

**Literature review on atmospheric emissions and associated
environmental effects from conventional thermal electricity generation**

Prepared for:
Clean Air Strategic Alliance
Electricity Project Team

Prepared by:
Heidi Swanson

March 12, 2008

Table of Contents

1	Introduction.....	4
1.1	Objective and summary of literature review.....	4
1.2	Literature search methodology	4
1.2.1	Peer-Reviewed Journal Articles.....	4
1.2.2	Grey Literature Reports	5
1.3	Organization of the literature review document	6
1.4	Summary of findings and key studies	7
1.4.1	Mercury.....	7
1.4.2	Sulphur dioxide.....	8
1.4.3	Nitrogen oxides.....	9
1.4.4	Particulate matter	9
1.4.5	List 2 substances (PAHs, particulate matter, trace metals, benzene, fluoride/fluoric acid, hydrochloric acid).....	10
2	Priority substances	13
2.1	Mercury.....	13
2.1.1	Emissions, atmospheric deposition, and modeling	13
2.1.2	Environmental effects and biomonitoring	29
2.1.3	Regulation, policy, and reduction technologies.....	38
2.2	Sulphur dioxide and nitrogen oxides	47
2.2.1	Emissions, atmospheric deposition, and modeling	47
2.2.2	Environmental effects and biomonitoring	52
2.2.2.1	Acidification	54
2.2.2.2	Nitrogen saturation and eutrophication.....	58
2.2.3	Regulation, policy, and abatement technologies.....	67
2.3	Particulate matter	72
2.3.1	Emissions, atmospheric deposition, and modeling	72
2.3.2	Environmental effects and biomonitoring	81
2.3.3	Regulation, policy, and abatement technologies.....	82
2.4	Carbon dioxide.....	84
2.4.1	Emissions, regulation, policy, and reduction technologies.....	84
2.5	Multiple pollutant studies	88
2.5.1	Emissions, atmospheric deposition and modelling.....	88
2.5.2	Environmental effects and biomonitoring	105
2.5.3	Regulations, guidelines, and abatement technologies.....	112
3	List 2 Substances.....	117
3.1	Emissions, atmospheric deposition, and modeling	117
3.1.1	Trace metals	117
3.1.2	Polycyclic aromatic hydrocarbons (PAHs).....	132
3.1.3	Dioxins and furans	140
3.1.4	Fluoride.....	143
3.1.5	Hydrogen chloride	144
3.1.6	Radionuclides.....	145
3.2	Environmental effects, ecotoxicity, and biomonitoring.....	149
3.2.1	Trace metals	149

3.2.2	Polycyclic aromatic hydrocarbons	159
3.2.3	Dioxins and furans	164
3.2.4	Fluoride	164
3.2.5	Radionuclides.....	167
3.3	Regulations, policies, and abatement technologies.....	168
4	Additional references on emissions	170
4.1	Primary publications	170
4.2	Grey literature	187

1 Introduction

1.1 Objective and summary of literature review

The objective of this review is to report on recent research (published since January 2002) that addresses: 1) atmospheric emissions from thermal electricity generation; and, 2) the direct and indirect environmental effects of these emissions. As well, published changes in environmental standards, guidelines, and emissions abatement technology are presented. This information will be used by CASA (Clean Air Strategic Alliance) as part of a five-year review of the Air Emissions Management Framework that was published in November 2003. Although all of the abstracts presented in this report were screened for relevance, no attempt was made to critically evaluate the quality of the science. Some of the papers included in the report are quite broad in scope (e.g., include pollutant sources other than thermal electricity). In these cases, an attempt was made to highlight relevant portions of the abstracts in italics.

The vast majority of papers published on thermal electricity generation since 2002 have been focused on pollutant reduction, pollutant monitoring, and regulatory evaluations. There has been considerable emphasis on research related to mercury emissions and abatement. Recent studies on direct and indirect environmental *effects* of air emissions from thermal electricity generation were primarily limited to local and regional studies (especially in eastern Europe and Greece) and to toxicity research on some List 2 substances. This was true regardless of the database or search engine employed (e.g., Web of Science, Cambridge Scientific Abstracts, Google Scholar, Science Direct). For certain pollutants, especially for particulate matter and PAHs, recent research was primarily directed toward human health effects; these abstracts were screened out of this report. Further investigation revealed that the bulk of research projects relating to environmental effects of thermal electricity generation were published between 1985 and 1999, and that these findings appear to be so well-documented that focus has now shifted to pollutant reduction. As such, part of this review is focused on technology and standard/guideline changes that have evolved since 2002. Many researchers are now conducting “life cycle” emissions studies, where the total emissions of electricity generation (including upstream processes such as mining and fuel transport) are accounted for and evaluated in economic and environmental terms.

No attempt was made to search for new or “emerging” pollutants from thermal electricity generation. Despite this, a number of studies on radionuclide emissions were encountered during the course of the review; these are included in the section that presents results for List 2 substances.

1.2 Literature search methodology

1.2.1 Peer-Reviewed Journal Articles

There are many search engines and databases available for searching peer-reviewed journal articles, conference proceedings, and book chapters. For environmental research, Scopus, Cambridge Scientific Abstracts, and Web of Science are among the most popular search engines. To test the effectiveness of various search engines and databases within search engines, fixed sequences of Boolean operators (e.g., air emission* AND environ* effect* AND (thermal electric* OR coal-fired power plant* OR power plant*)) were entered into the “advanced search” window of a variety of different search engine/database combinations. Results were evaluated for number of hits, relevance, ease of follow-on searching (e.g., linked cited reference search, related articles), and export options to reference software. The “biological sciences” database within Cambridge Scientific Abstracts was chosen as the primary vehicle for searching peer-reviewed journal articles. Additional searches were performed in specific subject areas using Web of

Science and Science Direct (via Google Scholar). Approximately 3500 articles were screened for relevance during the course of the review.

1.2.2 Grey Literature Reports

Searches for Grey Literature reports were completed on individual agency websites such as Environment Canada, Health Canada, and the US Environmental Protection Agency. Non-governmental organization websites (e.g., World Health Organization, Ontario Clean Air Alliance) were also searched. In general, searching for publications within agency websites was less effective than using google-based searches that included the name of the agency in the search (i.e., search =“US EPA Clean Air Mercury Rule”). Between the two teams (environmental effects and human health effects, see below), 28 websites were searched (Table 1).

Table 1. Government and non-governmental organization websites that were searched.

Agency or group	Country	Website
Air Impacts	Global	www.airimpacts.org
Alberta Environment	Canada	www.environment.gov.ab.ca
Alberta Health and Wellness	Canada	www.health.gov.ab.ca
ATSDR	USA	www.atsdr.cdc.gov
Brookhaven National Laboratory	USA	www.bnl.gov
Clean Air Task Force (CATF)	USA	www.catf.us
Commission for Environmental Cooperation	Canada/USA/Mexico	www.cec.org
Electric Power Research Initiative	USA	www.epri.com
Environment Canada	Canada	www.ec.gc.ca
Environmental Integrity Project	USA	www.environmentalintegrity.org
Environmental Protection Agency (EPA)	USA	www.epa.gov
European Commission-Environment	European Union	www.ec.europa.eu/environment
Geological Survey of Canada	Canada	www.gsc.nrcan.gc.ca
Government of British Columbia	Canada	www.gov.bc.ca
Government of Saskatchewan	Canada	www.gov.sk.ca
Greenpeace Canada	Canada	www.greenpeace.ca
Health Canada	Canada	www.hc-sc.gc.ca
Health Effects Institute (HEI)	USA	www.healtheffects.org
International Joint	Canada/USA	www.ijc.org

Agency or group	Country	Website
Commission (IJC)		
National Energy Technology Laboratory	USA	www.netl.doe.gov
New York State Energy Research and Development Authority	USA	www.nyserda.org
Ontario Clean Air Alliance	Canada	www.cleanairalliance.org
Ontario Power Generation	Canada	www.opg.com
Sustainable Energy and Economic Development Coalition	USA	www.seedcoalition.org
United Nations Economic Development	Global	www.unep.org
World Health Organization	Global	www.who.int
World Resources Initiative	USA	www.wri.org

1.3 Organization of the literature review document

For priority substances (mercury, sulphur dioxide, nitrogen oxide, particulate matter), abstracts are categorized by pollutant type and sub-categorized by the study objective. The sub-categories are arranged as follows (with some variation among pollutants):

- a. Emissions, atmospheric deposition, and modeling
- b. Environmental effects and biomonitoring
- c. Regulation and policy

Abstracts on List 2 substances were also divided into these sub-categories before being grouped by pollutant, wherever relevant studies were available. The document is organized in such a way that the reader can easily navigate through the sections by making use of MS Word's Document Map feature (see View menu) and the hyperlinks provided in the tables below.

Another researcher (Adrienne LeBlanc) completed a concurrent review on human health effects of air emissions from thermal electricity generation. The results she obtained on emissions characterization were forwarded to me for inclusion in this report. In total, 136 peer-reviewed abstracts and 31 gray literature articles were forwarded (please refer to her report for detailed search methodology and results). I merged all abstracts relating to emissions characterization, removed duplicates, and categorized the abstracts according to the scheme presented above. In some instances, however, results that she obtained had originally been screened out of this report and/or they did not fit well into the categorization scheme. These abstracts are included at the end of the report in a section entitled "extra emissions references." They include abstracts that relate to less common fuel types (e.g., oil shales) and contamination of the environment via fly ash disposal sites.

1.4 Summary of findings and key studies

A total of 445 abstracts related to emissions and environmental effects of pollutants associated with thermal electricity generation are presented. The abstracts cover a range of fuel types (coal, diesel, oil, natural gas, biomass), though the bulk of the studies consider emissions from coal-fired power plants. The following paragraphs provide a brief overview of the search results on a pollutant-by-pollutant basis, with links to studies considered particularly applicable to CASA's regulatory review.

1.4.1 Mercury

Mercury is a global pollutant with multiple anthropogenic and natural sources. As such it is difficult to attribute specific environmental effects to power plants, though it is clear that elevated atmospheric deposition rates and consequent accumulation of mercury in biota can be partially attributed to these emissions. The abstracts presented herein focus primarily on the characterization of Hg emissions from coal-fired power plants (e.g., Manolopoulos et al. 2007) and the response of environmental Hg concentrations to changes in atmospheric deposition rates (e.g., Berube et al. 2003; Drevnick et al. 2007; Harris et al. 2007). Much of the recent research with respect to power plant emissions has focused on historical patterns of Hg accumulation (Donahue et al. 2006), speciation of Hg in gaseous and particulate phases (e.g., Edgerton et al. 2006), leachability of Hg from fly ash (e.g., Gustin and Ladwig 2004), and cost benefit analyses of reducing Hg emissions (Griffiths et al. 2007). The following studies are considered to be particularly relevant to the CASA regulatory review:

Table 2. Key studies on mercury.

Author and year	Title	Page #
Berube et al. 2003	Assessing risks associated with the presence of mercury in the environment: The COMERN approach	13
Boylan et al. 2003	A New Method to Assess Mercury Emissions: A Study of Three Coal-Fired Electric-Generating Power Station Configurations	13
Charnley 2006	Assessing and managing methylmercury risks associated with power plant mercury emissions in the United States	38
Donahue et al. 2006	Impacts of coal-fired power plants on trace metals and polycyclic aromatic hydrocarbons (PAHs) in lake sediments in central Alberta, Canada	14
Drevnick et al. 2007	Deposition and cycling of sulfur controls mercury accumulation in Isle Royale fish	31
Edgerton et al. 2006	Mercury speciation in coal-fired power plant plumes observed at three surface sites in the southeastern US	15
Givelet et al. 2003	Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: Comparison with natural "background" values (past 8000 years)	15
Harris et al. 2007	Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition	31
Hrabik and Watras 2002	Isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake	32
Kotnick et al. 2002	Mercury in small freshwater lakes: A case study: Lake Velenje, Slovenia	20

Author and year	Title	Page #
Lipfert et al. 2005	Methylmercury, fish consumption, and the precautionary principle	40
Manolopoulos et al. 2007	Local and regional factors affecting atmospheric mercury speciation at a remote location	21
Paterson et al. 2006	Bioaccumulation of newly deposited mercury by fish and invertebrates: An enclosure study using stable mercury isotopes	35
Watras and Morrison 2008	The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulfate, and the water cycle	37

1.4.2 Sulphur dioxide

Current research on the environmental effects of sulphur dioxide are primarily focused on aspects of forest health (Akselsson et al. 2004), soil biogeochemistry (Hultberg and Ferm 2006), and acidification of terrestrial and aquatic ecosystems (e.g., Fenn et al. 2006). Key findings over the past five years include ecological responses to declines in atmospheric deposition of sulphur dioxide (e.g., Laudon and Bishop 2002; Watras and Morrison 2008), modeling forest response to changes in deposition rates (Gbondo-Tugbawa et al. 2002), and comparative assessments of emissions from different fuel types (e.g., de Castro Villela and Silveira 2006; Chatzimouratidis and Pilavachi 2007).

Table 3. Key studies on sulphur dioxide.

Author and year	Title	Page #
Chatzimouratidis and Pilavachi 2007	Objective and subjective evaluation of power plants and their non-radioactive emissions using the analytic hierarchy process	89
de Castro Villela and Silveira 2006	Thermoeconomic model considering the environment impacts on thermoelectric power plants: Natural gas versus diesel	92
Fenn et al. 2006	Status of soil acidification in North America	55
Gbondo-Tugbawa et al. 2002	A model to simulate the response of a northern hardwood forest ecosystem to changes in S deposition	47
Hultberg and Ferm 2006	Temporal changes and fluxes of sulphur and calcium in wet and dry deposition, internal circulation as well as in run-off and soil in a forest at Gardsjon, Sweden	56
Jeffries et al. 2003	Monitoring the results of Canada/U.S.A. acid rain control programs: Some Lake responses	48
Kaewboonsong et al. 2006	Minimizing fuel and environmental costs for a variable-load power plant (co-)firing fuel oil and natural gas - Part 1. Modeling of gaseous emissions from boiler units	96
Laudon and Bishop 2002	The rapid and extensive recovery from episodic acidification in northern Sweden due to declines in SO ₂ ⁺ deposition	57
Puig et al. 2008	Sulphur isotopes as tracers of the influence of a coal-fired power plant on a Scots pine forest in Catalonia (NE Spain)	53
Tzimas et al. 2007	Trade-off in emissions of acid gas pollutants and of carbon dioxide in fossil fuel power plants with carbon capture	114
Watras and Morrison 2008	The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulfate, and the water cycle	37

1.4.3 Nitrogen oxides

As with mercury and sulphur dioxide, nitrogen oxides are ubiquitous atmospheric pollutants with multiple anthropogenic sources. Consequently, it is difficult to attribute the environmental impacts of elevated nitrogen deposition exclusively to emissions from electrical generation. Researchers continue to focus on the impacts of anthropogenic nitrogen on forests, with studies throughout North America and Europe documenting increases in nitrate export (e.g., Dise and Gundersen 2004), changes in soil chemistry (Aber 2003), eutrophication (e.g., Rodriguez and Macias 2006), changes in plant growth rate and community composition (Kochy and Brakenhielm 2008), and loss of biodiversity (Dise and Stevens 2005). Other relevant studies examined aspects of nitrogen source apportionment (Fenn et al. 2003), monitoring of power plant emissions (e.g., Kim et al. 2006), and life-cycle assessment on the effect of GHG capture technologies on emissions of other pollutants (e.g., Tzimas et al. 2007).

Table 4. Key studies on nitrogen oxides.

Author and year	Title	Page #
Aber et al. 2003	Is nitrogen deposition altering the nitrogen status of northeastern forests?	58
Chatzimouratidis and Pilavachi 2007	Objective and subjective evaluation of power plants and their non-radioactive emissions using the analytic hierarchy process	89
de Castro Villela and Silveira 2006	Thermoeconomic model considering the environment impacts on thermoelectric power plants: Natural gas versus diesel	92
Dise and Gundersen 2004	Forest ecosystem responses to atmospheric pollution: Linking comparative with experimental studies	59
Dise and Stevens 2005	Nitrogen deposition and reduction of terrestrial biodiversity: evidence from temperate grasslands	59
Fenn et al. 2003	Nitrogen pollution in the northeastern United States: Sources, effects, and management options	55
Kim et al. 2006	Satellite-observed US power plant NO _x emission reductions and their impact on air quality	49
Kochy and Brakenhielm 2007	Separation of effects of moderate N deposition from natural change in ground vegetation of forests and bogs	62
Odeh and Cockerill 2008	Life cycle GHG assessment of fossil fuel power plants with carbon capture and storage	68
Rodriguez and Macias 2006	Eutrophication trends in forest soils in Galicia (NW Spain) caused by the atmospheric deposition of nitrogen compounds	64
Tzimas et al. 2007	Trade-off in emissions of acid gas pollutants and of carbon dioxide in fossil fuel power plants with carbon capture	114

1.4.4 Particulate matter

Relevant studies on the environmental impact of particulate matter emissions addressed issues related to source apportionment (e.g., Brook et al. 2007), spatial deposition patterns at local and regional scales (Sharma and Pervez 2004), the content and chemistry of particulate matter (e.g., Goodarzi 2006), and toxicity (e.g., Gilmour et al. 2007). There appears to a scarcity of research

on the ecological effects of particulate matter, though there are many studies addressing the environmental impacts of the contaminants contained in particulate matter, as cited in this report.

Table 5. Key studies on particulate matter.

Author and year	Title	Page #
Brook et al. 2007	Assessing sources of PM sub(2.5) in cities influenced by regional transport	72
Chow et al. 2002	Review of PM2.5 and PM10 apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model	74
Doraiswamy et al. 2006	Contribution of coal-fired power plants to ambient PM2.5 in TN	74
Gilmour et al. 2007	Comparative toxicity of size-fractionated airborne particulate matter obtained from different cities in the United States	81
Goodarzi 2006a	Morphology and chemistry of fine particles emitted from a Canadian coal-fired power plant	76
Goodarzi 2006b	The rates of emissions of fine particles from some Canadian coal-fired power plants	76
Greenbaum 2003	A historical perspective on the regulation of particles	82
Nielsen and Livbjerg 2002	Formation and emission of fine particles from two coal-fired power plants	78
Sharma and Pervez 2004	A case study of spatial variation and enrichment of selected elements in ambient particulate matter around a large coal-fired power station in central India	78
Triantafyllou et al. 2006	Levels and trend of suspended particles around large lignite power stations	79

1.4.5 List 2 substances (PAHs, particulate matter, trace metals, benzene, fluoride/fluoric acid, hydrochloric acid)

With the exception of PAHs and particulate matter, there were relatively few relevant studies published on the environmental impacts of List 2 substances emitted from thermal power plants. There were a number of studies on trace metal emissions, trace metal adsorption to particulate matter, and trace metal speciation in emissions, however. For trace metals that were specifically listed in the terms of reference (e.g., thallium, beryllium), abstracts relating to general toxicity and environmental effects are presented (e.g., Heim et al. 2002). There were also a number of studies on using mosses and lichens as biomonitoring tools for detecting trace metal and radionuclide emissions (e.g., Fernandez et al. 2002). Very few studies were found on fluoride, but the use of deer antlers as biomonitoring tools for fluoride was presented (Kierdof and Kierdof 2005).

Key studies on PAH emissions focused on source apportionment (e.g., Feng et al. 2007) and characterization of PAH compounds in flue gases and particulate matter (e.g., Liu et al. 2002). Few studies examined direct correlations between emissions and local effects of deposition to aquatic or terrestrial ecosystems.

Table 6. Key studies on List 2 substances.

Pollutant	Author and year	Title	Page #
<i>PAHs</i>	Donahue et al. 2006	Impacts of coal-fired power plants on trace metals and polycyclic aromatic hydrocarbons (PAHs) in lake sediments in central Alberta, Canada	14
	Arditsoglou et al. 2004	Size distribution of trace elements and polycyclic aromatic hydrocarbons in fly ashes generated in Greek lignite-fired power plants	132
	Feng et al. 2007	Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China	134
	Li et al. 2003	A study of the PAHs (polycyclic aromatic hydrocarbons) emissions resulting from the combustion of different ranks of coal	135
	Yan et al. 2004	Performance of PAHs emission from bituminous coal combustion	139
	Lampi et al. 2006	Photoinduced Toxicity of Polycyclic Aromatic Hydrocarbons to <i>Daphnia Magna</i> : Ultraviolet-Mediated Effects and the Toxicity of Polycyclic Aromatic Hydrocarbon Photoproducts	160
	Lehndorff and Schwark 2004	Biomonitoring of air quality in the Cologne Conurbation using pine needles as a passive sampler	160
	Mastral et al. 2002	Relationship between ecotoxicity and PAH content in coal combustion waste samples	161
	Simcik and Offenberg 2006	Polycyclic aromatic hydrocarbons in the Great Lakes	162
<i>Trace metals</i>	Goodarzi and Sanei 2002	The deposition of trace elements on the land/surface soil in the Wabamun Lake area, Alberta, Canada	120
	Goodarzi 2006	Assessment of elemental content of milled coal, combustion residues, and stack emitted materials: Possible environmental effects for a Canadian pulverized coal-fired power plant	120
	Huang et al. 2004	Trace elements (Mn, Cr, Pb, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler	122
	Naruwaka et al. 2005	Investigation on chemical species of arsenic, selenium and antimony in fly ash from coal fuel thermal power stations	127
	Hopkins et al. 2006	Reproduction, embryonic development, and maternal transfer of contaminants in the amphibian <i>Gastrophryne carolinensis</i>	152
	Pinochet et al. 2002	Selenium Concentration in Compartments of Aquatic Ecosystems in Central Chile	155
<i>Fluoride</i>	Franzaring et al. 2006	Environmental monitoring of fluoride emissions using precipitation, dust, plant and soil samples	164

Pollutant	Author and year	Title	Page #
	Kierdorf and Kierdorf 2005	Antlers as biomonitors of environmental pollution by lead and fluoride: A review	165
	Zemek et al. 2006	Spatial distribution of dental fluorosis in roe deer (<i>Capreolus capreolus</i>) from North Bohemia (Czech Republic) and its relationships with environmental factors	166
	Liteplo et al. 2002	Environmental health criteria 227: Fluorides	165
<i>Dioxins and furans</i>	Bochentin et al. 2007	Polychlorinated dibenzo-p-dioxins (PCDDs) and -furans (PCDFs) in pine needles of Poland	164
	Everaert and Bayens 2002	The formation and emission of dioxins in large scale thermal processes.	140
	Fernandez et al. 2004	First assessment of dioxin emissions from coal-fired power stations in Spain	140
<i>Radionuclides</i>	Chauhan and Chakarvarti 2002	Radon activity and exhalation rates in coal fired thermal power plants	146
	Flues et al. 2002	The influence of a coal-fired power plant operation on radionuclide concentrations in soil	147
	Flues et al. 2006	Radioactivity of coal and ashes from Figueira coal power plant in Brazil	146
	Papp and Deszo 2003	Estimate of the dose-increment due to outdoor exposure to gamma rays from uranium progeny deposited on the soil around a coal-fired power plant in Ajka town, Hungary	148
	Ugur et al. 2003	Biomonitoring of Po-210 and Pb-210 using lichens and mosses around a uraniferous coal-fired power plant in western Turkey	167

2 Priority substances

2.1 Mercury

2.1.1 Emissions, atmospheric deposition, and modeling

Berube, D., Lucotte, M., and Canuel, R. 2003. Assessing risks associated with the presence of mercury in the environment: The COMERN approach. Journal De Physique.IV : JP, Vol. 107, pp. 163-167.

Abstract: The presence of mercury (Hg) in the environment has become a source of great concern in the scientific community throughout the World. However, existing models describing Hg behavior in the environment and risks to communities health attributable to Hg exposure fail to cope with the complexity of this issue. We propose here a new modeling approach named the Mercury Environmental Vulnerability Index (MEVI) that takes into account notions such as ecosystems sensitivity and resilience, threshold levels of environmental effects, dynamic changes to the environment induced by human activities, and communities exposure and vulnerability to contaminants. The development of MEVI will be accomplished through the activities of a wide Canadian-based research network, the Collaborative Mercury Research Network, during the course of its five-years research plan.

Blanchard, P., Froude, F.A., Martin, J.B., Dryfhout-Clark, H., and Woods, J.T. 2002. Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada. Atmospheric Environment 36: 3735-3743.

Abstract: Total gaseous mercury (TGM) measurements have been conducted around the Great Lakes since 1997. At two of these sites (Egbert and Burnt Island), TGM concentrations presented significant seasonal variations. *Possible explanations for the larger winter-spring/smaller summer-fall concentrations included seasonal meteorological differences, a northern hemispherical increase in coal combustion for wintertime heating*, seasonal cycles of atmospheric oxidants and overall hemispherical source-sink relationship. The impact of populated/industrialized areas on the TGM concentrations at rural sites was demonstrated using pollution roses. Trend analyses for Egbert and Point Petre indicated relatively stable TGM concentrations between 1997 and 2000. Principal component analysis of TGM and trace metals confirmed the influence of the industrialized/populated area of Southwestern Ontario on both Egbert and Point Petre as well as metal recovery activities from Northern Ontario. For one episode of significant TGM concentrations, only a general geographical area could be implied as the source of atmospheric mercury.

Boylan, H.M., Cain, R.D., and Kingston, H.M. 2003. A New Method to Assess Mercury Emissions: A Study of Three Coal-Fired Electric-Generating Power Station Configurations. J. Air Waste Management Association 53: 1318-1325.

Abstract: U.S. Environmental Protection Agency (EPA) Method 7473 for the analysis of mercury (Hg) by thermal decomposition, amalgamation, and atomic absorption spectroscopy has proved successful for use in Hg assessment at coal-fired power stations. In an analysis time of 5 min per sample, this instrumental methodology can directly analyze total Hg-with no discrete sample preparation-in the solid matrices associated with a coal-fired power plant, including coal, fly ash, bottom ash, and flue gas desulfurization (FGD) material. This analysis technique was used to investigate Hg capture by coal combustion byproducts (CCBs) in three different coal-fired power plant configurations. Hg capture and associated emissions were estimated by partial

mass balance. The station equipped with an FGD system demonstrated 68% capture on FGD material and an emissions estimate of 18% (11 kg/yr) of total Hg input. The power plant equipped with low oxides of nitrogen burners and an electrostatic precipitator (ESP) retained 43% on the fly ash and emitted 57% (51 kg/yr). The station equipped with conventional burners and an ESP retained less than 1% on the fly ash, emitting an estimated 99% (88 kg/yr) of Hg. Estimated Hg emissions demonstrate good agreement with EPA data for the power stations investigated.

Cohen, M., Artz, R., Draxler, R., Miller, P., Poissant, L., Niemi, D., Ratte, D., Deslauriers, M., Duval, R., Laurin, R., Slotnick, J., Nettesheim, T., and McDonald, J. 2004. Modeling the atmospheric transport and deposition of mercury to the Great Lakes. *Environmental Research* 95: 247-265.

Abstract: A special version of the NOAA HYSPLIT_4 model has been developed and used to estimate the atmospheric fate and transport of mercury in a North American modeling domain. Spatial and chemical interpolation procedures were used to expand the modeling results and provide estimates of the contribution of each source in a 1996 anthropogenic US/Canadian emissions inventory to atmospheric mercury deposition to the Great Lakes. While there are uncertainties in the emissions inventories and ambient data suitable for model evaluation are scarce, model results were found to be reasonably consistent with wet deposition measurements in the Great Lakes region and with independent measurement-based estimates of deposition to Lake Michigan. Sources up to 2000km from the Great Lakes contributed significant amounts of mercury through atmospheric transport and deposition. While there were significant contributions from incineration and metallurgical sources, *coal combustion was generally found to be the largest contributor to atmospheric mercury deposition to the Great Lakes.*

CONSOL Energy. (2006) Evaluation of Mercury Emissions from Coal-Fired Facilities with SCR and FGD Systems. Retrieved Jan 13, 2007 from <http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/control-tech/pubs/DOE%20SCR-FGD%20FINAL%20REPORT.pdf>.

De Lacerda, L.D., Dos Santos, A.F., and Marins, R.V. 2007. Mercury emissions to the atmosphere from natural gas burning in Brazil. *Quimica nova* 30: 366-369.

Abstract: Increasing natural gas use in Brazil triggered a discussion of its role as a Hg source. We show that Hg emissions to the atmosphere from fossil fuel combustion for power generation in Brazil contribute with 6.2% (4.2 t yr⁻¹) to the total anthropogenic Hg atmospheric emissions, with coal combustion and biomass burning as major sources. Natural gas contributes with 0.04 t yr⁻¹, mostly from electricity generation (88%) and industrial uses (7.6%). Preliminary results on Hg concentrations in natural gas suggest that a large fraction of it is trapped during refining and transport, which may create Hg point sources between extraction and consumption.

Donahue, W.F., Allen, E.W., and Schindler, D.W. 2006. Impacts of coal-fired power plants on trace metals and polycyclic aromatic hydrocarbons (PAHs) in lake sediments in central Alberta, Canada. *Journal of Paleolimnology* 35: 111-128.

Abstract: Trace metals and polycyclic aromatic hydrocarbons (PAH) were analyzed in sediment cores from three central Alberta lakes to determine the contributions of local coal-fired power plants to contaminant loadings. In Wabamun Lake, with four power plants built since 1950 within a 35-km radius, sediment concentrations of mercury, copper, lead, arsenic and selenium have increased by 1.2- to 4-fold. Trace metal enrichments were less pronounced in Lac Ste. Anne and Pigeon Lake, situated 20 km north and 70 km south of Wabamun Lake, respectively. Total Hg flux to Wabamun Lake sediments (21-32 µg m⁻² yr⁻¹) has increased 6-fold since 1950, compared to 2- and 1.5-fold increases in Lac Ste. Anne and Pigeon Lake, respectively, since circa

1900. Total PAH flux to surface sediments was 730-1100 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ in Wabamun Lake, 290-420 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ in Lac Ste. Anne, and 140-240 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ in Pigeon Lake. Without adoption of pollution-abatement technology that compensates for increases in generating capacity, continued expansion of coal-burning industry in Alberta will result in increased contaminant deposition, primarily from local sources.

Edgerton, E.S., Hartsell, B.E., and Jansen, J.J. 2006. Mercury speciation in coal-fired power plant plumes observed at three surface sites in the southeastern US. Environmental Science & Technology 40: 4563-4570.

Abstract: Elemental Hg (Hg-0), reactive gaseous Hg (RGM) and fine particulate Hg (Hg-P) were measured intermittently at three sites in the southeastern U. S. from June 2001 through November 2004. Simultaneous measurements of SO₂ and NO_y were used to identify plumes from coal fired power plants (CFPPs). Emission signatures and back trajectories were used to identify specific CFPPs, and to compare observed (i.e., at the site) versus expected (i.e., at the stack) Hg speciation. Results for 41 precipitation-free plume events show that observed RGM: SO₂ is substantially lower (by a factor of 2-4) than expected RGM: SO₂. HgP represented 2%, or less, of total-Hg in CFPP plumes, in general agreement with emission estimates. Results for 21 events, where both RGM and Hg-0 could be estimated, show that total-Hg (i.e., RGM + Hg-0) was essentially conserved from the point of emission to the site, and that Hg-0 was the dominant form (average 84%). Emission estimates, based on coal analyses and the EPRI-ICR Hg speciation model, indicate that Hg-0 should represent about 42% of Hg in the observed plumes. Possible explanations for these differences include, but are not limited to, in-plume reduction of RGM to Hg-0, measurement error, errors in emission estimates, and depositional losses. Further work is needed to confirm these results and to determine if they apply to CFPPs in general, or the limited set of observed CFPPs.

Feng, X., Sommar, J., Lindqvist, O., and Hong, Y. 2002. Occurrence, emissions and deposition of mercury during coal combustion in the province Guizhou, China. Water Air Soil Pollut. 139: 311-324.

Abstract: Forty-eight coal samples from the major coal mines in Guizhou were collected by means of subterranean channel sampling. The average mercury content in coal from this Chinese province is 0.53 mg kg⁻¹, which is substantially higher than coal produced in any other province of China. A strong link is proposed to exist between atmospheric mercury emissions and the combustion of coal. During the last two decades, the amount of mercury emitted from coal combustion in Guizhou has increased invariably to 8.3 tons in 1998. Being concentrated to the pyrite fraction in the coal, the implementation of physical coal cleaning is likely to be an effective way to reduce the mercury content. Total and fractionated mercury in air and precipitation was measured in the provincial capital. During a measurement campaign in October 1999, the reactive gaseous mercury (RGM) concentration averaged at 450 pg m⁻³, which is much higher than that in pristine area (less than 20 pg m⁻³). The average total mercury in rainwater of 1996 was estimated to be 33 ng L⁻¹, and the total annual wet deposition of mercury in the area was 39 g km⁻² in 1996.

Givelet, N., Roos-Barraclough, F., and Shoty, W. 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: Comparison with natural "background" values (past 8000 years). Journal of Environmental Monitoring 5: 935-949.

Abstract: Peat cores from three bogs in southern Ontario provide a complete, quantitative record of net rates of atmospheric Hg accumulation since pre-industrial times. For comparison with modern values, a peat core extending back 8000 years was used to quantify the natural variations

in Hg fluxes for this region, and their dependence on climatic change and land use history. The net mercury accumulation rates were separated into "natural" and "excess" components by comparing the Hg/Br ratios of modern samples with the long-term, pre-anthropogenic average Hg/Br. The average background mercury accumulation rate during the pre-anthropogenic period (from 5700 years BC to 1470 AD) was $1.4 \pm 1.0 \text{ ?g m}^{-2}$ per year ($n = 197$). The beginning of Hg contamination from anthropogenic sources dates from AD 1475 at the Luther Bog, corresponding to biomass burning for agricultural activities by Native North Americans. During the late 17th and 18th centuries, deposition of anthropogenic Hg was at least equal to that of Hg from natural sources. Anthropogenic inputs of Hg to the bogs have dominated continuously since the beginning of the 19th century. The maximum Hg accumulation rates decrease in the order Sifton Bog, in the City of London, Ontario (141 ?g Hg m^{-2} per year), Luther Bog in an agricultural region (89 ?g Hg m^{-2} per year), and Spruce Bog which is in a comparatively remote, forested region (54 ?g Hg m^{-2} per year). Accurate age dating of recent peat samples using the bomb pulse curve of ^{14}C shows that the maximum rate of atmospheric Hg accumulation occurred during AD 1956 and 1959 at all sites. *In these (modern) samples, the Hg concentration profiles resemble those of Pb, an element which is known to be immobile in peat bogs. The correlation between these two metals, together with sulfur, suggests that the predominant anthropogenic source of Hg (and Pb) was coal burning. While Hg accumulation rates have gone into strong decline since the late 1950's, Hg deposition rates today still exceed the average natural background values by 7 to 13 times.*

Goodarzi, F. 2004. Speciation and mass-balance of mercury from pulverized coal fired power plants burning western Canadian subbituminous coals. Journal of Environmental Monitoring 6:792-798.

Abstract: This report summarizes the results of a study carried out on six pulverized coal-fired power plants in western Canada burning subbituminous coal for the mass-balance and speciation of mercury. The main objectives of this study were to: determine the total gaseous mercury (TGM) emitted from stacks of power plants using the Ontario Hydro method; identify the speciation of emitted mercury such as metallic (Hg⁰) and gaseous elemental (GEM) mercury; and perform mass-balance calculations of mercury for milled-coal, bottom ash, electrostatic precipitators (ESP) fly ash and stack-emitted mercury based on three tests. Sampling of mercury was carried out using the Ontario Hydro method and mercury was determined using the USEPA method 7473 by cold vapor atomic absorption (CVAAS). The sample collection efficiencies confirmed that both oxidized and the elemental mercury had been successfully sampled at all power plants. The total gaseous mercury emitted (TGM) is 6.95-15.66 g h⁻¹ and is mostly in gaseous elemental mercury (GEM, Hg⁰) form. The gaseous elemental mercury is emitted at a rate of 6.59-12.62 g h⁻¹. Reactive gaseous mercury (RGM, Hg²⁺) is emitted at a rate of 0.34-3.68 g h⁻¹. The rate of emission of particulate mercury (Hg^p) is low and is in the range 0.005-0.076 g h⁻¹. The range of mass-balances for each power plant is more similar to the variability in measured mercury emissions, than to the coal and ash analyses or process data. The mass-balance calculations for the six power plants, performed on results of the three tests at each power plant, are between 86% and 123%, which is acceptable and within the range 70-130%. The variation in mass-balance of mercury for the six power plants is mostly related to the variability of coal feed rate.

Goodarzi, F., Reyes, J., Schulz, J., Hollman, D., and Rose, D. 2006. Parameters influencing the variation in mercury emissions from an Alberta power plant burning high inertinite coal over thirty-eight weeks period. International Journal of Coal Geology 65: 26-34.

Abstract: Feed coals and fly ashes from a coal-fired power station burning Alberta subbituminous coal were examined for a period of thirty-eight weeks to determine the variation in

emitted mercury. Feed coal samples were analyzed for proximate, calorific value and Hg content, while fly ash samples were examined for C and Hg contents. The maceral content of the feed coal was also determined. The emitted mercury was calculated and compared to mercury emitted from the stack according to a mass-balance calculation from a previous study for the same station. Mercury contents ranged from 0.029 to 0.066 mg/kg for feed coal, and from 0.069 to 0.112 mg/kg for fly ash. The carbon/char in fly ash was separated into reactive (vitrinitic/bimacerate) and less reactive (inertinitic) chars using ZnBr₂ at specific gravities of 1.7, 2.0, and 2.25 to 2.4. The result shows that there is a positive correlation between the carbon and mercury content of the fly ash. The reactive char particles in the fly ash may be responsible for the capture mercury in fly ash. The percentage of estimated captured mercury by fly ash increases with increasing carbon content (%) in fly ash. The percentage of emitted mercury for the period of 38 weeks is estimated to be within the range of 49% to 76% of the total input of mercury.

Goodarzi, F., Reyes, J., and Abrahams, K. 2008. Comparison of calculated mercury emissions from three Alberta power plants over a 33 week period - Influence of geological environment. Fuel 87: 915-924.

Abstract: Feed coals and fly ashes from two coal-fired power plants burning Alberta subbituminous coal were analyzed for C, Cl, Hg, and S and calorific values (for feed coal only), every week for a period of 33 weeks. The feed coals used in this study were deposited in brackish water and are compared to the coals deposited in a freshwater environment. The Hg and char (unburnt carbon) content of the fly ash was monitored to determine the variation of Hg and its possible relationship to the char types in the fly ash. The feed coals have Hg content of 0.026-0.089 mg/kg and their fly ash contains 0.02-0.243 mg/kg of Hg. The C content of the fly ashes ranges from 0.15% to 0.51%. The carbon/char was separated from the fly ash using HF and HCl. Reactive vitrinitic (formed from woody part of plants) and less reactive inertinitic (natural char) chars were separated by density separations of various specific gravities using ZnBr₂. The char is mostly reactive vitrinitic (67-80 vol.%). Both stations have similar range of C content for their respective fly ashes. However, station 2 shows a much wider range of Hg in fly ash compared to station 1. In general, the fly ash from coal deposited under brackish water environment (stations 1 and 2) appears to have same or higher Hg content for lower C content compared to the fly ash from coal deposited under fresh water environment. The calculated emitted Hg for the period of 33 weeks for station 1 is estimated to be 64-90% of the total input of Hg with an average of 74%. The calculated emitted Hg shows a more complex pattern for station 2 and falls into two groups; with group (a) showing higher enrichment index for both Hg and S. The calculated emitted Hg for this group is 43-74% with an average of 57%, indicative of more Hg being captured by fly ash, possibly due to interaction between Hg and S. In the second group (b) the emitted Hg is calculated to be 74-95% with an average of 85%. The relative enrichment of both Hg and S in group (b) is low compared to group (a), indicative of possible slight paleo-weathering of the feed coal. The present study indicates that geological parameters such as paleo weathering and also depositional environment of the feed coal may influence the Hg content of fly ash.

Gray, J.E., Fey, D.L., Holmes, C.W., and Lasorsa, B.K. 2005. Historical deposition and fluxes of mercury in Narraguinnep Reservoir, southwestern Colorado, USA. Applied Geochemistry 20: 207-220.

Abstract: Narraguinnep Reservoir has been identified as containing fish with elevated Hg concentrations and has been posted with an advisory recommending against consumption of fish. There are presently no point sources of significant Hg contamination to this reservoir or its supply waters. To evaluate potential historical Hg sources and deposition of Hg to Narraguinnep Reservoir, the authors measured Hg concentrations in sediment cores collected from this reservoir. The cores were dated by the Cs-137 method and these dates were further refined by

relating water supply basin hydrological records with core sedimentology. Rates of historical Hg flux were calculated (ng/cm²/a) based on the Hg concentrations in the cores, sediment bulk densities, and sedimentation rates. The flux of Hg found in Narraguinnep Reservoir increased by approximately a factor of 2 after about 1970. The 3 most likely sources of Hg to Narraguinnep Reservoir are surrounding bedrocks, upstream inactive Au-Ag mines and several coal-fired electric power plants in the Four Corners region. Patterns of Hg flux do not support dominant Hg derivation from surrounding bedrocks or upstream mining sources. *There are 14 coal-fired power plants within 320 km of Narraguinnep Reservoir that produce over 80 x 10⁶ MWH of power and about 16,40 kg-Hg/a are released through stack emissions contributing significant Hg to the surrounding environment. Two of the largest power plants, located within 80 km of the reservoir, emit about 950 kg-Hg/a. Spatial and temporal patterns of Hg fluxes for sediment cores collected from Narraguinnep Reservoir suggest that the most likely source of Hg to this reservoir is from atmospheric emissions from the coal-fired electric power plants, the largest of which began operation in this region in the late-1960s and early 1970s.*

Gustin, M.S., and Ladwig, K. 2004. An Assessment of the Significance of Mercury Release from Coal Fly Ash. *Journal of the Air and Water Waste Associations* 54: 320-330.

Abstract: Some mercury (Hg) naturally present in coal is retained in the fly ash remaining after combustion. Concern has been raised regarding the potential for release of this Hg to the environment. The exchange of Hg between fly ash and the atmosphere was measured in the laboratory and in situ at a fly ash landfill. All samples of fly ash used in the laboratory study, with the exception of that derived from lignite-type coal, acted as a sink for atmospheric Hg. Deposition rates were found to increase as air Hg concentrations increased and to decrease with incident light and increased temperature. Addition of water to fly ash samples resulted in re-emission of deposited atmospheric Hg. Deposition was the dominant flux measured in situ at a fly ash landfill. Atmospheric Hg was deposited to all samples collected as part of two demonstration projects using carbon injection for enhanced Hg capture. Hg concentrations of extracts derived using U.S. Environmental Protection Agency Method 1312 (Synthetic Precipitation Leaching Procedure) were 14.4 ng/L. Data developed demonstrate that fly ash, including that collected from Hg removal projects, will release little Hg to the air or water, and under certain conditions, absorbs Hg from the air.

Heebink, L.V., and Hassett, D.J. 2002. Release of mercury vapor from coal combustion ash. *Journal of the Air and Water Waste Associations* 52: 927-930.

Abstract: The long-term stability of Hg in coal combustion by-products (CCBs) was evaluated at ambient and near-ambient temperatures. Six CCB samples with atypically high levels of total Hg were selected for study assuming a greater potential for release of measurable amounts of Hg vapor. The samples selected included two fly ash samples from U.S. eastern bituminous coal, two fly ash samples from South African low-rank coal, one fly ash from Powder River Basin (PRB) subbituminous coal blended with petroleum coke, and one PRB subbituminous coal fly ash incorporated with flue gas desulfurization material. Air scrubbed of Hg was passed through compacted 100-g aliquots of each sample at 1 mL/min and vented to a gold-coated quartz trap to collect released Hg vapor. The samples were maintained at ambient and near-ambient (37°C) temperatures. All samples released low-picogram levels of Hg after 90 days. No pattern was evident to link the total Hg content to the rate of release of Hg vapor. An average of 0.030 pg Hg/g CCB/day was released from the samples, which equates to 2.2 x 10⁻⁸ lb Hg/ton CCB/year. If this were applied to a coal-fired power plant production of 200,000 tons of fly ash per year, there would be a maximum potential release of 0.0044 lb, or 2.00 g, of Hg per year. Experiments are continuing to determine long-term vapor release of Hg from CCBs. All samples have been set

up in duplicate at ambient temperature with an improved apparatus to reevaluate results reported in this article.

Hodgson, S., Nieuwenhuijsen, M.J., Colvile, R., and Jarup, L. 2007. Assessment of exposure to mercury from industrial emissions: comparing "distance as a proxy" and dispersion modelling approaches. Occupational and Environmental Medicine 64 (6), p. 380-388.

Abstract: The Runcorn area, north-west England, contains many pollution sources, the health effects of which have been under discussion for over 100 years. Preliminary investigations revealed an excess risk of mortality from kidney disease in people living nearest to several point sources of pollution, using distance as a proxy for exposure. Ongoing epidemiological investigations into the effect of ambient mercury exposure on dose and renal effect required a more refined assessment of exposure. **METHODS:** Atmospheric dispersion modelling was used to assess mercury dispersion from three mercury-emitting sources (including a large chlor alkali plant), based on knowledge of emissions, local meteorology and topography. **RESULTS:** The model was sensitive to various input parameters, with different dispersion patterns and ground-level concentrations, and therefore different exposed populations identified when different input parameters were defined. The different approaches to exposure assessment also had an impact on the epidemiological findings. The model output correlated well with weekly monitoring data collected in the local area, although the model underestimated concentrations in close proximity to the chlor alkali plant. The model identified that one point source did not contribute significantly to ground-level mercury concentrations, so that inclusion of this source when using the "distance as a proxy" approach led to significant exposure misclassification. **CONCLUSIONS:** The model output indicates that assessment of ambient exposure should give consideration to the magnitude of emissions, point source characteristics, local meteorology and topography to ensure that the most appropriate exposure classification is reached. Even if dispersion modelling cannot be undertaken, these data can be used to inform and improve the distance as a proxy approach, and improve the interpretability of the epidemiological findings.

Jiang, J.K., Hao, J.M., Wu, Y., Streets, D.G., Duan, L., and Tian, H.Z. 2005. Development of mercury emission inventory from coal combustion in China. Huanjing Kexue 26: 34-39.

Abstract: Mercury emission inventory by province from coal combustion in China was developed by combining fuel consumption, mercury content in fuel and emission factors after combustion in this study. The study is intended to provide an understanding of mercury transformation, transportation and deposition in atmosphere, as well as propose measures to control mercury pollution in China. Mercury emission sources were classified into 65 categories by economic sectors, fuel types, boiler types and pollution control technologies. For two different data sets of mercury content in coal the total amounts of mercury released into atmosphere in 2000 in China were estimated at about 161.6 tons and 219.5 tons, respectively. The biggest three source sectors were industry, power plants, and residential use, contributing 46%, 35% and 14% of total mercury emissions, respectively. The shares of elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particulate mercury (Hg_p) were 16%, 61% and 23%, respectively. The spatial distribution of mercury emissions from coal combustion in China is not uniform. Henan, Shanxi, Hebei, Liaoning and Jiangsu contributed large amounts of mercury emissions, exceeding 10 t+a-1.

Kellie, S., Y. Cao, Y. F. Duan, L. C. Li, P. Chu, A. Mehta, R. Carty, J. T. Riley, and W. P. Pan. 2005. Factors affecting mercury speciation in a 100-MW coal-fired boiler with low-NOx burners. Energy & Fuels 19:800-806.

The Western Kentucky University mobile laboratory for monitoring mercury emissions measured the mercury levels in a 100-MW boiler with wall-fired low-NO_x burners. Mercury emissions were monitored while burning seven coals, using semicontinuous emission monitoring at the air preheater outlet and electrostatic precipitator outlet. The collected data was then scaled and analyzed using stepwise regression analysis. The results showed that initial mercury concentration in the coal, as well as chlorine and sulfur levels, all influence the amount of mercury emissions. After mercury content, chlorine had the major role in the levels of vapor-phase mercury present in the flue gas. Chlorine promotes the chemisorption of mercury onto fly ash. Sulfur was shown to be a major factor in the oxidation of elemental mercury but inhibited the adsorption of oxidized mercury onto the fly ash. Further experimental results suggest that both HCl and SO₂ may participate directly in the mercury oxidation mechanism.

Kotnik, J., Horvat, M., Fajon, V., and Logar, M. 2002. Mercury in small freshwater lakes: A case study: Lake Velenje, Slovenia. *Water Air and Soil Pollution* 134: 319-339.

Abstract: Lake Velenje is located in one of the most polluted regions of Slovenia, the Salek Valley. The major source of pollution is the coal-fired thermal power plant in Sostanj (STPP). In the past, dumping of coal ash directly into Lake Velenje and drainage water from the ash disposal site resulted in unique chemical characteristics of the lake water, such as very high pH (10-12) and high concentrations of heavy metals. The introduction of a closed cycle ash transport system in 1995 resulted in a very fast recovery of the lake water quality. The aim of our study was to establish the sources, fate and distribution of mercury in Lake Velenje. In order to establish recent sources of mercury, total mercury and methylmercury concentrations were measured in various environmental samples (lake inflows, outflow, rainwater, sediments, etc.). Total mercury and methylmercury concentrations were measured at the surface and at different depths to establish mercury cycling, its transport and chemical transformations in the lake. General water quality parameters (such as pH, Eh, O₂, temperature, TDS, conductivity) were also determined. The results show that the major sources of mercury in Lake Velenje are lake inflows and wet deposition. Total mercury and methylmercury concentrations in the water column are very low (total mercury: 0.2-2.7 ng L⁻¹; methylmercury: 20-86 pg L⁻¹) and can be compared to other non-contaminated freshwater lakes. *These results suggest that the major form of mercury emitted from thermal power plant stacks is volatile Hg⁰, which has no or very little influence on the nearby surroundings, but rather is subject to long-range atmospheric transport.*

Lee, S. J., Y. C. Seo, H. N. Jang, K. S. Park, J. I. Baek, H. S. An, and K. C. Song. 2006. Speciation and mass distribution of mercury in a bituminous coal-fired power plant. *Atmospheric Environment* 40:2215-2224.

Characterization and mass balance of mercury in a coal-fired power plant were carried out in a 500 MW, bituminous coal consuming electric utility boiler. This facility is equipped with a cold-side electrostatic precipitator (ESP) and a wet flue gas desulfurization (FGD) in series as air pollution control devices (APCDs). Mercury sampling points were selected at both the up and down streams of the ESP and outlet of the FGD, which is at stack. Two different types of sampling methods were employed, one is the Ontario Hydro (OH) method (ASTM D6784) and the other is US EPA 101A. Various samples were collected from the coal-fired power plant such as fuel coals, fly ash in hopper, lime/lime stone, gypsum, and effluent water from FGD. These samples were analyzed by US EPA 7470A and 7471A to understand the behavior and mass balance of mercury in the process of a coal-fired power plant. There are no significant differences between the two sampling methods, but the OH method seems to have more advantages for Hg sampling from a coal-fired power plant because mercury speciation is quite an important factor to estimate the mercury emission and control efficiency from combustion flue gas. Approximate Hg mass balance could be obtained from various samples in the study; however, a series of long-term

and comprehensive study is required to evaluate the reliable Hg mass distribution and behavior in a coal-fired power plant.

Liu, Q.Y., Dai, J.X., Li, J., and Hou, L. 2006. Mercury in oil and natural gas and its critical assessment. *Shiyou Kantan Yu Kaifa* 33: 542-547.

Abstract: Abundance and forms of mercury in oil and gas have been increasingly paid attention to. There are mercury and its compounds in natural gas, condensate gas and crude oil. In natural gas, mercury exists exclusively in its elemental forms. Condensate gas and crude oil contain Hg of different forms, including elemental, organic, inorganic and suspended mercury. Hg stems from the hydrocarbon sources in natural gas, with Hg abundance higher in coal derived gas than in the oil derived gas. The abnormally high abundance of mercury in natural gas is related to the deep structure. Owing to its strong adsorption, Hg can easily form amalgams with a variety of metals causing problems in transportation pipeline or tank and other processing equipments, and even resulting in catastrophic events. So the abnormally high mercury must be removed from natural gas.

Lohman, K., C. Seigneur, E. Edgerton, and J. Jansen. 2006. Modeling mercury in power plant plumes. *Environmental Science & Technology* 40:3848-3854.

Abstract: Measurements of speciated mercury (Hg) downwind of coal-fired power plants suggest that the Hg-II/(Hg-0+Hg-II) ratio (where Hg-II is divalent gaseous Hg and Hg-0 is elemental Hg) decreases significantly between the point of emission and the downwind ground-level measurement site, but that the SO₂/(Hg-0 + Hg-II) ratio is conserved. We simulated nine power plant plume events with the Reactive & Optics Model of Emissions (ROME), a reactive plume model that includes a comprehensive treatment of plume dispersion, transformation, and deposition. The model simulations fail to reproduce such a depletion in Hg-II. A sensitivity study of the impact of the Hg-II dry deposition velocity shows that a difference in dry deposition alone cannot explain the disparity. Similarly, a sensitivity study of the impact of cloud chemistry on results shows that the effect of clouds on Hg chemistry has only minimal impact. Possible explanations include Hg-II reduction to Hg-0 in the plume, rapid reduction of Hg-II to Hg-0 on ground surfaces, and/or an overestimation of the Hg-II fraction in the power plant emissions. We propose that a chemical reaction not included in current models of atmospheric mercury reduces Hg-II to Hg-0 in coal-fired power plant plumes. The incorporation of two possible reduction pathways for Hg-II (pseudo-first-order decay and reaction with SO₂) shows better agreement between the model simulations and the ambient measurements. These potential Hg-II to Hg-0 reactions need to be studied in the laboratory to investigate this hypothesis. Because the speciation of Hg has a significant effect on Hg deposition, models of the fate and transport of atmospheric Hg may need to be modified to account for the reduction of Hg-II in coal-fired power plant plumes if such a reaction is confirmed in further experimental investigations.

Manolopoulos, H., Schauer, J.J., Purcell, M.D., Rudolph, T.M., Olson, M.L., Rodger, B., and Krabbenhoft, D.P. 2007. Local and regional factors affecting atmospheric mercury speciation at a remote location. *Journal of Environmental Engineering and Science* 6: 491-501.

Abstract: Atmospheric concentrations of elemental (Hg-0), reactive gaseous (RGM), and particulate (PHg) mercury were measured at two remote sites in the midwestern United States. *Concurrent measurements of Hg-0, PHg, and RGM obtained at Devil's Lake and Mt. Horeb, located approximately 65 km apart, showed that Hg-0 and PHg concentrations were affected by regional, as well as local sources, while RGM was mainly impacted by local sources. Plumes reaching the Devil's Lake site from a nearby coal-fired power plant significantly impacted SO₂ and RGM concentrations at Devil's Lake, but had little impact on Hg-0.* Our findings suggest that

traditional modeling approaches to assess sources of mercury deposited that utilize source emissions and large-scale grids may not be sufficient to predict mercury deposition at sensitive locations due to the importance of small-scale sources and processes. We suggest the use of a receptor-based monitoring to better understand mercury source-receptor relationships.

Menounou, N., and Presley, B.J. 2003. Mercury and other trace elements in sediment cores from central Texas lakes. *Archiv fur Environmental Contamination and Toxicology* 45: 11-29.

Abstract: Metals released during fossil fuel use are important atmospheric pollutants. Mercury and other trace metals can be transferred to an aquatic environment through atmospheric deposition. In the work reported here, a number of sediment cores were retrieved from central Texas lakes in the proximity of a coal-fired power plant in search of local anthropogenic effects. Cores were collected along a transient parallel to the prevailing wind direction (S-SE) in the area. Trace element concentrations in the lignite and in effluents from the power plant showed that some elements remained constant (Al, Cu) throughout the different lignite combustion and power production processes. Some (like Cd and Se) showed an affinity for the smaller particles, whereas others (Hg) showed very low concentrations in all the solid wastes, indicating that they probably escaped with the flue gases. *Sediment cores from a lake next to the power plant showed higher trace metal concentration in the upper part of the cores (more recent sediment). For example, there was as much as a tenfold increase in Hg concentration between the core bottom (10 ng/g), where the sediment was approximately 100 years old and the surface (100 ng/g). Cd and Se at surface sediments were also found to be as high as 1.6 and 3.45 µg/g, respectively. The excess metal inventory was higher for the lakes located next to the power plant than for two lakes about 30 km away.*

Mukherjee, A.B., and Zevenhoven, R. 2006. Mercury in coal ash and its fate in the Indian subcontinent: A synoptic review. *Science of the Total Environment* 368: 384-392.

Abstract: In the Indian subcontinent power generation is mainly dependent upon the thermal power units and coal is burnt as a fuel for the production of heat and electricity. In India, bituminous and sub-bituminous coals are used which contain over 40% of ash. At present, 80-90 million tons of fly ashes are generated from 85 existing coal based thermal power plants. Coal contains trace metals of which mercury is most toxic for humans and aquatic fauna. The problem of mercury in the society is not new, but in recent years the Indian subcontinent has gained the reputation of being "a dumping ground for mercury". This study focuses on mercury in fly ash and its releases to the atmosphere and soils cross the country. The utilisation of coal ash in India is also addressed although it is still in its nascent stage. About 10% of produced fly ashes are used in India whereas in Western countries its use is typically over 70%. Regulations from India's Ministry of Environment and Forestry should increase coal fly ash utilisation, although this would require that cost-effective new technology is put to use. As to the release of Hg from ashes disposed of in the environment, the scarce literature suggests that this is negligible or zero, and less problematic than wet or dry deposition of Hg from flue gases.

Murray, M., and S. A. Holmes. 2004. Assessment of mercury emissions inventories for the Great Lakes states. *Environmental Research* 95:282-297.

Abstract: Anthropogenic mercury (Hg) air emissions for the eight Great Lakes states in 1999-2000 were evaluated by analyzing three inventories. The US Environmental Protection Agency (EPA) National Emissions Inventory (NEI) had the most complete coverage for all states, and total Hg emissions ranged from 4226 lb in Minnesota to 15,828 lb in Pennsylvania. Coal-fired electric utilities accounted for 52.7% of the region's Hg emissions, varying from 20.2% of the total in New York to 67.5% in Ohio. Other important contributors to regional emissions included

municipal waste combustion (5.6%), mercury-cell chlor-alkali plants and hazardous-waste incinerators (4% each), stationary internal combustion engines (ICEs) (3.5%), industrial, commercial, and institutional (ICI) boilers (3.3%), and lime manufacturing (3.0%). Although medical waste incineration accounted for just over 1% of regional emissions using the original classifications, the inclusion of health care facilities that may have been inappropriately identified with other sectors would increase the sector to 4.5% of regional emissions (and decrease the stationary ICE sector to 1.4% of the regional total). There were substantial differences for some sectors between the NEI and the Great Lakes Regional Air Toxics Emissions Inventory (GLEI), as well as unexplained differences within inventories between states (particularly for the cement, lime, and asphalt industries, and for lamp breakage). Toxics Release Inventory data for 2000 mainly covered electric utilities, and differences from the NET were significant for several states. An independent assessment indicates the possibility of underestimated Hg emissions by about twofold for ICI boilers, although data for the sector (in particular concerning fuel oil emissions) are highly uncertain. Limited data indicate the likelihood of significant underestimates of electric furnace mercury emissions in the NEI and GLEI inventories. Several measures are here identified for improving the reliability of the inventories, both for modeling of atmospheric transport and deposition modeling and for tracking progress in Hg reduction initiatives.

Nelson, P.F. 2007. Atmospheric emissions of mercury from Australian point sources. *Atmospheric Environment* 41: 1717-1724.

Abstract: The UN Global Mercury Assessment (GMA) estimates that atmospheric emissions of mercury from Australian stationary combustion sources were 97.0 tonnes for the year of 1995. This is more than 90% of the estimated emissions from stationary combustion for the whole of North America, and seems abnormally high for a country with a population of around 20 million, in spite of the fact that most of Australia's stationary energy supply is provided by coal. It is also significantly larger than previous estimates of mercury emissions from Australian sources. New estimates of Australian mercury emissions from stationary energy sources, based on both a top down and bottom up approach, are presented. These estimates can be reconciled for black coal fired power stations, but suggest that the bottom up approach (the Australian National Pollutant Inventory) significantly under-estimates emissions from brown coal fired plant, if mercury capture efficiencies in these plants are low, as observed for lignite-fired plant. The major uncertainties in these estimates are the coal mercury content in coals burnt in Australian power stations, and the mercury capture efficiency in particulate control devices used at these stations. Based on these estimates, Australian emissions of mercury from stationary energy are currently 2-8 tonnes/year, significantly lower than the GMA estimate.

Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., and Panasiuk, D. 2006. Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. *Science of the Total Environment* 370: 147-156.

Abstract: The paper reviews the current state of knowledge regarding European emissions of mercury and presents estimates of European emissions of mercury to the atmosphere from anthropogenic sources for the year 2000. This information was then used as a basis for Hg emission scenario development until the year 2020. Combustion of coal in power plants and residential heat furnaces generates about half of the European emissions being 239 megatonnes. The coal combustion is followed by the production of caustic soda with the use of the Hg cell process (17%). Major points of mercury emission generation in the mercury cell process include: by-product hydrogen stream, end box ventilation air, and cell room ventilation air. This technology is now being changed to other caustic soda production technologies and further reduction of Hg emissions is expected in this connection. The third category on the list of the

largest Hg emitters in Europe is cement production (about 13%). The largest emissions were estimated for Russia (the European part of the country), contributing with about 27% to the European emissions, followed by Poland, Germany, Spain, Ukraine, France, Italy and the United Kingdom. Most of these countries use coal as a major source of energy in order to meet the electricity and heat demands. In general, countries in the Central and Eastern Europe generated the main part of the European emissions in 2000. Emission reductions between 20% and 80% of the 2000 emission amounts can be obtained by the year 2020, as estimated by various scenarios.

Park, K. S., Y. C. Seo, S. J. Lee, and J. H. Lee. 2008. Emission and speciation of mercury from various combustion sources. Powder Technology 180:151-156.

Abstract: Characterization of mercury emission and behavior from various stationary combustion processes were carried out for the major sources including coal-fired power plants and incinerators. Emission sampling and analysis of mercury at inlet and outlet of air pollution control devices (APCDs) for various sources have been made as the first attempt in Korea and now several institutions in governmental sectors are preparing the inventory on mercury. Speciation whether mercury forms are elemental or oxidized, was also studied by employing two different types of sampling method: Ontario Hydro(OH) method and US EPA 101 A. Mercury emission and speciation depended on the Hg concentration in the fuels, type of APCDs, and flue gas temperature and composition. Measurement results showed that elemental mercury (Hg⁰) was dominant at stack of coal power plants, while oxidized mercury was dominant at stack of incinerators, which could be due to the formation of mercury compounds in furnaces and APCDs configuration differences between them. The data for other sources were also obtained to understand the mercury emission. More intensive investigations were performed for a power plant and a municipal waste incinerator for observing the distribution of mercury at all the effluents. Mass balance of mercury in the process was figured out from the emission data and analysis results of mercury at all the in- and out-streams such as fuel (coals or wastes) fed, lime/lime stone, fly ash, bottom ash, gypsum and effluent water from wet flue-gas desulfurization (FGD). Approximate Hg mass balance could be obtained from sampled and analyzed data for those processes. However, a series of long-term and comprehensive studies are required to evaluate the reliable Hg distribution at coal-fired power plants and municipal waste incinerators. There were no significant differences between two sampling methods, but OH method seemed to have more advantage for Hg sampling from plants because mercury speciation was a very important factor for estimating the mercury emission and control efficiency from combustion flue gas.

Ren, J.L., Zhou, J.S., Luo, Z.Y., and Cen, K.F. 2002. Study of mercury emission during coal combustion. Zhejiang Daxue Xuebao (Gongxue Ban)/Journal of Zhejiang University (Engineering Science Edition) 36: 397-403.

Abstract: Mercury in the environment is a serious issue and mercury emission from coal-fired power plants is a major source of environmental pollution. This work was focused on the mechanism of mercury emission with different coal and reaction conditions. Firstly, the mercury content of the residual after coal combustion and pyrolysis was investigated with different temperature and heating time. The results indicate that mercury in coal during coal combustion discharge faster than during coal pyrolysis. Nearly all of the mercury in coal samples discharge rapidly in the high temperature (above 700°C) during coal combustion or pyrolysis. Secondly, the experiments were carried out in a fixed-bed combustor and a bench-scale pulverized coal combustor. The experimental data showed that the speciation of mercury occurring under the above two systems were similar, but results from the latter are close to that from utility boilers. It shows that the gaseous mercury concentrations in the flue gas range from 10 and 15 (µg/Nm³), and that the content of Hg₂₊ in the flue gas was about 40%. The content of mercury in the ash

was below 20%, which suggested that most of the mercury went into the flue gas in gaseous state. These findings are similar to results reported from literature. In addition, the cooling rate of hot flue gas is considered to be an important factor tending to increase the conversion ratio of elemental mercury (Hg⁰) to divalent mercury (Hg²⁺) with slower cooling rate.

Schuster, P.F., Krabbenhoft, D.P., Naftz, D.L., Cecil, L.D., Olson, M.L., DeWild, J.F., Susong, D.D., Green, J.R., and Abbott, M.L. 2002. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. *Environmental Science & Technology* 36: 2303-2310.

Abstract: Mercury (Hg) contamination of aquatic ecosystems and subsequent methylmercury bioaccumulation are significant environmental problems of global extent. At regional to global scales, the primary mechanism of Hg contamination is atmospheric Hg transport. Thus, a better understanding of the long-term history of atmospheric Hg cycling and quantification of the sources is critical for assessing the regional and global impact of anthropogenic Hg emissions. Ice cores collected from the Upper Fremont Glacier (UFG), Wyoming, contain a high-resolution record of total atmospheric Hg deposition (ca. 1720-1993). Total Hg in 97 ice-core samples was determined with trace-metal clean handling methods and low-level analytical procedures to reconstruct the first and most comprehensive atmospheric Hg deposition record of its kind yet available from North America. The record indicates major atmospheric releases of both natural and anthropogenic Hg from regional and global sources. Integrated over the past 270-year ice-core history, anthropogenic inputs contributed 52%, volcanic events 6%, and background sources 42%. More significantly, during the last 100 years, anthropogenic sources contributed 70% of the total Hg input. Unlike the 2-7-fold increase observed from preindustrial times (before 1840) to the mid-1980s in sediment-core records, the UFG record indicates a 20-fold increase for the same period. The sediment-core records, however, are in agreement with the last 10 years of this ice-core record, indicating declines in atmospheric Hg deposition.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., and Scott, C. 2004. Modeling the atmospheric fate and transport of mercury over North America: power plant emission scenarios. *Fuel Processing Technology* 85: 441-450.

Abstract: A multiscale modeling system that consists of a global cycling model and a continental-scale model, TEAM, is applied to simulate the fate and transport of mercury over North America. The performance of the modeling system is shown to be satisfactory. TEAM is used to simulate three coal-fired power plant emission control scenarios that correspond to 47%, 30% and 16% reductions in mercury emissions from the 1999 base case. Changes in total mercury deposition are less than 10% over most of the United States. The latter two scenarios that include subcategorization of power plants by coal rank and stack temperature show little effect on mercury deposition compared to the first scenario.

Wangberg, I., Munthe, J., Berg, T., Ebinghaus, R., Kock, H.H., Temme, C., Bieber, E., Spain, T.G., and Stolk, A. 2007. Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area. *Atmospheric Environment* 41: 2612-2619.

Abstract: An evaluation of mercury observations from North Sea coastal stations during 1995-2002 has been performed. The mercury data originate from EMEP/OSPAR stations in Ireland, Netherlands, Germany, Norway and Sweden where mercury in precipitation and Total Gaseous Mercury (TGM) have been measured. A decreasing trend in mercury wet deposition is observed. The decrease is sufficiently large to be significant considering measurement precision and appears to occur at all the studied sites. The reduction in deposition is 10-30% when comparing the two periods 1995-1998 and 1999-2002. The trend is likely to be due to emission controls in Europe. In contrast, no decreasing trend in TGM could be observed during the same time periods.

A plausible explanation is that the TGM concentration measured in the OSPAR area to a larger extent than before is dominated by the hemispherical background concentration of TGM.

Wong, C.S.C., Duzgoren-Aydin, N.S., Aydin, A., and Wong, M.H. 2006. Sources and trends of environmental mercury emissions in Asia. Science of the Total Environment 368: 649-662.

Abstract: This paper focuses on environmental mercury emissions in Asia and elaborates its probable trend in the future and associated implications given the anticipated socioeconomic outlook and other macro-environmental factors. Among the various regions, Asia has become the largest contributor of anthropogenic atmospheric Hg, responsible for over half of the global emission. In the next few decades, a significant increase in anthropogenic Hg emissions in Asia is likely owing to rapid economic and industrial development, unless drastic measures are taken. In particular, the dominance of Asia in some Hg-emitting industries, such as coal combustion, steel production and gold mining, provokes a serious environmental concern over their potential contributions of incidental Hg in the region. Moreover, the increasing prevalence of electrical and electronic manufacturing industry as a user and a contributor of Hg in Asia is also worrying. Specifically, disposal of obsolete electrical and electronic wastes represents a phenomenon increasingly encountered in Asia. In addition to escalating anthropogenic Hg emissions in Asia, associated environmental and health implications may also exacerbate in the region for the probable effects of a unique combination of climatic (e.g. subtropical climate), environmental (e.g. acid rain) and socioeconomic factors (e.g. high population density). Hence, much effort is still needed to understand the role of Asia in global Hg cycle and associated environmental and health effects in the region.

Yan, R., D. T. Liang, and J. H. Tay. 2003. Control of mercury vapor emissions from combustion flue gas. Environmental Science and Pollution Research 10:399-407.

Goal, Scope and Background. Mercury (Hg) emission from combustion flue gas is a significant environmental concern due to its toxicity and high volatility. A number of the research efforts have been carried out in the past decade exploiting mercury emission, monitoring and control from combustion flue gases. Most recently, increasing activities are focused on evaluating the behavior of mercury in coal combustion systems and developing novel Hg control technologies. This is partly due to the new regulatory requirement on mercury emissions from coal-fired combustors to be enacted under the U.S. Title III of the 1990 Clean Air Act Amendments. The aim of this review work is to better understand the state-of-the-art technologies of flue gas mercury control and identify the gaps of knowledge hence areas for further opportunities in research and development. Main Features. This paper examines mercury behaviors in combustion systems through a comprehensive review of the available literature. About 70 published papers and reports were cited and studied. Results and Discussion. *This paper summarizes the mechanisms of formation of mercury containing compounds during combustion, its speciation and reaction in flue gas, as well as subsequent mobilization in the environment.* It also provides a review of the current techniques designed for real-time, continuous emission monitoring (CEM) for mercury. Most importantly, current flue gas mercury control technologies are reviewed while activated carbon adsorption, a technology that offers the greatest potential for the control of gas-phase mercury emissions, is highlighted. Conclusions and Recommendations. Although much progress has been achieved in the last decade, techniques developed for the monitoring and control of mercury from combustion flue gases are not yet mature and gaps in knowledge exist for further advancement. More R&D efforts are required for the effective control of Hg emissions and the main focuses are identified.

Yang, X. H., Y. Q. Zhuo, Y. F. Duan, L. Chen, L. G. Yang, L. A. Zhang, Y. M. Jiang, and X. C. Xu. 2007. Mercury speciation and its emissions from a 220 MW pulverized coal-fired boiler power plant in flue gas. Korean Journal of Chemical Engineering 24:711-715.

Distributions of mercury speciation of Hg⁰, Hg²⁺ and Hg-P in flue gas and fly ash were sampled by using the Ontario Hydro Method in a 220 MW pulverized coal-fired boiler power plant in China. The mercury speciation was varied greatly when flue gas going through the electrostatic precipitator (ESP). The mercury adsorbed on fly ashes was found strongly dependent on unburnt carbon content in fly ash and slightly on the particle sizes, which implies that the physical and chemical features of some elemental substances enriched to fly ash surface also have a non-ignored effect on the mercury adsorption. The concentration of chlorine in coal, oxygen and NO_x in flue gas has a positive correlation with the formation of the oxidized mercury, but the sulfur in coal has a positive influence on the formation of elemental mercury.

Yang, L., Duan, Y., Yang, X., Jiang, Y., Wang, Y., and Zhao, C. 2007. Mercury emission characteristics from coal-fired power plants. Dongnan Daxue Xuebao 37: 817-821.

Abstract: To evaluate the mercury emissions, and to comprehend and compare the speciation characteristics of mercury in different power plants, six representative coal-fired power plants were selected, of which there were five pulverized coal boilers and one circulating fluidized bed boiler, whose capacities ranged from 50 MW to 600 MW with different flue gas cleaning up devices such as electrostatic precipitator (ESP), fabric filter (FF) and flue gas desulfurization (FGD). Samples of feeding coal, bottom ash, fly ash, desulfurization sorbent and flue gas were taken at the inlet and outlet of pollution control devices from the six different coal-fired power plants. The results of mercury emission and mercury balance show that the mercury speciation distribution changes greatly depending on coal types, combustion boilers and different air pollution control devices (APCD). The fly ash exerts different influences on mercury adsorption, and the chlorine content in flue gas can convert more oxidized mercury. It is shown that circulating fluidized bed combustion (CFBC) can decrease the total gaseous mercury emission, however the mechanism needs to be further investigated.

Yudovich, Y., and Ketris, M.P. 2005. Mercury in coal: A review. Part 1. Geochemistry. International Journal of Coal Geology 62: 107-134.

Abstract: This is the first of two papers that review approximately 200 publications on mercury (Hg) in coal; topics reviewed in this paper include: (a) analytical and historical introduction; (b) some peculiarities of Hg environmental geochemistry; (c) estimation of the Hg coal Clarke value; (d) occurrence of high-Hg coals; (e) mode of Hg occurrence in coal; (f) factors influencing the distribution of Hg in coal; and (g) origins of Hg in coal. Aspects of the environmental impact of Hg due to coal combustion and coking are noted throughout the review, and are more fully examined in second and final paper of this review. The Clarke value for Hg in coal (world-wide average Hg content) is 0.10 (±0.01) ppm Hg, regardless of coal rank. However, if the Hg content is expressed on an ash basis, bituminous rank coals average 0.87 (±0.08) ppm Hg, and lower rank coals average 0.62 (±0.06) ppm. In general, Hg is a very "coalophile" element; that is, it has a strong affinity for organic and inorganic coal matter, but is obligatory authigenic. There are some coals that are enriched in Hg by 1 to 2 orders of magnitude above the Clarke value. Such coals are located in the Donbas (Ukraine), Appalachian basin and Texas (USA), Russian Far East, and Southern China. Mercury in these coals is usually accompanied by other chalcophile trace elements. In low-sulfur coals, which are generally poor in Hg, only two Hg sites dominate: Hg^{org} and Hg₂S (commonly pyritic mercury, Hg₂pyr). High-sulfur coals usually contain higher amounts of Hg, which is typically in the Hg₂pyr form. In the unique Hg-enriched Donbas coals, both HgS and metallic mercury (Hg⁰) also occur. Because of the extremely strong affinity of Hg²⁺ for humic matter, it is theoretically possible for syngenetic (or early epigenetic) Hg to

accumulate in peats and lignites. Indeed, the amount of Hg in some tropic and moderate zone peats is greater than or equal to the Hg content of typical coal. Until the recent discovery of syngenetic volcanic Hg accumulations in Canadian coals, such Hg accumulations in coal were unknown. The most important type of Hg enrichment in coals is an epigenetic, low-temperature hydrothermal process; the Nikitovka (Ukraine), Warrior (USA), and Guizhou (China) basins are good examples. In the two latter coal basins, the paragenetic association Hg-As-Au-Tl is similar to Carlin-type Au deposits. The most notably Hg-rich basin is the Donbas-Donetsk coal basin situated in the Ukraine and Russia. Numerous coalfields in the Donbas are enriched in Hg by one order of magnitude above the coal Clarke level. The Hg in the Donbas was due to hydrothermal mineralization passing through sheared zones. The extraction and use of Hg-bearing Donbas coals have created very difficult environmental problems for the Ukrainian people.

Yudovich, Y., and Ketris, M.P. 2005. Mercury in coal: A review Part 2. Coal use and environmental problems. *International Journal of Coal Geology* 62: 135-165.

Abstract: During combustion of pulverized coals, most of the Hg volatilizes. Variable amounts of Hg are captured by fly ash and essentially none accumulates in the bottom ash. Hg is emitted to the atmosphere as gaseous (dominate) and solid-phase (subordinate) pollutants. Because of the high toxicity of Hg and its compounds, it is desirable to reduce the Hg content of coals prior to utilization and in the process of combustion. There are several ways to achieve reduction: selective mining of low-sulfur and low-Hg coals; standard coal cleaning through pyrite removal; also, a rejection of coarse, often pyrite-rich, material in pulverization at power plant can be added; perhaps, combustion of some coarser-grained coals, which will lead to more Hg capture through the formation of unburned char particles in fly ash; change of combustion regime by lowering flue gas temperatures and increasing Hg capture on collected fly ash (low-NO_x burners and other devices); oxidation of elemental Hg in flue gases to more capturable HgCl₂ through the combustion of Cl-bearing coals and in ECO process; the wider use of dry and wet scrubber systems for flue gas desulfurization and Hg capture; the greater use of carbon sorbent injection into flue gas ducts for better Hg capture, and, especially, use of modified carbon sorbents with more capacity for Hg; the use of some other very promising sorbents and filters, especially of FF type (fabric filters) as more effective scavengers of Hg than ESPs (electrostatic precipitators). Because of the potentially serious environmental impacts, additional research is required on the Hg geochemistry of coals.

Zhang, L., and Wong, M.H. 2007. Environmental mercury contamination in China: Sources and impacts. *Environment International* 33: 108-121.

Abstract: This review article focused on the current status of mercury (Hg) contamination in different ecological compartments in China, and their possible environmental and health impacts, focusing on some major cities. Mercury emission from non-ferrous metals smelting (especially zinc smelting), coal combustion and miscellaneous activities (of which battery and fluorescent lamp production and cement production are the largest), contributed about 45%, 38% and 17%, respectively, to the total Hg emission based on the data of 1999. Mercury contamination is widespread in different ecological compartments such as atmosphere, soil and water. There is evidence showing bioaccumulation and biomagnification of Hg in aquatic food chains, with higher concentrations detected in carnivorous fish. In terms of human exposure to Hg, fish consumption is the major exposure pathway for residents living in coastal cities such as Hong Kong, but inhalation may be another major source, affecting human health in areas with severe atmospheric Hg, such as Guiyang City (Guizhou Province). The first case study indicated that after closure of the acetic acid plant 20 years at Songyuan City (Jilin Province), 16.7% of residents' hair still contained Hg concentration in excess of 1 mg/kg (the reference dosage value, RfD set by USEPA). The second case study indicated that the male residents of Hong Kong who

consumed more than four or more meals of fish per week tended to contain higher Hg in their hair, which was linked to their subfertility. There is also increasing evidence showing that skin disorders and autism in Hong Kong children are related to their high Hg body loadings (hair, blood and urine), through prenatal methyl Hg exposure. There seems to be an urgent need to identify the sources of Hg, speciation and concentrations in different ecological compartments, which may lead to high body loadings in human beings. Adverse health effects of residents living in places with a higher background level of Hg, due to long-term exposure to chronic levels of Hg through oral intake should not be overlooked.

Zheng, L., Liu, G., and Chou, C.L. 2007. The distribution, occurrence and environmental effect of mercury in Chinese coals. *Science of the Total Environment* 384: 374-383.

Abstract: Mercury (Hg) is a toxic, persistent, and globally distributed pollutant due to its characteristic properties such as low melting and boiling points, conversion between chemical forms and participation in biological cycles. During combustion mercury in coal is almost totally emitted to the atmosphere. With a huge amount of coal consumed, coal combustion is one of the main anthropogenic sources of this element in the environment. In this study, Hg data of 1699 coal samples of China has been compiled, and the concentration, distribution, modes of occurrence, and the impact of Hg emissions on the environment are investigated. Most Chinese coals have Hg content in the range of 0.1 to 0.3ppm, with an average of 0.19 ppm, which is slightly higher than the average Hg content of world coals and is close to that of the U.S. coals. The Hg content in coals varies in different coal basins, geological ages and coal ranks. The most likely mode of occurrences of Hg in high-sulfur and high Hg content coals is as solid solution in pyrite. But in low-sulfur coals, modes of occurrence of Hg are variable, and the organic-bound and sulfide-bound Hg may dominate. Silicate-bound Hg may be the main form in some coals because of magmatic intrusion. Mercury emissions during coal combustion have resulted in serious environmental contamination in China, particularly in the northeastern and southwestern China, where a high Hg content in the atmosphere occurs.

2.1.2 *Environmental effects and biomonitoring*

Basu, N., Scheuhammer, A., Grochowina, N., Klenavic, K., Evans, D., O'Brien, M., and Chan, H.M. 2005. Effects of mercury on neurochemical receptors in wild river otters (*Lontra canadensis*). *Environmental Science & Technology*. 39: 3585-3591.

Abstract: Fish-eating wildlife, such as river otters (*Lontra canadensis*), accumulate mercury (Hg) at concentrations known to impair animal behavior, but few studies have explored the underlying biochemical changes that precede clinical neurotoxicity. The objective of this study was to determine if Hg exposure can be related to concentrations of neurochemical receptors in river otters. River otter carcasses (n = 66) were collected in Ontario and Nova Scotia (Canada) by local trappers in 2002-2004. Concentrations of Hg (total and organic) were measured in the cerebral cortex and cerebellum. Saturation binding curves for the cholinergic muscarinic acetylcholine (mACh) receptor and dopamine-2 (D2) receptor were completed for each animal to calculate receptor density (B max) and ligand affinity (Kd). Negative correlations were found between concentrations of Hg and mACh receptor Bmax (r total Hg = -0.458, r inorganic Hg = -0.454, r organic Hg = -0.443) in the cerebral cortex. A negative correlation was also found between concentrations of total Hg and D2 receptor B max (r = -0.292) in the cerebral cortex. *These results suggest that neurochemical receptors may prove useful as novel biomarkers of Hg exposure and neurotoxic effects in wildlife. Given the importance of cholinergic and dopaminergic systems in animal physiology, the ecological implications of these changes need to be investigated.*

Burgess, N.M., Evers, D.C., and Kaplan, J.D. 2005. Mercury and other contaminants in common loons breeding in Atlantic Canada. *Ecotoxicology* 14: 241-252.

Abstract: Common loons (*Gavia immer*) were studied to assess the biomagnification of persistent contaminants in lake ecosystems in Atlantic Canada. Forty-two breeding adults and 20 juvenile loons were captured in August, 1995-1997 on lakes in four areas of southern New Brunswick (Lepreau and Fundy National Park) and Nova Scotia (Halifax and Kejimikujik National Park). Blood samples were collected for analysis of mercury, methylmercury, lead, and selenium. Plasma samples from adult loons were analyzed for PCB congeners and organochlorine pesticides. Secondary flight feathers were collected from adult loons for mercury analysis. Kejimikujik loons had significantly higher geometric mean concentrations of mercury in blood (adults: 5.5 µg/g, wet wt) and feathers (adults: 15 µg/g, fresh wt), and higher levels of PCBs, DDE, oxychlorane, trans-nonachlor, mirex and hexachlorobenzene than loons at Halifax or Lepreau. Blood selenium levels were lowest in Kejimikujik loons. Selenium and mercury concentrations were negatively related in blood of adults across all sites. Adult males had higher concentrations of mercury in blood and feathers and PCBs, DDE, and oxychlorane in plasma, and lower levels of selenium in blood, than adult females. Juvenile loons had lower blood mercury and selenium concentrations than adults. Several contaminants showed significant inter-lake variation within the study sites. Mean blood mercury concentrations in Kejimikujik loons are the highest found in breeding common loons across North America. Of adult loons at Kejimikujik, 92% had blood mercury levels >4 µg/g (wet wt), which have been associated with impaired reproduction, elevated corticosterone levels, asymmetry in plumage development, and altered breeding behavior in loons there and elsewhere.

Champoux, L., Masse, D.C., Evers, D., Lane, O.P., Plante, M., and Timmermans, S.T.A. 2006. Assessment of mercury exposure and potential effects on common loons (*Gavia immer*) in Quebec. *Hydrobiologia* 567: 263-274.

Abstract: Results from recent studies report increases in mercury in the environment and increased bioaccumulation in aquatic food webs. The Canadian Wildlife Service (CWS) and the Canadian National Park Service initiated this study to determine whether common loons (*Gavia immer*) are exposed to sufficiently high mercury concentrations in prey fish to impair their reproduction and survival. Monitoring of loon reproduction, measurement of lake physicochemistry, and fish sampling for mercury analysis were conducted in various regions in Quebec, Canada, during summers from 1997 to 2002. Reproductive success was assessed and loons were captured at night and banded. Blood and feathers were collected to measure mercury. Mean blood and feather Hg concentrations in males (2.6 µg/g w.w and 17.6 µg/g d.w.) and females (1.8 µg/g w.w and 8.9 µg/g d.w.) were within the normal range of samples from north-eastern North America. However, one third (33%) of the loons sampled had mercury levels in blood or feathers exceeding the high risk levels for health and reproduction. Loons from western Quebec showed significantly lower Hg levels than those from eastern Quebec, both in blood and feathers. *This study will help to determine the potential effects of mercury on the Quebec and North-American loon population and provide information to assist in decisions on pollution abatement policies.*

Devlin, E.W. 2006. Acute toxicity, uptake and histopathology of aqueous methyl mercury to fathead minnow embryos. *Ecotoxicology* 15: 97-110.

Abstract: Early life stages of fishes have been shown to be especially susceptible to the toxic effects of heavy metal pollution. In this study, fathead minnow (*Pimephales promelas*) embryos were exposed in the laboratory to a graded series of aqueous methyl mercury concentrations under continuous-flow conditions. A number of toxicological endpoints were examined including; acute toxicity, bioaccumulation, protein production, impact on mitosis, gross and histopathology. Acute toxicity, reported as LC50 values of methyl mercury, ranged from 221 µg/l (95% C.I. 246-196 µg/l) for 24-h tests to 39 µg/l (95% C.I. 54-24 µg/l) for 96-h exposures.

Fathead minnow embryos were shown to rapidly take up mercury from the surrounding water. Mercury levels in embryos reached levels of 2.80 µg/g wet weight after 96 h exposure to 40 µg/l methyl mercury. An initial elevation of total protein in embryo was observed in embryos exposed to 25 µg/l methyl mercury during the first 12 h of development. At later stages, significantly lower levels of protein/µg embryo were observed. Methyl mercury had no effect on mitotic stages ($p = 0.05$) in early, cleaving blastulastage embryos. Live embryos and serial sections were utilized to characterize changes in embryo morphology and histopathology.

Drevnick, P.E., Canfield, D.E., Gorski, P.R., Shinneman, A.L.C., Engstrom, D.R., Muir, D.C.G., Smith, G.R., Garrison, P.J., Cleckner, L.B., Hurley, J.P., Noble, R.B., Otter, R.R., and Oris, J.T. 2007. Deposition and cycling of sulfur controls mercury accumulation in Isle Royale fish. *Environmental Science & Technology* 41: 7266-7272.

Abstract: Mercury contamination of fish is a global problem. Consumption of contaminated fish is the primary route of methylmercury exposure in humans and is detrimental to health. Newly mandated reductions in anthropogenic mercury emissions aim to reduce atmospheric mercury deposition and thus mercury concentrations in fish. However, factors other than mercury deposition are important for mercury bioaccumulation in fish. In the lakes of Isle Royale, U.S.A., reduced rates of sulfate deposition since the Clean Air Act of 1970 have caused mercury concentrations in fish to decline to levels that are safe for human consumption, even without a discernible decrease in mercury deposition. Therefore, reductions in anthropogenic sulfur emissions may provide a synergistic solution to the mercury problem in sulfate-limited freshwaters.

Frescholtz, T.F., Gustin, M.S., Schorran, D.E., and Fernandez, G.C.J. 2003. Assessing the source of mercury in foliar tissue of quaking aspen. *Environmental Toxicology and Chemistry* 22: 2114-2119.

Abstract: Foliar accumulation of mercury has been demonstrated to occur as plants leaf out, yet the primary source of this mercury is not known. Using closed-system growth chambers, uptake of mercury by quaking aspen (*Populus tremuloides*) foliage was measured over time as a function of soil mercury concentrations (0.01, 6.2, and 25.6 µg/g) and atmospheric mercury exposure concentrations (1.4, 14.9, and 68.5 ng/m³). Foliar mercury concentrations increased as a function of time for all exposures. Twice during the experiment, leaf washes were analyzed for mercury to assess surface deposition, and little mercury was removed (0.02-0.04 ng/m²), suggesting that direct deposition to the leaf surface was not significant during this experiment. At the end of the four-month experiment, whole-plant mercury concentrations were determined. It was found that whereas mercury in the atmosphere primarily influenced foliar uptake, root concentrations were related to the soil mercury concentration. The implication of this study is that litterfall may serve as a pathway for new, atmospherically derived mercury to be deposited to forest soils. This has significant implications for watershed management of ecosystems where mercury is of concern

Harris, R.C., Rudd, J.W.M., Amyot, M., Babiarz, C.L., Beaty, K.G., Blanchfield, P.J., Bodaly, R.A., Branfireun, B.A., Gilmour, C.C., Graydon, J.A., Heyes, A., Hintelmann, H., Hurley, J.P., Kelly, C.A., Krabbenhoft, D.P., Lindberg, S.E., Mason, R.P., Paterson, M.J., Podemski, C.L., Robinson, A., Sandilands, K.A., Southworth, G.R., Louis, V.L., and Tate, M.T. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proceedings of the National Academy of Sciences of the United States of America* 104: 16586-16591.

Abstract: Methylmercury contamination of fisheries from centuries of industrial atmospheric emissions negatively impacts humans and wildlife worldwide. The response of fish methylmercury concentrations to changes in mercury deposition has been difficult to establish

because sediments/soils contain large pools of historical contamination, and many factors in addition to deposition affect fish mercury. To test directly the response of fish contamination to changing mercury deposition, we conducted a whole-ecosystem experiment, increasing the mercury load to a lake and its watershed by the addition of enriched stable mercury isotopes. The isotopes allowed us to distinguish between experimentally applied mercury and mercury already present in the ecosystem and to examine bioaccumulation of mercury deposited to different parts of the watershed. Fish methylmercury concentrations responded rapidly to changes in mercury deposition over the first 3 years of study. Essentially all of the increase in fish methylmercury concentrations came from mercury deposited directly to the lake surface. In contrast, <1% of the mercury isotope deposited to the watershed was exported to the lake. Steady state was not reached within 3 years. Lake mercury isotope concentrations were still rising in lake biota, and watershed mercury isotope exports to the lake were increasing slowly. Therefore, we predict that mercury emissions reductions will yield rapid (years) reductions in fish methylmercury concentrations and will yield concomitant reductions in risk. However, a full response will be delayed by the gradual export of mercury stored in watersheds. The rate of response will vary among lakes depending on the relative surface areas of water and watershed.

Hope, B. 2003. A basin-specific aquatic food web biomagnification model for estimation of mercury target levels. *Environmental Toxicology and Chemistry* 22: 2525-2537.

Abstract: In the Willamette River Basin (WRB, Oregon, USA), health advisories currently limit consumption of fish that have accumulated methylmercury (MeHg) to levels posing a potential health risk for humans. Under the Clean Water Act Water Act, these advisories create the requirement for a total maximum daily load (TMDL) for mercury in the WRB. A TMDL is a calculation of the maximum amount of a pollutant that a body of water can receive and still meet water-quality standards. Because MeHg is known to biomagnify in aquatic food webs, a basin-specific biomagnification factor can be used, given a protective fish tissue criterion, to estimate total mercury concentrations in surface waters required to lower advisory mercury concentrations currently in fish in the WRB. This paper presents an aquatic food web biomagnification model that simulates inorganic mercury (Hg(II)) and MeHg accumulation in fish tissue and estimates WRB-specific biomagnification factors for resident fish species of concern to stakeholders. Probabilistic (two-dimensional Monte Carlo) techniques propagate parameter variability and uncertainty throughout the model, providing decision makers with credible range information and increased flexibility in establishing a specific mercury target level. The model predicts the probability of tissue mercury concentrations in eight fish species within the range of concentrations measured in these species over 20 years of water-quality monitoring. Estimated mean biomagnification factor values range from 1.12×10^6 to 7.66×10^6 and are within the range of U.S. Environmental Protection Agency national values. Several WRB-specific mercury target levels are generated, which vary by their probability of affording human health protection relative to the federal MeHg tissue criterion of 0.30 mg/kg. Establishing a specific numeric target level is, however, a public policy decision, and one that will require further discussions among WRB stakeholders.

Hrabik, T.R., and Watras, C.J. 2002. Recent declines in mercury concentration in a freshwater fishery: Isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. *Science of the Total Environment* 297: 229-237.

Abstract: The atmospheric deposition of H⁺, SO₄, and Hg to Little Rock Lake in northern Wisconsin has declined substantially during the past decade. Parallel decreases have been observed in the surface waters of the lake. Here we extend the observations to the fish community and we present evidence of a contemporaneous decline in levels of Hg in fish tissue. By comparing data from two separated basins of the lake, we then make an initial effort to isolate and

quantify the relative importance of de-acidification and reduced Hg deposition on mercury contamination in fish. Statistical modeling indicates that fish Hg in both basins decreased by roughly 30% between 1994 and 2000 (-5%/y) due to decreased atmospheric Hg loading. De-acidification could account for an additional 5% decrease in one basin (-0.8%/y) and a further 30% decrease in the other basin (-5%/y), since the basins de-acidified at very different rates. These results are consistent with the hypothesis that depositional inputs of SO₄ and Hg(II) co-mediate the biosynthesis of methyl mercury and thereby co-limit bioaccumulation. And they suggest that modest changes in acid rain or mercury deposition can significantly affect mercury bioaccumulation over short-time scales.

Kraepiel, A.M.L., Keller, K., Chin, H.B., Malcolm, E.G., and Morel, F.M.M. 2003. Sources and Variations of Mercury in Tuna. *Environmental Science & Technology* 37: 5551-5558.

Abstract: While the bulk of human exposure to mercury is through the consumption of marine fish, most of what we know about mercury methylation and bioaccumulation is from studies of freshwaters. We know little of where and how mercury is methylated in the open oceans, and there is currently a debate whether methylmercury concentrations in marine fish have increased along with global anthropogenic mercury emissions. Measurements of mercury concentrations in Yellowfin tuna caught off Hawaii in 1998 show no increase compared to measurements of the same species caught in the same area in 1971. On the basis of the known increase in the global emissions of mercury over the past century and of a simple model of mercury biogeochemistry in the Equatorial and Subtropical Pacific ocean, we calculate that the methylmercury concentration in these surface waters should have increased between 9 and 26% over this 27 years span if methylation occurred in the mixed layer or in the thermocline. Such an increase is statistically inconsistent with the constant mercury concentrations measured in tuna. We conclude tentatively that mercury methylation in the oceans occurs in deep waters or in sediments

Kuzmick, D.M., Mitchelmore, C.L., Hopkins, W.A., and Rowe, C.L. 2007. Effects of coal combustion residues on survival, antioxidant potential, and genotoxicity resulting from full-lifecycle exposure of grass shrimp (*Palaemonetes pugio* Holthius). *Science of the Total Environment* 373: 420-430.

Abstract: Coal combustion residues (CCRs), largely derived from coal-fired electrical generation, are rich in numerous trace elements that have the potential to induce sublethal effects including oxidative stress, alterations in antioxidant status and DNA single strand breaks (SSB). CCRs are frequently discharged into natural and man-made aquatic systems. As the effects of CCRs have received relatively little attention in estuarine systems, the estuarine grass shrimp, *Palaemonetes pugio*, was chosen for this study. Grass shrimp were exposed in the laboratory to CCR-enriched sediments and food over a full life cycle. Survival to metamorphosis was significantly reduced in CCR-exposed larvae (17 ± 4 versus 70 ± 13% in the controls) but not in the juveniles or adults. The COMET assay, a general but sensitive assay for genotoxicity, was used to quantify DNA SSB in the adults. Total antioxidant potential was examined to assess the overall antioxidant scavenging capacity of CCR-exposed and non-exposed adult grass shrimp. Grass shrimp exposed to CCR significantly accumulated selenium and cadmium compared to unexposed shrimp, although an inverse relationship was seen for mercury accumulation. Chronic CCR exposure caused DNA SSB in hepatopancreas cells, as evidenced by the significantly increased percent tail DNA, tail moment, and tail length as compared to reference shrimp. However, no significant difference was observed in total antioxidant potential. Our findings suggest that genotoxicity may be an important mode of toxicity of CCR, and that DNA SSB may serve as a useful biomarker of exposure and effect of this very common, complex waste stream.

Lopez Alonso, M., Benedito, J.L., Miranda, M., Fernandez, J.A., Castillo, C., Hernandez, J., and Shore, R.F. 2003. Large-scale spatial variation in mercury concentrations in cattle in NW Spain. *Environmental Pollution* 125: 173-181.

Abstract: Mercury (Hg) is a highly toxic environmental contaminant and man-made emissions account for between a quarter and a third of total atmospheric levels. Point discharges, particularly coal-burning power stations, are major sources of atmospheric Hg and can result in marked spatial variation in mercury deposition and subsequent uptake by biota. The aims of this study were to quantify the extent to which major point and diffuse sources of atmospheric Hg emissions affected accumulation of Hg by biota throughout Galicia and Asturias, two of the major regions in northwest Spain. We did this by relating renal Hg concentrations in locally reared cattle (n=284) to the proximity of animals to point and diffuse sources of Hg emissions. Mercury residues in calf kidneys ranged between non-detected and 89.4 ug/kg wet weight. *Point discharges from coal-fired power plants in Galicia had the most dominant impact on Hg accumulation by calves in Galicia, affecting animals throughout the region and explaining some two-thirds of the variation in renal residues between animals located directly downwind from the plants. The effects of more diffuse emission sources on Hg accumulation in calves were not distinguishable in Galicia but were detected in cattle from neighbouring Asturias. The impact of both point and diffuse sources in elevating environmental levels of bioavailable Hg and subsequent accumulation by cattle extended to approximately 140-200 km downwind from source.*

Odsjo, T., Roos, A., and Johnels, A.G. 2004. The tail feathers of osprey nestlings (*Pandion haliaetus* L.) as indicators of change in mercury load in the environment of southern Sweden (1969-1998): A case study with a note on the simultaneous intake of selenium. *Ambio* 33: 133-137.

Abstract: The tail feathers of 104 osprey nestlings (*Pandion haliaetus*) from Lake A?snen, southern Sweden, were analyzed for total mercury and selenium content. Concentrations of mercury in feathers from the western part of the lake fell during the period 1969-1998, when pollution from industrial mercury had decreased and a paper mill upstream of the lake was closed down in 1979. Nestlings from the eastern part of the lake had initially lower levels of mercury, predominantly from atmospheric fallout. The levels did not decrease during the period. The reason for the differences seems to be the limited water flow between the western and the eastern part of the lake. The selenium concentrations were constant over time and approximately the same in both parts of the lake. The total-Hg/Se ratio in the western part of the lake was 2.94, which is somewhat higher than the 1:1 molar ratio constant (2.54). This indicates that the bioaccumulated quantity of selenium which is thought to be protective for the organisms against the toxic effects of mercury, is somewhat insufficient to bind all body mercury.

Outridge, P.M., Hobson, K.A., McNeely, R., and Dyke, A. 2002. A comparison of modern and preindustrial levels of mercury in the teeth of beluga in the Mackenzie Delta, Northwest Territories, and walrus at Igloodik, Nunavut, Canada. *Arctic* 55: 123-132.

Abstract: Mercury (Hg) concentrations were compared in modern and preindustrial teeth of belugas (*Delphinapterus leucas*) and walrus (*Odobenus rosmarus rosmarus*) at sites in the Canadian Arctic so that the relative amounts of natural and anthropogenic Hg in modern animals could be estimated. Mercury levels in the teeth of Beaufort Sea belugas captured in the Mackenzie Delta, Northwest Territories, in 1993 were significantly ($p = 0.0001$) higher than those in archeological samples dated A.D. 1450-1650. In terms of geometric means, the Hg levels in modern animals were approximately four times as high as preindustrial levels in 10-year-old belugas, rising with age to 17 times as high in 30-year-olds. Because Hg levels in modern teeth were highly correlated with those in soft tissues, including muscle and muktuk, which are part of

traditional human diets, it is likely that soft-tissue Hg has increased to a similar degree over the past few centuries. The increase was not due to dietary differences over time, as shown by analysis of stable-C and -N isotopes in the teeth, and was unlikely to be due to sex differences or to chemical diagenesis of historical samples. Industrially related Hg inputs to the Arctic Ocean and Canadian Arctic Archipelago may be the most likely explanation for the increase. If so, then 80-95% of the total Hg in modern Beaufort Sea belugas more than 10 years old may be attributed to anthropogenic activities. In contrast, tooth Hg concentrations in walrus at Igloodik, Nunavut, were no higher in the 1980s and 1990s than in the period A.D. 1200-1500, indicating an absence of industrial Hg in the species at this location.

Paterson, M.J., Blanchfield, P.J., Podemski, C., Hintelmann, H.H., Gilmour, C.C., Harris, R., Ogrinc, N., Rudd, J.W.M., and Sandilands, K.A. 2006. Bioaccumulation of newly deposited mercury by fish and invertebrates: An enclosure study using stable mercury isotopes. *Canadian Journal of Fisheries and Aquatic Sciences* 63: 2213-2224.

Abstract: Enriched stable mercury (Hg) isotopes were added to four 10 m diameter enclosures in Lake 239 at the Experimental Lakes Area to increase inorganic Hg loading. Our main objectives were to (i) follow low-level additions (spikes) of isotope-enriched Hg through the biogeochemical cycle and into the food web and (ii) determine the relative contribution of newly deposited Hg to methyl Hg (MeHg) accumulation by fish and other biota. The experiment ran for two summers (2000, 2001), with different enriched Hg isotopes being added each year. Within 1 month of beginning additions in 2000, spike Hg was detected in water, zooplankton, and benthic invertebrates as MeHg, and in fish as total Hg (THg; the sum of inorganic and organic Hg). In 2001, concentrations in water of inorganic spike Hg added in 2000 were near detection limits, but concentrations of 2000 spike MeHg in water and biota remained unchanged or greater. Despite comparatively large increases in inorganic Hg loading, accumulation of ambient, non-spike MeHg predominated in all organisms, and spike MeHg never comprised more than 15%, even after 1 year. Our results suggest that changes in Hg loading will affect MeHg concentrations in fish and other biota, but that steady state may not be achieved for at least 10-30 years under conditions similar to our enclosures.

Rea, A.W., Lindberg, S.E., Scherbatskoy, T., and Keeler, G.J. 2002. Mercury accumulation in foliage over time in two northern mixed-hardwood forests. *Water Air and Soil Pollution* 133: 49-67.

Abstract: Concentrations of mercury (Hg) in live foliage increased ten-fold from spring bud break (mean \pm std. dev. from both sites: 3.5 \pm 1.3 ng g⁻¹) to autumn litterfall (36.8 ng g⁻¹). Mercury in foliage did not behave similarly to eight other elements with known soil or aerosol sources (Aluminum (Al), Vanadium (V), Strontium (Sr), Rubidium (Rb), Copper (Cu), Zinc (Zn), Barium (Ba), and lead (Pb)), suggesting that Hg originated from a distinct pathway. Based on measured and modeled data, uptake of only 25% of the available ambient dry deposited Hg₀ could explain all of the Hg measured in foliage throughout the growing season. Estimates of gaseous elemental Hg (Hg₀) uptake from soil water accounted for 3-14% of the Hg in litterfall. Mercury deposition to forested sites in the Lake Champlain and Lake Huron basins was highest in litterfall (40%), followed by total throughfall (33%), and precipitation (27%). The Hg flux in litterfall was 15.8 \pm 1.9 ug m⁻² yr⁻¹ to the Lake Champlain Watershed in 1995 and was 11.4 \pm 2.8 ug m⁻² yr⁻¹ to the Lake Huron Watershed in 1996. In comparison, the Hg fluxes in precipitation and total throughfall were 9.0 \pm 0.6 and 11.6 \pm 0.7 ug m⁻² yr⁻¹ in the Lake Champlain Watershed (1995), and 8.7 \pm 0.5 and 10.5 \pm 1.0 ug m⁻² yr⁻¹ in the Lake Huron Watershed (1996).

Rimmer, C.C., Mcfarland, K.P., Evers, D.C., Miller, E.K., Aubry, Y., Busby, D., and Taylor, R.J. 2005. Mercury concentrations in Bicknell's thrush and other insectivorous passerines in montane forests of northeastern North America. *Ecotoxicology* 14: 223-240.

Abstract: Anthropogenic input of mercury (Hg) into the environment has elevated risk to fish and wildlife, particularly in northeastern North America. Investigations into the transfer and fate of Hg have focused on inhabitants of freshwater aquatic ecosystems, as these are the habitats at greatest risk for methylmercury (MeHg) biomagnification. Deviating from such an approach, we documented MeHg availability in a terrestrial montane ecosystem using a suite of insectivorous passerines. Intensive and extensive sampling of Bicknell's thrush (*Catharus bicknelli*) indicated significant heterogeneity in MeHg availability across 21 mountaintops in northeastern North America. Southern parts of the breeding range tended to be at greater risk than northern parts. Mean blood Hg concentrations for Bicknell's thrush at 21 distinct breeding sites ranged from 0.08 to 0.38 ug/g (ww) and at seven Greater Antillean wintering sites ranged from 0.03 to 0.42 ug/g (ww). Overall concentrations were significantly greater in wintering than in breeding areas. Mercury exposure profiles for four passerine species on Mt. Mansfield, Vermont indicated greatest MeHg uptake in Bicknell's thrush and yellow-rumped warbler (*Dendroica coronata*) and lowest in blackpoll warbler (*Dendroica striata*) and white-throated sparrow (*Zonotrichia albicollis*). The MeHg and total Hg ratio in blood in these four species was nearly 1:1. There was no correlation between blood and feather Hg concentrations in breeding Bicknell's thrush, in part because of apparent retention of winter Hg body burdens, within-season variation of MeHg availability, and confounding factors such as influences from age. Adult thrushes had significantly higher concentrations of feather Hg than did young-of-the-year. Although individual patterns of inter-year feather Hg concentrations were disordered, some individuals exhibited bioaccumulation of MeHg. Female blood Hg concentrations were significantly lower than males', in part because females have additional depurating mechanisms through eggs. Older male Bicknell's thrushes that breed in New England are therefore likely at greatest risk. Mechanisms for Hg methylation in montane areas without standing water are not yet fully understood. However, recent studies indicate that MeHg is present in forest tree leaves and leaf detritus; saturated soils and other moist microhabitats may also contribute to MeHg availability. Our finding of a correlation between regional litterfall Hg flux patterns and Bicknell's thrush blood Hg concentrations demonstrates on-site availability of MeHg. Further investigations into MeHg availability in montane environments are recommended to assess risk to insectivorous passerines, particularly the Bicknell's thrush.

Sensen, M., and Richardson, D.H.S. 2002. Mercury levels in lichens from different host trees around a chlor-alkali plant in New Brunswick, Canada. *Science of the Total Environment* 293: 31-45.

Abstract: Mercury concentrations were determined in the epiphytic lichen *Hypogymnia physodes* along five transects starting from a chlor-alkali plant located at Dalhousie, New Brunswick, a landfill site and a nearby electricity generating station. Lichen samples were collected from white birch (*Betula papyrifera*) and spruce (*Picea* sp.) or balsam fir (*Abies balsamea*). Average lichen background mercury values were 0.088±0.005 ug/g from white birch and 0.148±0.046 ug/g from spruce trees, with a detection limit of 0.05 ug/g. The chlor-alkali plant and a power plant were identified, respectively, as a major source and a minor source of elevated mercury levels in lichens. *At 125 m north-west of the New Brunswick Power plant, 0.28 ug/g Hg were found in Hypogymnia physodes from spruce trees, while at 250 m west (downwind) of the chlor-alkali plant, 3.66 ug/g of mercury were determined.* High values, 0.98 ug/g in lichens from spruce trees and 0.79 ug/g in lichen samples from white birch were also measured at 125 m south of the chlor-alkali plant and decreased exponentially with distance. The sphere of influence of the chlor-alkali plant with respect to mercury deposition was estimated to extend 2.4-3.4 km

from the plant. The mercury concentrations in *Hypogymnia physodes* collected from white birch were significantly lower than the concentrations in the same lichen from spruce trees in areas with elevated levels of mercury, but not in areas with low mercury levels. The magnitude of this difference dropped with distance from the source.

Sullivan, T. M., Bowerman, B., Adams, J., Lipfert, F. D., Morris, S. M., Bando, A., Pena, R. and Blake, R. (2005) Local Impacts of Mercury Emissions from Coal Fired Power Plants.

Retrieved Dec 6, 2007 from

http://204.154.137.14/technologies/coalpower/ewr/air_quality_research/health_effects/pdfs/ImpactsHgAnnualreport_3-2005.pdf, BNL-73967-2005.

Sullivan, T. M., Adams, J., Milian, L., Subramanian, S., Feagin, L., Williams, J. and Boyd, A. (2007) Local Impacts of Mercury Emissions from the Monticello Coal Fired Power Plant.

Retrieved Jan 14, 2007 from <http://www.pubs.bnl.gov/documents/33077.pdf>.

Watras, C.J. and Morrison, K.A. 2008. The response of two remote, temperate lakes to changes in atmospheric mercury deposition, sulfate, and the water cycle. Canadian Journal of Fisheries and Aquatic Sciences 65 (1), p. 100-116.

Abstract: Atmospheric deposition is the ultimate source of Hg to many remote lakes, but the response to depositional change remains uncertain because of potential buffering by historical pools of Hg in sediments and soils. We investigated the responsiveness of two lakes over time scales ranging from weeks to decades. For waterborne Hg, results indicated that a precipitation-dominated seepage lake and a wetland-dominated drainage lake responded similarly to depositional change, despite high loadings of terrigenous matter to the drainage lake. For methylmercury (MeHg), the response was more complicated, reflecting the influence of multiple factors on in-lake methylation. In the seepage lake, waterborne meHg was correlated with the atmospheric deposition of Hg super(II) and SO sub(4), and there was an indirect dependence on the water cycle. In the drainage lake, although wetland export was always the dominant external source of meHg, mass balance indicated that net in-lake methylation was four- to seven-fold greater than loading from the wetland. However, in-lake MeHg production was related to the export of Hg super(II), SO sub(4), dissolved organic carbon, and P from the wetland to the lake. The results suggest that atmospheric Hg deposition, weather, and microbial activity interactively effect the aquatic mercury cycle in ways that can be independent of historical pools of Hg in catchments.

Weis, I.M. 2004. Mercury concentrations in fish from Canadian Great Lakes areas of concern: An analysis of data from the Canadian Department of Environment database. Environ. Res. 95: 341-350.

Abstract: The tissue mercury concentrations in six species of fish collected at the 17 Areas of Concern identified by the International Joint Commission on the Canadian side of the Great Lakes were analyzed using an Environment Canada database. A linear increase in mercury concentration with fish length was found, but slopes differed among locations. The temporal pattern over the period 1971-1997 differed across species in fish collected in Lake St. Clair; in at least two species there was evidence of increased mercury concentration during the 1990s that had been suggested in an earlier analysis. Areas of Concern differed significantly in observed tissue concentrations. Differences observed did not consistently parallel expectations associated with the historical presence of chlor-alkali plants in the vicinities of some locations. An attempt to correlate the fish tissue mercury concentration with the frequency of occurrence of infantile cerebral palsy at Areas of Concern was unsuccessful.

2.1.3 Regulation, policy, and reduction technologies

Amar, P. 2004. Status of Mercury Control Technologies, Measurement Methods, and Emerging State Regulations for U.S. Coal-Fired Utility Sector.

http://www.cec.org/files/pdf/POLLUTANTS/Pres-Praveen-Amar%20_en.pdf

Charnley, G. 2006. Assessing and managing methylmercury risks associated with power plant mercury emissions in the United States. Medscape Gen. Med. 8 (1)

[http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1681952.](http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1681952)

Abstract: Until the Clean Air Mercury Rule was signed in March 2005, coal-fired electric utilities were the only remaining, unregulated major source of industrial mercury emissions in the United States. Proponents of coal-burning power plants assert that methylmercury is not a hazard at the current environmental levels, that current technologies for limiting emissions are unreliable, and that reducing mercury emissions from power plants in the United States will have little impact on environmental levels. Opponents of coal-burning plants assert that current methylmercury exposures from fish are damaging to the developing nervous system of infants, children, and the fetus; that current technology can significantly limit emissions; and that reducing emissions will reduce exposure and risk. One concern is that local mercury emissions from power plants may contribute to higher local exposure levels, or "hot spots." The impact of the Mercury Rule on potential hot spots is uncertain due to the highly site-specific nature of the relationship between plant emissions and local fish methylmercury levels. The impact on the primary source of exposure in the United States, ocean fish, is likely to be negligible due to the contribution of natural sources and industrial sources outside the United States. Another debate centers on the toxic potency of methylmercury, with the scientific basis of the US Environmental Protection Agency's (EPA's) recommended exposure limit questioned by some and defended by others. It is likely that the EPA's exposure limit may be appropriate for combined exposure to methylmercury and polychlorinated biphenyls (PCBs), but may be lower than the available data suggest is necessary to protect children from methylmercury alone. Mercury emissions from power plants are a global problem. Without a global approach to developing and implementing clean coal technologies, limiting US power plant emissions alone will have little impact.

Dronen, L. C., A. E. Moore, E. I. Kozliak, and W. S. Seames. 2004. An assessment of acid wash and bioleaching pre-treating options to remove mercury from coal. Fuel 83: 181-186.

Abstract: The United States Environmental Protection Agency is expected to begin regulating the release of vapor-phase mercury from coal-fired power plants in the year 2007. Chemical pre-treatment methods were investigated for mercury removal effectiveness from pulverized low-sulfur North Dakota lignite coal. More limited results were obtained for a pulverized high-sulfur Blacksville bituminous coal. A two-step acid wash treatment showed removal rates of 60-90%, compared to one-step treatments with concentrated HCl, which yielded removals of 30-38%. Removal effectiveness is similar for first step solvents of water, pH 5.0 acid, or pH 2.0 acid followed by concentrated HCl as the second step solvent, and is independent of first step incubation time. Neither of two bacterial strains, Thiobacillus ferrooxidans and T. thiooxidans, was found effective for mercury removal.

Griffiths, C., A. McGartland, and M. Miller. 2007. A Comparison of the Monetized Impact of IQ Decrements from Mercury Emissions. Environmental health perspectives 115:841-847.

Abstract: OBJECTIVE: The U.S. Environmental Protection Agency (EPA) reports that the upper

bound of benefits from removing mercury emissions by U.S. power plants after implementing its Clean Air Interstate Rule (CAIR) is \$210 million per year. In contrast, Trasande et al. [Environ Health Perspect 113:590-596 (2005)] estimated that American power plants impose an economic cost of \$1.3 billion due to mercury emissions. It is impossible to directly compare these two estimates for a number of reasons, but we are able to compare the assumptions used and how they affect the results. **DATA SOURCE AND DATA EXTRACTION:** We use Trasande's linear model with a cord/maternal blood ratio of 1.7 and calculate health effects to children whose mothers had blood mercury levels greater than or equal to 4.84 $\mu\text{g/L}$. **DATA SYNTHESIS:** We introduce the assumptions that the U.S. EPA used in its Clean Air Mercury Rule (CAMR) analysis and discuss the implications. Using this approach, it is possible to illustrate why the U.S. EPA assumptions produce a lower estimate. **CONCLUSIONS:** The introduction of all the U.S. EPA assumptions, except for those related to discounting, decreases the estimated monetized impact of global anthropogenic mercury emissions in the Trasande model by 81%. These assumptions also decrease the estimated impact of U.S. sources (including power plants) by almost 97%. When discounting is included, the U.S. EPA assumptions decrease Trasande's monetized estimate of global impacts by 88% and the impact of U.S. power plants by 98%.

Hylander, L.D., and Goodsite, M.E. 2006. Environmental costs of mercury pollution. Science of the Total Environment 368: 352-370.

Abstract: Mercury (Hg) has been used for millennia in many applications, primarily in artisanal mining and as an electrode in the chloralkali industry. It is anthropogenically emitted as a pollutant from coal fired power plants and naturally emitted, primarily from volcanoes. Its unique chemical characteristics enable global atmospheric transport and it is deposited after various processes, ultimately ending up in one of its final sinks, such as incorporated into deep sediment or bioaccumulated, primarily in the marine environment. All forms of Hg have been established as toxic, and there have been no noted biological benefits from the metal. Throughout time, there have been notable incidents of Hg intoxication documented, and the negative health effects have been documented to those chronically or acutely exposed. Today, exposure to Hg is largely diet or occupationally dependent, however, many are exposed to Hg from their amalgam fillings. This paper puts a tentative monetary value on Hg polluted food sources in the Arctic, where local, significant pollution sources are limited, and relates this to costs for strategies avoiding Hg pollution and to remediation costs of contaminated sites in Sweden and Japan. The case studies are compiled to help policy makers and the public to evaluate whether the benefits to the global environment from banning Hg and limiting its initial emission outweigh the benefits from its continued use or lack of control of Hg emissions. The cases we studied are relevant for point pollution sources globally and their remediation costs ranged between 2500 and 1.1 million US\$ kg^{-1} Hg isolated from the biosphere. Therefore, regulations discontinuing mercury uses combined with extensive flue gas cleaning for all power plants and waste incinerators is cost effective.

Johnson, M. L., H. Y. Lai, and D. Wortman. 2008. Preventing mercury emissions from coal-fired power plants using environmentally preferable coal purchasing practices. Journal of Cleaner Production 16:716-721.

Electric utilities in the United States will soon be required under the federal Environmental Protection Agency's Clean Air Mercury Rule to significantly reduce mercury emissions. Coal-fired power plants, including the Lower Colorado River Authority's (LCRA) Fayette Power Project (FPP) have demonstrated that the selective purchasing of coal with low mercury content can result in significant reduction of pollution. This selective activity, commonly known as "green purchasing", has been applied to the procurement of coal. For example, the use of low-sulfur coal from the Powder River Basin deposits of Wyoming results in the prevention of a

significant amount of sulfur dioxide (SO₂) releases to the atmosphere when compared to other sources of coal in the United States. This same philosophy (selective purchasing of coal) can be employed to prevent mercury emissions and substantially reduce mercury removal costs for electric utilities burning coal. Data analysis confirms that low-mercury coal is available and that selective purchasing of low-mercury coal is possible. LCRA has implemented an extensive pollution prevention program and their green purchasing efforts have been expanded to influence coal purchasing choices. Coal purchasing is limited to the Gillette Coal Field from the Powder River Basin (PRB) of Wyoming. Three sets of coal quality data which include LCRA's Coal Quality Database (CQD), a database created from the Information Collection Request (ICR) conducted by the EPA in 1999, and the U.S. Geological Survey (USGS) Coal Quality (COALQUAL) Database were analyzed. Lab accuracy issues were found to have undermined the reliability of certain records in both the CQD and ICR databases, however, both remain valuable resources. The independent sets of coal quality data and technical reports show measurable differences in mercury concentration in coal in the Gillette Coal Field, both geographically (coal mine) and by depth (coal seam). A preliminary cost benefit analysis indicates that substantial cost savings in operating and maintaining mercury control equipment will be realized with low-mercury coal. Currently, low-mercury coal can be purchased without a significant premium.

Lipfert, F., Morris, S., Sullivan, T., Moskowitz, P., and Renninger, S. 2005. Methylmercury, fish consumption, and the precautionary principle. Journal of the Air Waste Management Association 55: 388-398.

Abstract: This paper considers several broad issues in the context of probabilistic assessment of the benefits of curtailing mercury (Hg) emissions from U.S. coal-fired power plants, based on information developed from recent literature and epidemiology studies of health effects of methylmercury. Exposure of the U.S. population is considered on the national scale, in large part because of recent questions arising from survey and experimental data about the relative importance of local deposition of airborne Hg. Although epidemiological studies have provided useful information, safe levels of Hg exposure remain uncertain, in part because of other dietary considerations in the populations that were studied. For example, much of the sea-food consumed in one of the major studies was also contaminated with polychlorinated biphenyls, as are fish taken from some U.S. fresh waters. The primary epidemiological approach involves cross-study comparisons in relation to mean exposures, rather than detailed critiques of individual effects reported in each study. U.S. exposures are seen to be well below the levels at which adverse health effects are reported. This analysis supports the conclusion that unilateral reduction of Hg emissions from U.S. coal-fired power plants alone is unlikely to realize significant public health benefits.

Maltby, V. 2002. Literature review of emissions of mercury from fossil fuel and biomass combustion and emerging control technologies. NCASI Technical Bulletin 851.

Abstract: Further reductions in mercury emissions have become an EPA priority, with mercury emission standards under development for electric utility and industrial boilers. Regulations limiting mercury emissions from municipal waste and hazardous waste combustors, medical waste incinerators, and sewage sludge incinerators were issued. Options for further reductions in mercury emissions, by coal pre-treatment, combustion modification and add-on control technology, were actively explored.

Mazzi, E., Glesmann, S., and Bell, A. 2006. Canada wide standards mercury measurement methodologies for coal-fired power plants. Proceedings of the EPA-DOE-EPRI-A and WMA Power Plant Air Pollutant Control Mega Symposium 2006, Vol. 1, pp. 60-80.

Abstract: In support of the proposed Canada Wide Standards (CWSs) for Mercury Emissions from Coal-fired Electric Power generation Plants, the Canadian Council for Ministers of the Environment (CCME) commissioned a study of mercury monitoring options for Canada's coal-fired power plants. Broad study questions were developed to explore monitoring options. Questions posed were: what to measure, how to monitor, over what averaging timeframe, and how to minimize variability? A review was conducted of the spatial and temporal environmental health impacts and experience with measurement methodologies. CCME and the Canadian Electricity Association (CEA) coordinated a two year program of weekly coal and ash data collection (mass balance) from 20 Canadian power plants. Analyses using these coal and ash data are presented. Additionally, a smaller set of stack CEMS and Ontario Hydro Method stack test data are presented. One of CCME's goals is to develop predictive models for mercury emissions, and regression analyses were employed to develop statistical models of emission rates (kg/TWh) as a function of coal mercury and chlorine content using Canadian and U.S. data. The most useful model was a statistically significant regression equation for plants with a cold-side ESP, no post-combustion NO_x controls, and no post-combustion SO_x controls. The study recommended monitoring of total and oxidized mercury, although oxidized emissions would be for information only because the draft CWSs only specify total mercury for determining compliance. To benefit from anticipated performance and cost improvements in CEMS technology, mercury monitoring by mass balance is recommended for Canadian plants until one or two years after U.S. plants are required to have CEMS. Monitoring by CEMS or sorbent trap is recommended for the long run. A 12-month rolling average is recommended with exceedances corrected within 36 months. It is emphasized that this study was commissioned to perform analyses and make recommendations. However these results and recommendations were not intended to be automatically adopted into CCME's monitoring protocol.

Mohapatra, S. P., I. Nikolova, and A. Mitchell. 2007. Managing mercury in the Great Lakes: An analytical review of abatement policies. Journal of Environmental Management 83:80-92.

Abstract: Mercury, a toxic metal known to have several deleterious affects on human health, has been one of the principal contaminants of concern in the Great Lakes basin. There are numerous anthropogenic sources of mercury to the Great Lakes area. Combustion of coal, smelting of nonferrous metals, and incineration of municipal and medical waste are major sources of mercury emissions in the region. In addition to North American anthropogenic emissions, global atmospheric emissions also significantly contribute to the deposition of mercury in the Great Lakes basin. Both the USA and Canada have agreed to reduce human exposure to mercury in the Great Lakes basin and have significantly curtailed mercury load to this region through individual and joint efforts. However, many important mercury sources, such as coal-fired power plants, still exist in the vicinity of the Great Lakes. More serious actions to drastically reduce mercury sources by employing alternative energy sources, restricting mercury trade and banning various mercury containing consumer products, such as dental amalgam are as essential as cleaning up the historical deposits of mercury in the basin. A strong political will and mass momentum are crucial for efficient mercury management. International cooperation is equally important. In the present paper, we have analyzed existing policies in respective jurisdictions to reduce mercury concentration in the Great Lakes environment. A brief review of the sources, occurrence in the Great Lakes, and the health effects of mercury is also included.

Moore, D.R.J., Teed, R.S., and Richardson, G.M. 2003. Derivation of an ambient water quality criterion for mercury: Taking account of site-specific conditions. Environmental Toxicology and Chemistry 22: 3069-3080.

Abstract: Mercury is considered to be a serious risk to wildlife. As a result, the Great Lakes Water Quality Initiative and others have developed ambient water quality criteria (AWQC) for the protection of wildlife. These AWQC have been controversial, however, because the AWQC were single values that did not account for site-specific conditions, derivation of the AWQC relied on a single no-observed-adverse-effect level, and the AWQC had an unknown level of conservatism because of reliance on both average and conservative assumptions and uncertainty factors. Rather than develop a single-value AWQC for total mercury, we derived an AWQC model that explicitly incorporates factors controlling bioavailability, methylation rates, and bioaccumulation in the aquatic environment (e.g., pH, dissolved organic carbon). To derive our AWQC model, field data were collected from 31 lakes in Ontario and an additional 10 lakes in Nova Scotia (North America). In the field study, levels of total and methylmercury in water and fish as well as levels of key water quality variables were determined. We conducted multiple-regression analysis to derive a model that estimates mercury levels in prey of mink. Mink are very sensitive to mercury exposure. An independent dataset consisting of 51 water bodies in the United States was then used to confirm the validity and robustness of the AWQC model. Next, we combined the results of chronic-feeding studies with similar protocols and endpoints in a meta-analysis to derive a dose-response curve for mink exposed to mercury in the diet. In the final step, we used a probabilistic risk model to estimate the concentrations of methylmercury in water that would lead to levels in fish sufficient for a 10% probability of exceeding the lethal dose affecting 5% of the mink population. The result is an AWQC equation for mercury for the protection of wildlife that can be used with a variety of site-specific conditions.

Pavlish, J. H., E. A. Sondreal, M. D. Mann, E. S. Olson, K. C. Galbreath, D. L. Laudal, and S. A. Benson. 2003. State review of mercury control options for coal-fired power plants. Fuel Processing Technology 82:89-165.

Abstract: This paper presents an overview of research related to mercury control technology for coal-fired power plants and identifies areas requiring additional research and development. It critically reviews measured mercury emissions; the chemistry of mercury transformation and control; progress in the development of promising control technologies: sorbent injection, control in wet scrubbers, and coal cleaning; and projects costs for mercury control. Currently, there is no single best technology that can be broadly applied. Combinations of available control methods may be able to provide up to 90% control for some plants but not others. In August 2000, the National Research Council completed a study that determined that the U.S. Environmental Protection Agency's (EPA) conservative exposure reference dose of 0.1 *mg mercury/ kg body weight/day was scientifically justified to protect against harmful neurological effects during fetal development and early childhood. Subsequently, in December 2000, EPA made its regulatory decision that mercury emissions from coal-fired electric generating plants will need to be controlled on a schedule that calls for a proposed rule by December 2003, a final rule by December 2004, and full compliance by the end of 2007. Coal-fired utility boilers are currently the largest single-known source of mercury emissions in the United States. EPA's Information Collection Request (ICR) to coal-burning utilities indicated that there were 75 tons of mercury in the 900 million tons of coal used in U.S. power plants during 1999. Estimates of total mercury emissions from coal-fired plants based on ICR data range from 40 to 52 tons. On average, about 40% of the mercury entering a coal-fired power plant is captured and 60% emitted. Percentage emissions of mercury for individual plants tested under the ICR varied widely depending on coal type and emission control equipment. Western subbituminous coals on average contain only about half as much mercury as Appalachian bituminous coals, but the higher chlorine content of the latter promotes mercury oxidation and results in a higher percentage of mercury capture. Some iron minerals found in coal also catalyze mercury oxidation, whereas calcium and sulfur tend to impede oxidation. Review of ICR data on mercury capture in boilers and existing control

devices indicates very little mercury removal within a pulverized coal-fired boiler, and the level of mercury oxidation at the exit of the boiler was increased for higher coal chlorine contents and lower exit temperatures. Mercury removals across cold-side electrostatic precipitators (ESPs) averaged 27%, compared to 4% for hot-side ESPs. Removals for fabric filters (FFs) were higher, averaging 58%, owing to additional gas-solid contact time for oxidation. Both wet and dry flue gas desulfurization (FGD) systems removed 80% to 90% of the gaseous mercury(II), but elemental mercury (Hg₀) was not affected. High mercury removals, averaging 86%, in fluidized-bed combustors with FFs were attributed to mercury capture on high-carbon fly ash. Tests on the two coal-fired integrated gasification combined-cycle plants in the United States suggest that about half of the coal mercury was emitted predominantly in elemental form. ICR tests on selective catalytic reduction and selective noncatalytic reduction used for NO_x control were inconclusive, and additional full-scale tests are in progress. The mechanisms responsible for varied levels of mercury oxidation and capture are beginning to be understood. Mercury in coal occurs in association with pyrite and other sulfide minerals and may also be organically bound. Coal mercury is converted to gaseous Hg₀ in the combustion flame and is subsequently partially oxidized (35% to 95%) as the combustion gases cool. Mercury oxidation in boiler systems is kinetically controlled; homogeneous oxidation reactions are promoted by chlorine and atomic chlorine, and heterogeneous oxidation is promoted by fly ash and sorbents. The mechanisms responsible for varied levels of mercury oxidation and capture are beginning to be understood. Mercury in coal occurs in association with pyrite and other sulfide minerals and may also be organically bound. Coal mercury is converted to gaseous Hg₀ in the combustion flame and is subsequently partially oxidized (35% to 95%) as the combustion gases cool. Mercury oxidation in boiler systems is kinetically controlled; homogeneous oxidation reactions are promoted by chlorine and atomic chlorine, and heterogeneous oxidation is promoted by fly ash and sorbents. Acid gases critically influence the heterogeneous oxidation of mercury, particularly as it affects capture on sorbents. HCl, NO, and NO₂ all promote oxidation and capture both individually and in combination. However, the combination of SO₂ with NO₂ greatly reduces capture of Hg₀ on activated carbon, whereas oxidation continues on the solid surface. Mass transfer of gaseous mercury by diffusion from the bulk gas to the solid surface can also limit heterogeneous oxidation and capture of mercury, but diffusion within a porous sorbent is not believed to be rate-limiting. Reducing the size of the sorbent particles and increasing their dispersion can greatly enhance control where mass transfer is limiting. To achieve 90% control of a mercury concentration of 10 *mg/scm in 2-s residence time by activated carbon injection requires a minimum carbon-to-mercury (C/Hg) mass ratio of about 3000:1 for 4-*mm particles compared to 18,000:1 for 10-*mm particles. Mercury removals in some tests performed to characterize sorbents have been mass transfer-limited by the large particle size of the sorbents used. Mercury sorption capacities between about 200 and 5000 *mg Hg/g C have been reported for conditions applying to coal combustion. However, higher measured capacities do not always correlate with higher removal levels in practice because of the effect of other variables. What is important is that several of the activated carbons tested have sufficient capacity to capture mercury at carbon injection rates below a C/Hg mass ratio of 10,000, based on both laboratory and field sorption tests. Since capacity is defined in reference to an assumed sorption equilibrium, the equilibrium capacity of a sorbent determined over a period of hours in the laboratory may have limited relevance to the amount of mercury captured in a few seconds' time of flight or in minutes of contact time on an FF. Laboratory tests that are more representative of the conditions in an actual control device are needed to determine more useful capacity factors. Injection of activated carbon upstream of either an ESP or an FF baghouse is a retrofit control technology that has potential application to 75% of all coal-fired power plants in the United States that are not equipped with FGD scrubbers. Field and pilot-scale tests on activated carbon injection for mercury control have resulted in mercury removals between about 25% and 95% over the range of 2000-15,000 C/Hg mass ratio. The mercury removal data from some tests could be correlated with carbon injection rates by

assuming that the removal was mass transfer-limited, whereas in tests on other coals, removals appeared to be controlled by catalytic oxidation and capture on fly ash. Mercury capture on sorbents, therefore, depends on the properties of the coal being burned, and pilot-scale tests on particular coals should be performed before a full-scale sorbent injection system is designed. Development of low-cost, ultrafine sorbents with high effective sorption capacities and rapid reaction kinetics would revolutionize injection technology. Engineering development is also needed to improve sorbent dispersion and to optimize gas-solid contact time. Wet FGD units currently installed on about 25% of the U.S. coal-fired utility boilers remove nearly 90% of the mercury(II) entering but essentially none of the Hg⁰.

Romero, C. E., Y. Li, H. Bilirgen, N. Sarunac, and E. K. Levy. 2006. Modification of boiler operating conditions for mercury emissions reductions in coal-fired utility boilers. Fuel 85:204-212.

Abstract: US EPA's studies have determined that mercury emissions from coal-fired power plants pose significant hazards to public health and must be reduced. Coal-fired power plants represent a significant fraction of the anthropogenic emissions of mercury into the atmosphere. Mercury emissions are impacted by factors such as coal type, boiler operation, fly ash characteristics and type of environmental control equipment installed on the unit. Field data show a wide variation in the fraction of mercury that is emitted in the gaseous phase, as elemental and oxidized mercury vapor, and as particulate-bound mercury. Oxidized mercury is a preferable species because it is less volatile at stack temperatures, water-soluble, and tends to interact with mineral matter and char, and cold-end air pollution control devices. There is also evidence that boiler-operating conditions could be used to influence mercury behavior in the boiler, since they affect the thermo-chemical conditions for mercury formation and reduction. However, operation of boiler control settings, which result in mercury removal benefits, should also consider the tradeoff between mercury reduction and other emissions (for example, NO_x and CO), the level of unburned carbon in the fly ash, unit efficiency and the performance of particulate control equipment. This paper reports fieldwork performed to investigate the feasibility of affecting mercury emissions from coal-fired plants by manipulating boiler control settings. Full-scale testing was performed at two units. One of the units is equipped with a back-end train that includes a rotary air preheater followed by two electrostatic precipitators in series. The other unit is equipped with hot and cold precipitators and a tubular air preheater. A strategy for mercury control by selectively manipulating boiler control settings, if used in combination with other control measures such as sorbent injection, should provide a cost-effective option for mercury control.

Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., and Scott, C. 2004. Modeling the atmospheric fate and transport of mercury over North America: power plant emission scenarios. Fuel Processing Technology 85: 441-450.

Abstract: A multiscale modeling system that consists of a global cycling model and a continental-scale model, TEAM, is applied to simulate the fate and transport of mercury over North America. The performance of the modeling system is shown to be satisfactory. TEAM is used to simulate three coal-fired power plant emission control scenarios that correspond to 47%, 30% and 16% reductions in mercury emissions from the 1999 base case. Changes in total mercury deposition are less than 10% over most of the United States. The latter two scenarios that include subcategorization of power plants by coal rank and stack temperature show little effect on mercury deposition compared to the first scenario.

Spath, P.L., M.K. Mann, and D.R. Kerr 2000. Life Cycle Assessment of Coal-fired Power Production. National Renewable Energy Laboratory Report, U.S. Department of Energy, Boulder, CO. <http://www.nrel.gov/docs/fy99osti/25119.pdf>

Abstract: Coal has the largest share of utility power generation in the United States, accounting for approximately 56% of all utility-produced electricity (U.S. DOE, 1998). Therefore, understanding the environmental implications of producing electricity from coal is an important component of any plan to reduce total emissions and resource consumption. A life cycle assessment (LCA) on the production of electricity from coal was performed in order to examine the environmental aspects of current and future pulverized coal boiler systems. Three systems were examined: 1) a plant that represents the average emissions and efficiency of currently operating coal-fired power plants in the U.S. (this tells us about the status quo), 2) a new coal-fired power plant that meets the New Source Performance Standards (NSPS), and 3) a highly advanced coal-fired power plant utilizing a low emission boiler system (LEBS).

Swain, E. B., P. M. Jakus, G. Rice, F. Lupi, P. A. Maxson, J. M. Pacyna, A. Penn, S. J. Spiegel, and M. M. Veiga. 2007. Socioeconomic Consequences of Mercury Use and Pollution. *Ambio* 36:45-61.

Abstract: In the past, human activities often resulted in mercury releases to the biosphere with little consideration of undesirable consequences for the health of humans and wildlife. This paper outlines the pathways through which humans and wildlife are exposed to mercury. Fish consumption is the major route of exposure to methylmercury. Humans can also receive toxic doses of mercury through inhalation of elevated concentrations of gaseous elemental mercury. We propose that any effective strategy for reducing mercury exposures requires an examination of the complete life cycle of mercury. This paper examines the life cycle of mercury from a global perspective and then identifies several approaches to measuring the benefits of reducing mercury exposure, policy options for reducing Hg emissions, possible exposure reduction mechanisms, and issues associated with mercury risk assessment and communication for different populations.

United States Environmental Protection Agency. Clean Air Mercury Rule. <http://www.epa.gov/camr/>. Accessed February 10, 2008.

On March 15, 2005, EPA issued the first-ever federal rule to permanently cap and reduce mercury emissions from coal-fired power plants. This rule makes the United States the first country in the world to regulate mercury emissions from coal-fired power plants.

- The Clean Air Mercury Rule will build on EPA's Clean Air Interstate Rule (CAIR) to significantly reduce emissions from coal-fired power plants -- the largest remaining sources of mercury emissions in the country. When fully implemented, these rules will reduce utility emissions of mercury from 48 tons a year to 15 tons, a reduction of nearly 70 percent.
- EPA believes it makes sense to address mercury, SO₂ and NO_x emissions simultaneously through CAIR and the Clean Air Mercury Rule. These rules will protect public health and the environment without interfering with the steady flow of affordable energy for American consumers and business.
- The Clean Air Mercury Rule establishes "standards of performance" limiting mercury emissions from new and existing coal-fired power plants and creates a market-based cap-and-trade program that will reduce nationwide utility emissions of mercury in two distinct phases. The first phase cap is 38 tons and emissions will be reduced by taking advantage of "co-benefit" reductions -- that is, mercury reductions achieved by reducing sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions under CAIR. In the second

phase, due in 2018, coal-fired power plants will be subject to a second cap, which will reduce emissions to 15 tons upon full implementation.

- New coal-fired power plants (“new” means construction starting on or after Jan. 30, 2004) will have to meet stringent new source performance standards in addition to being subject to the caps.
- EPA’s modeling shows that CAIR will significantly reduce the majority of the coal-fired power plant mercury emissions that deposit in the United States, and those reductions will occur in areas where mercury deposition is currently the highest. The Clean Air Mercury Rule is expected to make additional reductions in emissions that are transported regionally and deposited domestically, and it will reduce emissions that contribute to atmospheric mercury worldwide.

Yang, H. Q., Z. H. Xu, M. H. Fan, A. E. Bland, and R. R. Judkins. 2007. Adsorbents for capturing mercury in coal-fired boiler flue gas. *Journal of Hazardous Materials* 146:1-11.

This paper reviews recent advances in the research and development of sorbents used to capture mercury from coal-fired utility boiler flue gas. Mercury emissions are the source of serious health concerns. Worldwide mercury emissions from human activities are estimated to be 1000 to 6000 t/annum. Mercury emissions from coal-fired power plants are believed to be the largest source of anthropogenic mercury emissions. Mercury emissions from coal-fired utility boilers vary in total amount and speciation, depending on coal types, boiler operating conditions, and configurations of air pollution control devices (APCDs). The APCDs, such as fabric filter (FF) bag house, electrostatic precipitator (ESP), and wet flue gas desulfurization (FGD), can remove some particulate-bound and oxidized forms of mercury. Elemental mercury often escapes from these devices. Activated carbon injection upstream of a particulate control device has been shown to have the best potential to remove both elemental and oxidized mercury from the flue gas. For this paper, NORIT FGD activated carbon was extensively studied for its mercury adsorption behavior. Results from bench-, pilot- and field-scale studies, mercury adsorption by coal chars, and a case of lignite-burned mercury control were reviewed. Studies of brominated carbon, sulfur-impregnated carbon and chloride-impregnated carbon were also reviewed. Carbon substitutes, such as calcium sorbents, petroleum coke, zeolites and fly ash were analyzed for their mercury-adsorption performance. At this time, brominated activated carbon appears to be the best-performing mercury sorbent. A non-injection regenerable sorbent technology is briefly introduced herein, and the issue of mercury leachability is briefly covered.

2.2 Sulphur dioxide and nitrogen oxides

2.2.1 Emissions, atmospheric deposition, and modeling

Fottova, D. 2003. Trends in sulphur and nitrogen deposition fluxes in the GEOMON network, Czech Republic, between 1994 and 2000. *Water Air and Soil Pollution* 150: 73-87.

Abstract: Deposition fluxes of sulphur and nitrogen in bulk and throughfall precipitation were monitored for the 1994-2000 period for seven small forest catchments in the GEOMON network, Czech Republic (CR). Four catchments are situated at similar elevations (roughly between 800 and 1000 m) and represent three areas: the Black Triangle near the Krusnehozy Mts. coalfield (catchments JEZ and LYS), the Orlickehozy Mts., close to the Polish industrial regions (UDL), and the Sumava Mts., a relatively unpolluted area (LIZ). Three catchments (GEM, POM, LES) lie at lower elevations (400-600 m) in Central Bohemia. A substantial decrease in the bulk and throughfall deposition of pollutants occurred as a result of the desulphurisation programme implemented in the Czech Republic between 1996 and 1998. A reduction has been described mainly in the Krusnehozy Mts. (JEZ), in Slavkovskyles (LYS) and also in Central Bohemia (GEM). The decrease in the throughfall to less than one half within a single year in POM (Central Bohemia) was an example of a direct response to the local emission reduction in the nearby Chvaletice power plant. However, in some areas, the throughfall deposition of sulphur, which includes wet and dry deposition, is still significant, especially at higher elevations. Recent forest degradation was observed in the Orlickehozy Mts., where, particularly in 1998, as much as 91.1 kg S was found in coniferous throughfall. The fraction of dry deposition in the coniferous forests of CR represents 30-70% of the total deposition. The difference between coniferous (higher) and deciduous (lower) throughfall fluxes is significant because of the larger surface area of conifers and year-round exposure to air-borne sulphur. At several of the GEOMON sites, the flux of nitrogen via throughfall increased during the observation period and, at the end of the studied period (2000), nitrogen became the main source of acidification, replacing sulphur compounds. The highest fluxes (81.7 kg N ha⁻¹ yr⁻¹) were measured in 2000 in the Orlickehozy Mts., which provide an example of multiple causes of forest decline - the direct impact of air pollution, abundance of nitrogen, acidification and secondary stressors (weather changes, insect pests, fungal infections). A comparison is given with data from other countries.

Gbondo-Tugbawa, S.S., Driscoll, C.T., Mitchell, M.J., Aber, J.D., and Likens, G.E. 2002. A model to simulate the response of a northern hardwood forest ecosystem to changes in S deposition. *Ecological Applications* 12: 8-23.

Abstract: Watershed studies across the northeastern United States have shown that stream losses of SO₄²⁻ exceed atmospheric sulfur (S) deposition. Understanding the processes responsible for this additional source of S is critical to quantifying ecosystem response to ongoing and potential future controls on SO₂ emission. An integrated biogeochemical model, PnET-BGC, was used to investigate inputs and dynamics of S in a northern hardwood forest at the Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA. The changes in soil S pools and stream-water SO₄²⁻ were simulated to assess the response to both atmospheric S deposition and forest clear-cutting disturbances. Model simulation using the measured dry-to-bulk deposition ratio of 0.21 resulted in an underprediction of soil S pools and stream-water SO₄²⁻ concentrations in the biogeochemical reference watershed (Watershed 6). However, the depiction of biotic processes (e.g., plant uptake, mineralization) in the model reduced the discrepancy in stream SO₄²⁻ concentration between measured and model predicted value by -50% compared to a previous modeling effort that only considered abiotic processes. Long-term simulations (-150 yr) indicated that elevated anthropogenic S deposition has increased stream SO₄²⁻ concentrations and

enhanced the incorporation of S in adsorbed SO₄²⁻ and organic S soil pools. Following the implementation of the 1970 and 1990 Amendments to the Clean Air Act, decreases in S deposition resulted in the net release of S from soil pools, including soil organic S. Model simulation of forest clear-cutting of Watershed 5 at the HBEF showed that NO₃⁻ leaching and associated acidification following this disturbance increased adsorption of SO₄²⁻ to soil. Compared to the reference watershed, stream-water SO₄²⁻ concentrations were slightly higher, and soil adsorbed SO₄²⁻ pools were substantially higher in the clear-cut watershed 4-5 yr after disturbance. Simulation of stable S isotopes showed that fractionation associated with the mineralization of soil organic S might explain the depletion in ³⁴S observed between throughfall and stream water in the reference watershed. There is a need for further research on: (1) the rates of dry S deposition and (2) the rate of weathering of various minerals and the isotopic composition of these minerals in order to fully assess the discrepancy (i.e., greater export of S than can be accounted for by atmospheric deposition) in watershed S mass balances. The results of forecasts of the future response to anticipated decreases in S deposition are highly dependent on the nature of this additional source of S to forest watersheds. However, the large size and relatively long turnover time of soil organic S pools compared to adsorbed SO₄²⁻ pools suggest that a model depicting only abiotic processes will not be suitable for predicting the long-term recovery of stream water from acidification by atmospheric deposition in northern forests.

Gormley, C. H., and S. Thompson. 2002. A lumped parameter NO_x emissions model for a coal-fired power station. *Journal of the Institute of Energy* 75:43-51.

Abstract: The development is described of a simple lumped parameter NO_x model suitable for on-line control of pollutant emissions. This NO_x model has the potential to deal with a wide range of operational conditions and was developed for a coal-fired power station in Northern Ireland. The plant is equipped with low NO_x burners, requiring the modelling of combustion and NO_x reactions in both fuel-rich and fuel-lean combustion zones. Both volatile and char-based NO_x are included, with fuel NO_x formation and reduction modelled in the fuel-rich region, whereas char NO_x and thermal NO_x were modelled in the outer fuel-lean zone. Model constants were determined by parameter estimation using existing plant data. The predicted NO_x output compared favourably with actual plant emissions.

Hu, Y., Odman, M.T., and Russell, A.G. 2006. Re-examination of the 2003 North American electrical blackout impacts on regional air quality. *Geophysical Research Letters* 33.

Abstract: Aircraft measurements have been utilized to capitalize on the 2003 North American electrical blackout as an unplanned event providing a unique opportunity to assess the impacts of power plants on air quality. Here we adopt a modeling approach using CMAQ with a direct sensitivity technique, DDM-3D, to quantify how emissions reductions from different sources impacted ozone and particulate matter. Simulated air quality fields were able to reproduce both the regular surface observations and airborne measurements before and during the blackout. Sensitivity results show that blackout-linked power plant SO₂ emissions reductions led to a sulfate concentration reduction of 22% at Selinsgrove, Pennsylvania, while power plant NO_x emissions reductions had very limited (4%) impacts on O₃. These results are lower than the estimates presented in previous studies. Results also suggest that over much of the region, on-road mobile NO_x emissions reductions linked to the blackout had a larger impact on O₃.

Jeffries, D.S., Brydges, T.G., Dillon, P.J., and Keller, W. 2003. Monitoring the results of Canada/U.S.A. acid rain control programs: Some Lake responses. *Environmental Monitoring and Assessment* 88: 3-19.

Abstract: Aquatic acidification by deposition of airborne pollutants emerged as an environmental issue in southeastern Canada during the 1970s. Drawing information from the extensive research and monitoring programs, a sequence of issue assessments demonstrated the necessity of reducing the anthropogenic emissions of acidifying pollutants, particularly sulphur dioxide (SO₂). The 1991 Canada-U.S. Air Quality Agreement (AQA) was negotiated to reduce North American SO₂ emissions by 40% relative to 1980 levels by 2010, and at present, both countries have reduced emissions beyond their AQA commitment. In response to reduced SO₂ emissions, atmospheric deposition of sulphate (SO₄²⁻) and SO₄²⁻ concentrations in many lakes have declined, particularly in south-central Ontario and southern Quebec. Sulphate deposition still exceeds aquatic critical loads throughout southeastern Canada however. Increasing pH or alkalinity (commonly deemed 'recovery') has been observed in only some lakes. Several biogeochemical factors have intervened to modify the lake chemistry response to reduced SO₄²⁻ input, notably release of stored SO₄²⁻ from wetlands following periods of drought and reduction in the export of base cations from terrestrial soils. Three examples from Ontario are presented to illustrate these responses. Significant increases in pH and alkalinity have been observed in many lakes in the Sudbury area of Ontario due to the large reductions in local SO₂ emissions; 'early-stage' biological recovery is evident in these lakes. An integrated assessment model predicts that AQA emission reductions will not be sufficient to promote widespread chemical or biological recovery of Canadian lakes. Monitoring and modeling are mutually supporting assessment activities and both must continue.

Kaldellis, J. K., G. T. Vlachos, A. G. Paliatsos, and E. M. Kondili. 2005. Detailed examination of the Greek electricity sector nitrogen oxides emissions for the period 1995-2002. Environmental Science & Policy 8:502-514.

Abstract: The importance of energy in economic development has been globally recognised, A considerable electricity consumption increase has taken place in Greece since the country's incorporation in the European Union. Unfortunately, the electricity generation up to now is mainly based on fossil fuels. As a direct result of this policy, electricity generation is one of the main contributors to the Greek air pollutant emissions. The present work is focused on investigating in detail the corresponding nitrogen oxides emissions for the period 1995-2002. One of the most negative observations resulting from the presented analysis is that the undesirable NO_x emissions factors increase, mainly during the last 3 years of the period analysed. Moreover, annual NO_x emissions continue to increase, as a result of the noteworthy electricity consumption amplification registered during the concerned period. Therefore, local data were compared with similar information from the literature regarding other territories and then used accordingly to evaluate the Greek compliance with the existing EU decisions (e.g. Directive 2001/80/EC). Finally, considering that more than 90% of national electricity production is based on carbon containing fuels, further emissions of noxious nitrogen oxides increase is expected for the next decade, unless the appropriate abatement technologies are promptly applied.

Kim, S. W., A. Heckel, S. A. McKeen, G. J. Frost, E. Y. Hsie, M. K. Trainer, A. Richter, J. P. Burrows, S. E. Peckham, and G. A. Grell. 2006. Satellite-observed US power plant NO_x emission reductions and their impact on air quality. Geophysical Research Letters 33.

Abstract: Nitrogen oxide (NO_x) emissions resulting from fossil fuel combustion lead to unhealthy levels of near-surface ozone (O₃). One of the largest U. S. sources, electric power generation, represented about 25% of the U. S. anthropogenic NO_x emissions in 1999. Here we show that space-based instruments observed declining regional NO_x levels between 1999 and 2005 in response to the recent implementation of pollution controls by utility companies in the eastern U. S. Satellite-retrieved summertime nitrogen dioxide (NO₂) columns and bottom-up emission estimates show larger decreases in the Ohio River Valley, where power plants dominate

NO_x emissions, than in the northeast U. S. urban corridor. Model simulations predict lower O₃ across much of the eastern U. S. in response to these emission reductions.

Li, K., S. Thompson, and J. X. Peng. 2004. Modelling and prediction of NO_x emission in a coal-fired power generation plant. Control Engineering Practice 12:707-723.

Abstract: In this paper NO_x emissions modelling for real-time operation and control of a 200 MWe coal-fired power generation plant is studied. Three model types are compared. For the first model the fundamentals governing the NO_x formation mechanisms and a system identification technique are used to develop a grey-box model. Then a linear AutoRegressive model with exogenous inputs (ARX) model and a non-linear ARX model (NARX) are built. Operation plant data is used for modelling and validation. Model cross-validation tests show that the developed grey-box model is able to consistently produce better overall long-term prediction performance than the other two models.

Luria, M., R. E. Imhoff, R. J. Valente, and R. L. Tanner. 2003. Ozone yields and production efficiencies in a large power plant plume. Atmospheric Environment 37:3593-3603.

Abstract: The plume of Tennessee Valley Authority's coal-fired Cumberland power plant was sampled during four different days in the summer of 1998 and 1999 from an instrumented helicopter. The extent of formation of ozone and various secondary NO_x species in the plume was measured and the rates of loss processes estimated. The rates of these processes were found to be similar during three of the four sampling days. On the fourth day conversion and removal processes within the plume were significantly slower apparently due to lower ambient temperatures, and poor dispersion conditions. On the three more 'reactive' days ozone yield (Y) was found to be in the range of 1.5-2.6 molecules of O₃ produced per molecule of NO_x emitted. The ozone production efficiency, estimated from Y and the average chemical age of the farthest distance sampled, varied from 2.3 to 5.4.

Martins, C.R., and De Andrade, J.B. 2002. Atmospheric chemistry of sulfur (IV): Emissions, aqueous phase reactions and environmental effects. Quimica nova 25: 259-272.

Abstract: The oxidation process of sulfur(IV) species by oxygen, ozone and nitrogen oxides, catalysed by trace metal ions, can play an important role in atmospheric chemistry processes like acid rain, visibility degradation and health hazard. An overview of the more relevant investigations on emissions sources, aqueous phase conversion process and environmental impact is presented.

McGonigle, A. J. S., C. L. Thomson, V. I. Tsanev, and C. Oppenheimer. 2004. A simple technique for measuring power station SO₂ and NO₂ emissions. Atmospheric Environment 38:21-25.

Abstract: Emissions of SO₂ and NO₂ from fossil fuel power stations can have serious environmental consequences via conversion to sulphuric and nitric acids and subsequent deposition. Consequently, there is considerable interest in techniques capable of monitoring these emissions, in order to ensure compliance with environmental legislation. Here we present a novel approach to measuring power station SO₂ and NO₂ emissions by traversing underneath the plume by car or on-foot or scanning the power station's plume from a fixed position with a compact and lightweight UV spectrometer. This work was performed at a power station in eastern England during January, February and June 2003, resulting in a SO₂ flux of 5.2 kg s⁻¹, which is in close correspondence with the in-stack measured value of 5.3 kg s⁻¹. This technique is considerably simpler and cheaper than other remote sensing approaches to monitoring these emissions.

McKeen, S.A. 2003. Measuring reactive nitrogen emissions from point sources using visible spectroscopy from aircraft. *Journal of Environmental Monitoring* 5: 29-34.

Abstract: Accurate measurements of nitrogen dioxide (NO₂), a key trace gas in the formation and destruction of tropospheric ozone, are important in studies of urban pollution. Nitrogen dioxide column abundances were measured during the Texas Air Quality Study 2000 using visible absorption spectroscopy from an aircraft. The method allows for quantification of the integrated total number of nitrogen dioxide molecules in the polluted atmosphere and is hence a useful tool for measuring plumes of this key trace gas. Further, we show how such remote-sensing observations can be used to obtain information on the fluxes of nitrogen dioxide into the atmosphere with unique flexibility in terms of aircraft altitude, and the height and extent of mixing of the boundary layer. Observations of nitrogen dioxide plumes downwind of power plants were used to estimate the flux of nitrogen oxide emitted from several power plants in the Houston and Dallas metropolitan areas and in North Carolina. Measurements taken over the city of Houston were also employed to infer the total flux from the city as a whole.

Say, N. P. 2006. Lignite-fired thermal power plants and SO₂ pollution in Turkey. *Energy Policy* 34:2690-2701.

Abstract: About 80% of the electric energy production in Turkey is provided by thermal power plants which use fossil fuels. Lignite, the most abundant domestic energy source, is consumed in most of these plants. Turkey has approximately 0.85% of the world's lignite reserves; however, the Turkish lignites have low calorific value and contain relatively higher amounts of ash, moisture, and sulfur. Nearly 80% of the lignite mined in Turkey is consumed in the thermal power plants since it is not appropriate for use in other types of industry and heating. In Turkey, 13 large-scale lignite-fired thermal power plants are responsible for a considerable amount of air pollution. Therefore, it is crucial to decide on the optimal place and technology for the future thermal power plants, and to equip the currently operating plants with newer technologies that will reduce amount of contaminants released into the air. In this study, the effects of the lignite-fired thermal power plants which have an important place in the energy politics in Turkey on the air pollution are investigated. We focused on SO₂ pollution and the regions in which the SO₂ emissions were concentrated and diffused. The pollutant diffusion areas were projected and mapped based on parameters such as wind data, isotherm curves, population density, and topographic features by using Geographical Information System (GIS) software, ArcView. The contribution of the thermal power plants to SO₂ pollution was also examined.

Shen, S.S., Miller, D.P., and Lewis, P.E. 2007. Analysis of SO₂ point source emissions using NASA Atmospheric Infrared Sounder data. *Proceedings of SPIE - The International Society for Optical Engineering*, Vol. 6565.

Abstract: Determining the extent to which large power plant emission sources interacting with atmospheric constituents affect the environment could play a significant role in future U.S. energy production policy. The effects on the environment caused by the interaction between power plant emissions and atmospheric constituents has not been investigated in depth due to the lack of calibrated spectral data on a suitable temporal and spatial scale. The availability of NASA's space-based Atmospheric Infrared Sounder (AIRS) data makes it possible to explore, and begin the first steps toward establishing, a correlation between known emission sources and environmental indicators. An exploratory study was conducted in which a time series of 26 cloud-free AIRS data containing two coal-fired power plants in northern New Mexico were selected, acquired, and analyzed for SO₂ emissions. A generic forward modeling process was also developed to derive an estimate of the expected AIRS pixel radiance containing the SO₂ emissions from the two power plants based on published combustion analysis data for coal and available power plant documentation. Analysis of the AIRS NEAR calculated in this study and

subsequent comparison with the radiance values for SO₂ calculated from the forward model provided essential information regarding the suitability and risk in the use of a modified AIRS configuration for monitoring anthropogenic point source emissions. The results of this study along with its conclusions and recommendations in conjunction with additional research collaboration in several specific topics will provide guidance for the development of the next generation infrared spectrometer system that NASA is considering building for environmental monitoring.

Sotiropoulos, D., A. Georgakopoulos, and N. Kolovos. 2005. Impact of free calcium oxide content of fly ash on dust and sulfur dioxide emissions in a lignite-fired power plant. *Journal of the Air & Waste Management Association* 55:1042-1049.

Abstract: Emitted pollutants from the Agios Dimitrios lignite-fired power plant in northern Greece show a very strong linear correlation with the free calcium oxide content of the lignite ash. Dust (fly ash) emissions are positively correlated to free calcium oxide content, whereas sulfur dioxide (SO₂) emissions are negatively correlated. As a result, at present, the Agios Dimitrios Power Plant operates very strictly within the legislative limits on atmospheric particulate emission. In the present study, the factors to be considered in assessing the impact of lignite combustion on the environment are presented and evaluated statistically. The ash appears to have a remarkable SO₂ natural dry scrubbing capability when the free calcium oxide content ranges between 4 and 7%. Precipitator operating problems attributable to high ash resistivity can be overcome by injecting sulfur trioxide to reduce the ash resistivity, with, of course, a probable increase in operating costs.

2.2.2 *Environmental effects and biomonitoring*

Al Sayegh Petkovsek, S., Batic, F., and Ribaric Lasnik, C. 2008. Norway spruce needles as bioindicator of air pollution in the area of influence of the Sostanj Thermal Power Plant, Slovenia. *Environmental Pollution* 151: 287-291.

Abstract: This paper reports the results of total sulphur content, photosynthetic pigments, ascorbic acid (vitamin C) and [alpha]-tocopherol (vitamin E) analysed in current-year needles of Norway spruce (*Picea abies* (L.) Karst.) in the area influenced by sulphur emissions from the Sostanj Thermal Power Plant (STPP), Slovenia, in the period 1991-2004. Ten differently polluted sampling sites in the emission area of STPP were selected. After desulphurization of emission gases from STPP total sulphur content in needles decreased and vitality parameters of needles increased. Moreover, a strong correlation between the average annual emissions of SO₂ from STPP and average annual sulphur content (increase) or average annual chlorophyll content (decrease) in current-year needles was found. The results showed that spruce needles may be an useful bioindicator for detecting changes in the emission rates of SO₂.

Hijano, C., Domínguez, M., Giménez, R, Sánchez, P. and García, I. 2005. Higher plants as bioindicators of sulphur dioxide emissions in urban environments. *Environmental Monitoring and Assessment*. 111. 75-88.

Abstract: The evaluation of certain vascular plants that grow in the city of Madrid as biomonitors of SO₂ air pollution in urban environments has been carried out. Total concentration of sulphur in leaves of the chosen higher plants as well as other parameters in close relation to this contaminant (visible injury symptoms, chlorophyll a- and b-content and peroxidase activity) have been determined in order to study the spatial distribution and temporal changes in SO₂ deposition. Results obtained show that coniferous species such as *Pinus pinea*, were more sensitive to SO₂

atmospheric concentration than leafy species as *Quercus ilex* subspecies *ballota* and, in the same way, bush species, such as *Pyracantha coccinea* and *Nerium oleander*, were more sensitive than wooded species, such as *Cedrus deodara* and *Pinus pinea*, respectively. There is a higher accumulation of sulphur in vegetable species located near highways and dense traffic incidence roads and near areas with high density of population. The minimum values for accumulation of SO₂ were registered in winter and spring seasons (from January to April) due to the vegetative stop; while maximum values are obtained during the summer season (from June to September), due to the stoma opening. The highest increments in sulphur concentration, calculated as the difference between two consecutive months, are obtained in May and June for all considered species except for *Cedrus deodara* and *Pyracantha coccinea*, both species have few seasonal changes during the whole year. Some species are more sensitive to natural washing than others, showing a decrease in sulphur concentration after rainfall periods.

Ponikvar, M., J. Snajder, and B. Sedej. 2005. Honey as a bioindicator for environmental pollution with SO₂. *Apidologie* 36:403-409.

Abstract: Honey was proven to be a highly sensitive bioindicator for estimation of the environmental pollution with SO₂. A bee monitoring net consisting of 32 apiaries and covering an area of about 700 km² was configured surrounding the Sostanj coal-fired power plant. The results of investigations revealed that the amount of sulphate determined in honey from this area correlated with total yearly emissions of SO₂ observed by an electronic monitoring. When exhaust gases at the power plant were purified, a corresponding decrease in the amounts of sulphate in honey was observed. The proposed bee monitoring net is an example of using biomonitoring for tracing environmental pollution, which could be also applied to estimate the impact of NO_x gases or to trace other pollutants.

Puig, R., Avila, A., and Soler, A. 2008. Sulphur isotopes as tracers of the influence of a coal-fired power plant on a Scots pine forest in Catalonia (NE Spain). *Atmospheric Environment* 42: 733-745.

Abstract: Stable sulphur isotopes and major ionic composition were analysed in precipitation and throughfall samples from a Scots pine (*Pinus sylvestris*, L.) forest near the Cercs coal-fired power plant (Catalonia, NE Spain). The purpose of the study was to determine the main sources of sulphur deposition on this pine forest. Sulphur isotope measurements from the SO₂ power plant stack emissions were used to identify the isotopic signature of this source. Net throughfall fluxes of sulphur (26.1 kg S ha⁻¹ yr⁻¹) and nitrogen (16.3 kg N ha⁻¹ yr⁻¹) were higher--5-25 times higher for S and 5-15 times for N--at this site than in other forests in Catalonia. Sulphur isotope analysis confirmed that the net throughfall fluxes of sulphur were mostly due to the dry deposition of the SO₂ power plant emissions onto the pine canopies. Two potential atmospheric end-members were distinguished: regional background rainwater ($\delta^{34}\text{S}=+7.2$ [per mille sign]) and power plant emissions ($\delta^{34}\text{S}=-2.8$ [per mille sign]). By applying a two-component sulphur isotope mixing model, we found that during periods of low power plant activity (≤ 10 emission h day⁻¹), 62% of the throughfall sulphate could be attributed to the power plant emissions. At higher activity periods (≥ 14 emission h day⁻¹), this contribution rose to 73%. Although power plant contribution to bulk deposition was lower in both cases (34% and 45%), the possible influence of sulphate coming with long-range transport events from the polluted areas in the Mediterranean basin ($\delta^{34}\text{S} \approx 0$ [per mille sign]) was not discarded.

Yao, X. H., N. T. Lau, M. Fang, and C. K. Chan. 2006. Use of stationary and mobile measurements to study power plant emissions. *Journal of the Air & Waste Management Association* 56:144-151.

Abstract: This paper presents a technique to study air pollution by combining high spatial resolution data obtained by a mobile platform and those measured by conventional stationary stations. Conventional stations provide time-series point data but cannot yield information, that is distant from the sites. This can be complemented or supplemented by mobile measurements in the vicinity of the conventional sites. Together, the combined dataset yields a clearer and more precise picture of the dispersion and the transformation of pollutants in the atmosphere in a fixed time frame. Several experiments were conducted in the years 2002-2003 to track the impact of power plant plumes on ground receptors in the immediate vicinity (within a radius of 30 km) of the plants, using a combined mobile and stationary dataset. *The mobile data allowed the identification of emissions from coal-fired and gas-fired power plants. Coal-fired power plants were the major source of sulfur dioxide (SO₂), whereas nitrogen oxides (NO_x) emitted from the gas-fired power plant played an important role in the formation of ozone (O₃) at ground level.* The mobile data showed that two particle size distribution regimes were detected: one had a dominant accumulation mode at 0.40-0.65 µm and the other at 0.65-1 µm. The existence of particles characterized by their mode at 0.65-1 µm and formed by in-cloud processes suggests that vehicular emissions were not the, important source. Other local sources, such as power plants (elevated emission), were the likely sources, because Hong Kong does not have much manufacturing industry.

2.2.2.1 Acidification

Akselsson, C., Ardo, J., and Sverdrup, H. 2004. Critical loads of acidity for forest soils and relationship to forest decline in the Northern Czech Republic. Environmental Monitoring and Assessment 98: 363-379.

Abstract: Critical load calculations in the Czech part of 'the Black Triangle' show exceedance of critical load in 75% of the forest area. A comparison with forest damage data shows an insignificant tendency toward more forest damage in areas with high exceedance. We conclude that high exceedance of critical load is a probable contributing factor to forest damage in the area.

Alpay, S., Veillette, J.J., Dixit, A.S., and Dixit, S.S. 2006. Regional and historical distributions of lake-water pH within a 100-km radius of the Horne smelter in Rouyn-Noranda, Quebec, Canada. Geochemistry: Exploration, Environment, Analysis 6: 179-186.

Abstract: The spatial distribution of lake-water pH near the Horne smelter in Rouyn-Noranda, Quebec, Canada, is affected not only by industrial sulphur dioxide emissions, but also by other anthropogenic and natural factors. Regional calcareous glaciolacustrine deposits from glacial lakes Barlow and Ojibway provide buffering capacity. Locally, some kettle lakes are buffered by silicate weathering. Small mines, tailings, and natural sources of acidity (e.g. peat basins, forested catchment areas with acidic soils) also contribute to lake acidification. Interpreting the modern regional distribution of lake-water pH, ranging from 3.7 to 9.3 in 99 lakes, is equivocal in this area where wind-transported emissions and buffering from calcareous glaciolacustrine deposits can yield similar spatial trends. However, in a parallel study, diatom assemblages have been used as bio-indicators of past lake-water pH since they respond to temporal shifts in environmental conditions, including lake-water acidity. The historical pH reconstructions for two lakes within a 100-km radius of Rouyn-Noranda suggest that they were naturally acidic before industrialization and have further acidified. Lac de la Pepiniere was naturally acidic in the 1800s (pH 5.5) and reached a pH of 4.8 by 1998; its increased rate of acidification since 1927 corresponds to the beginning of mining and smelting operations.

Brouwer, E., and Roelofs, J.G.M. 2002. Oligotrophication of acidified, nitrogen-saturated softwater lakes after dredging and controlled supply of alkaline water. Archiv fur Hydrobiologie 155: 83-97.

Abstract: After acidification of shallow softwater lakes as a consequence of atmospheric sulphur and nitrogen deposition, the concentrations of nitrogen and carbon dioxide in the water layer are raised and the cation reserves in the sediment are depleted. Liming can counteract acidification, but can also lead to further nutrient mobilisation. Controlled supply of calcareous groundwater is an alternative method to restore the pH and alkalinity of the water layer. Sediment removal and subsequent restoration of pH leads to a reversal of the nutrient status towards pre-acidification levels. However, rapid re-acidification may occur as a consequence of supplying water from the catchment which is acid and rich in nitrogen. After three years of repeated groundwater supply, the base saturation of the sediment was higher than that of adjacent reference lakes where the sediment had been removed simultaneously. This base saturation is possibly a key factor in the prevention of re-acidification. During a five-year period after the start of groundwater supply, CO₂ and nitrogen concentrations in the water layer decreased and were not higher compared to adjacent reference lakes. Characteristic softwater macrophytes returned, but not in the reference lakes.

Fenn, M.E., Huntington, T.G., Mclaughlin, S.B., Eagar, C., Gomez, A., and Cook, R.B. 2006. Status of soil acidification in North America. Journal of Forest Science 52: 3-13.

Abstract: Forest soil acidification and depletion of nutrient cations have been reported for several forested regions in North America, predominantly in the eastern United States, including the northeast and in the central Appalachians, but also in parts of southeastern Canada and the southern U.S. Continuing regional inputs of nitrogen and sulfur are of concern because of leaching of base cations, increased availability of soil Al, and the accumulation and ultimate transmission of acidity from forest soils to streams. Losses of calcium from forest soils and forested watersheds have now been documented as a sensitive early indicator and a functionally significant response to acid deposition for a wide range of forest soils in North America. For red spruce, a clear link has been established between acidic deposition, alterations in calcium and aluminum supplies and increased sensitivity to winter injury. Cation depletion appears to contribute to sugar maple decline on some soils, specifically the high mortality rates observed in northern Pennsylvania over the last decade. While responses to liming have not been systematically examined in North America, in a study in Pennsylvania, restoring basic cations through liming increased basal area growth of sugar maple and levels of calcium and magnesium in soil and foliage. In the San Bernardino Mountains in southern California near the west coast, the pH of the A horizon has declined by at least 2 pH units (to pH 4.0-4.3) over the past 30 years, with no detrimental effects on bole growth; presumably, because of the Mediterranean climate, base cation pools are still high and not limiting for plant growth.

Flues, M., Hama, P., Lemes, M.J.L., Dantas, E.S.K., and Fornaro, A. 2002. Evaluation of the rainwater acidity of a rural region due to a coal-fired power plant in Brazil. Atmospheric Environment 36: 2397-2404.

Abstract: Rainwater samples (73) of a rural region surrounding a coal plant in the northeast of Parana State (Brazil) were evaluated. Samples of bulk and wet deposition were analysed during a 1-year period (June 1999-June 2000). A large number of rain samples (51) presented pH values below 5.6 (volume weight mean (VWM) was pH=4.7±0.7), indicating that the region rainwater was slightly acidic. The anions and cations concentrations in rainwater samples showed a high sulphate concentration (69µeqL⁻¹), followed by sodium, calcium and ammonium (35, 32 and 30µeqL⁻¹, respectively). The analysis of different data of the region indicates that one probable source of the high sodium concentration is fly ash, after the coal burning process. Due to a large

contribution of these cations to the sulphate neutralization action, the rainwater of this region displays only a moderate acidity, which does not cause significant environmental impact.

Hultberg, H., and Ferm, M. 2004. Temporal changes and fluxes of sulphur and calcium in wet and dry deposition, internal circulation as well as in run-off and soil in a forest at Gardsjon, Sweden. *Biogeochemistry* 68: 355-364.

Abstract: Sulphur dioxide in air as well as dry deposition of sulphur dioxide to a forest has decreased by a factor of 20 during the last two decades. It was earlier found that the internal circulation of calcium in Norway spruce follows the dry deposition of sulphur dioxide. The sulphur and calcium fluxes from 1992 were calculated from wet deposition, throughfall and a surrogate surface. Earlier fluxes from 1981 to 1991 were calculated using assumptions of the dry deposition of non-marine sulphate and calcium. The new estimates confirm the earlier studies that the internal circulation of calcium in a coniferous forest is directly related to the dry deposition of sulphur dioxide to the canopies and that the internal circulation of calcium decreases at the same rate as the deposition of sulphur decreased during the last two decades. The deposition fluxes were also compared to run-off and uptake of calcium in the forest as well as on modelled weathering rates from severely acidified forested catchments near the coast and inland and the soil pool. A reconstruction of changes in the soil pool of calcium over the last 100 years indicate that the soil pool has decreased by ca. 70% in catchments with complete harvest of the forest and ca. 40% if branches and needles are left on the ground. In a natural forest without acid deposition the soil pool of calcium would have increased by 6%. Estimates for the 21st century show that harvesting of stems+branches and needles may almost empty the soil pool of calcium in the next 100 years. Increased nitrogen deposition has increased forest growth, which indirectly increased uptake of calcium by the trees and indirectly caused a further decrease of the soil pool of calcium.

Klose, S., K. D. Wernecke, and F. Makeschin. 2004. Microbial activities in forest soils exposed to chronic depositions from a lignite power plant. *Soil Biology and Biochemistry* 36:1913-1923.

Abstract: Atmospheric emissions of fly ash and SO₂ from lignite-fired power plants strongly affect large forest areas in Germany. The impact of different deposition loads on the microbial biomass and enzyme activities was studied at three forest sites (*Picea abies* (L.) Karst.) along an emission gradient of 3, 6, and 15 km downwind of a coal-fired power plant (sites Ia, II, and III, respectively), representing high, moderate and low emission rates. An additional site (site Ib) at a distance of 3 km from the power plant was chosen to study the influence of forest type on microbial parameters in coniferous forest soils under fly ash and SO₂ emissions. Soil microbial biomass C and N, CO₂ evolved and activities of L-asparaginase, L-glutaminase, beta-glucosidase, acid phosphatase and arylsulfatase (expressed on dry soil and organic C basis) were determined in the forest floor (L, Of and Oh horizon) and mineral top soil (0-10 cm). The emission-induced increases in ferromagnetic susceptibility, soil pH, concentrations of mobile (NH₄)NO₃ extractable Cd, Cr, and Ni, effective cation exchange capacity and base saturation in the humus layer along the 15 km long transect significantly (P<0.05) reflected the effect of past depositions of alkaline fly ash. Soil microbial and biochemical parameters were significantly (P<0.05) affected by chronic fly ash depositions. The effect of forest type (i.e. comparison of sites Ia and Ib) on the studied parameters was generally dominated by the deposition effect. Alkaline depositions significantly (P<0.05) decreased the microbial biomass C and N, microbial biomass C-to-N ratios and microbial biomass C-to-organic C ratios. Microbial respiration, metabolic quotient (qCO₂) and the activities of L-asparaginase, L-glutaminase, beta-glucosidase, acid phosphatase and arylsulfatase were increased by long-term depositions from the power plants. Acid phosphatase had the highest specific (enzyme activities expressed per unit organic C) activity values among the enzymes studied and arylsulfatase the lowest. The

responses of the microbial biomass and soil respiration data to different atmospheric deposition loads were mainly controlled by the content of organic C and cation exchange capacity, while those of enzyme activities were governed by the soil pH and concentrations of mobile heavy metals. We concluded that chronic fly ash depositions decrease litter decomposition by influencing specific microbial and enzymatic processes in forest soils.

Kozlov, M. V. 2003. Density fluctuations of the leafminer *Phyllonorycter strigulatella* (Lepidoptera: Gracillariidae) in the impact zone of a power plant. *Environmental Pollution* 121:1-10.

Abstract: Populations of a tiny moth *Phyllonorycter strigulatella*, whose larvae develop in leaves of *Alnus incana*, were monitored around a coal fired power plant (annually emitting 11-29 Kt of SO₂) near Apatity, northwestern Russia, during 1991-2001. The periodicity in density fluctuation was not affected by pollution; the peak densities of the leafminer in both polluted and clean localities were observed in 1993 and 1999. Densities of *P. strigulatella* showed no correlation with pollution between the outbreaks but strongly increased near the power plant during the outbreaks. In polluted localities the density increased by a factor of 15-20, whereas in clean localities it increased by a factor of 3-4, relative to the latent density. Mine distribution among individual leaves was more aggregated near the power plant. *P. strigulatella* demonstrated higher preference of long shoots in the contaminated sites, but mine distributions within a shoot and within a leaf did not change with the distance from the polluter. Thus, moderate contamination by SO₂ favoured *P. strigulatella*, leading to an increase in the intensity of outbreaks (the ratio between outbreak and latent densities) by a factor of five, but did not change either frequency of outbreaks or timing of density increase.

Laudon, H., and Bishop, K.H. 2002. The rapid and extensive recovery from episodic acidification in northern Sweden due to declines in SO₂⁴⁻ deposition. *Geophysical Research Letters* 29: 35.1-35.4.

Abstract: Reductions in acid deposition have led to rapid and substantial recovery from episodic acidification associated with spring snow melt in circumpolar waters including 80,000 lakes and 1,000,000 km of watercourses in northern Sweden. Our results are based on the correlation between SO₄²⁻ concentration in snow and the anthropogenic component of spring flood ANC decline. An empirical model of spring flood response to acid deposition built around that correlation predicts that the 65% reduction in sulphur deposition between 1970 and 1990 has reduced the area of seriously acidified spring floods across 250,000 km² of northern Sweden by 75%. The study suggests that much of what has been achieved so far by the large and costly emission reductions in Europe and North America the last decades lies not primarily in chronically acidified regions but rather in more marginally impacted areas where episodic acidification.

Wood, Y.A., Fenn, M., Meixner, T., Shouse, P.J., Breiner, J., Allen, E., and Wu, L. 2007. Smog nitrogen and the rapid acidification of forest soil, San Bernardino Mountains, southern California. *The Scientific World Journal* 7: 175-180.

Abstract: We report the rapid acidification of forest soils in the San Bernardino Mountains of southern California. After 30 years, soil to a depth of 25 cm has decreased from a pH (measured in 0.01 M CaCl₂) of 4.8 to 3.1. At the 50-cm depth, it has changed from a pH of 4.8 to 4.2. We attribute this rapid change in soil reactivity to very high rates of anthropogenic atmospheric nitrogen (N) added to the soil surface (72 kg ha⁻¹ year⁻¹) from wet, dry, and fog deposition under a Mediterranean climate. Our research suggests that a soil textural discontinuity, related to a buried ancient landsurface, contributes to this rapid acidification by controlling the spatial and temporal movement of precipitation into the landsurface. As a result, the depth to which dissolved

anthropogenic N as nitrate (NO₃) is leached early in the winter wet season is limited to within the top 130 cm of soil where it accumulates and increases soil acidity. has been the primary chemical impact of SO₂⁴⁻ - deposition.

Zapletal, M. 2006. Atmospheric deposition of nitrogen and sulphur in relation to critical loads of nitrogen and acidity in the Czech Republic. Journal of Forest Science 52: 92-100.

Abstract: Estimates of dry and wet deposition of sulphur and nitrogen were compared with critical loads of sulphur and nitrogen in the Czech Republic on 1 + 1 km grid. Deposition was estimated from monitored and modelled concentrations in the atmosphere and in precipitation where the most important acidifying compounds are sulphur dioxide, nitrogen oxides and ammonia, and their reaction products. Wet deposition was derived from concentration values for SO₄²⁻, NO₃⁻ and NH₄⁺ in precipitation and from precipitation amounts. Dry deposition was derived from concentrations of gaseous components and aerosol in the air, and from their deposition velocities. A simple mass balance model was used to calculate critical loads of sulphur and nitrogen. The annual average value of total (potential) acid decreased from 4,147 to 2,185 mol H⁺/ha/year between 1991 and 2000. A reduction in total sulphur and nitrogen (total potential acid) deposition by about 60% would protect 98% of the area of sensitive forests.

2.2.2.2 Nitrogen saturation and eutrophication

Aber, J.D., Goodale, C.L., Ollinger, S.V., Smith, M.L., Magill, A.H., Martin, M.E., Hallett, R.A., and Stoddard, J.L. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? BioScience 53: 375-389.

Abstract: Concern is resurfacing in the United States over the long-term effects of excess nitrogen (N) deposition and mobility in the environment. We present here a new synthesis of existing data sets for the northeastern United States, intended to answer a single question: Is N deposition altering the N status of forest ecosystems in this region? Surface water data suggest a significant increase in nitrate losses with N deposition. Soil data show an increase in nitrification with decreasing ratio of soil carbon to nitrogen (C:N) but weaker relationships between N deposition and soil C:N ratio or nitrification. Relationships between foliar chemistry and N deposition are no stronger than with gradients of climate and elevation. The differences in patterns for these three groups of indicators are explained by the degree of spatial and temporal integration represented by each sample type. The surface water data integrate more effectively over space than the foliar or soil data and therefore allow a more comprehensive view of N saturation. We conclude from these data that N deposition is altering N status in northeastern forests.

Aber, J.D., and Magill, A.H. 2004. Chronic nitrogen additions at the Harvard Forest (USA): The first 15 years of a nitrogen saturation experiment. Forest Ecology and Management 196: 1-5.

Abstract: The delivery of reactive forms of nitrogen to the environment through the sum of agricultural and industrial activities now exceeds that from natural processes. Potential negative effects on forests were first proposed in 1985, and in the ensuing two decades, the process of N saturation has become a well-established and generally understood phenomenon, with a few remaining, significant unknowns. One goal of this special section in Forest Ecology and Management is to report in detail on results from the first 15 years of chronic nitrogen additions to two contrasting forest types at the Harvard Forest in Petersham, MA, USA, with special reference to these two central questions. As similar projects elsewhere come to an end, the Harvard Forest experiment remains as one of the few on-going, long-term N saturation

experiments. Longevity has enhanced the value of the chronic N experiment, and lead to a series of collaborative studies on plant, soil and microbial responses. Another goal of this special issue is to bring together and present the findings resulting from a diverse set of measurements enabled by the presence of this long-term experiment. A total of 11 papers are presented, in addition to this brief introduction.

Dise, N.B., and Gundersen, P. 2004. Forest ecosystem responses to atmospheric pollution: Linking comparative with experimental studies. *Water, Air, and Soil Pollution: Focus* 4: 207-220.

Abstract: The impact on an ecosystem of an environmental stress, such as climate change or air pollution, can be studied through experimentation, through comparisons of sites across a gradient of the stress, through long-term studies at a single site, or through theoretical or modelling approaches. Although the former three techniques often are used to develop and test models, it is much rarer to explicitly link experimental, comparative or long-term studies together. Here we present a concept for combining experimental and comparative research to assess the direction and rate of change, the expected long-term state, and the rate at which the long-term state is achieved after an ecosystem is exposed to an environmental stress. We do this by comparing the response of a forest in Denmark to experimentally increased N deposition with the expected long-term response based on a European database of forests exposed to different levels of N deposition over long time periods. The analysis suggests that if N deposition were to increase by 3-fold to about 50 kg N ha⁻¹ a⁻¹ at the Danish site, and remain at this level, the N concentration in needles would respond within 2-4 yr after the onset of the enhanced N deposition, and would rapidly plateau to an expected mean value of 18.0 mg N g⁻¹ dry mass (95% confidence interval ±2.5 mg g⁻¹). The N concentration of new litter also would respond rapidly (1-2 yr) to reach an expected value of 16.6 mg N kg⁻¹ dry mass (±3). The N concentration of the organic layer in the soil would increase much more slowly, but a significant increase would be expected within 5-10 yr. Mineral soil pH would take more than 7 yr to change. Finally, the flux of dissolved inorganic N in leachate would begin to increase immediately, but would take many years to reach the expected level of 22.4 kg N ha⁻¹ a⁻¹ (±4).

Dise, N.B., and Stevens, C.J. 2005. Nitrogen deposition and reduction of terrestrial biodiversity: evidence from temperate grasslands. *Science in China. Series C, Life sciences / Chinese Academy of Sciences*. 48: 720-728.

Abstract: Biodiversity is thought to be essential for ecosystem stability, function and long-term sustainability. Since nitrogen is the limiting nutrient for plant growth in many terrestrial ecosystems, reactive nitrogen has the potential to reduce the diversity of terrestrial vegetation and associated biota through favouring species adapted to quickly exploiting available nutrients. Although the potential has long been recognised, only recently has enough evidence come together to show beyond reasonable doubt that these changes are already occurring. Linked together, experimental, regional/empirical, and time-series research provide a powerful argument that enhanced deposition of reactive nitrogen across Great Britain, and potentially the rest of Europe, has resulted in a significant and ongoing decline in grassland species richness and diversity.

Driscoll, C., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C., Groffman, P., Hopkinson, C., Lambert, K., Lawrence, G., and Ollinger, S. 2003. Nitrogen pollution: Sources and consequences in the U.S. Northeast. *Environment* 45: 8-22.

Abstract: Nitrogen pollution is increasing in the Northeast and contributes to a wide array of environmental problems. As a single nitrogen molecule cascades through the environment, it contributes to air-quality degradation, acidification of soil and surface waters, disruption of forest

processes, and overenrichment of coastal waters. Solving the nitrogen problem will require a multipronged approach. Computer model results show that the current Clean Air Act has not had a substantial effect on airborne nitrogen emissions and further reductions are needed to mitigate the impacts of high nitrogen deposition on sensitive ecosystems. Another computer model determined that nitrogen loading to estuaries in the Northeast is high and dominated by nitrogen discharged from wastewater treatment plants. Adding nitrogen control technology to treatment plants would significantly reduce nitrogen pollution in the region's estuaries. The results of this study show that policy efforts in the Northeast should include concentrated efforts to reduce airborne nitrogen emissions from vehicles and electric utilities and increased investment in improved wastewater treatment to address nitrogen pollution.

Driscoll, C.T., Whitall, D., Aber, J., Boyer, E., Castro, M., Cronan, C., Goodale, C.L., Groffman, P., Hopkinson, C., Lambert, K., Lawrence, G., and Ollinger, S. 2003. Nitrogen pollution in the northeastern United States: Sources, effects, and management options. *BioScience* 53: 357-374.

Abstract: The northeastern United States receives elevated inputs of anthropogenic nitrogen (N) largely from net imports of food and atmospheric deposition, with lesser inputs from fertilizer, net feed imports, and N fixation associated with leguminous crops. Ecological consequences of elevated N inputs to the Northeast include tropospheric ozone formation, ozone damage to plants, the alteration of forest N cycles, acidification of surface waters, and eutrophication in coastal waters. We used two models, PnET-BGC and WATERSN, to evaluate management strategies for reducing N inputs to forests and estuaries, respectively. Calculations with PnET-BGC suggest that aggressive reductions in N emissions alone will not result in marked improvements in the acid-base status of forest streams. WATERSN calculations showed that management scenarios targeting removal of N by wastewater treatment produce larger reductions in estuarine N loading than scenarios involving reductions in agricultural inputs or atmospheric emissions. Because N pollution involves multiple sources, management strategies targeting all major pollution sources will result in the greatest ecological benefits.

Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., and Neitlich, P. 2003. Ecological effects of nitrogen deposition in the western United States. *BioScience* 53: 404-420.

Abstract: In the western United States vast acreages of land are exposed to low levels of atmospheric nitrogen (N) deposition, with interspersed hotspots of elevated N deposition downwind of large, expanding metropolitan centers or large agricultural operations. Biological response studies in western North America demonstrate that some aquatic and terrestrial plant and microbial communities are significantly altered by N deposition. Greater plant productivity is counterbalanced by biotic community changes and deleterious effects on sensitive organisms (lichens and phytoplankton) that respond to low inputs of N (3 to 8 kilograms N per hectare per year). Streamwater nitrate concentrations are elevated in high-elevation catchments in Colorado and are unusually high in southern California and in some chaparral catchments in the southwestern Sierra Nevada. Chronic N deposition in the West is implicated in increased fire frequency in some areas and habitat alteration for threatened species. Between hotspots, N deposition is too low to cause noticeable effects or has not been studied.

Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O. 2003. Nitrogen emissions, deposition, and monitoring in the western United States. *BioScience* 53: 391-403.

Abstract: Nitrogen (N) deposition in the western United States ranges from 1 to 4 kilograms (kg) per hectare (ha) per year over much of the region to as high as 30 to 90 kg per ha per year

downwind of major urban and agricultural areas. Primary N emissions sources are transportation, agriculture, and industry. Emissions of N as ammonia are about 50% as great as emissions of N as nitrogen oxides. An unknown amount of N deposition to the West Coast originates from Asia. Nitrogen deposition has increased in the West because of rapid increases in urbanization, population, distance driven, and large concentrated animal feeding operations. Studies of ecological effects suggest that emissions reductions are needed to protect sensitive ecosystem components. Deposition rates are unknown for most areas in the West, although reasonable estimates are available for sites in California, the Colorado Front Range, and central Arizona. National monitoring networks provide long-term wet deposition data and, more recently, estimated dry deposition data at remote sites. However, there is little information for many areas near emissions sources

Fenn, M.E., Geiser, L., Bachman, R., Blubaugh, T.J., and Bytnerowicz, A. 2007. Atmospheric deposition inputs and effects on lichen chemistry and indicator species in the Columbia River Gorge, USA. *Environmental Pollution* 146: 77-91.

Abstract: Topographic and meteorological conditions make the Columbia River Gorge (CRG) an 'exhaust pipe' for air pollutants generated by the Portland-Vancouver metropolis and Columbia Basin. We sampled fog, bulk precipitation, throughfall, airborne particulates, lichen thalli, and nitrophytic lichen distribution. Throughfall N and S deposition were high, 11.5-25.4 and 3.4-6.7 kg ha⁻¹ over 4.5 months at all 9 and 4/9 sites, respectively. Deposition and lichen thallus N were highest at eastern- and western-most sites, implicating both agricultural and urban sources. Fog and precipitation pH were frequently as low as 3.7-5.0. Peak NO_x, NH₃, and SO₂ concentrations in the eastern CRG were low, suggesting enhanced N and S inputs were largely from particulate deposition. Lichens indicating nitrogen-enriched environments were abundant and lichen N and S concentrations were 2+ higher in the CRG than surrounding national forests. The atmospheric deposition levels detected likely threaten Gorge ecosystems and cultural resources.

Gundersen, P., Schmidt, I.K., and Raulund-Rasmussen, K. 2006. Leaching of nitrate from temperate forests - Effects of air pollution and forest management. *Environmental Reviews* 14: 1-57.

Abstract: We compiled regional and continental data on inorganic nitrogen (N) in seepage and surface water from temperate forests. Currently, N concentrations in forest waters are usually well below water quality standards. But elevated concentrations are frequently found in regions with chronic N input from deposition (>8-10 kg ha⁻¹ a⁻¹). We synthesized the current understanding of factors controlling N leaching in relation to three primary causes of N cycle disruption: (i) Increased N input (air pollution, fertilization, N₂ fixing plants). In European forests, elevated N deposition explains approximately half of the variability in N leaching, some of the remaining variability could be explained by differences in N availability or "N status". For coniferous forests, needle N content above 1.4% and (or) forest floor C:N ratio lower than 25 were thresholds for elevated nitrate leaching. At adjacent sites conifer forests receive higher N deposition and exhibit higher nitrate loss than deciduous forests; an exception is alder that shows substantial nitrate leaching through N fixation input. Fertilization with N poses limited risk to water quality, when applied to N-limited forests, (ii) Reduced plant uptake (clear-cut, thinning, weed control). The N cycle responses to plant cover disturbance by clear-cut are well studied. Nitrate losses peak after 2-3 years and are back to pre-cut levels after 3-5 years. Nitrogen losses increase with deposition and are higher at N rich sites. The extent and duration of the nitrate response is especially connected to the recovery of the vegetation sink. Less intensive disturbances like thinning have only minor effects on N loss. (iii) Enhanced mineralization of soil N (liming, ditching, climate change). Responses in nitrate leaching after liming may increase with N deposition and in older stands. However data on these types of N cycle disruption are too

sparse to allow general conclusions on controlling factors. Nitrate leaching occurs when N deposition (input) and net mineralization (N status) exceed plant demand. A combined N flux to the soil of 50 to 60 kg ha⁻¹ a⁻¹ from N deposition and litterfall may be a threshold for nitrate leaching in undisturbed forests. This threshold also indicates risk of increasing losses in case of a disturbance (e.g., clear-cut). We conclude by discussing forest management options for water quality protection. These options focus on decreasing input, increasing plant uptake, increasing biomass removal, and (re)establishing immobilization and denitrification processes at the catchment scale.

Heijmans, M.M.P.D., Klees, H., De Visser, W., and Berendse, F. 2002. Response of a Sphagnum bog plant community to elevated CO₂ and N supply. *Plant Ecology* 162: 123-134.

Abstract: The response of plant growth to rising CO₂ levels appears to depend on nutrient availability, but it is not known whether the growth of bog plants reacts similarly. We therefore studied the effects of elevated CO₂ in combination with N supply on the growth of Sphagnum mosses and vascular plants in ombrotrophic bog vegetation. Because the growth of Sphagnum is less nutrient-limited than that of vascular plants, we hypothesized that Sphagnum would benefit from elevated CO₂. In our greenhouse experiment, peat monoliths (34 cm diameter, 40 cm deep) with intact bog vegetation were exposed to ambient (350 ppmv) or elevated (560 ppmv) atmospheric CO₂ combined with low (no N addition) or high (5 g N m⁻² yr⁻¹ added) N deposition for two growing seasons. Elevated atmospheric CO₂ had unexpected deleterious effects on the growth of Sphagnum magellanicum, the dominant Sphagnum species. Growth was greatly reduced, particularly in the second growing season when, regardless of N supply, the mosses looked unhealthy. The negative CO₂ effect was strongest in the warmest months, suggesting a combined effect of elevated CO₂ and the raised temperatures in the greenhouse. High N deposition favored Rhynchospora alba, which became the dominant vascular plant species during the experiment. Biomass increased more when N supply was high. There were no significant effects of elevated CO₂ on vascular plants, although elevated CO₂ combined with high N supply tended to increase the aboveground vascular plant biomass. As Sphagnum is the main carbon-sequestering species in bogs and rising atmospheric CO₂ levels are likely to be followed by increases in temperature, there is an urgent need for further research on the combined effects of elevated CO₂ and increased temperature on Sphagnum growth in bog ecosystems.

Kochy, M., and S.Brakenhielm 2008. Separation of effects of moderate N deposition from natural change in ground vegetation of forests and bogs. *Forest Ecology and Management* 255: 1654-1663.

Abstract: The effect of moderate rates of nitrogen deposition on ground floor vegetation is poorly predicted by uncontrolled surveys or fertilization experiments using high rates of nitrogen (N) addition. We compared the temporal trends of ground floor vegetation in permanent plots with moderate (7-13 kg ha⁻¹ year⁻¹) and lower bulk N deposition (4-6 kg ha⁻¹ year⁻¹) in southern Sweden during 1982-1998. We examined whether trends differed between growth forms (vascular plants and bryophytes) and vegetation types (three types of coniferous forest, deciduous forest, and bog). Trends of site-standardized cover and richness varied among growth forms, vegetation types, and deposition regions. Cover in spruce forests decreased at the same rate with both moderate and low deposition. In pine forests cover decreased faster with moderate deposition and in bogs cover decreased faster with low deposition. Cover of bryophytes in spruce forests increased at the same rate with both moderate and low deposition. In pine forests cover decreased faster with moderate deposition and in bogs and deciduous forests there was a strong non-linear increase with moderate deposition. The trend of number of vascular plants was constant with moderate and decreased with low deposition. We found no trend in the number of

bryophyte species. We propose that the decrease of cover and number with low deposition was related to normal ecosystem development (increased shading), suggesting that N deposition maintained or increased the competitiveness of some species in the moderate-deposition region. Deposition had no consistent negative effect on vegetation suggesting that it is less important than normal successional processes.

Meixner, T., Allen, E.B., Tonnessen, K., Fenn, M., and Poth, M. 2002. Atmospheric nitrogen deposition: Implications for managers of western U.S. parks. *Park Science* 21: 30-33.

Abstract: A comparison of three ecosystems highlights differences in the susceptibility of natural resources to the effects of atmospheric nitrogen deposition.

Nilsson, L.O., Wallander, H., th, E., and Falkengren-Grerup, U. 2006. Soil N chemistry in oak forests along a nitrogen deposition gradient. *Biogeochemistry* 80: 43-55.

Abstract: Anthropogenic N deposition may change soil conditions in forest ecosystems as demonstrated in many studies of coniferous forests, whereas results from deciduous forests are relatively scarce. Therefore the influence of N deposition on several variables was studied in situ in 45 oak-dominated deciduous forests along a N deposition gradient in southern Sweden, where the deposition ranged from 10 to 20 kg N ha⁻¹ year⁻¹. Locally estimated NO₃⁻ deposition, as measured with ion-exchange resins (IER) on the soil surface, and grass N concentration (%) were positively correlated with earlier modelled regional N deposition. Furthermore, the δ¹⁵N values of grass and uppermost soil layers were negatively correlated with earlier modelled N deposition. The data on soil NO₃⁻, measured with IER in the soil, and grass N concentration suggest increased soil N availability as a result of N deposition. The δ¹⁵N values of grass and uppermost soil layers indicate increased nitrification rates in high N deposition sites, but no large downward movements of NO₃⁻ in these soils. Only a few sites had NO₃⁻ concentrations exceeding 1 mg N l⁻¹ in soil solution at 50 cm depth, which showed that N deposition to these acid oak-dominated forests has not yet resulted in extensive leaching of N. The δ¹⁵N enrichment factor was the variable best correlated with NO₃⁻ concentrations at 50 cm and is thus a variable that potentially may be used to predict leaching of NO₃⁻ from forest soils.

Nilsson, L.O., th, E., Falkengren-Grerup, U., and Wallander, H. 2007. Growth of ectomycorrhizal mycelia and composition of soil microbial communities in oak forest soils along a nitrogen deposition gradient. *Oecologia* 153: 375-384.

Abstract: Deciduous forests may respond differently from coniferous forests to the anthropogenic deposition of nitrogen (N). Since fungi, especially ectomycorrhizal (EM) fungi, are known to be negatively affected by N deposition, the effects of N deposition on the soil microbial community, total fungal biomass and mycelial growth of EM fungi were studied in oak-dominated deciduous forests along a nitrogen deposition gradient in southern Sweden. In-growth mesh bags were used to estimate the production of mycelia by EM fungi in 19 oak stands in the N deposition gradient, and the results were compared with nitrate leaching data obtained previously. Soil samples from 154 oak forest sites were analysed regarding the content of phospholipid fatty acids (PLFAs). Thirty PLFAs associated with microbes were analysed and the PLFA 18:26,9 was used as an indicator to estimate the total fungal biomass. Higher N deposition (20 kg N ha⁻¹ y⁻¹ compared with 10 kg N ha⁻¹ y⁻¹) tended to reduce EM mycelial growth. The total soil fungal biomass was not affected by N deposition or soil pH, while the PLFA 16:17,5, a biomarker for arbuscular mycorrhizal (AM) fungi, was negatively affected by N deposition, but also positively correlated to soil pH. Other PLFAs positively affected by soil pH were, e.g., i14:0, a15:0, 16:19, a17:0 and 18:17, while some were negatively affected by pH, such as i15:0, 16:17t, 10Me17:0 and cy19:0. In addition, N deposition had an effect on the PLFAs 16:17c and 16:19 (negatively) and cy19:0 (positively). The production of EM mycelia is probably more sensitive to N

deposition than total fungal biomass according to the fungal biomarker PLFA 18:26,9. Low amounts of EM mycelia covaried with increased nitrate leaching, suggesting that EM mycelia possibly play an important role in forest soil N retention at increased N input.

Paulissen, M.P.C.P., Van Der Ven, P.J.M., Dees, A.J., and Bobbink, R. 2004. Differential effects of nitrate and ammonium on three fen bryophyte species in relation to pollutant nitrogen input. *New Phytologist* 164: 451-458.

Abstract: In Dutch fens, subjected to high nitrogen (N) deposition, *Scorpidium* and other brown mosses have declined markedly. A concurrent strong increase of *Sphagnum* and *Polytrichum* has promoted acidification. We measured nitrate (NO₃⁻) and ammonium (NH₄⁺) availability in Dutch fens. We also tested preference for either N form of *Scorpidium scorpioides*, *Sphagnum squarrosum* and *Polytrichum commune*. Ion exchange membranes were installed in the field. In a hydroponic experiment, plants were grown on 100 μM (reflecting concentrations in Dutch precipitation since 1980), provided as NO₃⁻, NH₄NO₃, or NH₄⁺. NH₄⁺ availability in *Sphagnum* and *Polytrichum* stands and NH₄⁺:NO₃⁻ ratio in *Sphagnum* stands were higher than in brown moss stands. In the experiment, *Scorpidium* performed best on NO₃⁻. NH₄NO₃ tended to decrease its growth, whereas NH₄⁺ was very toxic. N treatment did not significantly affect growth of *Sphagnum* and *Polytrichum*. Tissue pH and nutrient concentrations confirmed the growth patterns and indicated that *Scorpidium* was most sensitive to NH₄⁺ stress. We conclude that high NH₄⁺ inputs pose a serious threat to the brown moss flora of rich fens.

Rodriguez, L., and Macias, F. 2006. Eutrophication trends in forest soils in Galicia (NW Spain) caused by the atmospheric deposition of nitrogen compounds. *Chemosphere* 63: 1598-1609.

Abstract: We calculated the sensitivity of Galician forest soils to eutrophication caused by atmospheric deposition of nitrogen compounds, using the Simple Mass Balance (SMB) method as described by [Posch, M., de Vries, W., Hettelingh, J.-P., 1995. Critical loads of sulphur and nitrogen. In: Posch, M., de Smet, P.A.M., Hettelingh, J.-P., Downing, R.J. Calculation and Mapping of Critical Thresholds in Europe. Status Report 1995, Coordination Center for Effects, National Institute for Public Health and the Environment, Bilthoven, The Netherlands, pp. 31-42]. Deposition values were used to calculate critical loads exceedance. Galician natural forest ecosystems can support nitrogen deposition loads of more than 10 kg N ha⁻¹ yr⁻¹. The lowest critical loads (approximately 10 kg N ha⁻¹ yr⁻¹) mainly occurred in forest stands in the interior zone, while highest critical load values (approximately 68 kg N ha⁻¹ yr⁻¹) were observed in eucalyptus stands at low altitudes in the littoral area. Exceedances based on N deposition levels, calculated from data recorded in 2001, occurred in 40% of the forest soils, showing the need to control N emissions in these areas to prevent possible eutrophication of soils and waters. Analysis of rainfall bulk composition revealed that ammonium, probably derived from agricultural and cattle activities, was the main compound responsible for N deposition in Galicia.

Silvola, J., Saarnio, S., Foot, J., Sundh, I., Greenup, A., Heijmans, M., Ekberg, A., Mitchell, E., and van Breemen, N. 2003. Effects of elevated CO₂ and N deposition on CH₄ emissions from European mires. *Global Biogeochemical Cycles* 17: 37-1.

Abstract: Methane fluxes were measured at five sites representing oligotrophic peatlands along a European transect. Five study plots were subjected to elevated CO₂ concentration (560 ppm), and five plots to NH₄NO₃ (3 or 5 g N yr⁻¹). The CH₄ emissions from the control plots correlated in most cases with the soil temperatures. The depth of the water table, the pH, and the DOC, N and SO₄ concentrations were only weakly correlated with the CH₄ emissions. The elevated CO₂ treatment gave nonsignificantly higher CH₄ emissions at three sites and lower at two sites. The N treatment resulted in higher methane emissions at three sites (nonsignificant). At one site, the

CH₄ fluxes of the N-treatment plots were significantly lower than those of the control plots. These results were not in agreement with our hypotheses, nor with the results obtained in some earlier studies. However, the results are consistent with the results of the vegetation analyses, which showed no significant treatment effects on species relationships or biomass production.

Stevens, C.J., Dise, N.B., Mountford, J.O., and Gowing, D.J. 2004. Impact of Nitrogen Deposition on the Species Richness of Grasslands. *Science* 303: 1876-1879.

Abstract: A transect of 68 acid grasslands across Great Britain, covering the lower range of ambient annual nitrogen deposition in the industrialized world (5 to 35 kg N ha⁻¹ year⁻¹), indicates that long-term, chronic nitrogen deposition has significantly reduced plant species richness. Species richness declines as a linear function of the rate of inorganic nitrogen deposition, with a reduction of one species per 4-m² quadrat for every 2.5 kg N ha⁻¹ year⁻¹ of chronic nitrogen deposition. Species adapted to infertile conditions are systematically reduced at high nitrogen deposition. At the mean chronic nitrogen deposition rate of central Europe (17 kg N ha⁻¹ year⁻¹), there is a 23% species reduction compared with grasslands receiving the lowest levels of nitrogen deposition.

Stevens, C.J., Dise, N.B., Gowing, D.J.G., and Mountford, J.O. 2006. Loss of forb diversity in relation to nitrogen deposition in the UK: Regional trends and potential controls. *Global Change Biology* 12: 1823-1833.

Abstract: In this study we investigate the impact of nitrogen (N) deposition on the diversity of three different vegetation functional groups - forbs, grasses and mosses - using a field survey of acid grasslands across Great Britain. Our aim is to identify the vegetation types that are most vulnerable to enhanced N deposition, and to shed light on the mechanisms that may be driving N-initiated species changes in the UK. Sixty-eight randomly selected grasslands belonging to the UK National Vegetation Classification group U4 (*Festuca ovina*-*Agrostis capillaris*-*Galium saxatile* grassland) were studied along a gradient of atmospheric N deposition ranging from 6 to 36 kg N ha⁻¹ yr⁻¹. At each site, vegetation was surveyed and samples were taken from the topsoil and subsoil. Aboveground plant material was collected from three species: a forb, grass and moss. Both the species richness and cover of forbs declined strongly with increasing N deposition, from greater than eight species/20% cover per m² quadrat at low levels of N to fewer than two species/5% cover at the highest N deposition levels. Grasses showed a weak but significant decline in species richness, and a trend toward increasing cover with increasing N input. Mosses showed no trends in either species richness or cover. Most of the decline in plant species richness could be accounted for by the level of ammonium deposition. Soil KCl-extractable ammonium concentration showed a significant positive correlation with N input, but there was no relationship between N deposition and extractable nitrate. In the soil O/ A horizon, there was no relationship between N deposition and %N, and only a very weak positive relationship between the level of N deposition and the C:N ratio. Finally, in the vegetation, there was no relationship between N deposition and either shoot tissue N concentration or N:P ratio for any of the three reference species. Combining our regional survey with the results of published N-addition experiments provides compelling evidence that there has been a significant decline in the species richness and cover of forbs across Great Britain, and that the primary cause is competition due to an increase in the cover of grasses in response to enhanced deposition of reactive N, primarily NH₄⁺.

Stoddard, J.L. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *BioScience* 53: 375-389.

Abstract: Concern is resurfacing in the United States over the long-term effects of excess nitrogen (N) deposition and mobility in the environment. We present here a new synthesis of existing data sets for the northeastern United States, intended to answer a single question: Is N

deposition altering the N status of forest ecosystems in this region? Surface water data suggest a significant increase in nitrate losses with N deposition. Soil data show an increase in nitrification with decreasing ratio of soil carbon to nitrogen (C:N) but weaker relationships between N deposition and soil C:N ratio or nitrification. Relationships between foliar chemistry and N deposition are no stronger than with gradients of climate and elevation. The differences in patterns for these three groups of indicators are explained by the degree of spatial and temporal integration represented by each sample type. The surface water data integrate more effectively over space than the foliar or soil data and therefore allow a more comprehensive view of N saturation. We conclude from these data that N deposition is altering N status in northeastern forests.

Van Den Berg, L.J.L., Tomassen, H.B.M., Roelofs, J.G.M., and Bobbink, R. 2005. Effects of nitrogen enrichment on coastal dune grassland: A mesocosm study. *Environmental Pollution* 138: 77-85.

Abstract: Mesocosms filled with dune sand were planted with graminoid (*Calamagrostis epigejos*, *Carex arenaria*) and herbaceous species (*Carlina vulgaris*, *Galium verum*). Strong effects of nitrogen addition on the vegetation were found within two to three years. The above-ground biomass of *C. epigejos* and *C. arenaria* increased at deposition rates between 10 and 80 kg N ha⁻¹ yr⁻¹. Both grasses were limited by N. In latter stages P limitation was suggested for *C. arenaria*. At high N-levels, *C. epigejos* dominated the vegetation within two years. *C. vulgaris* and *G. verum* declined drastically as a result of increased competition for light by the highly competitive grass *C. epigejos*. It is concluded that increased (ambient) N inputs are of major importance for the increased dominance of tall grasses in stable dune grasslands.

Venterea, R. T., P. M. Groffman, M. S. Castro, L. V. Verchot, I. J. Fernandez, and M. B. Adams. 2004. Soil emissions of nitric oxide in two forest watersheds subjected to elevated N inputs. *Forest Ecology and Management* 196:335-349.

Abstract: The production of nitric oxide (NO) in forest soils can indicate that the ecosystem is progressing toward a state of nitrogen (N) saturation. Soil NO emissions may also have impacts on local tropospheric ozone (O₃) levels. During 2000-2001, we made first-time measurements of NO emissions in two paired watershed studies. In each study, one watershed had been amended with aerial applications of 2.5-3.5 g N m⁻² per year above background atmospheric deposition rates since 1989, and an adjacent watershed served as a reference. In plots at the Fernow Experimental Forest (FEF) in West Virginia and the Bear Brook Watershed in Maine (BBWM), NO emissions in N-amended watersheds (0.61-6.8 μg NO-N m⁻² h⁻¹) were higher than in the reference watersheds (0.21-1.4 μg NO-N m⁻² h⁻¹). In the N-amended watershed at BBWM, NO fluxes in plots dominated by hardwood species were higher than in plots dominated by softwood species, in contrast to previous studies in other forests. Field NO fluxes were correlated with mineral soil nitrate (NO₃⁻) concentrations ($r^2=0.65$, $P=0.016$) across all plots, suggesting that NO emissions may be a reliable indicator of NO₃⁻ leaching potential. Laboratory experiments indicated that nitrification was the dominant source of NO at both sites. At BBWM, increased NO emissions in N-amended soil appeared to result from more rapid nitrification. In contrast, reduced soil pH in N-amended soil at FEF may have caused increased protonation of nitrification-derived nitrite, and the subsequent abiotic formation of NO, even though nitrification rates were not significantly higher than in unamended soil. The results suggest that enhanced soil NO emissions are a characteristic response in forests subjected to elevated N inputs. One possible consequence of higher NO emissions is an increase in O₃-related phytotoxicity. This effect may mitigate the ability of forests to accumulate carbon in response to N inputs or increasing atmospheric CO₂.

Vitt, D.H., Wieder, K., Halsey, L.A., and Turetsky, M. 2003. Response of Sphagnum fuscum to Nitrogen Deposition: A Case Study of Ombrogenous Peatlands in Alberta, Canada. Bryologist 106: 235-245.

Abstract: Peatlands cover about 30% of northeastern Alberta and are ecosystems that are sensitive to nitrogen deposition. In polluted areas of the UK, high atmospheric N deposition (as a component of acid deposition) has been considered among the causes of Sphagnum decline in bogs (ombrogenous peatlands). In relatively unpolluted areas of western Canada and northern Sweden, short-term experimental studies have shown that Sphagnum responds quickly to nutrient loading, with uptake and retention of nitrogen and increased production. Here we examine the response of Sphagnum fuscum to enhanced nitrogen deposition generated during 34 years of oil sands mining through the determination of net primary production (NPP) and nitrogen concentrations in the upper peat column. We chose six continental bogs receiving differing atmospheric nitrogen loads (modeled using a CALPUFF 2D dispersion model). Sphagnum fuscum net primary production (NPP) at the high deposition site (Steepbank - mean of 600 g/m²; median of 486 g/m²) was over three times as high than at five other sites with lower N deposition. Additionally, production of S. fuscum may be influenced to some extent by distance of the moss surface from the water table. Across all sites, peat nitrogen concentrations are highest at the surface, decreasing in the top 3 cm with no significant change with increasing depth. We conclude that elevated N deposition at the Steepbank site has enhanced Sphagnum production. Increased N concentrations are evident only in the top 1-cm of the peat profile. Thus, 34 years after mine startup, increased N-deposition has increased net primary production of Sphagnum fuscum without causing elevated levels of nitrogen in the organic matter profile. A response to N-stress for Sphagnum fuscum is proposed at 14-34 kg ha⁻¹ yr⁻¹. A review of N-deposition values reveals a critical N-deposition value of between 14.8 and 15.7 kg ha⁻¹ yr⁻¹ for NPP of Sphagnum species.

Zechmeister, H.G., Dirnbock, T., Hulber, K., and Mirtl, M. 2007. Assessing airborne pollution effects on bryophytes - lessons learned through long-term integrated monitoring in Austria. Environmental Pollution 147: 696-705.

Abstract: The study uses measured and calculated data on airborne pollutants, particularly nitrogen (ranges between 28 to 43 kg N*ha⁻¹*yr⁻¹) and sulphur (10 to 18 kg SO₄-S*ha⁻¹*yr⁻¹), in order to assess their long-term (1992 to 2005) effects on bryophytes at the UN-ECE Integrated Monitoring site 'Zobelboden' in Austria. Bryophytes were used as reaction indicators on 20 epiphytic plots using the IM monitoring method and on 14 terrestrial plots using standardised photography. The plots were recorded in the years 1992, 1993, 1998, and 2004/2005. Most species remained stable in terms of their overall population size during the observed period, even though there were rapid turnover rates of a large percentage of species on all investigated plots. Only a few bryophytes (Hypnum cupressiforme, Leucodon sciuroides) responded unambiguously to N and S deposition. Nitrogen deposition had a weak but significant effect on the distribution of bryophyte communities. However, the time shifts in bryophyte communities did not depend on total deposition of N and S.

2.2.3 Regulation, policy, and abatement technologies

Acharya, C., R. N. Kar, and L. B. Sukla. 2004. Microbial Desulfurization of Different Coals. Applied Biochemistry and Biotechnology 118:047-064.

Abstract: Coal is the most important nonrenewable energy source of fossil origin. It is also the most common fuel in thermal power plants. However, during coal incineration in power plants,

high sulfur content of coal poses serious environmental problems owing to sulfur dioxide emission. We studied the application of microbial methods for removal of sulfur from three types of high sulfur coals—two samples collected from Assam and Rajasthan in India and one from Libiaz, Poland. These coal samples were desulfurized using indigenous *Acidithiobacillus* sp. After investigation of the effect of various parameters, the conditions optimized for the maximum removal of total sulfur (91.87% for lignite, 63.13% for Polish coal, and only 9.44% for Assam coal) were as follows: initial pH of 1.5 (2.5 in the case of Assam coal), particle size of 45 μ , pulp density of 2% (w/v), incubation period of 30 d at -35 degree C in presence of 44.2 g/L of ferrous sulfate in the media with shaking at 140 rpm. Poor removal of sulfur in the case of Assam coal was owing to extensive precipitation of jarosites. In addition, the sulfur in Assam coal is mostly found in organic form, which is difficult to remove with *Acidithiobacillus* sp. The removal of sulfur from the three coal samples was demonstrated with photomicrographic studies.

Odeh, N.A., and Cockerill, T.T. 2008. Life cycle GHG assessment of fossil fuel power plants with carbon capture and storage. *Energy Policy* 36: 367-380.

Abstract: The evaluation of life cycle greenhouse gas emissions from power generation with carbon capture and storage (CCS) is a critical factor in energy and policy analysis. The current paper examines life cycle emissions from three types of fossil-fuel-based power plants, namely supercritical pulverized coal (super-PC), natural gas combined cycle (NGCC) and integrated gasification combined cycle (IGCC), with and without CCS. Results show that, for a 90% CO₂ capture efficiency, life cycle GHG emissions are reduced by 75-84% depending on what technology is used. With GHG emissions less than 170 g/kWh, IGCC technology is found to be favorable to NGCC with CCS. Sensitivity analysis reveals that, for coal power plants, varying the CO₂ capture efficiency and the coal transport distance has a more pronounced effect on life cycle GHG emissions than changing the length of CO₂ transport pipeline. *Finally, it is concluded from the current study that while the global warming potential is reduced when MEA-based CO₂ capture is employed, the increase in other air pollutants such as NO_x and NH₃ leads to higher eutrophication and acidification potentials.*

Sampattagul, S., S. Kato, T. Kiatsiroat, and A. Widiyanto. 2004. Life cycle considerations of the flue gas desulphurization system at a lignite-fired power plant in Thailand. *International Journal of Life Cycle Assessment* 9:387-393.

Abstract: Goal, Scope and Background. The Flue Gas Desulphurization (FGD) system has been installed at the biggest lignite-fired power generation plant in Thailand to reduce the large amount of SO₂ emission. In order to understand the costs and benefits, both in ecological and economic terms, the lignite-fired plant was studied both before and after the installation of the FGD system. The focus of this study is to consider not only the Life Cycle Assessment (LCA) outcome but also the Life Cycle Costing (LCC) factors. The results can provide valuable information when selecting appropriate technologies to minimize the negative impact that lignite-fired power plants have on the environment.

Methods. The Life Cycle Assessment - Numerical Eco-load Total Standardization (LCA-NETS) system was used to evaluate the impact on the environment of both the lignite-fired plant and the FGD system. Life Cycle Costing (LCC) was used to provide a comparison between alternative before and after installation of FGD. LCC, a powerful analytical tool, examines the total cost, in net present value terms, of a FGD system over its entire service lifetime.

Results and Discussion. The results of the study are shown in the eco-load values over the entire life cycle of the lignite-fired plant. Comparative models of the power plant, before and after the installation of the FGD system, are evaluated using the LCA-NETS system. The results indicate that the installation of the FGD system can reduce the acidification problem associated with lignite-fired plants by approximately 97%. The LCC estimation shows the major costs of the

FGD system: capital investment, operating and maintenance, and miscellaneous costs. The LCC provides the decision-making information when considering the cost of the FGD system in terms of protecting the environment.

Conclusion and Outlook. LCA is an important decision-making tool for environmental policies, especially with regard to the selection of pollution control equipment for lignite-fired plants. Green coal technologies and strategies to reduce the negative impact on the environment are essential to produce more environmentally-friendly power plants with a sustainable future.

Schmiedeman, E.C., Van Ierland, E.C., and Hordijk, L. 2002. Dynamic efficiency with multi-pollutants and multi-targets: The case of acidification and tropospheric ozone formation in Europe. *Environmental and Resource Economics* 23: 133-148.

Abstract: In this paper we consider two important aspects in the complex problem of transboundary air pollution in Europe, namely (i) the interdependence of the problems of tropospheric ozone and acidification and (ii) the dynamic processes related to soil acidification. We develop an optimal control model to analyse the interaction between acidification as a stock pollutant and tropospheric ozone as a flow pollutant for several countries. *Using a cost-benefit framework an analysis is performed to determine efficient emission paths for nitrogen oxides, sulphur dioxide and volatile organic compounds.* The model jointly analyses acidification and ozone. The current European reduction plans do not fully take into account the multi-pollutants multi-targets nature of the problem. In addition, the plans allow for temporary exceedance of critical loads without considering the consequences for the temporal development of the soil quality. This paper shows the complex relations and interactions which one should deal with while designing policies that are efficient with respect to the cross-effects between the different environmental problems. It also shows how dynamic efficient abatement strategies would look if the cross effects and the dynamic processes in soil acidification are explicitly incorporated in the analysis.

Seppala, J., Posch, M., Johansson, M., and Hettelingh, J.P. 2006. Country-dependent characterisation factors for acidification and terrestrial eutrophication based on accumulated exceedance as an impact category indicator. *International Journal of Life Cycle Assessment* 11: 403-416.

Abstract: Background, Aims and Scope. Several authors have shown that spatially derived characterisation factors used in life cycle impact assessment (LCIA) can differ widely between different countries in the context of regional impact categories such as acidification or terrestrial eutrophication. Previous methodology studies in Europe have produced country-dependent characterisation factors for acidification and terrestrial eutrophication by using the results of the EMEP and RAINS models and critical loads for Europe. The unprotected ecosystem area (UA) is commonly used as a category indicator in the determination of characterisation factors in those studies. However, the UA indicator is only suitable for large emission changes and it does not result in environmental benefits in terms of characterisation factors if deposition after the emission reduction is still higher than the critical load. For this reason, there is a need to search for a new category indicator type for acidification and terrestrial eutrophication in order to calculate site-dependent characterisation factors. The aim of this study is to explore new site-dependent characterisation factors for European acidifying and eutrophying emissions based on accumulated exceedance (AE) as the category indicator, which integrates both the exceeded area and amount of exceedance. In addition, the results obtained for the AE and UA indicators are compared with each other. Methods. The chosen category indicator, accumulated exceedance (AE), was computed according to the calculation methods developed in the work under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP). Sulphur and nitrogen depositions to 150x150 km² grid cells over Europe

were calculated by source-receptor matrices derived from the EMEP Lagrangian model of long-range transport of air pollution in Europe. Using the latest critical load data of Europe, the site-dependent characterisation factors for acidification and terrestrial eutrophication were calculated for 35 European countries and 5 sea areas for 2002 emissions and emissions predicted for 2010. In the determination of characterisation factors, the emissions of each country/area were reduced by various amounts in order to find stable characterisation factors. In addition, characterisation errors were calculated for the AE-based characterisation factors. For the comparison, the results based on the use of UA indicator were calculated by 10% and 50% reductions of emissions that corresponded to the common practice used in the previous studies. Results and Discussion. The characterisation factors based on the AE indicator were shown to be largely independent of the reduction percentage used to calculate them. Small changes in emissions (± 100 t) produced the most stable characterisation factors in the case of the AE indicator. The characterisation errors of those characterisation factors were practically zero. This means that the characterisation factors can describe the effects of small changes in national emissions that are mostly looked at in LCAs. The comparison between country-dependent characterisation factors calculated by the AE and UA indicators showed that these two approaches produce differences between characterisation factors for many countries/areas in Europe. The differences were mostly related to the Central and Northern European countries. They were greater for terrestrial eutrophication because the contribution of ammonia emission differ remarkably between the two approaches. The characterisation factors of the AE indicator calculated by the emissions of 2002 were greater than the factors calculated by the predicted emissions for 2010 in almost all countries/sea areas, due to the presumed decrease of acidifying and eutrophying emissions in Europe. Conclusions and Recommendations. In this study, accumulated exceedance was shown to be an appropriate category indicator in LCIA applications for the determination of site-dependent characterisation factors for acidification and terrestrial eutrophication in the context of integrated assessment modelling. In the future, it would be useful to calculate characterisation factors for emissions of separate parts of large countries and sea areas in Europe. In addition, it would also be useful to compare the approach based on the AE indicator with the method of the hazard index, as recommended in the latest CML guidebook.

Taylor, M. R., E. S. Rubin, and D. A. Hounshell. 2003. Effect of Government Actions on Technological Innovation for SO₂ Control. Environmental Science & Technology 37:4527.

Abstract: The relationship between government actions and innovation in environmental control technology is important for the design of cost-effective policies to achieve environmental goals. This paper examines such relationships for the case of sulfur dioxide control technology for U.S. coal-fired power plants. The study employs several complementary research methods, including analyses of key government actions, technology patenting activity, technology performance and cost trends, knowledge transfer activities, and expert elicitations. Our results indicate that government regulation appears to be a greater stimulus to inventive activity than government-sponsored research support alone, and that the anticipation of regulation also spurs inventive activity. Regulatory stringency focuses this activity along particular technical pathways and is a key factor in creating markets for environmental technologies. We also find that with greater technology adoption, both new and existing systems experience notable efficiency improvements and capital cost reductions. The important role of government in fostering knowledge transfer via technical conferences and other measures is also seen as an important factor in promoting environmental technology innovation.

Wang, Y. D., D. McIlveen-Wright, Y. Huang, N. Hewitt, P. Eames, S. Rezvani, J. McMullan, and A. P. Roskilly. 2007. The application of FLOX/COSTAIR technologies to

reduce NO_x emissions from coal/biomass fired power plant: A technical assessment based on computational simulation. Fuel 86:2101-2108.

Abstract: Nitrogen oxides (NO_x) is one of the harmful emissions from power plants. Efforts are made to reduce NO_x emissions by researchers and engineers all the times. NO_x emissions are from three resources during the combustion: prompt NO, fuel NO and thermal NO. The last one - thermal NO, which is described by 'Zeldovich-mechanism', is the main source for NO_x emissions. The thermal NO emission mainly results from the high combustion temperature in the combustion process. In order to control the NO formation, the control of peak combustion temperature is the key factor, as well as the oxygen concentration in the combustion areas. Flameless oxidation (FLOX) and continuous staged air combustion (COSTAIR) are two relatively new technologies to control the combustion temperature and the reaction rate and consequently to control the NO_x emissions. In this study both FLOX and COSTAIR technologies are assessed based on a 12 MW_e, coal-fired, circulating fluidised bed combustion (CFBC) power plant by using ECLIPSE simulation software, together with a circulating fluidised bed gasification (CFBG) plus normal burner plant. Two different fuels - coal and biomass (straw) are used for the simulation. The technical results from the study show that the application of FLOX technology to the plant may reduce NO_x emissions by 90% and the application of COSTAIR technology can reduce NO_x emissions by 80-85% from the power plant. The emissions from the straw-fuelled plants are all lower than that of coal-fuelled ones although with less plant efficiencies.

2.3 Particulate matter

2.3.1 Emissions, atmospheric deposition, and modeling

Balasubramanian, R., and Qian, W.B. 2004. Characterization and source identification of airborne trace metals in Singapore. *Journal of Environmental Monitoring* 6: 813-818.

Abstract: Airborne particulate trace metals have important health implications. As a consequence, their concentrations are increasingly monitored in many urban locations worldwide. In this study, fine atmospheric particles (PM 2.5) were collected in Singapore over a period of 83 consecutive days during 2000, and analysed to determine the concentration of trace elements using ICP-MS. Altogether, eighteen airborne trace metals were quantified: Al, Ag, Ba, Cd, Cr, Co, Cu, Fe, Ga, Li, Mn, Ni, Pb, Sr, Zn, V, Si, and Ti. While Li was the least abundant trace metal with a mean concentration of 0.2 ng m⁻³, Zn showed the maximum mean concentration of 279.1 ng m⁻³. Calculation of enrichment factors indicated that the elements Pb, Zn, Cd, V, Ni, Cr, and Cu were enriched by factors of 30 to 5000 relative to their natural abundance in crustal soil. The extent of metal pollution in the study area was assessed by comparing the measured concentrations to those reported in the literature for a selected number of urban sites in other parts of the world. Factor analysis was used to identify the major sources affecting particulate air pollution in Singapore. The sources that contribute to the loading of trace metal-bearing aerosols in the Singapore urban atmosphere include fuel oil-fired power plants, metal processing industry, land reclamation and construction activities, municipal solid waste incinerators, and traffic emissions.

Bhanarkar, A.D., Gavane, A.G., Tajne, D.S., Tamhane, S.M., and Nema, P. Composition and size distribution of particulate emissions from a coal-fired power plant in India. *Fuel In Press, Corrected Proof*: 291.

Abstract: Particulate matter in fly ash from ESP inlet and outlet of a coal fired power plant in India was measured for five units of 120 MW and 210 MW of the power plant. Samples of the pulverised coal and bottom and fly ashes were also collected. The size distribution and chemical composition of particulate matter were determined using a laser particle analyser, an ion chromatograph (IC) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The observed particle mass concentration at the ESP inlet was 5443-21483 mg Nm⁻³ whereas the outlet concentration was found as 12-315 mg Nm⁻³ thereby giving total removal efficiency of 95.7-99.8%. A fine particle mode appeared at the particle size of 0.4-0.9 [µ]m and coarse particle mode appeared at the particle size greater than 1 [µ]m. Magnesium and iron remained in bottom ash and showed high concentrations 99 and 2154 [µ]g g⁻¹ (ppmw) respectively, while other elements such as lead, chromium and zinc were observed in higher concentration in ESP inlet flue gas. Relative enrichment of trace elements (except Fe) in fly ash was observed higher than that in bottom ash.

Brook, J. R., R. L. Poirot, T. F. Dann, P. K. H. Lee, C. D. Lillyman, and T. Ip. 2007. Assessing Sources of PM sub(2.5) in Cities Influenced by Regional Transport. *Journal of Toxicology and Environmental Health, Part A: Current Issues* 70:191-199.

Abstract: The human health effects of fine particulate matter (PM sub(2.5)) have provided impetus for the establishment of new air quality standards or guidelines in many countries. This has led to the need for information on the main sources responsible for PM sub(2.5). In urban locations being impacted by regional-scale transport, source-receptor relationships for PM sub(2.5) are complex and require the application of multiple receptor-based analysis methods to

gain a better understanding. This approach is being followed to study the sources of PM sub(2.5) impacting southern Ontario, Canada, and its major city of Toronto. Existing monitoring data in the region around Toronto and within Toronto itself are utilized to estimate that 30-45% of the PM sub(2.5) is from local sources, which implies that 55-70% is transported into the area. In addition, there are locations in the city that can be shown to experience a greater impact from local sources such as motor vehicle traffic. Detailed PM sub(2.5) chemical characterization data were collected in Toronto in order to apply two different multivariate receptor models to determine the main sources of the PM sub(2.5). Both approaches produced similar results, indicating that motor-vehicle-related emissions, most likely of local origin, are directly responsible for about 20% of the PM sub(2.5). Gasoline engine vehicles were found to be a greater overall contributor (13%) compared to diesel vehicles (8%). ***Secondary PM sub(2.5) from coal-fired power plants continues to be a significant contributor (20-25%) and also played a role in enhancing production of secondary organic carbon mass (15%) on fine particles.*** Secondary fine particle nitrate was the single most important source (35%), with a large fraction of this likely related to motor vehicle emissions. Independent use of different receptor models helps provide more confidence in the source apportionment, as does comparison of results among complementary receptor-based data analysis approaches.

Carnevale, C., V. Gabusi, and M. Volta. 2006. POEM-PM: an emission model for secondary pollution control scenarios. *Environmental Modelling & Software* 21:320-329.

Abstract: The paper describes the POEM-PM (Pollutant Emission Model for gas and Particulate Matter) emission model design. The model, providing actual and alternative emission scenarios, represents a decision support tool to evaluate emission control strategy effectiveness. It estimates emissions at local and mesoscale level and implements a combined top-down and bottom-up approach. The POEM-PM emission fields answer the GAMES (Gas Aerosol Modelling Evaluation System) multiphase modelling system requirements: grid distribution, hourly time modulation, NMVOC split and lumping, PM10 granulometric and chemical description. The emission model has been validated performing episodic and seasonal simulations over Northern Italy by GAMES. POEM-PM is at present the emission model for air quality chemical and transport applications recommended by the Italian National Environmental Agency.

Cheng, J., Yuan, T., Wu, Q., Zhao, W., Xie, H., Ma, Y., Ma, J., and Wang, W. 2007. PM10-bound polycyclic aromatic hydrocarbons (PAHs) and cancer risk estimation in the atmosphere surrounding an industrial area of Shanghai, China. *Water Air Soil Pollut.* 183: 437-446.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the urban atmosphere. In particular, atmospheric pollution has increasingly become severe in China due to its rapid urbanization and industrialization. In recent years, a few studies have presented information about POPs (such as PAHs, PCBs, OCPs) in aerosols at a molecular level in a limited number of cities such as Beijing, Qingdao and Guangzhou, as well as Hong Kong. Whereas, these cities are located in northern and southern China, respectively, where characteristics of atmospheric pollution might be different from those in the eastern cities, such as Shanghai. Atmospheric particle pollution is a persistent problem in Shanghai, a typical metropolis of China, which has several huge industrial regions. In order to gain a comprehensive understanding of the present state, properties and sources of PAHs pollution in Shanghai, PM10 samples were collected at Coal-Fired Power Plant (CFP), Chlor-Alkali Chemical factory (CAC) and Coking and Chemical factory (CCF) in an industrial area, during the period, November 2004-September 2005. The concentrations of 16 PAHs were analyzed using the HPLC with UV visible detector. The results showed that the mean value of total PAHs in the industrial area was 64.85 ng m⁻³; 3-ring PAHs were found at low levels, while 4-, 5- and 6-ring PAHs were found at high levels. The

levels of BaP were 3.07 and 7.16 ng m⁻³ at Chlor-Alkali Chemistry Factory and Coking and Chemistry Factory sites, respectively. PAHs levels exhibited distinct seasonal variation, with the highest level in autumn and the lowest in summer. The major source of PAHs at the industrial area was fossil fuel combustion, coal-burning, industrial furnaces including others. There was a very significant correlation of PAHs levels between CCF and CAC ($R^2=0.91$). The average concentration of BaP in the industrial area during the sampling period was 5.95 ng m⁻³. It could be concluded the local population appears to be exposed to significantly high cancer risk (exceeding 2 ng m⁻³ in autumn and winter) as compared to the population of other areas.

Chow, J. C., and J. G. Watson. 2002. Review of PM_{2.5} and PM₁₀ apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model. *Energy & Fuels* 16:222-260.

Abstract: This review examines how the Chemical Mass Balance (CMB) receptor model has been used to quantify source contributions from fossil fuel combustion and other sources to ambient concentrations of PM_{2.5} and PM₁₀ for urban and regional scales. Nonfossil fuel sources, such as fugitive dust, cooking, vegetative burning, and natural or human-caused biogenics must be considered together with fossil-fuel sources in a CMB analysis to obtain closure for PM_{2.5} and PM₁₀ mass. CMB analyses in 22 different studies have found fossil fuel combustion to be a large contributor to PM_{2.5} and PM₁₀ concentrations, with most of the primary contributions originating from diesel- and gasoline-powered vehicle exhaust. Primary contributions from ducted sources, such as coal- and oil-fired power stations, are negligible when these facilities have been modernized with effective pollution controls, but they have been shown to be large contributors without these controls. Secondary sulfates and nitrates from fossil fuel combustion are recognized, but their attribution to specific precursor gas emitters is uncertain using either the CMB or source-oriented chemical transport models. Using source and receptor models together improves source contribution estimates and the confidence in those estimates.

Doraiswamy, P., Davis, W.T., Miller, T.L., and Fu, J.S. 2006. Contribution of coal-fired power plants to ambient PM_{2.5} in TN. *Electric Utilities Environmental Conference, EUEC 2005: 8th Annual Joint EPA, DOE, EEI, EPRI Conference on Air Quality, Global Climate Change and Renewable Energy, Vol. 2006.*

Abstract: Fine particle concentrations in the south eastern US consist of more than 50% secondary particles, of which sulfates form a major fraction. These secondary fine particles are formed from photochemical and other reactions involving precursor gases such as sulfur dioxide, NO_x, ammonia and VOCs. Source apportionment of PM_{2.5} is important to identify the source categories that are responsible for the concentrations observed at a particular receptor. Although receptor models have been used to do source apportionment, they do not fully take into account the chemical reactions (including photochemical reactions) involved in the formation of secondary fine particles. This work utilized the Models3/CMAQ modeling system for the photochemical/secondary particulate matter modeling. Point source and on-road mobile source inventories for the State of TN were estimated and compiled by the research group at the University of Tennessee (UT). The national emissions inventory (NEI) for the year 1999 was used for the other states. Hourly emissions data from the continuous emissions monitoring systems (CEMS) were used for the electric generating utilities in the modeling domain. The modeling domain consisted of a nested 36-12-4 km domain. The 4 km domain covered the entire state of TN. The episode chosen for the modeling runs was August 29 to September 9, 1999. This paper attempts to quantify the contribution of power plants to ambient fine particle concentrations in TN. This paper also shows the relative magnitude of the power plant contributions in comparison to other major source categories such as on-road mobile sources.

Garcia-Nieto, P. J. 2006. Study of the evolution of aerosol emissions from coal-fired power plants due to coagulation, condensation, and gravitational settling and health impact. Journal of Environmental Management 79:372-382.

Abstract: This paper studies the scavenging efficiencies of aerosol emissions from coal-fired power plants under different removal mechanisms (coagulation, heterogeneous nucleation and gravitational settling) as a function of time. It also analyses the 'health impact' of the aerosol before and after the above dynamic mechanisms by comparing the respirable dust fractions. The well-known equations of evolution are applied to an average PSD that represents the exhaust particulate emissions from coal-fired power plants (i.e. Abono power plant in Asturias that belongs to Hidrocantabrico Group, S.A.). From this study it is inferred that respirable dust is scavenged with the greatest difficulty and when compared with the initial volume of respirable dust, roughly 20% remains after 15 h of gravitational settling. Therefore, gravitational settling is the main removal mechanism of respirable dust compared to condensation and coagulation.

Gatari, M.J., Boman, J., Wagner, A., II, S., and Isakson, J. 2006. Assessment of inorganic content of PM_{2.5} particles sampled in a rural area north-east of Hanoi, Vietnam. Science of the Total Environment 368: 675-685.

Abstract: Atmospheric aerosols from seven rural sites in northern Vietnam, east of Hanoi, were sampled and analyzed. The aim of the study was to evaluate trace elemental and black carbon (BC) concentrations in fine particles (PM_{2.5}) and to investigate the influence of the Pha Lai power plant and other pollution sources on regional air quality. Seven measurement stations were set up at selected rural sites and a campaign consisting of 12 two-day measurement periods was conducted from the end of May until the end of October 2000. At each location a pair of samplers was installed consisting of a cyclone loaded with Teflon filters and a modified Millipore air monitoring cartridge loaded with glass fibre filters. The obtained samples were analyzed for trace elements by Energy Dispersive X-ray Fluorescence (EDXRF), while a black smoke detector was used for BC analysis. Seventeen trace elements were analyzed; Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Se, Sr, Ti, V and Zn and their concentrations evaluated. The results showed that BC, Ca, Cl, Fe, K and S dominated in the sampled atmospheric aerosols. The measured concentrations of the potentially hazardous trace elements Cr, Mn, Ni and Pb were all below the limits defined by Vietnamese standards of ambient air quality. Statistical evaluations indicated that coal and heavy fuel oil combustion were major sources of atmospheric pollutants in the area and that biomass burning and road transport had a marked influence on regional air quality. It was concluded that the Pha Lai power plant was the major source of coal combustion emissions. Trace element emissions originating from river transportation were suggested as another major source of atmospheric pollutants. The results indicate that the elemental concentrations in PM_{2.5} are strongly influenced by seasonal variations. Further measurements are required to identify the impact of long-range transported continental air masses on the air quality of the investigated rural area.

Giere, R., Blackford, M., and Smith, K. 2006. TEM study of PM_{2.5} emitted from coal and tire combustion in a thermal power station. Environmental Science & Technology 40: 6235-6240.

Abstract: The research presented here was conducted within the scope of an experiment investigating technical feasibility and environmental impacts of tire combustion in a coal-fired power station. Previous work has shown that combustion of a coal+tire blend rather than pure coal increased bulk emissions of various elements (e.g., Zn, As, Sb, Pb). The aim of this study is to characterize the chemical and structural properties of emitted single particles with dimensions <2.5 μm (PM_{2.5}). This transmission electron microscope (TEM)-based study revealed that, in addition to phases typical of coal fly ash (e.g., aluminum-silicate glass, mullite), the emitted PM

2.5 contains amorphous selenium particles and three types of crystalline metal sulfates never reported before from stack emissions. Anglesite, PbSO_4 , is ubiquitous in the $\text{PM}_{2.5}$ derived from both fuels and contains nearly all Pb present in the PM. Gunningite, $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$, is the main host for Zn and only occurs in the PM derived from the coal+tire blend, whereas yavapaiite, $\text{KFe}_3(\text{SO}_4)_2$, is present only when pure coal was combusted. We conclude that these metal sulfates precipitated from the flue gas, may be globally abundant aerosols, and have, through hydration or dissolution, a major environmental and health impact.

Goodarzi, F. 2006a. Morphology and chemistry of fine particles emitted from a Canadian coal-fired power plant. *Fuel* 85:273-280.

Abstract: Particles emitted from coal-fired power plants burning subbituminous coal from Alberta, Canada were examined for total particulates (PM) and size fractions $\text{PM}(> 10)$, PM_{10} , and $\text{PM}_{2.5}$. The sampling was carried out following EPA Method 201A. Three tests were performed at each station. The emitted particles were examined using SEM/EDX and gravimetric method for the determination of their sizes. The elemental composition of particles was determined using INAA and ICP-MS. The particles emitted from the stack are classified based on their morphologies and chemistries to the following: unburnt carbon, feed-coal minerals such as quartz, and by-products of the dissociation, fractionation, and contamination by minerals in coal. The emitted particles are mostly spherical and their matrices are composed of aluminosilicate minerals containing calcium. The $\text{PM}> 10$ fraction contains small spheres, fragments of char, and angular quartz and feldspar particles. The PM_{10} fraction contains solid spheres and cenospheres, gypsum needles, and particles of char. The $\text{PM}_{2.5}$ particle size fraction is mostly composed of solid spherical aluminosilicates with some surface enrichment of elements such as Ba, Ca, and Fe. The composition of emitted particles is ferrocalsialic. Most elements in the particle size fractions are Class I or II, such as Al, Ca, and Fe. Cd, Cu, Mo, and Ti were only detected in $\text{PM}_{2.5}$ fraction.

Goodarzi, F. 2006b. The rates of emissions of fine particles from some Canadian coal-fired power plants. *Fuel* 85:425-433.

Particles emitted from three coal-fired power plants burning subbituminous coals from Alberta, Canada were examined for total particulate matter (PM) and size fractions $\text{PM}> 10$, PM_{10} , and $\text{PM}_{2.5}$. The sampling was carried out following EPA Method 201 A, which requires a 6 inch port. Three tests were performed at each station. The rates of emitted particulates from the three power plants are 9.9-53.4 mg/m^3 (dry), 30-90 kg/hr (dry), and 0.039-0.118 kg/MWh , respectively. The emission rates of the various particle sizes for these three power plants are 8.7-39.5 kg/hr of $\text{PM}> 10$, 10.7-40.8 kg/hr of PM_{10} , and 9.65-10.7 kg/hr of $\text{PM}_{2.5}$. The present results indicate that 29-44% of emitted particles are $\text{PM}> 10$. The total emissions of particulates from two power plants are below the Canadian Guideline for emission from a coal-fired power plant (0.095 kg/MWh), while the third power plant is slightly higher than the Guideline (0.118 kg/MWh). The malfunctioning of control technology may result in unrealistic and wide variation in the measured rates of emitted particles.

Harrad, S., Hassoun, S., Romero, M.S., and Harrison, R.M. 2003. Characterisation and source attribution of the semi-volatile organic content of atmospheric particles and associated vapour phase in Birmingham, UK. *Atmospheric Environment* 37: 4985-4991.

Abstract: Concentrations of n-alkanes, petroleum biomarkers such as hopanes and steranes, n-alkanoic acids, n-alkanols, polycyclic aromatic hydrocarbons (PAH), dicarboxylic acids, and selected oxygenated PAH were separately determined in total suspended particulate matter and associated vapour phase in ambient air in Birmingham, UK. Samples were taken simultaneously at two locations on 24 separate occasions every 1-2 weeks between August 1999 and August

2000. Site A was 10m from a busy road, 800m from site B that was located within the "green space" of the University of Birmingham campus. Despite some differences in concentrations of some compounds, data from this study is in line with that reported in London, UK and in California. Differences between Sites A and B in both concentrations and carbon preference indices are consistent with greater traffic inputs at Site A, with some evidence of an appreciable biogenic input of n-alkanols and n-alkanes at the less-traffic influenced and more vegetated Site B. The biogenic input at Site B appears greater in the spring and summer months and suggests that biogenic emissions are appreciable even in British urban areas. Secondary formation mechanisms for some compounds including dicarboxylic acids and oxygenated PAH like fluoren-9-one are indicated by the lack of any significant intersite difference in concentrations. Intersite differences in concentrations provide new evidence that while petroleum biomarkers arise predominantly from local traffic, regional as well as local sources play an important role for the higher molecular weight PAH which exist predominantly in the particle phase.

Hynes, T., Campbell, J., Wong, H., Skaeff, J., Lamoureux, M., Somonetti, A. and Chatt, A. (2004) Physical and Chemical Evolution of Aerosols in Smelter and Power Plant Plumes. Retrieved Dec 21, 2007 from http://www.hc-sc.gc.ca/sr-sr/finance/tsri-irst/proj/metals-metaux/tsri-153_e.html.

Karar, K., and Gupta, A.K. 2007. Source apportionment of PM10 at residential and industrial sites of an urban region of Kolkata, India. Atmospheric Research 84: 30-41.

Abstract: PM10 and its chemical species mass concentrations were measured once in a week at residential (Kasba) and industrial (Cossipore) sites of an urban region of Kolkata for a period of 24h during November 2003 to November 2004. At each monitoring site, 53 sets of daily average PM10 samples were collected during the study period. Approximately 55% of the monitoring days are weekdays, while 45% are weekends. The PM10 mass concentrations ranged from 68.2 to 280.6 $\mu\text{g m}^{-3}$ at the residential site, and 62.4 to 401.2 $\mu\text{g m}^{-3}$ at the industrial site. Polycyclic aromatic hydrocarbon compounds (PAH), fluoranthene (Fl), pyrene (Py), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF) and benzo(a)pyrene (BaP) have been analyzed using Gas Chromatography. Metals in PM10 deposited on quartz microfibre filter papers were measured using an Inductively Coupled Plasma-Atomic Emission Spectrometer. Chromium (Cr), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), manganese (Mn) and iron (Fe) are the seven toxic trace metals quantified from the measured PM10 concentrations. Total carbon (TC), inorganic carbon (IC) and organic carbon (OC) were analyzed using a Carbon analyzer. Exposed quartz microfibre filter papers were also analyzed for water-soluble anions of fluoride (F⁻), chloride (Cl⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻) and sulfate (SO₄²⁻) using ion chromatography. In this study, principal component analysis (PCA)/absolute principal component scores (APCS) model was applied to the mass concentrations of PM10 and its chemical species. Principal component analysis with varimax rotation identified five possible sources; solid waste dumping, vehicular emission, coal combustion, cooking and soil dust at residential site. The extracted possible sources at the industrial site were vehicular emissions, coal combustion, electroplating industry, tyre wear and secondary aerosol. A quantitative estimation by principal component analysis-multiple linear regression (PCA-MLR) model indicated that solid waste dumping contributed 36%, vehicular emissions 26%, coal combustion 13%, cooking 8% and soil dust 4% at the residential site. The PCA-MLR apportioned 37% to vehicular emissions, 29% to coal combustion, 18% to electroplating industry, 8% to tyre wear and 1% to secondary aerosol at the industrial site. Due to the limitation in source marker species analyzed, 13% at Kasba and 7% at Cossipore could not be apportioned to any possible sources by this technique.

Nielsen, M. T., and H. Livbjerg. 2002. Formation and emission of fine particles from two coal-fired power plants. *Combustion Science and Technology* 174:79-113.

Abstract: The generation and emission of combustion particles from two full-scale coal-fired power plants was studied by field measurements during which particles are sampled for size classification and chemical analysis simultaneously at three positions in the plants: before the electrostatic precipitator, before the desulfurisation plant, and in the stack. The following sampling techniques are used: scanning mobility particle sizer, low pressure cascade impactor, dichotomous PM2.5 sampler, and total particle filter. The so-called multi-platform method used in this work Proves useful for gaining insight into the many particle-affecting processes in a power plant. In the boiler the size of particles extends over four decades, from approximately 20 nm to 200 nm, with the largest mass contained in particles in the size range 10-100 µm. Approximately 99.9% of the particles are removed in the electrostatic precipitator and the desulfurization scrubber. The mass fraction of submicron particles, i.e., PM1, increases from similar to 0.3% at the exit of the boiler, just before the electrostatic precipitator, to similar to 30% in the aerosol emitted via the stack. In the stack aerosol 50-80% of the particles are in the PM2.5 range. The emitted particles primarily stem from the coal ash with a minor contribution of particles of entrained, dried-out droplets of scrubber slurry. The large emitted particles are compact, almost-spherical single particles originating from the ash mineral inclusions in the coal. The small ones, corresponding in mass approximately to the PM0.45 fraction in terms of number concentration by far the dominant fraction are dendritic clusters, each consisting of several partly fused, even smaller particles. The cluster particles are generated in the burner by volatilization of Si, Al, Ca, and Fe under reducing conditions. Several other ash-contained elements, e.g., P, Ba, Co, Cu, Mn, Ni, Ph, V, and Zn, are partly vaporized in the boiler and enrich the small particles when they condense during cooling of the flue gas. Due to the higher penetration of the small particles through the filter and scrubber, these elements, tend to have an enhanced concentration in the emitted particles.

Schnelle-Kreis, J., Sklorz, M., Orasche, J., Izel, M., Peters, A., and Zimmermann, R. 2007. Semi volatile organic compounds in ambient PM2.5. Seasonal trends and daily resolved source contributions. *Environmental Science & Technology* 41: 3821-3828.

Abstract: Concentrations of ambient semivolatile organic compounds (SVOC) in the PM2.5 fraction of Augsburg, Germany, have been monitored on a daily basis from January 2003 through December 2004. Samples were taken in a large garden in the city center. Quantitative analysis of n-alkanes, alkanones, alkanolic acid methylesters, long chain linear alkyl benzenes and toluenes, hopanes, polycyclic aromatic hydrocarbons (PAH) and oxidized PAH, and some abietan type diterpenes was done. All compounds showed distinct seasonal variations in concentration. Most compounds showed highest concentrations during the cold seasons, but some n-alkanones and 6,10,14-trimethylpentadecanone showed maximum concentration during summer. Changes in patterns between and within compound classes were obvious, e.g., the hopane pattern exhibited a strong seasonal variation. The main source related contributions to changes observed were discussed. Using positive matrix factorization (PMF) for the statistical investigation of the data set, five factors have been separated. These factors are dominated by the pattern of single sources or groups of similar sources: factor 1, lubricating oil; factor 2, emissions of unburned diesel and heating oil consumption; factor 3, wood combustion; factor 4, brown coal combustion; and factor 5, biogenic emissions and transport components. Like the SVOC, the factors showed strong seasonality with highest values in winter for factors 1-4 and in summer for factor 5.

Sharma, R., and S. Pervez. 2004. A case study of spatial variation and enrichment of selected elements in ambient particulate matter around a large coal-fired power station in central India. *Environmental Geochemistry and Health* 26:373-381.

Abstract: The dominant use of coal in power sectors has been associated with adverse environmental impacts. Ambient air monitoring, for the two size fractions of particulate matter, respirable suspended particulate matter (RSPM) and non-respirable suspended particulate matter (NRSPM) in the downwind and upwind directions of a large coal-fired power station in central India, was carried out. Collected samples of ambient particulate matter were analysed atomic absorption spectrophotometrically for 15 elements. Spatial variability in elemental composition of RSPM and NRSPM and the degree of enrichment of these toxic metals in RSPM were investigated. A significant spatial variability for the elements in RSPM and NRSPM and higher degrees of enrichment of the elements were observed.

Sharma, R., Pervez, Y., and Pervez, S. 2005. Seasonal evaluation and spatial variability of suspended particulate matter in the vicinity of a large coal-fired power station in India - A case study. Environmental Monitoring and Assessment 102: 1-13.

Abstract: Coal combustion in the power sector gives rise to the emission of primary and secondary particulate pollutants. Since the emission of pollutants depends on coal quality and combustion technology, and given that transport, transformation and deposition of contaminants depend on regional climatic conditions, specific studies for the power stations is needed to evaluate their environmental impacts. Monitoring of ambient respirable suspended particulate matter (RSPM) and suspended particulate matter (SPM) levels around a large coal-fired power station in India was carried out. The specific objectives were the determination of spatial and seasonal variability in RSPM and SPM levels, and their relationship with meteorological parameters such as wind velocity and relative humidity. The results have shown a marked seasonal trend and spatial variability in RSPM and SPM levels in the study area. Higher concentrations of ambient RSPM and SPM were found in downwind monitoring stations compared to upwind direction. Ratios of RSPM to SPM and correlation coefficient values between RSPM and SPM along with meteorological parameters were also worked out. Relative humidity and wind velocity have shown an inverse relation with particulate deposition pattern.

Sui, J.C., Xu, M.H., Du, Y.G., Liu, Y., Yu, D.X., and Yi, G.Z. 2007. Emission characteristics and chemical composition of PM10 from two coal fired power plants in China. Journal of the Energy Institute 80 : 192-198.

Abstract: By using low pressure impactor, fly ash was sampled in the entrance and exit of the dust cleaning equipments, such as ESP and venturi scrubber, in a 50 and 100 MW utility boiler. The composition, mass size distribution and microstructure of fly ash were measured. A similar bimodal distribution of PM10 was obtained in the studied boilers. The small and large modes are formed at 0.1 and 4.0 μm respectively. Based on the comparison of concentrations of Si and Al in the size segregated ash, it is concluded that the ash with size smaller than 0.377 μm is formed by the nucleation of vaporised mineral components and growth via coagulation and heterogeneous condensation. The results by microstructure measurements showed that the typical microstructure of submicron and coarse PM is spherical, except for a few irregular particles in shape. The collection efficiency of the dust cleaning equipments had a minimum in particle size range of 0.01-1 μm .

Triantafyllou, A. G. 2003. Levels and trend of suspended particles around large lignite power stations. Environmental Monitoring and Assessment 89:15-34.

Abstract: The results of a 16 year long sampling program in a heavily industrialized area of NW Greece are presented and analyzed. Four lignite power stations are operated in this area, which account for about 70% of the total electrical energy produced in Greece. Ambient concentrations of Total Suspended Particles (TSP) over much of the period 1983-1998 as well as of particles of less than 10 μm aerodynamic diameter (PM10) for three years were measured. Emphasis is

given on the assessment of the levels of the daily average concentrations for the data period as well as the determination of the spatial and temporal variation of suspended particle concentrations. Based on the data analysis, useful information is provided about air quality levels after taking into account air quality standards. The interannual concentrations trend is also investigated and an attempt is made to examine the effectiveness of antipolluting procedures, which have occasionally been implemented in this industrial area. Finally the results are compared to those in the literature.

Triantafyllou, A. G., S. Zoras, and V. Evagelopoulos. 2006. Particulate matter over a seven year period in urban and rural areas within, proximal and far from mining and power station operations in Greece. *Environmental Monitoring and Assessment* 122:41-60.

Abstract: Lignite mining operations and lignite-fired power stations result in major particulate pollution (fly ash and fugitive dust) problems in the areas surrounding these activities. The problem is more complicated, especially, for urban areas located not far from these activities, due to additional contribution from the urban pollution sources. Knowledge of the distribution of airborne particulate matter into size fraction has become an increasing area of focus when examining the effects of particulate pollution. On the other hand, airborne particle concentration measurements are useful in order to assess the air pollution levels based on national and international air quality standards. These measurements are also necessary for developing air pollutants control strategies or for evaluating the effectiveness of these strategies, especially, for long periods. In this study an attempt is made in order to investigate the particle size distribution of fly ash and fugitive dust in a heavy industrialized (mining and power stations operations) area with complex terrain in the northwestern part of Greece. Parallel total suspended particulates (TSP) and particulate matter with an aerodynamic diameter less than 10 μm (PM10) concentrations are analyzed. These measurements gathered from thirteen monitoring stations located in the greater area of interest. Spatial, temporal variation and trend are analyzed over the last seven years. Furthermore, the geographical variation of PM10 - TSP correlation and PM10/TSP ratio are investigated and compared to those in the literature. The analysis has indicated that a complex system of sources and meteorological conditions modulate the particulate pollution of the examined area.

Xie, R., Seip, H.M., Wibetoe, G., Nori, S., and McLeod, C.W. 2006. Heavy coal combustion as the dominant source of particulate pollution in Taiyuan, China, corroborated by high concentrations of arsenic and selenium in PM10. *Science of the Total Environment* 370: 409-415

Abstract: Coal burning generates toxic elements, some of which are characteristic of coal combustion such as arsenic and selenium, besides conventional coal combustion products. Airborne particulate samples with aerodynamic diameter less than 10 μm (PM10) were collected in Taiyuan, China, and multi-element analyses were performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Concentrations of arsenic and selenium from ambient air in Taiyuan (average 43 and 58 ng m^{-3} , respectively) were relatively high compared to what is reported elsewhere. Arsenic and selenium were found to be highly correlated ($r = 0.997$), indicating an overwhelmingly dominant source. Correlation between these two chalcophile elements and the lithophile element Al is high (r is 0.75 and 0.72 for As and Se, respectively). This prompted the hypothesis that the particles were from coal combustion. The enrichment of the trace elements could be explained by the volatilization-condensation mechanism during coal combustion process. Even higher correlations of arsenic and selenium with PM10 ($r = 0.90$ and 0.88) give further support that airborne particulate pollution in Taiyuan is mainly a direct result of heavy coal consumption. This

conclusion agrees with the results from our previous study of individual airborne particles in Taiyuan.

Yi, H., Hao, J., Duan, L., Li, X., and Guo, X. 2006. Characteristics of inhalable particulate matter concentration and size distribution from power plants in China. Journal of the Air and Water Waste Management Associations 56: 1243-1251.

Abstract: In this investigation, the collection efficiency of particulate emission control devices (PECDs), particulate matter (PM) emissions, and PM size distribution were determined experimentally at the inlet and outlet of PECDs at five coal-fired power plants. Different boilers, coals, and PECDs are used in these power plants. Measurement in situ was performed by an electrical low-pressure impactor with a sampling system, which consisted of an isokinetic sampler probe, pre-cut cyclone, and two-stage dilution system with a sample line to the instruments. The size distribution was measured over a range from 0.03 to 10 μm . Before and after all of the PECDs, the particle number size distributions display a bimodal distribution. The PM_{2.5} fraction emitted to atmosphere includes a significant amount of the mass from the coarse particle mode. The controlled and uncontrolled emission factors of total PM, inhalable PM (PM₁₀), and fine PM P(M_{2.5}) were obtained. Electrostatic precipitator (ESP) and baghouse total collection efficiencies are 96.38-99.89% and 99.94%, respectively. The minimum collection efficiency of the ESP and the baghouse both appear in the particle size range of 0.1-1 μm . In this size range, ESP and baghouse collection efficiencies are 85.79-98.6% and 99.54%. Real-time measurement shows that the mass and number concentration of PM₁₀ will be greatly affected by the operating conditions of the PECDs. The number of emitted particles increases with increasing boiler load level because of higher combustion temperature. During test run periods, the data reproducibility is satisfactory.

2.3.2 Environmental effects and biomonitoring

Brown, L.E., Trought, K.R., Bailey, C.I., and Clemons, J.H. 2005. 2,3,7,8-TCDD equivalence and mutagenic activity associated with PM 10 from three urban locations in New Zealand. Science of the Total Environment 349: 161-174.

Abstract: Ambient particulate matter (PM₁₀) in urban centres varies depending on emission sources, geography, demography, and meteorology. Hence physical (PM₁₀, wind speed, rainfall, temperature), chemical (polycyclic aromatic hydrocarbons, PAH), and toxicological (Ames Test, H4IIE EROD Assay) analyses were done on daily PM₁₀ (1640 m³/day) collected from three New Zealand urban sites where winter emissions were predominantly due to domestic home heating. Daily PM₁₀ levels ranged between 9.7 and 20.8 in summer and between 21.8 and 61.0 $\mu\text{g}/\text{m}^3$ in winter. Daily PAH concentrations were 0.5, 0.45, and 1.5 ng/m^3 in summer and 52.1, 128.9, and 5.8 ng/m^3 in winter at sites Christchurch, Alexandra and Dunedin, respectively. During winter, 74% of PM₁₀ extracts from all three sites showed significant mutagenicity in the Ames Test (TA 98, -S9), whereas approximately 25% of the daily PM 10 was mutagenic in summer. Benzo[a]pyrene and BaP carcinogenic equivalence concentrations during winter were strongly correlated to both mutagenicity and TCDD-like activity at two sites. Daily levels of TCDD toxicity equivalence concentrations ranged from 0.5 to 3.6 pg TCDD/m³ air in summer and from 0.3 to 4009 pg TCDD/m³ air in winter. Chemically and biologically derived TCDD toxicity equivalent concentrations were significantly correlated in all study locations indicating that PAH may represent most of the TCDD-like activity present in the PM₁₀.

Gilmour, M.I., McGee, J., Duvall, R.M., Dailey, L., Daniels, M., Boykin, E., Cho, S.H., Doerfler, D., Gordon, T., and Devlin, R.B. 2007. Comparative toxicity of size-fractionated

airborne particulate matter obtained from different cities in the United States. *Inhalation Toxicology* 19 : 7-16.

Abstract: Hundreds of epidemiological studies have shown that exposure to ambient particulate matter (PM) is associated with dose-dependent increases in morbidity and mortality. While early reports focused on PM less than 10 μm (PM₁₀), numerous studies have since shown that the effects can occur with PM stratified into ultrafine (UF), fine (FI), and coarse (CO) size modes despite the fact that these materials differ significantly in both evolution and chemistry. Furthermore the chemical makeup of these different size fractions can vary tremendously depending on location, meteorology, and source profile. For this reason, high-volume three-stage particle impactors with the capacity to collect UF, FI, and CO particles were deployed to four different locations in the United States (Seattle, WA; Salt Lake City, UT; Sterling Forest and South Bronx, NY), and weekly samples were collected for 1 mo in each place. The particles were extracted, assayed for a standardized battery of chemical components, and instilled into mouse lungs (female BALB/c) at doses of 25 and 100 μg . Eighteen hours later animals were euthanized and parameters of injury and inflammation were monitored in the bronchoalveolar lavage fluid and plasma. Of the four locations, the South Bronx coarse fraction was the most potent sample in both pulmonary and systemic biomarkers, with a strong increase in lung inflammatory cells as well as elevated levels of creatine kinase in the plasma. These effects did not correlate with lipopolysaccharide (LPS) or total zinc or sulfate content, but were associated with total iron. Receptor source modeling on the PM_{2.5} samples showed that the South Bronx sample was heavily influenced by emissions from coal fired power plants (31%) and mobile sources (22%). Further studies will assess how source profiles correlate with the observed effects for all locations and size fractions.

2.3.3 Regulation, policy, and abatement technologies

Greenbaum, D. S. 2003. A historical perspective on the regulation of particles. *Journal of Toxicology and Environmental Health, Part A: Current Issues* 66:1493-1498.

Abstract: The modern era of attention to particle air pollution began to emerge in the mid-20th century with a series of widely reported and significant incidents of intense industrial air pollution followed by increases in mortality. Starting with incidents in the Meuse Valley in Belgium in 1931, and in Donora, Pennsylvania, in 1948, these incidents grew to new prominence with the now well-documented London, England, incident in December 1952 (United Kingdom Ministry of Health, 1954). In each of these cases, best documented in the London case, substantial increases in particle air pollution (up to levels in excess of 1000 $\mu\text{g}/\text{m}^3$) were followed by substantial increases in mortality. These incidents precipitated the first broad-based public action to address PM air pollution beginning with the British Clean Air Act of 1956; this was the first such effort in the industrialized world and led to reductions in the use of smoky fuels, in emissions from industries, and in the use of coal and peat for home heating. In the 1960s, epidemiological studies of the health effects of exposure to PM began to emerge in North America and initial efforts to control industrial emissions were undertaken. This was followed, in 1969, by the publication by the U.S. Department of Health, Education, and Welfare (the predecessor of the Environmental Protection Agency [EPA]), of the first "Criteria Document" in which the existing literature on exposure to, and health effects of, total suspended particles (TSP) and sulfur dioxide (SO₂) was summarized (U.S. Department of Health, Education, and Welfare, 1969).

Ortiz, F. J. G., B. Navarrete, L. Canadas, and L. Salvador. 2007. A technical assessment of a particle hybrid collector in a pilot plant. *Chemical Engineering Journal* 127:131-142.

Abstract: We developed a hybrid collector (ESP+FF) to improve particulate matter removal from flue gases from coal power plants and then tested it in a pilot plant that processes up to 15,000 m³/h of real flue gas. The tests were designed to achieve economic and operating optimization of the hybrid collector. The removal efficiency in relation to the PM₁₀ and PM_{2.5} and trace metals emissions, according to the legal limits in the European Union and the United States of America, was specifically considered. The efficiencies obtained were very high: PM₁₀ removal efficiency of more than 99.95% and PM_{2.5} removal efficiency of between 96 and 98%, and a metal deposition greater than 99% depending on the metal, overcoming the limitations of ESPs with regard to achieving the particulate matter emission limits. However, a lower efficiency was obtained for the capture of mercury in the vapor phase (only 30%). We discovered a relationship between the rate of pressure loss and both the filtration velocity and the number of active fields in ESP. Likewise, we found a relation between these two parameters and the number of cleaning cycles. Within the study a database was created and considered as a basis for designing hybrid collectors and retrofitting existing ESPs. Based on these results, we determined the criteria for a full-scale design of hybrid collectors, and we have proposed a basic retrofitting of an existing ESP to convert it into a hybrid collector, for both a 550 MWe and a 220 MWe pulverized coal power station.

2.4 Carbon dioxide

2.4.1 Emissions, regulation, policy, and reduction technologies

Frimpong, S., K. Makowecki, and A. Hachiya. 2002. Stochastic simulation of aquifer CO₂ sub(2) disposal economics for Alberta. *World Resource Review* 14:590-594.

Abstract: Canada's commitment to reductions in CO₂ emissions presents a serious economic challenge to Alberta. Alberta accounts for about 30 percent of Canada's total emissions. Coal-fired power plants and the fossil fuels industry account for about 90 percent of Alberta's CO₂ emissions. Disposal of CO₂ in land aquifers is a potentially viable option for Alberta in dealing with long-term storage. In this study, the authors develop a computer simulation model of a scaled aquifer disposal system. The scaled model consists of an injector well, aquifer environment with dominant Ca⁺⁺ and Mg⁺⁺ cations. Liquefied CO₂ is injected at an appropriate pressure and concentration through an injector well. The injected CO₂ migrates from the point of contact between the injector well and the aquifer domain to the main regime of the latter. These models are validated using flue gas data from the 500 MW Wabamum Power Plant in Alberta. The MRT5 methodology is used to formulate a comprehensive model to predict CO₂ emissions for Alberta within 1999 and 2012. Economic modeling of CO₂ disposal is carried out based on capacity optimization, capital and operating costs requirements and the fundamental profiles of the Canadian and Alberta economies. The design results show that the respective energy requirements for capturing, liquefying, transporting and injecting CO₂ in the Glauconitic aquifer are 7,567 kW, 65.34 MW, 98.36 kW and 912.27 kW. The results also show that CO₂ emissions in Alberta will increase from current levels of 122 to 215 million tonnes in 2012. The annualized equivalent cost for CO₂ disposal ranges between \$1.8 and \$3.0 billion for the period from 1999 to 2012. The expected cost of disposal within this period is between \$56.03 and \$64.17 per tonne of CO₂. This will increase energy cost from \$0.043/kWh by 7% up to \$0.046/kWh.

Han, F. X., J. S. Lindner, and C. Wang. 2007. Making carbon sequestration a paying proposition. *Naturwissenschaften* 94:170-182.

Abstract: Atmospheric carbon dioxide (CO₂) has increased from a preindustrial concentration of about 280 ppm to about 367 ppm at present. The increase has closely followed the increase in CO₂ emissions from the use of fossil fuels. Global warming caused by increasing amounts of greenhouse gases in the atmosphere is the major environmental challenge for the 21st century. Reducing worldwide emissions of CO₂ requires multiple mitigation pathways, including reductions in energy consumption, more efficient use of available energy, the application of renewable energy sources, and sequestration. Sequestration is a major tool for managing carbon emissions. In a majority of cases CO₂ is viewed as waste to be disposed; however, with advanced technology, carbon sequestration can become a value-added proposition. There are a number of potential opportunities that render sequestration economically viable. In this study, we review these most economically promising opportunities and pathways of carbon sequestration, including reforestation, best agricultural production, housing and furniture, enhanced oil recovery, coalbed methane (CBM), and CO₂ hydrates. Many of these terrestrial and geological sequestration opportunities are expected to provide a direct economic benefit over that obtained by merely reducing the atmospheric CO₂ loading. Sequestration opportunities in 11 states of the Southeast and South Central United States are discussed. Among the most promising methods for the region include reforestation and CBM. The annual forest carbon sink in this region is estimated to be 76 Tg C/year, which would amount to an expenditure of \$11.1-13.9 billion/year. Best management practices could enhance carbon sequestration by 53.9 Tg C/year, accounting for

9.3% of current total annual regional greenhouse gas emission in the next 20 years. Annual carbon storage in housing, furniture, and other wood products in 1998 was estimated to be 13.9 Tg C in the region. Other sequestration options, including the direct injection of CO₂ in deep saline aquifers, mineralization, and biomineralization, are not expected to lead to direct economic gain. More detailed studies are needed for assessing the ultimate changes to the environment and the associated indirect cost savings for carbon sequestration.

Hondo, H. 2005. Life cycle GHG emission analysis of power generation systems: Japanese case. *Energy* 30:2042-2056.

Abstract: This study presents the results of a life cycle analysis (LCA) of greenhouse gas emissions from power generation systems in order to understand the characteristics of these systems from the perspective of global warming. Nine different types of power generation systems were examined: coal-fired, oil-fired, LNG-fired, LNG-combined cycle, nuclear, hydropower, geothermal, wind power and solar-photovoltaic (PV). Life cycle greenhouse gas (GHG) emission per kW h of electricity generated was estimated for the systems using a combined method of process analysis and input-output analysis. First, average power generation systems reflecting the current status in Japan were examined as base cases. Second, the impacts of emerging and future nuclear, wind power and PV technologies were analyzed. Finally, uncertainties associated with some assumptions were examined to help clarify interpretation of the results.

Kara, M., S. Syri, A. Lehtila, S. Helynen, V. Kekkonen, M. Ruska, and J. Forsstrom. 2008. The impacts of EU CO₂ emissions trading on electricity markets and electricity consumers in Finland. *Energy Economics* 30:193-211.

In this paper, the likely impacts of the EU emission trading system on the Nordic electricity market and on the position of various market actors are assessed. In its first phase, the EU CO₂ emission trading system includes power plants with thermal capacity greater than 20 MW, metals industry, pulp and paper industry, mineral industry and oil refineries. This paper describes the assessment done for the Finnish Minister of Trade and Industry, analysing the likely impacts on power plant operators, on energy-intensive industries, on other industries and on other consumer groups. The impacts of emissions trading were studied with the VTT electricity market model and with the TIMES energy system model. The annual average electricity price was found to rise 0.74 EUR MW h⁻¹ for every 1 (sic) tonne CO₂-1 in the Nordic area. Large windfall profits were estimated to incur to electricity producers in the Nordic electricity market. In Finland, metals industry and private consumers were estimated to be most affected by the electricity market price increases. Expanded nuclear power generation could limit the increases in the prices of electricity to one-third compared to those in the base case.

Kim, S., and B. E. Dale. 2005. Life cycle inventory information of the United States electricity system. *International Journal of Life Cycle Assessment* 10:294-304.

Abstract: Goal and Scope. This study estimates the life cycle inventory (LCI) of the electricity system in the United States, including the 10 NERC (North American Electric Reliability Council) regions, Alaska, Hawaii, off-grid non-utility plants and the US average figures. The greenhouse gas emissions associated with the United States electricity system are also estimated. Methods. The fuel mix of the electricity system based on year 2000 data is used. The environmental burdens associated with raw material extraction, petroleum oil production and transportation for petroleum oil and natural gas to power plants are adopted from the DEAM (TM) LCA database. Coal transportation from a mining site to a power plant is specified with the data from the Energy Information Administration (EIA), which includes the mode of transportation as well as the distance traveled. The gate-to-gate environmental burdens associated

with generating electricity from a fossil-fired power plant are obtained from the DEAM (TM) LCA database and the eGRID model developed by the United States Environmental Protection Agency. For nuclear power plants and hydroelectric power plants, the data from the DEAM (TM) LCA database are used. Results and Discussion. Selected environmental profiles of the US electricity system are presented in the paper version, while the on-line version presents the whole LCI data. The overall US electricity system in the year 2000 released about 2,654 Tg CO₂ eq. of greenhouse gas emissions based on 100-year global warming potentials with 193 g CO₂ eq. MJ⁻¹ as an weighted average emission rate per one MJ electricity generated. Most greenhouse gases are released during combusting fossil fuels, accounting for 78-95% of the total. The greenhouse gas emissions released from coal-fired power plants account for 81% of the total greenhouse gas emissions associated with electricity generation, and natural gas-fired power plants contribute about 16% of the total. The most significant regions for the total greenhouse gas emissions are the SERC (Southeastern Electric Reliability Council) and ECAR (East Central Area Reliability Coordination Agreement) regions, which account for 22% and 21% of the total, respectively. A sensitivity analysis on the generation and consumption based calculations indicates that the environmental profiles of electricity based on consumption are more uncertain than those based on generation unless exchange data from the same year are available because the exchange rates (region to region import and export of electricity) vary significantly from year to year. Conclusions and Outlook. Those who are interested in the LCI data of the US electricity system can refer to the on-line version. When the inventory data presented in the on-tine version are used in a life cycle assessment study, the distribution and transmission losses should be taken into account, which is about 9.5% of the net generation [1]. The comprehensive technical information presented in this study can be used in estimating the environmental burdens when new information on the regional fuel mix or the upstream processes is available. The exchange rates presented in this study also offer useful information in consequential LCI studies.

Odeh, N. A., and T. T. Cockerill. 2008. Life cycle analysis of UK coal fired power plants. Energy Conversion and Management 49:212-220.

This paper examines the life cycle GHG emissions from existing UK pulverized coal power plants. The life cycle of the electricity Generation plant includes construction, operation and decommissioning. The operation phase is extended to upstream and downstream processes. Upstream processes include the mining and transport of coal including methane leakage and the production and transport of limestone and ammonia, which are necessary for flue gas clean up. Downstream processes, on the other hand, include waste disposal and the recovery of land used for surface mining. The methodology used is material based process analysis that allows calculation of the total emissions for each process involved. A simple model for predicting the energy and material requirements of the power plant is developed. Preliminary calculations reveal that for a typical UK coal fired plant, the life cycle emissions amount to 990 g CO₂-e/kWh of electricity generated, which compares well with previous UK studies. The majority of these emissions result from direct fuel combustion (882 g/kWh 89%) with methane leakage from mining operations accounting for 60% of indirect emissions. In total, mining operations (including methane leakage) account for 67.4% of indirect emissions, while limestone and other material production and transport account for 31.5%. The methodology developed is also applied to a typical IGCC power plant. It is found that IGCC life cycle emissions are 15% less than those from PC power plants. Furthermore, upon investigating the influence of power plant parameters on life cycle emissions, it is determined that, while the effect of changing the load factor is negligible, increasing efficiency from 35% to 38% can reduce emissions by 7.6%. The current study is funded by the UK National Environment Research Council (NERC) and is undertaken as part of the UK Carbon Capture and Storage Consortium (UKCCSC). Future work will investigate the life cycle emissions from other power generation technologies with and without carbon

capture and storage. The current paper reveals that it might be possible that, when CCS is employed, the emissions during generation decrease to a level where the emissions from upstream processes (i.e. coal production and transport) become dominant, and so, the life cycle efficiency of the CCS system can be significantly reduced. The location of coal, coal composition and mining method are important in determining the overall impacts. In addition to studying the net emissions from CCS systems, future work will also investigate the feasibility and technoeconomics of these systems as a means of carbon abatement.

Raghuvanshi, S. P., A. Chandra, and A. K. Raghav. 2006. Carbon dioxide emissions from coal based power generation in India. *Energy Conversion and Management* 47:427-441.

Abstract: Coal is the major fossil fuel used in industrial units and power plants for power generation in India. The carbon dioxide emitted as a product of combustion of coal (fossil fuels) is currently responsible for over 60% of the enhanced greenhouse effect. The present communication is an attempt to provide a brief investigation Of CO₂ emission from coal based power generation in India. Energy indicators, trends in energy consumption and carbon dioxide emissions have been thoroughly investigated. Methodology for analysis of carbon emissions and possible sinks is also provided.

Zhang, Y., S. Habibi, and H. L. MacLean. 2007. Environmental and Economic Evaluation of Bioenergy in Ontario, Canada. *Journal of the Air & Waste Management Association* 57: 919-933.

Abstract: We examined life cycle environmental and economic implications of two near-term scenarios for converting cellulosic biomass to energy, *generating electricity from cofiring biomass in existing coal power plants*, and producing ethanol from biomass in stand-alone facilities in Ontario, Canada. The study inventories near-term biomass supply in the province, quantifies environmental metrics associated with the use of agricultural residues for producing electricity and ethanol, determines the incremental costs of switching from fossil fuels to biomass, and compares the cost-effectiveness of greenhouse gas (GHG) and air pollutant emissions abatement achieved through the use of the bioenergy. Implementing a biomass cofiring rate of 10% in existing coal-fired power plants would reduce annual GHG emissions by 2.3 million metric tons (t) of CO₂ equivalent (7% of the province's coal power plant emissions). The substitution of gasoline with ethanol/gasoline blends would reduce annual provincial light-duty vehicle fleet emissions between 1.3 and 2.5 million t of CO₂ equivalent (3.5-7% of fleet emissions). If biomass sources other than agricultural residues were used, additional emissions reductions could be realized. At current crude oil prices (\$70/barrel) and levels of technology development of the bioenergy alternatives, the biomass electricity cofiring scenario analyzed is more cost-effective for mitigating GHG emissions (\$22/t of CO₂ equivalent for a 10% cofiring rate) than the stand-alone ethanol production scenario (\$92/t of CO₂ equivalent). The economics of biomass cofiring benefits from existing capital, whereas the cellulosic ethanol scenario does not. Notwithstanding this result, there are several factors that increase the attractiveness of ethanol. These include uncertainty in crude oil prices, potential for marked improvements in cellulosic ethanol technology and economics, the province's commitment to 5% ethanol content in gasoline, the possibility of ethanol production benefiting from existing capital, and there being few alternatives for moderate-to-large-scale GHG emissions reductions in the transportation sector.

2.5 Multiple pollutant studies

2.5.1 Emissions, atmospheric deposition and modelling

Ali, M., Athar, M., and Ali, E. 2007. The emissions and environmental impact of power plants operating on fossil fuel at Distt. Kasur, Pakistan. *Ekoloji* 16: 74-80.

Abstract: A comprehensive assessment of four power plants operating on fossil fuel (Diesel Power Plant) was conducted near the industrial area of Raiwind, Distt. Kasur, Pakistan. The installed capacity of these power plants is 117 MW, 112 MW, 90 MW, and 60MW respectively. The emissions of all the engines of the individual plants were monitored for six months at an interval of fifteen days. The emissions of priority pollutants Carbon Monoxide (CO), Oxides of Nitrogen (NO_x), Sulfur Dioxide (SO₂), Suspended Particulate Matter (SPM), Lead (Pb) and Mercury (Hg) were monitored. The emission results of the four plants were compared and some of the pollutant parameters were found higher when compared with local National Environmental Quality Standards (NEQS) as well as the World Bank guidelines for Power Plants. The ground level ambient air quality at 1 km downwind was also monitored for 24 hours at each individual plant site to evaluate the impact of these pollutants on ambient air quality.

Babbitt, C. W., and A. S. Lindner. 2005. A life cycle inventory of coal used for electricity production in Florida. *Journal of Cleaner Production* 13:903-912.

Abstract: Coal-fired power plants are anticipated to be increasingly used as a source of energy in the United States, particularly in states such as Florida that are experiencing rapid population growth and energy demands. While the emissions from coal combustion are a focus of intense study, little attention has been given to the emissions' contributions from other stages involved in the life cycle of coal used for electricity generation. This study inventories material and energy inputs and emissions in not only the Materials Processing stage (coal combustion) but also in the Raw Material Extraction (including coal mining and preparation) and Material Disposal (involving coal combustion products) stages, using data collected from four coal-burning utilities in Florida and SimaPro software (version 5. 1, PRe Consultants, The Netherlands). Total emissions to air from all three stages are significantly higher than to water or land, with 78% of the air emissions attributed to carbon dioxide from coal combustion. Coal mining and preparation contributes the largest quantities of non-methane volatile organic compounds and methane (over 98%) as well as the most total dissolved solids to water (over 76%). Disposal of coal combustion products, typically by either landfilling or surface impoundment, results in the largest emissions of particulate matter (PM 10) to air (41 %), a significant emission of total dissolved solids to water (over 22%).. and a variety of metals to land. These results verify the major contributions of coal combustion to air emissions and show that the emissions from the Raw Material Extraction and Material Disposal stages may result in a significant enough negative environmental impact to warrant pursuit of pollution control and prevention opportunities in these stages as well.

Balat, M. 2007. Influence of coal as an energy source on environmental pollution. *Energy Sources Recovery Util. Environmental Efficiency* 29: 581-589.

Abstract: This article considers the influence of coal energy on environmental pollution. Coal is undoubtedly part of the greenhouse problem. The main emissions from coal combustion are sulfur dioxide (SO₂), nitrogen oxides (NO_x), particulates, carbon dioxide (CO₂), and mercury (Hg). Since 1980, despite a 36% increase in electricity generation and more than a 50% increase in coal use, electric utility SO₂ and NO_x emissions have declined significantly. Globally, the largest source of anthropogenic greenhouse gas (GHG) emissions is CO₂ from the combustion of

fossil fuels - around 75% of total GHG emissions covered under the Kyoto Protocol. At the present time, coal is responsible for 30-40% of world CO₂ emission from fossil fuels.

Banic, C., W. R. Leaitch, K. Strawbridge, R. Tanabe, H. Wong, C. Gariepy, A. Simonetti, Z. Nejedly, J. L. Campbell, J. Lu, J. Skeaff, D. Paktunc, J. I. MacPherson, S. Daggupaty, H. Geonac'h, A. Chatt, and M. Lamoureux. 2006. The physical and chemical evolution of aerosols in smelter and power plant plumes: an airborne study. *Geochemistry-Exploration Environment Analysis* 6:111-120.

Abstract: National and international concern about the health effects and continued use of Pb, Cd, As and Hg as well as other metals has defined a need for improved estimates of the long-term risks to ecosystems and human health from metals released from mining, metallurgical and energy production activities. A research aircraft was used to determine the microphysical and chemical properties of airborne particulate metal emissions from the Nanticoke coal-fired power-generating station located on the north shore of Lake Erie, Ontario, and the Horne copper smelter at Rouyn-Noranda, Quebec. These properties are critical to the determination of the deposition rates of the metals emitted, and hence the potential for these species to have impacts on local or distant ecosystems. An overview of the measurements made during the study is given. The size distributions of particles emitted from the stacks and observed within 5 km of the point of emission are briefly described. After dilution by ambient air, the concentration of particles smaller than 0.135 μm in diameter in the plumes is tens of thousands per cubic centimetre, far exceeding the concentrations found in ambient air. However, in the size range 0.135 to 3 μm diameter the plumes generally contribute about one to four times more particles than present in ambient air.

Bhanarkar, A.D., Rao, P.S., Gajghate, D.G., and Nema, P. 2005. Inventory of SO₂, PM and toxic metals emissions from industrial sources in Greater Mumbai, India. *Atmospheric Environment* 39: 3851-3864.

Abstract: A comprehensive and spatial emission inventory was carried out for sulphur dioxide (SO₂), particulate matter (PM) and toxic metals from industrial sources in Greater Mumbai, India. Fuel consumption database was developed for industrial sources. Emission factors for various pollutants were compiled from the literature, scrutinized and used appropriately as applicable under Indian conditions. Emissions of SO₂, PM and toxic metals were estimated for 2001-02 and extrapolated to 2010. SO₂ emissions from fossil fuel combustion covering 215 point sources for 2001-02 were computed as 55.591 Gg y⁻¹ whereas those for PM were calculated as 9.794 Gg y⁻¹. The total metal emissions from industrial sources were computed as 0.375 Gg y⁻¹. Total fossil fuel energy consumption in industrial sector during 2001-02 was 145 PJ, which included fuel consumption (29%) in power plants. Amongst the industries, thermal power plants (TPP) were the major source of emissions in the region contributing 27% share towards SO₂, 19% PM and 62% metals. Projected scenario for 2010 indicates that there would be substantial reduction in PM and metal emission load while the gaseous pollutant concentration would show a decreasing trend.

Chatzimouratidis, A.I., and Pilavachi, P.A. 2007. Objective and subjective evaluation of power plants and their non-radioactive emissions using the analytic hierarchy process. *Energy Policy* 35: 4027-4038.

Abstract: Non-nuclear power plant emissions are of great concern to the public and to scientists alike. As energy demand tends to rise rapidly, especially in the developing countries, the negative effects to human health and to the environment from gaseous emissions together with hazardous particulate matter released by power plants can no longer be ignored. In this study, the impact of non-radioactive emissions is evaluated with the Analytic Hierarchy Process (AHP) by

synthesizing objective and subjective criteria. There are five main emissions to be evaluated, non-methane volatile organic compounds (NMVOC), carbon dioxide equivalent (CO₂-eq), nitrogen oxides (NO_x), sulphur dioxide (SO₂) and particulates or particulate matter (PM). Objective evaluation is achieved by expressing the impact of each emission released in monetary terms following generally accepted market rules, international agreements and protocols. That is, the Euro per kilogram of each emission exceeding a specific limit that should be paid as a penalty for environmental pollution and human health damage. Subjective assessment requires an intuitive expression of the percentage of damage to human health and to the ecosystem that each emission causes. Sensitivity analysis is then used in order to examine how change of input data affects final results. Finally, 10 main types of power plant are evaluated according to the level and kind of emissions they release. These types are coal/lignite, oil, natural gas turbine, natural gas combined cycle (NGCC), nuclear, hydro, wind, photovoltaic, biomass and geothermal.

Chow, J. C., Watson, J. G., Chen, L. A., Ho, S. S. H., Koracin, D., Zielinska, B., Tang, D., Perera, F., Cao, J. and Lee, S. C. (2006) Exposure to PM_{2.5} and PAHs from the Tong Liang, China epidemiological study. *J. Environ. Sci. Health A*. 41, 517-542.

Abstract: Chemically speciated PM_{2.5} and particle-bound polycyclic aromatic hydrocarbon (PAH) measurements were made at three sites near urban Tong Liang, Chongqing, a Chinese inland city where coal combustion is used for electricity generation and residential purposes outside of the central city. Ambient sampling was based on 72-hr averages between 3/2/2002 and 2/26/2003. Elevated PM_{2.5} and PAH concentrations were observed at all three sites, with the highest concentrations found in winter and the lowest in summer. This reflects a coupling effect of source variability and meteorological conditions. The PM_{2.5} mass estimated from sulfate, nitrate, ammonium, organics, elemental carbon, crustal material, and salt corresponded with the annual average gravimetric mass within ±10%. Carbonaceous aerosol was the dominant species, while positive correlations between organic carbon and trace elements (e.g. As, Se, Br, Pb, and Zn) were consistent with coal-burning and motor vehicle contributions. Ambient particle-bound PAHs of molecular weight 168-266 were enriched by 1.5 to 3.5 times during the coal-fired power plant operational period. However, further investigation is needed to determine the relative contribution from residential and utility coal combustion and vehicular activities.

Coltro, L., E. E. C. Garcia, and G. D. Queiroz. 2003. Life cycle inventory for electric energy system in Brazil. *International Journal of Life Cycle Assessment* 8:290-296.

Abstract: Goal, Scope and Background. The goal of this paper is to present the modeling of life cycle inventory (LCI) for electric energy production and delivery in Brazil for the reference year 2000 by application of ISO 14040. Site specific data along with sector production data have been combined to construct an energy production model, which has been applied to emissions estimation. Background-data of all the inputs and outputs from the system have been inventoried as follows: gross electric energy generation, installed nameplate capacity, flooded area, losses, emissions to air / water, process waste, used fuel, efficiency and land use.

Main Features. In Brazil, electricity is supplied to the various regions by an interconnected system composed of 418 electric companies, consisting of 389 hydraulic power plants and 29 thermal power stations. Due to this enormous number of companies, life cycle inventory for the electricity grid mix was developed on the basis of the following hierarchy: information received from companies (15), data from Brazilian Industrial Information System for the energy Sector (SIESE) and Brazilian Ministries. The functional unit was 1,000 MJ (278 kWh) of electricity distributed to electricity users. The main emissions from power stations, as well as those from fuel production, were investigated. The hydraulic process was not considered emission-free - a

model was proposed where emissions of renewable CO₂ and CH₄ (hydro) are attributed to the degradation of plants submerged in the reservoir areas.

Result. The production and distribution of 1,000 MJ of electricity by the interconnected system in Brazil requires approx. 1,600 MJ of process energy, 230 kg of water (evaporated at thermal plants), 116 m³ of waterflow through the turbines, 13 kg of coal, 5 kg of biotic reserves and 0.25 m² of land use. Emissions related to the 1,000 MJ electricity distributed were 18 kg of non-renewable CO₂, 17 kg of renewable CO₂, 540 g of CH₄, 575 g of NO_x, 116 g of SO₂, 149 g of CO₂ among others. Thermal power stations are the main contributors to these emissions, except for CH₄ and renewable CO₂ being contributions from coal production and hydraulic power plants, respectively.

Conclusions. In spite of considering the emissions of CO₂ and CH₄ by the submerged plants in the flooded area of dams in hydropower stations, it has been shown that electric energy production is a very clean process due to the characteristics of the electric energy production in Brazil - 93.5% hydraulic. This means 1,000 MJ of delivered electricity produces approx. 34 kg of CO₂, being 18 kg (53%) of non-renewable CO₂ emitted by fossil fuel burning at thermal power plants that participate with only 6.5% of the electric energy production in Brazil. This was the first tentative model to express electric energy generation and distribution in Brazil in terms of LCA. In future, a more detailed study should be made in order to improve this model.

Outlook. A complementary paper will be produced in which future scenarios of the Brazilian electricity grid mix will be discussed, including possible alternatives to minimize the environmental impacts of hydropower plants.

Commission for Environmental Cooperation of North America (CEC). (2005a) Canada 2002 Power Plant Emissions. Retrieved Dec 18, 2007 from <http://www.cec.org/news/details/index.cfm?varlan=English&ID=2648>.

Commission for Environmental Cooperation of North America (CEC). (2005b) Mexico 2002 Power Plant Emissions. Retrieved Dec 18, 2007 from <http://www.cec.org/news/details/index.cfm?varlan=English&ID=2648>.

Commission for Environmental Cooperation of North America (CEC). (2005c) United States 2002 Power Plant Emissions. Retrieved Dec 18, 2007 from <http://www.cec.org/news/details/index.cfm?varlan=English&ID=2648>.

Dallarosa, J.B., Teixeira, E.C., and Alves, R.C.M. 2007. Application of numerical models in the formation of ozone and its precursors in areas of influence of coal-fired power station - Brazil. Water Air Soil Pollut. 178: 385-399.

Abstract: The purpose of the present study is to simulate concentrations of ozone and its precursors (NO and NO₂) in an area under the influence of the Candiota coal-fired power station by applying numerical models. The photochemical simulations were conducted during two distinct periods: in summer (from 24 to 26 January 2003) and in winter (from 10 to 12 August, 2004). With the RAMS atmospheric model (Regional Atmospheric Modelling System) we obtained meteorological fields to initialize the CIT photochemical model. The emission data were based on the AP-42 and only compounds emitted during coal burning were considered. The simulated results revealed high ozone levels in warmer periods, being related to high temperatures and water vapor concentrations. The simulated concentrations are located far from the emitting source, favoring reaction and mixing time between precursors to form ozone. Simulated winds of small intensity favored ozone transport, mixing and accumulation in areas far from the emitting source.

Danihelka, P., Z. Volna, J. M. Jones, and A. Williams. 2003. Emission of trace toxic metals during pulverized fuel combustion of Czech coals. International Journal of Energy Research 27:1181-1203.

Abstract: A study of the trace elements emission (As, Se, Cd, Co, Cr, Cu, Zn, Hg, Tl, Pb, Ni, Sn, Sb, V, Mn and Fe) from pulverized coal combustion has been made at six heating and power stations situated in the Czech Republic. The amount of chlorine in coal has considerable influence on volatilization of some elements such as Zn, Cu, Pb, Hg and Tl, which is explained by the formation of thermodynamically stable compounds of these elements with chlorine. Generally, the affinities for Cl follows the order $Tl > Cu > Zn > Pb > Co > Mn > Sn > Hg$. The experimental data indicates enrichment of some of the trace toxic elements in the emissions (Cu, Zn, As, Se, Cd, Sit, Sb, Hg and Pb) and good agreement was obtained by thermodynamic equilibrium calculations with a few exceptions. In the case of Fe, Mn, Co, Cr and Sri calculated values are overestimated in the bottom ash and there are zero predicted amounts of these elements in the fly ash. In comparison, the results from experiments show up to 80% of these elements retained in fly ash. This implies that there exist additional steps leading to the enrichment by Fe, Mn, Co, Cr and Sn of small particles. Such mechanisms could include the ejection during devolatilization of small inorganic particles from the coal of bottom ash particles, or disintegration of the char containing these metals to small particles of fly ash. On the other hand, there are slightly overestimated or similar values of relative enrichment factors for As, V, Cu, Cd, Sb, Tl and Pb in the fly ashes and zero predicted values for bottom ashes. Our experimental results show about 5% or less of these elements are retained in bottom ashes, so they probably remain in the bottom ash inside unburned parts of coal.

de Castro Villela, I.A. and Silveira, J.L. 2006. Thermoeconomic model considering the environment impacts on thermoelectric power plants: Natural gas versus diesel. Proceedings of the ASME Turbo Expo, Vol. 2, pp. 945-951.

Abstract: In this paper a comparative analysis of the environmental impact caused by the use of natural gas and diesel in thermoelectric power plants utilizing combined cycle is performed. The objective is to apply a thermoeconomical analysis in order to compare the two proposed fuels. In this analysis, a new methodology that incorporates the economical engineering concept to the ecological efficiency once Cardu and Baica [1, 2], which evaluates, in general terms, the environmental impacts caused by CO₂, SO₂, NO_x and Particulate Matter (PM), adopting as reference the air quality standards in vigour is employed. The thermoeconomic model herein proposed utilizes functional diagrams that allow the minimization the Exergetic Manufacturing Cost, which represents the cost of production of electricity incorporating the environmental impact effects to study the performance of the thermoelectric power plant [3,4], It follows that it is possible to determine the environmental impact caused by thermoelectric power plants and, under the ecological standpoint, the use of natural gas as a fuel is the best option compared to the use of the diesel, presenting ecological efficiency values of 0.944 and 0.914 respectively. From the Exergoeconomic point of view of, it was found out that the EMC (Exergetic Manufacturing Cost) is better when natural gas is used as fuel compared to the diesel fuel.

de Castro Villela, I.A., and Silveira, J.L. 2007. Ecological efficiency in thermoelectric power plants. Applied Thermal Engineering 27: 840-847.

Abstract: This work evaluates the environmental impact resulting from the natural gas and diesel combustion in thermoelectric power plants that utilize the combined cycle technology (CC), as regarding to Brazilian conditions according to Thermopower Priority Plan (TPP). In the regions where there are not natural gas the option has been the utilization of diesel and consequently there are more emission of pollutants. The ecological efficiency concept, which evaluates by and large the environmental impact, caused by CO₂, SO₂, NO_x and particulate matter (PM)

emissions. The combustion gases of the thermoelectric power plants working with natural gas (less pollutant) and diesel (more pollutant) cause problems to the environment, for their components harm the human being life, animals and directly the plants. The resulting pollution from natural gas and diesel combustion is analyzed, considering separately the CO₂, SO₂, NO_x and particulate matter gas emission and comparing them with the in use international standards regarding the air quality. It can be concluded that it is possible to calculate thermoelectric power plant quantitative and qualitative environment factor, and on the ecological standpoint, for plant with total power of 41 441 kW, being 27 170 kW for the gas turbine and 14271 kW for the steam turbine. The natural gas used as fuel is better than the diesel, presenting ecological efficiency of 0.944 versus 0.914 for the latter, considering a thermal efficiency of 54% for the combined cycle.

Demirak, A., Balci, A., Dalman, O., and Tufekci, M. 2005. Chemical investigation of water resources around the Yatagan thermal power plant of Turkey. *Water, Air, and Soil Pollution* 162: 171-181.

Abstract: In this work, trace metals such as Hg, Pb, As, Cd, Cu, Fe, Mn and Zn in underground water samples obtained from three wells, an ash-pond and drinking water located near the Yatagan Thermal Power Plant were measured. As, Hg, Cu and Zn contents of the underground water were lower than those reported in the EEC (European Economic Community) and WHO (World Health Organization) guidelines. In contrast, the levels of Fe, Pb, Cd and Mn in some groundwater samples were higher than EEC and WHO guideline values. The trace metal concentrations in coal ash-pond water were observed to be lower than water quality standards with the exception of Pb. The obtained results indicated that the trace metal concentration in the sampled drinking water site did not exceed WHO limits.

Di, X., Nie, Z., Yuan, B., and Zuo, T. 2007. Life cycle inventory for electricity generation in China. *International Journal of Life Cycle Assessment* 12: 217-224.

Abstract: Background, Goal and Scope. The objective of this study was to produce detailed a life cycle inventory (LCI) for the provision of 1 kWh of electricity to consumers in China in 2002 in order to identify areas of improvement in the industry. The system boundaries were processes in power stations, and the construction and operation of infrastructure were not included. The scope of this study was the consumption of fossil fuels and the emissions of air pollutants, water pollutants and solid wastes, which are listed as follows: (1) consumption of fossil fuels, including general fuels, such as raw coal, crude oil and natural gas, and the uranium used for nuclear power; (2) emissions of air pollutants from thermal power, hydropower and nuclear power plants; (3) emissions of water pollutants, including general water waste from fuel electric plants and radioactive waste fluid from nuclear power plants; (4) emissions of solid wastes, including fly ash and slag from thermal power plants and radioactive solid wastes from nuclear power plants. Methods. Data were collected regarding the amount of fuel, properties of fuel and the technical parameters of the power plants. The emissions of CO₂, SO₂, NO_x, CH₄, CO, non-methane volatile organic compound (NMVOC), dust and heavy metals (As, Cd, Cr, Hg, Ni, Pb, V, Zn) from thermal power plants as well as fuel production and distribution were estimated. The emissions of CO₂ and CH₄ from hydropower plants and radioactive emissions from nuclear power plants were also investigated. Finally, the life cycle inventory for China's electricity industry was calculated and analyzed. Results. Related to 1 kWh of usable electricity in China in 2002, the consumption of coal, oil, gas and enriched uranium were 4.57E-01, 8.88E-03, 7.95E-03 and 9.03E-08 kg; the emissions of CO₂, SO₂, NO_x, CO, CH₄, NMVOC, dust, As, Cd, Cr, Hg, Ni, Pb, V, and Zn were 8.77E-01, 8.04E-03, 5.23E-03, 1.25E-03, 2.65E-03, 3.95E-04, 1.63E-02, 1.62E-06, 1.03E-08, 1.37E-07, 7.11E-08, 2.03E-07, 1.42E-06, 2.33E-06, and 1.94E-06 kg; the emissions of waste water, COD, coal fly ash, and slag were 1.31, 6.02E-05, 8.34E-02, and 1.87E-02 kg; and the emissions of inactive gas, halogen and gasoloid, tritium, non-tritium, and

radioactive solid waste were 3.74E+01 Bq, 1.61E-01 Bq, 4.22E+01 Bq, 4.06E-02 Bq, and 2.68E-10 m³ respectively. Conclusions. The comparison result between the LCI data of China's electricity industry and that of Japan showed that most emission intensities of China's electricity industry were higher than that of Japan except for NMVOC. Compared with emission intensities of the electricity industry in Japan, the emission intensities of CO₂ and Ni in China were about double; the emission intensities of NO_x, Cd, CO, Cr, Hg and SO₂ in China were more than 10 times that of Japan; and the emission intensities of CH₄, V, Pb, Zn, As and dust were more than 20 times. The reasons for such disparities were also analyzed. Recommendations and Perspectives. To get better LCI for the electricity industry in China, it is important to estimate the life cycle emissions during fuel production and transportation for China. Another future improvement could be the development of LCIs for construction and operation of infrastructure such as factory buildings and dams. It would also be important to add the information about land use for hydropower.

dos Santos, C. Y. M., D. D. Azevedo, and F. R. D. Neto. 2004. Atmospheric distribution of organic compounds from urban areas near a coal-fired power station. Atmospheric Environment 38:1247-1257.

Abstract: Atmospheric particulate matter and volatile organic compounds (VOCs) from three sites surrounding a thermoelectric complex, VOCs from the power plant stack gas and aliphatic and aromatic fractions obtained from a coal sample utilized by the thermoelectric complex were monitored in Tubarao and Capivari de Baixo cities, State of Santa Catarina, Brazil, in December 1997. Literature data were reviewed in order to outline differences and similarities among sources and levels of pollutants from coal combustion. Concentrations of benzo[a]pyrene, which is a well-known carcinogenic chemical, were relatively high compared to large urban agglomerations worldwide and similar compared to Asian cities as Beijing in China, a substantial producer and consumer of coal. Concentrations of benzene were lower than other Brazilian urban areas. Quantitation of the compounds identified showed that they were present within the recommended limits of exposure for substances present in air.

Environment Canada. National Pollutant Release Inventory.
http://www.ec.gc.ca/pdb/npri/npri_data_e.cfm. Accessed February 10, 2008.

Environmental Integrity Project. (2006) Dirty Kilowatts - America's Most Polluting Power Plants. Retrieved Nov 28, 2007 from
http://www.dirtykilowatts.org/Dirty_Kilowatts.pdf.

Environmental Integrity Project. (2007) Dirty Kilowatts - America's Most Polluting Power Plants. Retrieved Nov 28, 2007 from
http://www.dirtykilowatts.org/Dirty_Kilowatts2007.pdf.

Freitas, M. C., M. M. Farinha, M. G. Ventura, S. M. Almeida, M. A. Reis, and A. G. Pacheco. 2005. Gravimetric and chemical features of airborne PM₁₀ AND PM_{2.5} in mainland Portugal. Environmental Monitoring and Assessment 109:81-95.

Abstract: This paper describes concentration amounts of arsenic (As), particulate mercury (Hg), nickel (Ni) and lead (Pb) in PM₁₀ and PM_{2.5}, collected since 1993 by the Technological and Nuclear Institute (ITN) at different locations in mainland Portugal, featuring urban, industrial and rural environments, and a control as well. Most results were obtained in the vicinity of coal- and oil-fired power plants. Airborne mass concentrations were determined by gravimetry. As and Hg concentrations were obtained through instrumental neutron activation analysis (INAA), and Ni

and Pb concentrations through proton-induced X-ray emission (PIXE). Comparison with the EU (European Union) and the US EPA (United States Environmental Protection Agency) directives for Ambient Air has been carried out, even though the sampling protocols herein - set within the framework of ITN's R&D projects and/or monitoring contracts - were not consistent with the former regulations. Taking this into account, 1) the EU daily limit for PM₁₀ was exceeded a few times in all sites except the control, even if the number of times was still inferior to the allowed one; 2) the EU annual mean for PM₁₀ was exceeded at one site; 3) the EPA daily limit for PM_{2.5} was exceeded one time at three sites; 4) the EPA annual mean for PM_{2.5} was exceeded at most sites; 5) the inner-Lisboa site approached or exceeded the legislated PMs; 6) Pb levels stayed far below the EU limit value; and 7) concentrations of As, Ni and Hg were also far less than the reference values adopted by EU. In every location, Ni appeared more concentrated in PM_{2.5} than in coarser particles, and its levels were not that different from site to site, excluding the control. The highest As and Hg concentrations were found in the neighbourhood of the coal-fired, utility power plants. The results may be viewed as a "worst-case scenario" of atmospheric pollution, since they have been obtained in busy urban-industrial areas and/or near major power-generation and waste-incineration facilities.

Goodarzi, F., Peel, W. P., Huggins, F. E., Brown, J. R., Charland, J. and Percival, J. (2002) Chemical and mineralogical characteristics of milled coal, ashes, and stack-emitted material from Unit No. 5, Battle River coal-fired power station, Alberta, Canada. Retrieved Jan 8, 2008 from <http://geoscan.ess.nrcan.gc.ca/cgi-bin/starfinder/0?path=geoscan.fl&id=fastlink&pass=&search=R%3D213901&format=FULL>.,

Goodarzi, F., Huggins, F.E., and Sanei, H. 2008. Assessment of elements, speciation of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal. International Journal of Coal Geology 74: 1-12.

Abstract: A detailed assessment of elements was carried out at a power plant rated at 150 MW burning western Canadian medium volatile bituminous coal with an ash content of 34 wt.%. The distributions of elements of environmental concern (As, Cd, Cr, Hg, Ni and Pb) in feed coals, ashes, and stack-emitted materials were determined using NAA, ICPEs and ICP-MS, GFAA for Pb, and CVAA for Hg. The speciation of As, Cr, and Ni was examined using XANES spectroscopy. The results show that the elements in the feed coal are within the same range for As, Hg and Pb and higher for Cd, Cr and Ni compared to other Canadian feed coals and within range for world coals. The combination of a Mechanical Cyclone Separator (MCS) and Fabric Filter (FF) removes a significant portion of the elements of environmental concern, as indicated by their relative enrichment (RE) ratios greater than 0.7. The fly ash from within the FF has a higher content of elements, such as Hg (1.58 mg/kg) than the MSC (0.13 mg/kg) due its lower temperature (130 [degree sign]C) and the ability for finer particles to be captured by the baghouse. Arsenic in the feed coal is dominated by arsenical pyrite and less toxic As+ 5 in arsenate forms. Arsenic is very low in the bottom ash, while in the fly ash it is largely (> 90%) present as As+ 5. Chromium in the milled coal is present as Cr+ 3 in association primarily with illite. This occurrence gives rise to an aluminosilicate association in ash materials, with the chromium oxidation state remaining as Cr+ 3. Nickel in both the feed coal and ashes occurs as Ni+ 2 predominantly in coordination with oxygen. No evidence for carcinogenic Ni sub-sulfides was observed. Mercury is emitted from the plant at a rate of 1.8 g/h and is mostly in the form of reactive gaseous mercury, followed by elemental mercury and particulate mercury. The rates of input of elements of environmental concern, As, Cd, Cr, Hg, Ni and Pb, for this station were 10.45, 1.13, 123.3, 0.29, 36.3 and 23.1 kg/day, respectively, of which only 0.08, 0.01, 0.71, 0.04, 0.44, and 0.17 kg/day were emitted from the stack. Indicating that most of these elements (>

99%) were captured by the particulate removing devices. The concentrations of elements in the air and in the vicinity of this power plant are low or within the range of published data for ambient air in urban and rural areas.

Hao, J., Wang, L., Shen, M., Li, L., and Hu, J. 2007. Air quality impacts of power plant emissions in Beijing. Environ. Pollut. 147: 401-408.

Abstract: The CALMET/CALPUFF modeling system was applied to estimate the air quality impacts of power plants in 2000 and 2008 in Beijing, and the intake fractions (IF) were calculated to see the public health risks posed. Results show that in 2000 the high emission contribution induced a relatively small contribution to average ambient concentration and a significant impact on the urban area (9.52 $\mu\text{g}/\text{m}^3$ of SO_2 and 5.29 $\mu\text{g}/\text{m}^3$ of NO_x). The IF of SO_2 , NO_x and PM_{10} are 7.4×10^{-6} , 7.4×10^{-6} and 8.7×10^{-5} , respectively. Control measures such as fuel substitution, flue gas desulfurization, dust control improvement and flue gas denitration planned before 2008 will greatly mitigate the SO_2 and PM_{10} pollution, especially alleviating the pressure on the urban area to reach the National Ambient Air Quality Standard (NAAQS). NO_x pollution will be mitigated with 34% decrease in concentration but further controls are still needed.

Ichikawa, Y., and K. Sada. 2001. A method of evaluating the topographical effect on atmospheric dispersion using a numerical model. International Journal of Environment and Pollution 16:439-450.

Abstract: A method of evaluating topographical effects on exhaust gas dispersion using a numerical model is proposed. The numerical model consists of a turbulence closure model and a Lagrangian particle dispersion model. The topographical effect was evaluated in terms of the ratios of maximum concentration and the distance of the point of maximum concentration from the source on the topography to the respective values on a flat plane and the relative concentration distribution along the ground surface plume axis normalized for the maximum concentration on a flat plane. The proposed method was applied to the prediction of the dispersion of exhaust gas from a thermal power plant in a complex terrain. Good agreement was obtained between topographical effects evaluated by the numerical model and wind-tunnel experiments.

Kaewboonsong, W., V. I. Kuprianov, and N. Chovichien. 2006. Minimizing fuel and environmental costs for a variable-load power plant (co-)firing fuel oil and natural gas - Part 1. Modeling of gaseous emissions from boiler units. Fuel Processing Technology 87:1085-1094.

Abstract: This work was aimed at modeling of major gaseous emissions (NO_x , SO_3 , SO_2 , CO_2) from boiler units of a power plant firing (or co-firing) fuel oil and natural gas for variable operating conditions (load and load-related variables: excess air, flue gas recirculation, etc.). The emission rate of the pollutants for the co-firing was estimated for a particular boiler using these characteristics for the burning of each fuel in the boiler on its own and taking into account energy fractions (contributions) of fuel oil and natural gas to the boiler heat input. The gaseous emissions (in terms of emission concentrations, emission rates and specific emissions) from a 200-MW boiler unit firing low-S fuel oil and from a 310-MW boiler unit firing (or co-firing) medium-S fuel oil and natural gas were estimated and compared for 50-100% unit loads based on actual fuel properties and load-related operating variables of these units. Upper limit for the energy fraction of medium-S fuel oil was determined for the 310-MW boiler unit co-firing the two fuels with the aim to meet the national emission standard for SO_2 .

Kaldellis, J. K., G. Spyropoulos, and K. Chalvatzis. 2004. The impact of Greek electricity generation sector on the national air pollution problem. Fresenius Environmental Bulletin 13:647-656.

Abstract: Since the early sixties, the Greek electricity production sector has been based on local lignite and heavy-oil, being gradually replaced by imported natural gas only quite recently. Therefore, the electricity generation process -beyond the economic and macroeconomic cost- is assumed to be responsible for significant air pollution. In this context, an extensive and thorough analysis is carried out concerning the quantities of air pollutants that have resulted from the electricity sector during the 1995-2002 period. For this purpose, all obtainable data are initially considered and analysed, followed by an integrated numerical model developed from basic-principles, in order to estimate the air pollutants created from electricity generation. The results presented are based on official data, analysing the SO₂, NO_x and CO₂ gasses produced on the basis of the fuel utilized. Among the most interesting results of the present survey emerges the continuous increase of air pollutants with time, mainly attributable to the electricity demand amplification and the state policy of using Northern Greece lignite and imported natural gas in the mainland and diesel-oil in the Aegean Sea territories. This strategy practically leads to remarkable air pollution rise during the next decade, a fact that is also validated by the application of the analytical model developed.

Kannan, R., K. C. Leong, R. Osman, and H. K. Ho. 2007. Life cycle energy, emissions and cost inventory of power generation technologies in Singapore. Renewable & Sustainable Energy Reviews 11:702-715.

Abstract: Singapore is one of the most industrialised and urbanised economics in South-East Asia. Power supply is an important sub-system in its economy and heavily reliant on imported oil and natural gas. Due to its geographical area, clean/renewable energy sources for power generation are limited. At the same time, in its deregulated electricity market, the adoption of clean/renewable based power generation technology may be hindered by a market pricing mechanism that does not reflect externality costs. For a sustainable power supply, there is a need to change the conventional appraisal techniques. Life cycle assessment (LCA) and life cycle cost analysis (LCCA) are good tools to quantify environmental impacts and economic implications. LCA and LCCA are performed for centralised and distributed power generation technologies in Singapore, namely, oil and Orimulsion-fired steam turbines, natural gas-fired combined cycle plant, solar PV and fuel cell systems. A life cycle energy, emission and cost inventory is established. The results are discussed from the perspectives of fuel security, environmental protection and cost effectiveness of future power generation strategies for Singapore.

Kouprianov, V. I. 2002. Influence of lignite quality on airborne emissions from power generation in the Russian Far East and in Northern Thailand. Fuel Processing Technology 76:187-199.

Abstract: Domestic low rank lignites are widely used for power production in the Far East of Russia and in Northern Thailand. The quality of lignites fired in boilers of the power plants in both regions is somewhat variable because of significant fluctuations in the moisture and ash content as well as in the ultimate analysis of fuel. The effect of the fuel quality on airborne emissions (NO_x, SO_x, CO₂ and PM) from the power plant boilers is the focus of this work. The emission concentrations of NO, (as NO₂) in flue gas leaving the boiler are predicted based on the fuel analysis, as well as the boiler furnace geometry and operating conditions. The rates of SO_x (as SO₂) emitted into the atmosphere are estimated taking into account the sulfur content in fuel together with the effect of absorption of sulfur dioxide by fly ash and also efficiency of the FGD units. The emission concentration and rate, as well as the specific emission (per kW h) for the pollutants of interest, were quantified for the selected 55- and 100-MW units (Russian case study) and for the 150- and 300-MW units (Thai case study) fired with lignite of different qualities.

Krylov, D. A. 2002. Effect of heating and power plants on the environment. Atomic Energy

92:523-528.

Abstract: The OAO Gazprom has proposed that the consumption of natural gas by heating and power plants in Russia be decreased by 30 billion m³ per year and that this volume of gas be replaced by coal. Data on the environmental effects and effects on human health resulting from enterprises in the coal industry and heating and power plants burning coal and natural gas are analyzed. The volume of emissions of harmful substances into the atmosphere when 30 billion m³ of gas are replaced at heating and power plants by kamsko-achinsk and hard kuznets coal is calculated (for three variants). The calculations show that decreasing the amount of gas burned by heating and power plants and increasing at the same time the consumption of coal results in a substantial increase in harmful emissions into the environment.

Lee, K. M., S. Y. Lee, and T. Hur. 2004. Life cycle inventory analysis for electricity in Korea. Energy 29:87-101.

Abstract: A life cycle inventory analysis (LCI) database that encompasses the entire Korean electrical energy grid was developed. The CO₂ emission per functional unit of electricity, 1 kWh of usable electricity, was 0.49 kg/f.u. Contribution of direct emission of CO₂ to the total CO₂ emission was around 95%. In the case of emissions of SO_x, NO_x, and PM, contribution of the upstream processes including raw energy material extraction, transport, and fuel processing to the total emissions were 29%, 26%, and 43%, respectively. Emissions of air pollutants from power generation or direct emissions are much greater in quantity than those from the upstream processes. On the other hand, the opposite is true for the emissions of water pollutants. Bituminous coal was the largest source of emissions of air and water pollutants including CO₂. Natural gas was the best fuel and anthracite coal was the worst fuel with respect to the direct and upstream emissions of air and water pollutants and wastes.

Levy, J. I., J. D. Spengler, D. Hlinka, D. Sullivan, and D. Moon. 2002. Using CALPUFF to evaluate the impacts of power plant emissions in Illinois: model sensitivity and implications. Atmospheric Environment 36:1063-1075.

Abstract: Air pollution emissions from older fossil-fueled power plants are often much greater than emissions from newer facilities, in part because older plants are exempt from modern emission standards required of new plants under the Clean Air Act. To quantify potential health benefits of emission reductions, there is a need to apply atmospheric dispersion models that can estimate the incremental contributions of power plants to ambient concentrations with reasonable accuracy over long distances. We apply the CALPUFF atmospheric dispersion model with meteorological data derived from NOAA's Rapid Update Cycle model to a set of nine power plants in Illinois to evaluate primary and secondary particulate matter impacts across a grid in the Midwest. In total, the population-weighted annual average concentration increments associated with current emissions are estimated to be 0.04 mug m⁻³ of primary fine particulate matter (PM_{2.5}), 0.13 mug m⁻³ of secondary sulfate particles, and 0.10 mug m⁻³ of secondary nitrate particles (maximum impacts of 0.3, 0.2, and 0.2 mug m⁻³, respectively). The aggregate impact estimates are moderately insensitive to parametric assumptions about chemical mechanism, wet/dry deposition, background ammonia concentrations, and size of the receptor region, with the largest uncertainties related to nitrate particles and long-range transport issues. Additional uncertainties may be associated with inherent limitations of CALPUFF, but it appears likely that the degree of uncertainty in atmospheric modeling will not dominate the total uncertainty associated with health impact or benefit estimation. Although the annual average concentration increments from a limited number of sources are relatively small, the large population affected by long-range transport and the number of power plant sources around the US imply potentially significant public health impacts using standard epidemiological assumptions. Our analysis

demonstrates an approach that is applicable in any setting where source controls are being evaluated from a public health or benefit-cost perspective.

Liamsanguan, C., and Gheewala, S.H. 2007. Environmental assessment of energy production from municipal solid waste incineration. International Journal of Life Cycle Assessment 12: 529-536.

Abstract: Background, Aims and Scope. During the combustion of municipal solid waste (MSW), energy is produced which can be utilized to generate electricity. However, electricity production from incineration has to be evaluated from the point view of the environmental performance. In this study, environmental impacts of electricity production from waste incineration plant in Thailand are compared with those from Thai conventional power plants. Methods. The evaluation is based on a life cycle perspective using life cycle assessment (LCA) as the evaluation tool. Since MSW incineration provides two services, viz., waste management and electricity production, the conventional power production system is expanded to include landfilling without energy recovery, which is the most commonly used waste management system in Thailand, to provide the equivalent function of waste management. Results. The study shows that the incineration performs better than conventional power plants vis-a-vis global warming and photochemical ozone formation, but not for acidification and nutrient enrichment. Discussion. There are some aspects which may influence this result. If landfilling with gas collection and flaring systems is included in the analysis along with conventional power production instead of landfilling without energy recovery, the expanded system could become more favorable than the incineration in the global warming point of view. In addition, if the installation of deNO_x process is employed in the MSW incineration process, nitrogen dioxide can be reduced with a consequent reduction of acidification and nutrient enrichment potentials. However, the conventional power plants still have lower acidification and nutrient enrichment potentials. Conclusions. The study shows that incineration could not play the major role for electricity production, but in addition to being a waste management option, could be considered as a complement to conventional power production. To promote incineration as a benign waste management option, appropriate NO_x and dioxin removal processes should be provided. Separation of high moisture content waste fractions from the waste to be incinerated and improvement of the operation efficiency of the incineration plant must be considered to improve the environmental performance of MSW incineration. Recommendations. This study provides an overall picture and impacts, and hence, can support a decision-making process for implementation of MSW incineration. The results obtained in this study could provide valuable information to implement incineration. But it should be noted that the results show the characteristics only from some viewpoints. Outlook. Further analysis is required to evaluate the electricity production of the incineration plant from other environmental aspects such as toxicity and land-use.

Mahlia, T. M. I. 2002. Emissions from electricity generation in Malaysia. Renewable Energy 27:293-300.

Abstract: Emissions in the process utilization produce adverse effects on the environment that influence human health, organism growth, climatic changes and so on. The Kyoto protocol, produced by the United Nations Framework Convention on Climate change (UNFCCC) in December 1997, prescribed a legally binding greenhouse gas emission target about 5% below their 1990 level. About 160 countries including Malaysia now adopt this protocol. Electricity generation is one of the main contributors to emissions in the country. In order to calculate the potential emissions produced by this activity, the type of fuel use should be identified. Malaysia hopes to gradually change fuel use from 70% gas, 15% coal, 10% hydro, and 5% petroleum in the year 2000 to 40% gas, 30% hydro, 29% coal, and only 1% petroleum by the year 2020. The changes in fuel type have changed the pattern of emission production. This study attempts to

predict the pattern of emissions from 2002 to 2020 due to the changes in fuel use. The calculation is based on emissions for unit electricity generated and the percentages of fuel use for electricity generation. The study found that the electricity generation company has produced huge emissions from their power plants in this country.

Meij, R., and H. T. Winkel. 2004. The emissions and environmental impact of PM10 and trace elements from a modern coal-fired power plant equipped with ESP and wet FGD. Fuel Processing Technology 85:641-656.

Abstract: This study focused on the local environmental impact of a coal-fired power station with a net capacity of 600 MW, The atmospheric emissions of numerous possible flue gas components were calculated using the KEMA TRACE MODEL(R). The STACKS model was used to calculate annual average immission levels or ground-level concentrations. Also calculated were the levels of wet and dry deposition of plume components in the vicinity of a power station. The calculated immission and deposition levels were then compared with the prevailing background concentrations and deposition levels in the Netherlands.

It appears that the concentrations of air pollutants prevailing in the Netherlands are low, and that with the exception of fine dust and NO₂/NO_x-the levels do not exceed or even approach any air quality standards or limits. The present fine dust concentrations are close to the air quality standard. while the standards for NO₂/NO_x, sometimes are exceeded, mainly as a result of increased traffic emissions. For NO₂, the contribution of power plant emission to background concentrations is less than 2%. The increase in background fine dust concentrations attributable to fly dust ground level concentrations (immissions) is no more than 0.03%. Where the elements present in fly dust are concerned, the increase in the elemental background concentrations is smaller than 1%. The contribution to atmospheric fine dust concentrations in the vicinity of a power station attributable to the formation of secondary aerosols is negligible. The reason is that a distance of approximately 100 km, only about 3% of the gaseous sulphur dioxide and nitrogen oxides present in the plume are converted into secondary aerosols.

Total wet and dry fly dust deposition over a 40 x 40-km area around the power station averages 1.7 mg/m²/year, with a maximum of 25 mg/m²/year. Depositions of this will not cause any nuisance. Trace element deposition levels are very low. The increases in background depositions are negligible, varying between 2.5% and 0.01%, depending on the element concerned.

The background level of deposition of potentially acidifying substances in the Netherlands has fallen by more than 50% in the last 20 years to a value of about 3 100 mol/ha/year in 2000. The main contributors to potential acid deposition are foreign sources (43%) and the agricultural industry (41%,). The hypothetical power station was calculated to contribute on average only 15 acid equivalents/year across the area referred to above. This represents barely any increase in the background level of deposition (0.5%).

Meij, R., and H. T. Winkel. 2007. The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations. Atmospheric Environment 41:9262-9272.

Extensive research for establishing the emissions of heavy metals from coal-fired power stations is performed in the Netherlands for the past 25 years. In the Netherlands coal is fired from all over the world. This means that the emissions are established for coal of various origins. In the eighties, the emissions of installations equipped with ESPs (electrostatic precipitators) were measured. In the nineties, the influence of wet FGD (flue gas desulphurisation) on the emissions was studied. The effect of co-combustion of biomass and other secondary fuels is the main item for the last 10 years. Fifty-five elements were measured in the solid state and eight elements in the gaseous phase. It appeared that at low particulate concentration the influence of calcium containing evaporated water droplets downstream the wet FGD on the emissions of heavy metals is bigger than the composition of the coal. Also it appeared that at modern coal-fired power

stations the emissions are hardly influenced by co-combustion of biomass. All the results are used for modelling, resulting in the KEMA TRACE MODEL (R), by which the emissions can be predicted. The established emission factors are for most elements in good agreement with literature values for comparable modern installations. Persistence organic pollutants (POPs) that were detected in the flue gases of coal-fired power stations are polycyclic aromatic hydrocarbons (PAH) and dioxins/furans. Measurements during full coal-firing and during co-firing of biomass have indicated that these emissions are negligible.

Miller, P., Patterson, Z. and Vaughan, S. (2002) Estimating Future Air Pollution from New Electric Power Generation. Retrieved Dec 18, 2007 from http://www.ccc.org/files/pdf//2_airemissions-e.pdf.

Nansai, K., Y. Moriguchi, and S. Tohno. 2003. Compilation and application of Japanese inventories for energy consumption and air pollutant emissions using input-output tables. Environmental Science & Technology 37:2005-2015.

Abstract: Preparing emission inventories is essential to the assessment and management of our environment. In this study, Japanese air pollutant emissions, energy consumption, and CO₂ emissions categorized by approximately 400 sectors (as classified by Japanese input-output tables in 1995) were estimated, and the contributions of each sector to the total amounts were analyzed. The air pollutants examined were nitrogen oxides (NO_x), sulfur oxides (SO_x), and suspended particulate matter (SPM). Consumptions of about 20 fossil fuels and five other fuels were estimated according to sector. Air pollutant emission factors for stationary sources were calculated from the results of a survey on air pollution prevention in Japan. Pollutant emissions from mobile sources were estimated taking into consideration vehicle types, traveling speeds, and distances. This work also counted energy supply and emissions from seven nonfossil fuel sources, including nonthermal electric power, and CO₂ emissions from limestone (for example, during cement production). The total energy consumption in 1995 was concluded to be 18.3 EJ, and the annual total emissions of CO₂, NO_x, SO_x, and SPM were, respectively, 343 Mt-C, 3.51 Mt, 1.87 Mt, and 0.32 Mt. An input-output analysis of the emission inventories was used to calculate the amounts of energy consumption and emissions induced in each sector by the economic final demand.

Oguz, M. 2003. An Application of Geographic Information System (GIS) to a Fictitious Thermal Power Plant in Mersin, Tuerkiye: An Application of Dispersion Modelling Coupled with GIS. Water, Air, & Soil Pollution 148:389-406.

Abstract: In this study, local air quality impacts of a proposed conventional coal-fired power plant in the Icel region has been investigated using numerical dispersion modeling studies coupled with a GIS application. Within the impact area of the facility, Industrial Source Complex Short Term (ISCST2) dispersion model has been used to estimate ground-level concentrations of air pollutants originating from the power plant. For the same impact area, GIS applications have been utilised to determine the agricultural yield distribution. For this purpose, relevant satellite images were digitised, classified and statistically analyzed. Based on the predicted ground-level pollutant concentrations and sensitivity of the agricultural crops to the pollutants, agricultural yield loss was estimated for the impact area. The results have been quantified and valued in monetary terms for the purpose of performing an environmental cost benefit analysis. Comparison of the conventional cost benefit analysis with the environmental cost benefit analysis showed the significance of the external cost of the proposed facility, resulting from the environmental damages.

Ontario Clean Air Alliance. (2007) OPG: Ontario's Pollution Giant. Retrieved Jan 14, 2008 from <http://www.cleanairalliance.org/resource/opggiant.pdf>.

Otero-Rey, J. R., J. M. Lopez-Vilarino, J. Moreda-Pineiro, E. Alonso-Rodriguez, S. Muniategui-Lorenzo, P. Lopez-Mahia, and D. Prada-Rodriguez. 2003. As, Hg, and Se flue gas sampling in a coal-fired power plant and their fate during coal combustion. *Environmental Science & Technology* 37:5262-5267.

As, Hg, and Se are the most volatile elements in the flue gas from a coal-fired power plant. Significant amounts of these elements cause an undesired direct gaseous emission, which leads to a serious environmental health risk. The main focus of this study is to evaluate the possibility of simultaneous sampling of these volatile elements using an accurate official method for Hg (the most volatile element). A study of As, Hg, and Se emissions from a 1400 MW coal-fired power plant equipped with electrostatic precipitators (ESPs) was carried out for the combustion of a mixture of two types of coal. Simultaneous sampling of coal, bottom ash, fly ash, flue gas, and particles associated with the gas phase has been performed. Flue gas has been sampled by the Ontario Hydro Method Sampling Train, an ASTM method for Hg speciation. This sampling method was tested for As and Se sampling. As and Se determinations have been performed by HG-AAS, and Hg has been determined by CV-AAS. The results were used to examine the following: overall mass balances, relative distribution of these elements in the coal-fired power plant; As, Hg, and Se concentrations in coal and combustion residues; and predominant oxidation state for Hg in flue gas. The mass balances obtained for As, Hg, and Se were satisfactory in all cases; nevertheless, relative enrichment values in fly ash for As and Se were low; therefore, we concluded that As sampling in flue gas can be conducted by application of the Ontario Hydro Method; nevertheless Se released in the gas phase is not completely collected by this sampling train. Application of this sampling method allowed for performance of Hg speciation. The results indicated that Hg(II) was the predominant species in flue gas. It has also been proven that 24%, more than 99.8%, and 90% for As, Hg, and Se in the stack emissions, respectively, were in the gaseous phase.

Rang, S. (2002) Up The Stack: Coal-Fired Electricity's Toxic Impact. Retrieved Jan 14, 2008 from <http://www.cleanairalliance.org/resource/upthestack.pdf>.

Rotatori, M., E. Guerriero, A. Sbrilli, L. Confessore, M. Bianchini, F. Marino, L. Petrilli, and I. Allegrini. 2003. Characterisation and evaluation of the emissions from the combustion of Orimulsion-400, coal and heavy fuel oil in a thermoelectric power plant. *Environmental Technology* 24:1017-1023.

Abstract: An experimental campaign was carried out in a thermoelectric power plant in Southern Italy in order to evaluate the emissions released during the utilisation of three different fuels, Orimulsion-400, coal and heavy fuel oil (HFO) with high content of sulphur. Macropollutant concentrations in the exhaust gases were recorded by the continuous monitoring system and the Institute on Atmospheric Pollution of the Italian National Research Council (CNR) carried out samplings and analysis of Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorodibenzo-p-dioxins (PCDD) and Polychlorodibenzofurans (PCDF), halogenidric acids and metals. The pollutant concentrations, mass flows and emission factors were compared. Each fuel met the air emission limits for all the pollutants. Coal showed the highest emission levels, whilst HFO and Orimulsion were fairly similar. NO_x, SO₂ and particulate matter showed constant concentration for all the fuels, while Orimulsion and HFO SO₂ concentrations were critical at the highest operating power. Orimulsion showed the lowest PAHs values and PCDDs and PCDFs were much lower than the limits, for all the fuels. Particular attention must be paid with vanadium and nickel during Orimulsion utilisation. For these metals mass balances were carried out.

Silveira, J.L., de Carvalho, Jr.J.A., and de Castro Villela, I.A. 2007. Combined cycle versus one thousand diesel power plants: pollutant emissions, ecological efficiency and economic analysis. *Renewable and Sustainable Energy Reviews* 11: 524-535.

Abstract: The increase in the use of natural gas in Brazil has stimulated public and private sectors to analyse the possibility of using combined cycle systems for generation of electrical energy. Gas turbine combined cycle power plants are becoming increasingly common due to their high efficiency, short lead times, and ability to meet environmental standards. Power is produced in a generator linked directly to the gas turbine. The gas turbine exhaust gases are sent to a heat recovery steam generator to produce superheated steam that can be used in a steam turbine to produce additional power. In this paper a comparative study between a 1000 MW combined cycle power plant and 1000 kW diesel power plant is presented. In first step, the energetic situation in Brazil, the needs of the electric sector modification and the needs of demand management and integrated means planning are clarified. In another step the characteristics of large and small thermoelectric power plants that use natural gas and diesel fuel, respectively, are presented. The ecological efficiency levels of each type of power plant is considered in the discussion, *presenting the emissions of particulate material, sulphur dioxide (SO₂), carbon dioxide (CO₂) and nitrogen oxides (NO_x).*

Springston, S. R., L. I. Kleinman, F. Brechtel, Y. N. Lee, L. J. Nunnermacker, and J. Wang. 2005. Chemical evolution of an isolated power plant plume during the TexAQS 2000 study. *Atmospheric Environment* 39:3431-3443.

Abstract: Stack emissions from a coal-burning power plant were measured during a research flight of the DOE G-I during the Texas Air Quality Study (TexAQS 2000) on 10 September 2000. Clean upstream air and an isolated location allowed the plume to be unambiguously sampled during 12 successive downwind transects to a distance of 63 km-corresponding to a processing time of 4.6 h. The chemical transformation rates of sulfur and nitrogen primary pollutants into aerosol SO₄²⁻ and HNO₃ yield independent values of OH concentration (8.0 and 11 x 10⁽⁻³⁾ cm⁽⁻³⁾, respectively) that are consistent within experimental uncertainty and qualitatively agree with constrained steady-state (CSS) box model calculations. Ozone production efficiency increases with plume age as expected. Primary aerosol emissions with D-P > 5 μm were sampled near the stack. As the plume ages, aerosol size distributions adjusted for dilution show constant number concentrations of aerosols D-P > 10 nm and a marked increase in accumulation-mode particles (D-P > 0.1 μm) as gas-to-particle-conversion causes smaller particles to grow.

Suarez, A. E., and J. M. Ondov. 2002. Ambient aerosol concentrations of elements resolved by size and by source: Contributions of some cytokine-active metals from coal- and oil-fired power plants. *Energy & Fuels* 16:562-568.

Abstract: Size-segregated aerosol samples were collected with Micro-Orifice Impactors in Baltimore, MD, a typical northeastern port city where air quality is influenced by urban and industrial sources. The size fractions were analyzed for up to 32 elements by Instrumental Neutron Activation Analysis and the results were used in a chemical mass balance model to resolve the contributions to ambient levels by size and by source. Resolution by size improves interpretation of the results as primary accumulation aerosol populations from different sources are frequently resolved in the size spectra of their marker species. With a 15-source model, agreement between measured and predicted concentrations was within 40% for all elements except Co, Cr, Cs, Ti, and W. The results suggest that coal-fired power plants are minor sources of the respirable fractions of several metals, including Cr (19%), V (5%), and Zn (<1%), which are known to be active in cytokine assays, a metric of inflammatory response that is linked to

reactive oxygen species production and lung cell necrosis in in vitro and animal studies. Coal combustion contributions to ambient levels of As, Fe, Co, Mn, and Sb were 16, 13, 11, 2.7, and 4.8%, respectively. In addition, coal contributions are likely 30% less than these after correction of the source signature for vapor-phase Se emissions. Major fractions of respirable airborne V and Co (each about 55%), and Zn (70%) were attributed to aerosol emitted from fuel oil combustion and incinerators, respectively. Steel production was the major source for airborne Cr (45%), Fe (52%), and Mn (52%); whereas large (70 and 57%) fractions of airborne As and Sb were attributed to an unidentified source which was resolved in the size spectra. Metal concentrations attributed to long-range transport, owing to their association with secondary sulfate were typically negligible, except for Mn (15%), Se (28%), and Zn (5%).

Thompson, L. and White, M. (2002) Canadian Inventory of SO_x, PM_{2.5} and PM₁₀ Emissions Resulting from the Combustion of Fuel Oils. Retrieved Dec 30, 2007 from http://www.ec.gc.ca/cleanair-airpur/CAOL/OGEB/fuels/reports/cnslt_rpts/cdn_inv/em_inv_e.pdf.

United States Environmental Protection Agency. 2002 National Emissions Inventory Data & Documentation. <http://www.epa.gov/ttn/chief/net/2002inventory.html#inventorydata>. Accessed February 8, 2008.

United States Environmental Protection Agency (US EPA). (2006a) Year 2004 eGRID Plant, Boiler, and Generator Data Files. Retrieved Jan 14, 2008 from <http://www.epa.gov/cleanenergy/energy-resources/egrid/index.html>.

United States Environmental Protection Agency (US EPA). (2006b) Year 2004 eGRID State, EGC Location (operator)-based, EGC Owner-based, Parent Company Location (operator)-based, Parent Company Owner-based, PCA, eGRID Subregion, NERC Region, and U.S. Data Files. Retrieved Jan 14, 2008 from <http://www.epa.gov/cleanenergy/energy-resources/egrid/index.html>.

United States Environmental Protection Agency. National Emissions Inventory (NEI) Air Pollutant Emissions Trends Data. 2006. <http://www.epa.gov/ttn/chief/trends/index.html#tables>. Accessed February 8, 2008. Pollutant-specific data in excel format that provides pollutant- and industry-specific data on emissions from 1970 to 2006.

Vijay, S., Molina, L. T. and Molina, M. J. (2004) Estimating Air Pollution Emissions from Fossil Fuel Use in the Electricity Sector in Mexico. Retrieved Dec 18, 2007 from http://www.cec.org/files/PDF/POLLUTANTS/Estimating-AirPollutionEmmission-FossilFuel_en.pdf.

Voutsas, D., H. Terzi, L. Muller, C. Samara, and T. Kouimtzis. 2004. Profile analysis of organic micropollutants in the environment of a coal burning area, NW Greece. Chemosphere 55:595-604.

Abstract: The concentrations and profiles of dibenzo-p-dioxins, dibenzofurans, polychlorinated biphenyls and polynuclear aromatic compounds in various environmental matrices are presented in this study. The examined environmental matrices are total suspended particles, fly ash and soil collected in NW Greece, an area characterized by intensive coal burning for electrical power generation. Moreover, the occurrence of organic micropollutants in soot after an accidental fire was examined and the possible impact on the outdoor environment was evaluated. Results were statistically treated to obtain information on representative PCDD/F profiles in each matrix and to

compare these profiles with the compositional patterns of possible sources from literature. Coal combustion, fly ash and vehicle exhausts appeared to be the most possible sources in local atmosphere.

Yousif, S. A., A. A. Salem, Y. F. Nassar, and I. F. Bader. 2006. Investigation of pollutants dispersion from power stations. International Journal of Energy Research 30:1352-1362.

Abstract: Theoretical investigations were conducted of pollutants dispersion, NO_x, SO₂ and Particulate Matter (PM), from stacks of arbitrary four power plants in Libya, e.g. North Benghazi, South Tripoli, Zweitina, Khoms. The first four stations are gas power plants, while the last one is gas and steam station. Gaussian plume model has been used to identify ground-level NO_x concentrations profile downwind and crosswind of the chimneys through urban regions and also the location of maximum pollutant concentrations. The study is based on the worst-case emission conditions of Pasquill stability categories (class D). Results indicate that maximum ground-level NO_x impacts for all plants locate at a distance of approximately 1.0-2.5 km from stacks. The site most critical to ambient air NO_x impact is Zweitina, where the plant site is in direct vicinity to residential areas. Khoms electric station exhibits the maximum emitted NO_x, SO₂, and PM intensity, about 305, 48, and 0.7 $\mu\text{g}/\text{m}^3$, respectively, that is lower than allowable concentrations recommended by World Health Organization.

Zhao, F., Peng, S., Zheng, B., Tang, Y., Cong, Z., and Ren, D. 2006. The leaching behavior of cadmium, arsenic, zinc, and chlorine in coal and its ash from coal-fired power plant. Environmental Engineering Science 23: 68-76.

Abstract: The leaching experiment of feed coal (C) and its laboratory high-temperature ash (HA), fly ash (FA), and bottom ash (BA) from a Chinese coal-fired power plant were carried out using column leaching under different pH conditions (pH = 2.0, 4.0, 6.0, and 7.5, respectively) and different leaching durations (up to 80 h). The leaching behaviors of As, Cd, Zn, and Cl were investigated. The results showed that the elements occurring in water-soluble, ion-exchangeable, and Fe-Mn oxide phases are potentially leachable, whereas those in association with organic matter and silicate are less likely to be leached. The cumulative percent of Zn, As, Cl, and Cd leached from C and ash samples increase with decrease in pH. The leaching rate of As and Cl in C and ash samples are higher in comparison with Zn and Cd. However, the maximum concentrations of Cd in the leachate from C, HA, FA, and BA are in excess of or very close to the maximum standard concentrations permitted in the Chinese Standards for Drinking Water and Surface Water. The ultimate concentrations of As, Cd, and Cl in the leachates did not attain equilibrium after the leaching of 80 h; therefore, longer leaching experiments are necessary to evaluate the impact of these hazardous trace elements on aqueous environment.

2.5.2 Environmental effects and biomonitoring

Boone, R., J. Tardif, and R. Westwood. 2004. Radial Growth of Oak and Aspen Near a Coal-Fired Station, Manitoba, Canada. Tree-Ring Research 60:45-58.

Abstract: Eighteen stands of bur oak (*Quercus macrocarpa* Michx.) and trembling aspen (*Populus tremuloides* Michx.) were sampled and analyzed using dendrochronological methods to study the potential effects on tree growth of emissions from a 132 MW coal-fired generating station. Sixteen stands were sampled within a 16-km radius of the station, and two control stands were sampled outside of the range of influence, at distances > 40 km. All stands showed similar radial growth patterns from 1960-2001, regardless of distance from or direction relative to the generating station, and a number of stands, including the controls, had below average growth

after 1970. Both species were significantly affected by climatic factors, showing decreased radial growth with increasing June temperature. The species differed in their growth responses to spring precipitation and temperature in the previous October. One bur oak site displayed marked radial growth decline beginning in the mid-1970s, strongly pronounced following 1977. This decline does not appear to be related to emissions from the station, but is suspected to be a result of poor site conditions (shallow soil developed over calcareous till), confounded by a change in drainage (a road was built adjacent to the stand in 1977, perpendicular to the direction of drainage). The below average growth seen in 1970- 2001 across most stands is likely attributable to stand dynamics and age effects.

Cape, J. N., D. Fowler, and A. Davison. 2003. Ecological effects of sulfur dioxide, fluorides, and minor air pollutants: recent trends and research needs. *Environment international* 29:201-211.

Abstract: The regulation of the emissions of 'traditional' primary air pollutants (fluorides, sulfur dioxide) has changed the pattern of exposure of ecological systems, with greatly reduced exposure close to sources, but with a smaller effect in some remote areas. Measurements show that recovery is occurring at some sites, in fresh water chemistry (reduced acidity) and in sensitive biota (sustainable fish populations). However, the pattern of change in exposure has not always been simply related to emission reductions. An understanding of responses to recent changes will improve our predictions of the response to future emission changes, both locally and globally. As exposure to 'traditional' pollutants is reduced, the potential for other pollutants to have effects becomes more evident. In the aqueous phase, we need to understand the role of soluble and suspended organics, but this also means explicit recognition of the possibility of phase exchange, and the role of photolytic reactions on plant, soil, and water surfaces. Do highly reactive free radicals in the atmosphere, formed by the action of sunlight on volatile organic compounds, have direct effects on plants? Organic compounds and heavy metals may be bioactive as gases and particles, but for many potentially toxic compounds, the experimental evidence for biotic response is very limited. To evaluate the potential effects of pollutants, we need to understand the pathways by which airborne pollutants enter and react within ecosystems. For vegetation, we have to consider bidirectional fluxes, and distinguish among uptake through stomata, through leaf surfaces, or through roots. There are several challenges for the future. (1) Can we devise experiments that permit exposure of vegetation to gases, particles, and/or aqueous pollutants at 'realistic' concentrations? (2) Can we include the potential interactions with photolytically derived free radicals, and the dynamics of exchange? (3) How do we allow for responses to pollutant mixtures, or the simultaneous exposure to pollutants in gas, particle, and aqueous phases? The recognition of the importance of the dynamic exchange of pollutants between phases will be the key to the development of effective experimental approaches to evaluating cause-effect relationships between pollutant mixtures and ecosystem responses.

Cicek, A., and A. S. Koparal. 2004. Accumulation of sulfur and heavy metals in soil and tree leaves sampled from the surroundings of Tuncbilek Thermal Power Plant. *Chemosphere* 57:1031-1036.

Abstract: In this study, the quantities of sulfur and heavy metals, resulting from the Tuncbilek Thermal Power Plant (TPP) in Turkey, have been assessed in tree leaves and soil samples within a 10 km radius of the plant. Leaves of *Salix alba* L., *Populus tremula* L., *Robinia pseudoacacia* L., *Quercus infectoria* L., *Pinus nigra* Arn. ssp. *pallasiana* (Lamb) Holmboe. trees have been used with the aim of determining how far the gas and particles emitted from the TPP are carried, and for assessment of environmental impact. The results obtained from locations chosen at various distances to the TPP, indicate that the contaminating agents are very dense and effective; particularly in the prevailing wind direction and within 10 km of the plant. They gradually lose

their density and effect beyond this distance. The sulfur and heavy metal analyses made in soils taken from these locations indicate a similarity with the data obtained from the leaves.

Cicek, A., and Koparal, A. 2006. Assessment of environmental effects of the coal used in the Seyitomer thermal power plant (Turkey) on white willow. Communications in Soil Science and Plant Analysis 37: 1795-1804.

Abstract: Thermal power plants increase local pollution through SO_x, NO_x, volatile organic compounds (VOCs), and oils containing primarily particulates (including heavy metals) and increase global pollution through CO₂, the greenhouse gas that causes global warming. These strong pollutants have harmful effects on living organisms and the entire ecosystem. In this study, we analyzed the heavy metals iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), and sulfur (S) induced by sulfur dioxide found in the both washed and unwashed leaves of *Salix alba* L. tree, grown in six distinct localities in the vicinity of the Seyitomer thermal power plant, to assess the environmental impact. All parameters were examined in the surface soils (0-30 cm), and the most intense concentration of the pollutants in both soils and leaves was observed to be in the direction of the prevailing wind.

Fan, S., B. Freedman, and J. Gao. 2007. Potential Environmental Benefits from Increased Use of Bioenergy in China. Environmental management 40:504-515.

Abstract: Because of its large population and rapidly growing economy, China is confronting a serious energy shortage and daunting environmental problems. An increased use of fuels derived from biomass could relieve some demand for nonrenewable sources of energy while providing environmental benefits in terms of cleaner air and reduced emissions of greenhouse gases. In 2003, China generated about 25.9 x 10⁸ metric tons of industrial waste (liquid + solid), 14.7 x 10⁸ metric tons/year (t/y) of manure (livestock + human), 7.1 x 10⁸ t/y of crop residues and food-processing byproducts, 2 x 10⁸ t/y of fuelwood and wood manufacturing residues, and 1.5 x 10⁸ t/y of municipal waste. Biofuels derived from these materials could potentially displace the use of about 4.12 x 10⁸ t/y of coal and 3.75 x 10⁶ t/y of petroleum. An increased bioenergy use of this magnitude would help to reduce the emissions of key air pollutants: SO₂ by 11.6 x 10⁶ t/y, NO_x by 1.48 x 10⁶ t/y, CO₂ by 1.07 x 10⁹ t/y, and CH₄ by 50 x 10⁶ t/y. The reduced SO₂ emissions would be equivalent to 54% of the national emissions in 2003, whereas those for CO₂ are 30%. It is important to recognize, however, that large increases in the use of biomass fuels also could result in socioeconomic and environmental problems such as less production of food and damage caused to natural habitats.

Gupta, M. C., and M. Iqbal. 2005. Ontogenetic histological changes in the wood of mango (*Mangifera indica* L. cv Deshi) exposed to coal-smoke pollution. Environmental and Experimental Botany 54:248-255.

Trees of *Mangifera indica* L. cv *Deshi* growing at two sites, one heavily polluted due to coal-smoke emanating from a thermal power plant and the other free from such pollution, were examined across their boles (from pith to cambium) to trace ontogenetic changes induced by coal-smoke pollutants in the wood structure with special reference to vessels and fibres. Wood formation was hampered in the polluted environment, as evident from the width of annual rings, indicating an adverse influence of coal-smoke pollutants on the cambial activity. The pollutants inhibited dimensional growth of tracheal elements and promoted frequency and grouping of vessels since early growth stages. The increasing vessel number per square millimeter of wood and the decreasing dimensions of vessel elements and fibres resulted in low values for vulnerability and mesomorphic ratios in the polluted trees. The ratio of the length of fibres to that of vessel elements also decreased. With the growing age, the decline in vulnerability ratio and

mesomorphic ratio was enhanced whereas that in the fibre/vessel-element length ratio was minimized.

Inyang, H. I., G. F. Fisher, and G. E. Mbamalu. 2003. A quantitative methodology for indexing environmental sensitivity and pollution potential. *Environmental Monitoring and Assessment* 84:159-173.

Abstract: A methodology for rating the suitability of sites for the location of industrial facilities is formulated and applied to the case of a coal-fired power plant location. The methodology comprises two major interlinked components: the environmental plant location indexing component, which involves the identification, scaling and weighting of environmental sensitivity factors; and the impact analysis component, which involves the superimposition of the pollution generation impacts of an industrial facility on spatially gridded zones of various environmental sensitivities. For each rectangular areal unit defined by a square grid, the Unit Pollution Potential Index is determined by the severity and distribution of key environmental sensitivity factors and the coverage of superimposed pollutant effects as determined by contaminant fate and transport models. For any alternative site of a planned facility, the summation of the unit indices over the area of influence of the facility provides the quantitative Pollution Index, which can be used as a basis for comparison of alternative sites for planned facilities. For this paper, this methodology is applied to the hypothetical case of the siting of a coal-fired power plant in the northeastern region of the United States, in which three alternative sites are considered. The three sites: A, B and C yielded indices of 47.83, 47.91 and 47.6, respectively, indicating that site C is the most suitable for siting the power plant.

Klose, S., K. D. Wernecke, and F. Makeschin. 2004. Microbial activities in forest soils exposed to chronic depositions from a lignite power plant. *Soil Biology and Biochemistry* 36:1913-1923.

Abstract: Atmospheric emissions of fly ash and SO₂ from lignite-fired power plants strongly affect large forest areas in Germany. The impact of different deposition loads on the microbial biomass and enzyme activities was studied at three forest sites (*Picea abies* (L.) Karst.) along an emission gradient of 3, 6, and 15 km downwind of a coal-fired power plant (sites Ia, II, and III, respectively), representing high, moderate and low emission rates. An additional site (site Ib) at a distance of 3 km from the power plant was chosen to study the influence of forest type on microbial parameters in coniferous forest soils under fly ash and SO₂ emissions. Soil microbial biomass C and N, CO₂ evolved and activities of L-asparaginase, L-glutaminase, beta-glucosidase, acid phosphatase and arylsulfatase (expressed on dry soil and organic C basis) were determined in the forest floor (L, Of and Oh horizon) and mineral top soil (0-10 cm). The emission-induced increases in ferromagnetic susceptibility, soil pH, concentrations of mobile (NH₄)NO₃ extractable Cd, Cr, and Ni, effective cation exchange capacity and base saturation in the humus layer along the 15 km long transect significantly (P<0.05) reflected the effect of past depositions of alkaline fly ash. Soil microbial and biochemical parameters were significantly (P<0.05) affected by chronic fly ash depositions. The effect of forest type (i.e. comparison of sites Ia and Ib) on the studied parameters was generally dominated by the deposition effect. Alkaline depositions significantly (P<0.05) decreased the microbial biomass C and N, microbial biomass C-to-N ratios and microbial biomass C-to-organic C ratios. Microbial respiration, metabolic quotient (qCO₂) and the activities of L-asparaginase, L-glutaminase, beta-glucosidase, acid phosphatase and arylsulfatase were increased by long-term depositions from the power plants. Acid phosphatase had the highest specific (enzyme activities expressed per unit organic C) activity values among the enzymes studied and arylsulfatase the lowest. The responses of the microbial biomass and soil respiration data to different atmospheric deposition loads were mainly controlled by the content of organic C and cation exchange capacity, while

those of enzyme activities were governed by the soil pH and concentrations of mobile heavy metals. We concluded that chronic fly ash depositions decrease litter decomposition by influencing specific microbial and enzymatic processes in forest soils.

Kouprianov, V. I., V. N. Bashkin, S. Towprayoon, J. Milindalekha, and K. Wongyai. 2002. Emission of arsenic and gaseous pollutants from power generation in northern Thailand: Impact on ecosystems and human health. World Resource Review 14:99-116.

Abstract: The lignite-fired 2,625 MW Mae Moh power plant located in the North of Thailand is the focus of this study. For more than 20 years of the Mae Moh power plant's operation, enforced anthropogenic activity has led to an increase in the pollutant loading of all the biosphere compartments, including humans as well as terrestrial and aquatic ecosystems in the region around the power plant. A detailed analysis of NO_x, SO₂, CO₂, and As emissions from the power plant was carried out, taking into consideration actual boiler loads and seasonal changes in fuel quality. Annual rates of the pollutants were calculated for the period of 1996-1999, and relevant statistical data for the preceding period were involved, in order to assess the environmental impact of the power plant. It was shown that contribution of the CO₂ emission from the Mae Moh power plant to the total global emission of this pollutant from the fossil fuels combustion is about 0.08%. The critical load (CL) values for acidity were calculated based on both SO₂ and NO_x emissions in order to estimate the sensitivity of local ecosystems to sulfur and nitrogen loading. The calculated CLs across most of the studied area were found to be low, and the sensitivity of most ecosystems to acidification loading was shown to be very high. The 20-year period of exploitation of the Mae Moh power plant has led to significant accumulation of As and other metals in biogeochemical food webs. Some data of the preliminary study on the AS contamination of the surface water and deep groundwater in the Mae Moh area are discussed.

Mishra, U. C. 2004. Environmental impact of coal industry and thermal power plants in India. Journal of Environmental Radioactivity 72:35-40.

Abstract: Coal is the only natural resource and fossil fuel available in abundance in India. Consequently, it is used widely as a thermal energy source and also as fuel for thermal power plants producing electricity. India has about 90,000 MW installed capacity for electricity generation, of which more than 70% is produced by coal-based thermal power plants. Hydro-electricity contributes about 25%, and the remaining is mostly from nuclear power plants (NPPs). The problems associated with the use of coal are low calorific value and very high ash content. The ash content is as high as 55-60%, with an average value of about 35-40%. Further, most of the coal is located in the eastern parts of the country and requires transportation over long distances, mostly by trains, which run on diesel. About 70% oil is imported and is a big drain on India's hard currency. In the foreseeable future, there is no other option likely to be available, as the nuclear power programme envisages installing 20,000 MWe by the year 2020, when it will still be around 5% of the installed capacity. Hence, attempts are being made to reduce the adverse environmental and ecological impact of coal-fired power plants. The installed electricity generating capacity has to increase very rapidly (at present around 8-10% per annum), as India has one of the lowest per capita electricity consumptions. Therefore, the problems for the future are formidable from ecological, radio-ecological and pollution viewpoints. A similar situation exists in many developing countries of the region, including the People's Republic of China, where coal is used extensively. The paper highlights some of these problems with the data generated in the author's laboratory and gives a brief description of the solutions being attempted. The extent of global warming in this century will be determined by how developing countries like India manage their energy generation plans. Some of the recommendations have been implemented for new plants, and the situation in the new plants is much better. A few coal

washeries have also been established. It will be quite some time before the steps to improve the environmental releases are implemented in older plants and several coal mines due to resource constraints.

Nuhoglu, Y. 2004. Air pollution modelling of the Calabrian pine forests withered by the Yatagan thermal power plant, Turkey. *International Journal of Environment and Pollution* 21:400-410.

The emissions from the chimney of the Yatagan thermal power plant have caused a 3050-hectare forest to wither. Such air pollutants as sulfur dioxide, nitrogen oxides and fly ash are carried towards the Bencikdagi Calabrian pine forests on the prevailing north-east winds. To study these effects, the Q-Basic computer program developed for the Gaussian puff model was used with meteorological data provided by the Yatagan Meteorological Office and the pollutant loads formed by the thermal power plant. In the grid system on the map showing the surroundings of the thermal power plant, the concentrations of the pollutants in each grid square were determined. The Yatagan plant has three units containing 9000 mg/m³ sulfur dioxide, 1800 mg/m³ nitrogen oxides and 680 mg/m³ fly ash in its chimneys. The minimum pollutant emissions were found to be 100 mug/m³ SO₂, 20 mug/m³ NO_x, and 5 mug/m³ fly ash; the maximum emissions were found to be 385 mug/m³ SO₂, and 77 mug/m³ NO_x, and 25 g/m³ fly ash.

Prisyazhniuk, V. A. 2006. Strategies for emission reduction from thermal power plants. *Journal of Environmental Management* 80:75-82.

Abstract: Major polluters of man's environment are thermal power stations (TPS) and power plants, which discharge into the atmosphere the basic product of carbon fuel combustion, CO₂, which results in a build-up of the greenhouse effect and global warm-up of our planet's climate. This paper is intended to show that the way to attain environmental safety of the TPS and to abide by the decisions of the Kyoto Protocol lies in raising the efficiency of the heat power stations and reducing their fuel consumption by using nonconventional thermal cycles. Certain equations have been derived to define the quantitative interrelationship between the growth of efficiency of the TPS, decrease in fuel consumption and reduction of discharge of dust, fuel combustion gases, and heat into the environment. New ideas and new technological approaches that result in raising the efficiency of the TPS are briefly covered: magneto-hydrodynamic resonance, the Kalina cycle, and utilizing the ambient heat by using, as the working medium, low-boiling substances.

Rabl, A. 2002. Health and environmental impacts of energy systems. *International Journal of Global Energy Issues* 18.

Abstract: The assessment of health and environmental impacts of energy production has undergone a major evolution in recent years, reflecting progress in the underlying scientific domains. This paper reviews these developments and draws conclusions. The paper begins with a discussion of the relation between purpose and scope of an assessment. The following sections describe the methodology, with particular attention to key issues such as dispersion modelling, epidemiology, discounting, and the valuation of mortality. In the light of this discussion the major fuel chain studies since 1990 are reviewed and compared, to lead up to the present authors' best estimate of the impacts and damage costs of the most important energy technologies. The generalisability of the results to other sites and variations in emissions is discussed. Expressed in monetary terms as cost per kWh, the impacts of electricity from fossil fuels are not negligible: even for new power plants they are in the range of 10 to 100% of the market price of electricity, being about two to four times higher for coal than for gas. The damage costs of nuclear are much smaller, a few percent of the market price of electricity even at zero discount rate, assuming normal functioning in a stable mature society. Not surprisingly, the damage costs of renewable energies are, in most cases, very small. In view of the controversies surrounding far future

impacts, we also present some comparisons of physical impacts, for example showing that the increase in radiation dose from an all nuclear scenario would be small relative to natural background.

Shemwell, B.E., Ergut, A., and Levendis, Y.A. 2002. Economics of an integrated approach to control SO₂, NO_x, HCl, and particulate emissions from power plants. Journal of Air & Waste Management Association. 52: 521-534.

Abstract: An integrated approach for the simultaneous reduction of major combustion-generated pollutants from power plants is presented along with a simplified economic analysis. With this technology, the synergistic effects of high-temperature sorbent/coal or sorbent/natural gas injection and high-temperature flue gas filtration are exploited. Calcium-based (or Na-based, etc.) sorbents are sprayed in the post-flame zone of a furnace, where they react with S- and Cl-containing gases to form stable salts of Ca (or Na, etc.). The partially reacted sorbent is then collected in a high-temperature ceramic filter, which is placed downstream of the sorbent injection point, where it further reacts for a prolonged period of time. With this technique, both the likelihood of contact and the length of time of contact between the solid sorbent particles and the gaseous pollutants increase, because reaction takes place both in the furnace upstream of the filter and inside the filter itself. Hence, the sorbent utilization increases significantly. Several pollutants, such as SO₂, H₂S, HCl, and particulate (soot, ash, and tar), may be partially removed from the effluent. The organic content of the sorbents (or blends) also pyrolyzes and reduces NO_x. Unburned carbon in the ash may be completely oxidized in the filter. The filter is cleaned periodically with aerodynamic regeneration (back pulsing) without interrupting furnace operation. The effectiveness of this technique has been shown in laboratory-scale experiments using either rather costly carboxylic salts of Ca or low- to moderate-cost blends of limestone, lime, or sodium bicarbonate with coal fines. Injection occurred in the furnace at 1150 °C, while the filter was maintained at 600 °C. Results showed that 65 or 40% SO₂ removal was obtained with calcium formate or a limestone/coal blend, respectively, at an entering calcium-to-sulfur molar ratio of 2. A sodium bicarbonate/coal blend resulted in 78% SO₂ removal at a sodium-to-sulfur molar ratio of 2. HCl removal efficiencies have been shown to be higher than those for SO₂. NO_x reductions of 40% have been observed with a fuel (coal)-to-air equivalence ratio, ϕ around 2. The filter has been shown to be 97-99% efficient in removing PM_{2.5} particulates. Calculations herein show that this integrated sorbent/filter method is cost-effective, in comparison with current technologies, on both capital cost (\$/kW) and levelized cost (\$/ton pollutant removed) bases, if a limestone/coal mixture is used as the sorbent for fossil fuel plants. Capital costs for the filter/sorbent combination are estimated to be in the range of \$61-\$105/kW for a new plant. Because current technologies are designed for removing one pollutant at a time, both their cost and space requirements are higher than those of this integrated technique. At the minimum projected removal efficiencies for HCl/SO₂/NO_x of about 40%, the levelized costs are projected to be \$203-\$261/ton of combined pollutant SO₂/HCl/NO_x and particulates removed from coal-fired power plants.

Thormann, M.N. 2006. Lichens as indicators of forest health in Canada. Forestry Chronicle 82: 335-343.

Abstract: Canadian forests are naturally dynamic ecosystems, changing species composition and abundance as the ecosystem evolves through succession or reacts to disturbances, such as wind and insects. Pollution and climate change will be the largest stressors to Canada's forests in the future. Their future impact on the health of Canada's forests remains speculative. Lichens have been identified as valuable indicators of forest health; however, there are no comprehensive datasets on which lichens are indicative of forest health in Canada. An analysis of the existing literature reveals a large number of lichens that can be used to monitor levels of various pollutants

(general pollution: 51 species; sulphur dioxide: 42 species; photochemicals: 23 species; fluoride: 18 species; heavy metals: 3 species; acid precipitation: 8 species; sulphite: 2 species; nitrate: 2 species). The use of lichens as indicators of climate change is also reported in the literature but, there are insufficient data to monitor the effects of climate change on lichen communities in North America. While various provincial and federal government departments and industries have been monitoring lichen communities across Canada for up to nearly three decades, there exists no standard monitoring protocol for lichens in Canada, which makes comparisons among studies challenging. The development of a standard monitoring protocol would allow integration of the various initiatives into a nationwide lichen monitoring program

Yilmaz, K., S. Inac, H. Dikici, and A. C. Reyhanii. 2004. The effects of a coal power plant on the environment and wildlife in southeastern Turkey. *Journal of Environmental Biology* 25:423-429.

Abstract: This study was carried out to determine the possible effects of the Afsin-Elbistan Coal Power Plant (AECPP) on the environment.. The soil and plant samples were collected, based on the dominant wind direction, which is from northeast to southwest and we defined the northeast part of the plant as the less contaminated direction (LCD) and the southwest part as the more contaminated direction (MCD). The results indicated that the AECPP created environmental problems and caused contaminations especially in the MCD. The results of the statistical analysis for the measured attributes between the LCD and the MCD showed that there were significant differences for pH, SO₄-2-S, Ni and Pb. Significant correlations were found between the distance from the AECPP and some of the measured soil and plant parameters in the MCD. The concentrations of SO₄-2-S, Ni and Pb decreased as the distance increased. The discharge water carries a potential risk for the aquatic life and soil health in the area. The honey quality was also affected negatively by fly ash and emission.

2.5.3 Regulations, guidelines, and abatement technologies

May, J. R., and D. J. Brennan. 2003. Life Cycle Assessment of Australian fossil energy options. *Process Safety and Environmental Protection* 81:317-330.

Abstract: Electricity generation in Australia has been almost entirely derived from combustion of its abundant fossil fuel resources. The consumption of these resources, and the emissions produced consequently, are known to impact upon the health of the local, regional, and global environment. To assist in planning Australia's future electricity supply, the environmental impacts from a number of likely fossil electricity production systems have been quantified using Life Cycle Assessment (LCA) method, and conclusions about their suitability derived. Extended systems from cradle to delivery have been defined for brown coal, black coal, and natural gas, utilizing both currently practised and advanced electricity generation technology. The export of black coal and natural gas (as LNG) for power generation overseas was also considered. For currently practised technologies, no one-fuel system has the most significant contribution to all impacts, and no single impact dominates. The most significant impacts were climate change for brown coal systems, acidification, eutrophication, and solid waste generation for black coal systems, and photochemical smog for natural gas systems. For each fuel, advanced technology systems showed reduced impacts compared with conventional technology systems, elucidating the considerable potential for environmental benefits from technological substitution. For immediate implementation, natural gas CCGT systems have distinct advantages for most impact categories.

Nadadur, S. S., C. A. Miller, P. K. Hopke, T. Gordon, S. Vedal, J. J. Vandenberg, and D. L. Costa. 2007. The Complexities of Air Pollution Regulation: the Need for an Integrated

Research and Regulatory Perspective. Toxicological Sciences 100:318-327.

Abstract: The Clean Air Act mandates the U.S. Environmental Protection Agency to periodically reassess existing and new science that underlie the regulation of major ambient pollutants-particulate matter (PM) and tropospheric ozone being most notable. While toxic effects have been ascribed individually to these and other pollutants in the air, it is clear that mixtures of these contaminants have the potential to interact and thereby influence their overall toxic outcomes. It follows that a more comprehensive assessment of the potential health effects of the air pollution complex might better protect human health; however, traditional regulatory drivers and funding constraints have impeded progress to such a goal. Despite difficulties in empirically conducting studies of complex mixtures of air pollutants and acquiring relevant exposure data, there remains a need to develop integrated, interdisciplinary research and analytical strategies to provide more comprehensive (and relevant) assessments of associated health outcomes and risks. The research and assessment communities are endeavoring to dissect this complexity using varied approaches. Here we present five interdisciplinary perspectives of this evolving line of thought among researchers and those who use such data in assessment: (1) analyses that coordinate air quality-health analyses utilizing representative polluted U.S. air sheds to apportion source and component-specific health risks; (2) novel approaches to characterize air quality in terms of emission sources and how emission reduction strategies might effectively impact pollutant levels; (3) insights from present-day studies of effects of single ambient pollutants in animal and controlled clinical toxicology studies and how these are evolving to address air pollution; (4) refinements in epidemiologic health assessments that take advantage of the complexities of existent air quality conditions; and (5) new approaches to integrative analyses to establish the criteria for regulation of PM and other criteria pollutants. As these examples illustrate, implementing multidisciplinary and integrative strategies offer the promise of more realistic and relevant science, greater reductions in uncertainty, and improved overall air pollution assessment. The regulatory mandate may lag behind the science, but real gains both in public health benefit and the science to dissect complex problems will result.

Patino-Echeverri, D., Morel, B., Apt, J., and Chen, C. 2007. Should a coal-fired power plant be replaced or retrofitted? Environmental Science & Technology 41: 7980-7986.

Abstract: In a cap-and-trade system, a power plant operator can choose to operate while paying for the necessary emissions, allowances, retrofit emissions controls to the plant, or replace the unit with a new plant. Allowance prices are uncertain, as are the timing and stringency of requirements for control of mercury and carbon emissions. We model the evolution of allowance prices for SO₂, NO_x, Hg, and CO₂ using geometric Brownian motion with drift, volatility, and jumps, and use an options-based analysis to find the value of the alternatives. In the absence of a carbon price, only if the owners have a planning horizon longer than 30 years would they replace a conventional coal-fired plant with a high-performance unit such as a supercritical plant, otherwise, they would install SO₂ and NO_x controls on the existing unit. An expectation that the CO₂ price will reach \$50/t in 2020 makes the installation of an IGCC with carbon capture and sequestration attractive today, even for planning horizons as short as 20 years. A carbon price below \$40/t is unlikely to produce investments in carbon capture for electric power.

Rabl, A., J. Nathwani, M. Pandey, and F. Hurley. 2007. Improving Policy Responses to The Risk of Air Pollution. Journal of Toxicology and Environmental Health, Part A: Current Issues 70:316-331.

Abstract: This paper offers a brief review of the need for cost-benefit analysis (CBA) and the available policy instruments for air pollution. To prioritize different possible actions, one needs to know which source of pollution causes how much damage. This requires an impact pathway analysis, that is, an analysis of the chain emission → right dispersion → right dose-

response function arrow right monetary valuation. The methodology for this is described and illustrated with the results of the ExternE (External Costs of Energy) project series of the European Commission. Two examples of an application to CBA are shown: one where a proposed reduction of emission limits is justified, and one where it is not. It is advisable to subject any proposed regulation to a CBA, including an analysis of the uncertainties. Even if the uncertainties are large and a policy decision may have to take other considerations into account, a well-documented CBA clarifies the issues and provides a basis for rational discussion. One of the main sources of uncertainty lies in the monetary valuation of premature mortality, the dominant contribution to the damage cost of air pollution. As an alternative, an innovative policy tool is described, the Life Quality Index (LQI), a compound indicator comprising societal wealth and life expectancy. It is applied to the Canada-wide standards for particulate matter and ozone. Regardless of monetary valuation, a 50% reduction of PM sub(10) concentrations in Europe and North America has been shown to yield a population-average life expectancy increase on the order of 4 to 5 mo.

Skodras, G., E. Someus, P. Grammelis, A. Palladas, P. Amarantos, P. Basinas, P. Natas, M. Prokopidou, I. Diamantopoulou, E. Kakaras, and G. P. Sakellaropoulos. 2007. Combustion and environmental performance of clean coal end products. International Journal of Energy Research 31:1237-1250.

Thermal desorption recycle-reduce-reuse technology (TDT-3R) is based on the low-temperature carbonization fuel pre-treatment principles. Clean coal samples were produced according to this method in an indirectly heated rotary kiln and were examined for their combustion efficiency and environmental performance. Raw material included coal and biomass, such as willow and straw. Investigations were realized via on-site measurements both in the clean coal procurement and combustion facilities and the characterization of end products and by-products. Clean coals were proved to be less reactive than raw coal samples, while biomass chars increased the reactivity of fuel blends during combustion. *In the clean coal production and combustion processes, flue gases emissions, such as CO, SO₂, NO_x, were particularly low, while polychlorinated dibenzo-p-dioxins and dibenzofuran emissions were in an order of magnitude less than anticipated from the EU legislation. Reduced total CO₂ emissions are anticipated with the implementation of TDT-3R process compared to the conventional combustion of raw fuels.* All ash leachates were accepted by the EPA-TCLP test, since none of them exceeded the EPA limits for safe disposal. The mercury content of all samples was very low and was reduced by about 90% after the leaching treatment. The pilot scale combustion tests demonstrated the major advantage offered by the TDT-3R process, which is the production of clean fuels with much lower pollutants content. High added value commercial application of the technology is feasible, provided that the ash content of raw fuel does not exceed 20% w/w. ***It is expected that the employment of produced clean coal originating from high-grade coal in combination with biomass derived materials may result in almost zero emission power plant operation.***

Tzimas, E., A. Mercier, C. C. Cormos, and S. D. Peteves. 2007. Trade-off in emissions of acid gas pollutants and of carbon dioxide in fossil fuel power plants with carbon capture. Energy Policy 35:3991-3998.

This paper investigates the impact of capture of carbon dioxide (CO₂) from fossil fuel power plants on the emissions of nitrogen oxides (NO_x) and sulphur oxides (SO_x), which are acid gas pollutants. This was done by estimating the emissions of these chemical compounds from natural gas combined cycle and pulverized coal plants, equipped with post-combustion carbon capture technology for the removal of CO₂ from their flue gases, and comparing them with the emissions of similar plants without CO₂ capture. The capture Of CO₂ is not likely to increase the emissions of acid gas pollutants from individual power plants; on the contrary, some NO_x and SO_x will also

be removed during the capture of CO₂. The large-scale implementation of carbon capture is however likely to increase the emission levels of NO_x from the power sector due to the reduced efficiency of power plants equipped with capture technologies. Furthermore, SO_x emissions from coal plants should be decreased to avoid significant losses of the chemicals that are used to capture CO₂. The increase in the quantity of NO_x emissions will be however low, estimated at 5% for the natural gas power plant park and 24% for the coal plants, while the emissions of SO_x from coal fired plants will be reduced by as much as 99% when at least 80% of the CO₂ generated will be captured.

United States Environmental Protection Agency. Clean Air Interstate Rule.

<http://www.epa.gov/cair/>. Accessed February 9, 2008.

On March 10, 2005, EPA issued the Clean Air Interstate Rule (CAIR), a rule that will achieve the largest reduction in air pollution in more than a decade. CAIR will ensure that Americans continue to breathe cleaner air by dramatically reducing air pollution that moves across state boundaries. In 2015, CAIR will provide health and environmental benefits valued at more than 25 times the cost of compliance.

CAIR will permanently cap emissions of sulfur dioxide (SO₂) and nitrogen oxides (NO_x) in the eastern United States. CAIR achieves large reductions of SO₂ and/or NO_x emissions across 28 eastern states and the District of Columbia. When fully implemented, CAIR will reduce SO₂ emissions in these states by over 70 percent and NO_x emissions by over 60 percent from 2003 levels. This will result in \$85 to \$100 billion in health benefits and nearly \$2 billion in visibility benefits per year by 2015 and will substantially reduce premature mortality in the eastern United States. The benefits will continue to grow each year with further implementation.

Unterberger, S. and Hein, K.R.G. 2003. Air toxic emissions from coal-fired power plants - Regulation, applied technologies and recent research activities in Europe. Proceedings of the 2003 5th International Symposium on Coal Combustion, pp. 377-381.

Abstract: In Europe large-scale coal fired power plants are identified as a significant contributor to the environment pollution by the emission of sulphur and nitrogen oxides as well as dust and heavy metals. Accordingly, the European Commission has recently passed two new directives giving among others emission limiting values and national emission ceilings which has to be applied all over Europe within a tight time frame. Actions have to be taken for complying with the given targets, based either on application of well established flue gas cleaning technologies or developing new multi-pollutant approaches are described and discussed in the challenging field of a liberalised European energy market. Objective and already achieved results of recently ongoing European research and development projects once specify future needs and prospects in line with the long term strategic considerations of the European Community.

Zhang, Q.Y., Wei, Y.M., Chen, Y.X., and Guo, H. 2007. Environmental damage costs from fossil electricity generation in China, 2000-2003. Journal of Zhejiang University: Science A 8: 1816-1825.

Abstract: Electricity consumption increases rapidly with the rapid development of China. The environmental damage costs of electricity generation are very important for both policy analysis and the proper management of the environment. A method was developed in this work to estimate gross environmental damage costs according to emission inventory and environmental cost factors, and to extend the costs from provincial to national level with population density. In this paper, sulfur dioxide (SO₂), nitrogen oxides (NO_x), particulate matter less than 10 µm in diameter (PM₁₀), and carbon dioxide (CO₂) from fossil fired power plants over 6000 kW were selected as index pollutants to quantify the environmental costs of damages on human health and global warming. With the new developed method, environmental damage costs, caused by 3 types

of fired power plants in 30 provinces and 6 economic sectors during the years 2000 to 2003, were evaluated and analyzed. It can be seen that the calculated total national environmental damage costs of electricity have rapidly increased from 94930.87 + 10⁶ USD in 2000 to about 141041.39 + 10⁶ USD in 2003, with an average annual growth rate of 14.11%. Environmental damage costs of SO₂, NO_x, PM₁₀, and CO₂ are 69475.69 + 10⁶, 30079.29 + 10⁶, 28931.84 + 10⁶, and 12554.57 + 10⁶ USD and account for 49.26%, 21.33%, 20.51%, and 8.90% of total environmental costs in fossil electricity generation, respectively. With regard to regional distribution, external costs caused by fossil electricity generation are mainly concentrated in the more populated and industrialized areas of China, i.e., the Eastern Central and Southeastern areas.

3 List 2 Substances

3.1 Emissions, atmospheric deposition, and modeling

3.1.1 Trace metals

Chaudhary, S., and D. K. Banerjee. 2007. Speciation of some heavy metals in coal fly ash. *Chemical Speciation and Bioavailability* 19:95-102.

Selected heavy metals Cu, Ni, Zn and Pb were studied in two different types of coal fly ash samples, dyke and field, collected from Badarpur Thermal Power Station, Delhi, India for their total metal concentration as well as geochemical differentiation in different chemical fraction namely exchangeable, easily reducible or Fe-Mn bound, organic or sulfide bound and residual fractions. The total concentration of heavy metals in both types of fly ash samples followed the order $Cr > Zn > Pb > Ni > Cu$. Among the two types of samples, field fly ash samples were more enriched in these heavy metals compared with the dyke type samples. The fine grain size of field type samples possibly provided the sufficiently large surface area for the adsorption of these metals, resulting in higher concentrations compared with those in the coarse grained dyke samples. But, interestingly, the dyke type fly ash samples contain most of the metals in the exchangeable fraction. Metals in this fraction are easily mobilisable or can be made mobile depending upon the environmental conditions of Eh and pH. This suggests that the dyke type samples with low bulk metal content can even pose serious environmental hazards compared to the high total metal containing samples of field type. This suggests that it is the presence of metal in particular fraction(s) and not the total metal concentrations which are harmful to the environment, in particular to the soil and aquatic life.

Duzgoren-Aydin, N.S. 2007. Sources and characteristics of lead pollution in the urban environment of Guangzhou. *Science of the Total Environment* 385: 182-195.

Abstract: Guangzhou, the capital of the southeastern province of Guangdong, is one of the largest and most rapidly developing industrial cities in China. In recent years its rapid economic development has brought great prosperity to the Pearl River Delta (PRD) region, but has also given rise to a wide variety of environmental problems. The current level of lead (Pb) contamination (75-926 μ g/kg) in the surface environment of Guangzhou remains a major concern, even though the use of leaded petrol in the city was banned in 1997. The Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ min-max : 1.1612-1.1961 and $^{208}\text{Pb}/^{207}\text{Pb}$ min-max : 2.4495-2.4838) of the urban dusts from unconfined (road dusts and gully sediments) and relatively confined (vehicular tunnel) settings in Guangzhou remains in a relatively narrow range, comparable with those of the regional natural and anthropogenic sources. This study highlights the inherent shortcomings of the Pb isotope fingerprinting technique for provenancing Pb sources, as both the target media (urban dusts) and potential sources have similar and highly radiogenic Pb isotope values. This could not only lead to an overestimation of the effectiveness of phasing-out of leaded petrol, but also an underestimation of the ever-increasing relative contributions from other potential sources of pollution, including coal combustion, industrial emissions of local Pb-ores and non-additive Pb contents of crude oils. Re-suspended Pb-bearing particulates deposited from early vehicular exhaust emission of leaded petrol with distinctly low Pb isotope compositions are still an important source of Pb pollution in the region.

Ceburnis, D., J. Sakalys, K. Armolaitis, D. Valiulis, and K. Kvietkus. 2002. In-stack emissions of heavy metals estimated by moss biomonitoring method and snow-pack analysis. *Atmospheric Environment* 36:1465-1474.

Abstract: Data from the chemical analysis of moss growing close to a thermal power station and snowpack have been used for the estimation of heavy metal deposition close to the point pollution sources. A semi-empirical model was proposed to describe atmospheric trace metal deposition close to the point pollution source. Model parameters were derived from experimental data, and nickel and vanadium quantities, washed out with snow and rain, were calculated. Using long-term meteorological observation data of rain and snow duration and metal uptake efficiencies in moss, the average emission rates of vanadium and nickel from the stack were calculated. The coincidence between data from emission inventory and model results was within 25%. It was estimated that in the vicinity of pollution source (within 30km) about 15% out of total emitted metals were washed out by rain and snow events. Metal concentrations in the environment become indistinguishable from the background at a distance: of about 20 km from the stack.

Electric Power Research Institute (EPRI). (2005) Arsenic and Selenium Speciation in Fly Ash and Wastewater. Retrieved Jan 13, 2008 from <http://my.epri.com/portal/server.pt?>

Eskenazy, G.M. 2006. Geochemistry of beryllium in Bulgarian coals. International Journal of Coal Geology 66: 305-315.

Abstract: The beryllium content of about 3000 samples (coal, coaly shales, partings, coal lithotypes, and isolated coalified woods) from 16 Bulgarian coal deposits was determined by atomic emission spectrography. Mean Be concentrations in coal show great variability: From 0.9 to 35 ppm for the deposits studied. There was no clear-cut relationship between Be content and rank. The following mean and confidence interval Be values were measured: lignites, 2.6 ± 0.8 ppm; sub-bituminous coals, 8.2 ± 3.3 ppm; bituminous coals, 3.0 ± 1.2 ppm; and anthracites, 19 ± 9.0 ppm. The Be contents in coal and coaly shales for all deposits correlated positively suggesting a common source of the element. Many samples of the coal lithotypes vitrain and xylain proved to be richer in Be than the hosting whole coal samples as compared on ash basis. Up to tenfold increase in Be levels was routinely recorded in fusain. The ash of all isolated coalified woods was found to contain 1.1 to 50 times higher Be content relative to its global median value for coal inclusions. Indirect evidence shows that Be occurs in both organic and inorganic forms. Beryllium is predominantly organically bound in deposits with enhanced Be content, whereas the inorganic form prevails in deposits whose Be concentration approximates Clarke values. The enrichment in Be exceeding the coal Clarke value 2.4 to 14.5 times in some of the Bulgarian deposits is attributed to subsynchronous at the time of coal deposition hydrothermal and volcanic activity.

Freitas, M. C., and A. M. G. Pacheco. 2007. Elemental concentrations of aerosols near Portuguese power plants by INAA and PIXE. Journal of Radioanalytical and Nuclear Chemistry 271:185-189.

Abstract: Mass and elemental concentrations in PM10 and PM2.5 - airborne particulate matter with an aerodynamic diameter below 10 µm and 2.5 µm, respectively - have been evaluated in mainland Portugal since 1993. The data herein refer to areas generally impacted by emissions from electrical power plants, either coal- or oil-fired, which are mostly large, state-of-the-art facilities. Background areas have been sampled as well, and results from one of them are given for comparison. Through the country, lead levels are well below the European enacted values, particularly since unleaded fuels became mandatory in the late 1990s. Nickel appears especially concentrated in PM2.5 and, apart from extreme cases (rural sites, coal-fired plants), its levels are not significantly different from place to place. Highest values for arsenic and mercury have been found in the vicinity of the coal-fired plants. Cadmium data, if only available for metropolitan Lisbon, seems to confirm the trend for anthropogenic elements appearing mainly in fine particulates.

Galbreath, K.C., and Zygarlicke, C.J. 2004. Formation and chemical speciation of arsenic-, chromium-, and nickel-bearing coal combustion PM2.5. Fuel Processing Technology 85: 701-726.

Abstract: The chemical analysis of the arsenic (As), chromium (Cr) and nickel (Ni) speciation of PM2.5 samples, formed during coal combustion was discussed. The samples were determined using X-ray absorption fine-structure spectroscopy (XAFS). Chemical analysis of Illinois No. 6 fly ash samples indicated that As, Cr and Ni concentrations and relative enrichment/depletion (RED) factors generally increased and decreasing particle size which was consistent with an elemental vaporization-particle surface deposition process. It was found that the differences in Illinois No.6 and coal combustion conditions did not significantly effect As, Cr, or Ni speciation.

Giere, R., M. Blackford, K. L. Smith, H. Li, C. T. Williams, and C. Kirk. 2007. Metal sulfates in PM emissions from a coal-fired power plant. Geochimica Et Cosmochimica Acta 71:A322-A322.

Abstract: Coal combustion facilities represent a major source of fine particulate matter (PM) in the atmosphere. The particle capture efficiency of air pollution control devices is size-dependent, and is considerably lower for particles with diameters <2.5 micrometers (PM2.5) than for larger ones. These particles are thus emitted preferentially and, moreover, exhibit relatively long atmospheric residence times. To assess the environmental and health impacts of such PM, it is necessary to obtain information about its mineralogical composition. We report results from SEM, TEM and XRD investigations on PM emitted from a stoker boiler. The samples, collected on filters placed in the smokestack above all air pollution control devices, represent PM that would have escaped into the atmosphere. Our study demonstrates that these fugitive particles in the PM2.5 fraction consist of amorphous material (Al-Si-glass, soot, native Se) and a variety of crystalline phases, including lime, mullite, and various euhedral metal sulfates. Electron diffraction patterns and chemical compositions obtained by quantitative analytical TEM revealed the presence in the PM of the following sulfates (Gieré *et al.* 2006): anglesite (PbSO₄) as main host of Pb; anhydrite (CaSO₄); gunningite (ZnSO₄.H₂O); and yavapaiite (KFe(SO₄)₂), a mineral that is exceedingly rare in the geosphere. In the larger size fraction, we have identified the following additional phases: voltaite and zincvoltaite K₂(Fe²⁺,Zn)₅(Fe³⁺,Al)₄(SO₄)₁₋₁₈H₂O, millosevichite - Al₂(SO₄)₃, meta-aluminite - Al₂(SO₄)(OH)₄-5H₂O, and tamarugite - NaAl(SO₄)₆-6H₂O. It is concluded that most of these metal sulfates were precipitated from the flue gas, that large quantities of these phases may be emitted globally into the atmosphere through combustion processes, and that they have, through hydration and dissolution, a major environmental and health impact.

Godoy, M., J. M. Godoy, and P. Artaxo. 2005. Aerosol source apportionment around a large coal fired power plant - Thermoelectric Complex Jorge Lacerda, Santa Catarina, Brazil. Atmospheric Environment 39:5307-5324.

Abstract: The Thermoelectric Complex Jorge Lacerda (TCJL) is located in the Southern part of Brazil, at the community of Capivari de Baixo, in the state of Santa Catarina, 130km from Florianopolis. The TCJL is the largest coal burning thermoelectric complex of Latin America, formed by seven power plants and with a total capacity of 832 MW. Two aerosol-sampling campaigns were performed, during summer and winter seasons, in 12 different sites around the TCJL with aerosol collection for 10 sampling days each site. Stacked filter units were used to collect fine and coarse aerosol particles and trace element analysis by inductively coupled plasma-mass spectrometry (ICP-MS) was performed in both size fractions. Gravimetric analysis and reflectance measurements provided aerosol mass and black carbon concentrations. Very good detection limits for up to 42 elements were obtained. Receptors models such as principal factor

analysis, cluster analysis and absolute principal factor analysis were applied in order to identify and quantify the aerosol particle sources. Emissions from the TCJL are the main source of elements such as As, Bi, Cd, Pb, Sb and Se in both aerosol fractions, ranging from 34% up to 83% in mass. Based on absolute principal component analysis, source profiles were calculated. These profiles were compared with those observed on the EPA Speciate 3.1 data bank and a good similarity was observed. The ICP-MS analysis of trace elements in aerosols has proven to be reliable and feasible for large amount of samples, and the coupling with receptor models provided an excellent method for quantitative aerosol source apportionment in industrial complexes.

Gomez, D., M. Dos Santos, F. Fujiwara, G. Polla, J. Marrero, L. Dawidowski, and P. Smichowski. 2007. Fractionation of metals and metalloids by chemical bonding from particles accumulated by electrostatic precipitation in an Argentine thermal power plant. *Microchemical Journal* 85:276-284.

Abstract: A study was undertaken to evaluate the distribution of Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn in fly ashes collected in the electrostatic precipitator of a thermal power plant in San Nicolas (Argentina). Five samples were collected during one week of operation. For the fractionation, the scheme applied consisted in extracting the elements in four fractions namely (i) soluble and exchangeable elements; (ii) carbonates, oxides and reducible elements; (iii) bound to sulfidic metals; and (iv) residual elements. Metals and metalloids at $\mu\text{g g}^{-1}$ level were determined in each fraction by inductively coupled plasma optical emission spectrometry (ICP OES). For validation, a standard reference material (SRM 1633 coal fly ash) from NIST was subjected to the same chemical sequential extraction procedure that the samples. X-ray diffraction powder (XRD) analysis and scanning electron microscopy (SEM) were used to characterize the major minerals present in the matrix. Total analyte concentration (in $\mu\text{g g}^{-1}$) varied from 10.6 for Pb to 17,622 for Al. Minimum and maximum concentrations (in gg g^{-1}) found in individual samples in the four fractions were: Al, 92.7-9668; As, < 0.3-143; Cr, 2.0-10.4; Cu, < 0.2-35.6; Fe, < 0.3-4992; Mn, < 0.1-128; Ni, < 0.3-139; Pb, < 0.5-9.1; Ti, < 0.3-2243; V, 17.0-112.9; and Zn, < 0.1-68.2. The leachability of the 11 elements under study proved to be different. Low percentages of Al (1%), V (7%) and Cr (8%) were detected in the most bioavailable fraction. Arsenic was found to be most abundant in the non-silicate phase, represented by the second and third fractions, while Cr, Fe, Ni, Pb and Zn were mostly associated to the residual fraction.

Goodarzi, F. and Sanei, H. (2002) The deposition of trace elements on the land/surface soil in the Wabamun Lake area, Alberta, Canada. Retrieved Jan 8, 2008 from <http://geoscan.ess.nrcan.gc.ca/cgi-bin/starfinder/0?path=geoscan.fl&id=fastlink&pass=&search=R%3D213042&format=FLFULL..>

Goodarzi, F. 2006. Assessment of elemental content of milled coal, combustion residues, and stack emitted materials: Possible environmental effects for a Canadian pulverized coal-fired power plant. *International Journal of Coal Geology* 65: 17-25.

Abstract: Two monitoring studies were carried out at four-year intervals on a power plant that uses western Canadian subbituminous coal and generates approximately 800 Mw/h of electricity. The distributions of elements of environment concern (As, Hg, Ni, Pb, and Cd) and elements of environmental interest (B, Ba, Be, Cl, Co, Cr, Cu, Mn, Mo, Th, Se, V, U, and Zn) in milled coals, power plant ashes, and emitted materials from the stack were determined using neutron activation analysis (NAA), Inductively Coupled Plasma Emission Spectroscopy (ICPES), and Inductively Coupled Plasma-Mass spectroscopy (ICP-MS) for most elements, Graphite Furnace Atomic Absorption (GFAA) for Pb, and Cold Vapor Atomic Absorption (CVAA) for Hg. The concentrations of most of elements in milled coal are low as compared to world coals and other Canadian milled coals. For example, in both studies mercury is within the lower range of world

coal. Bottom ashes from both studies have low concentrations of As, Cd, Hg, Pb, and Zn, as well as low relative enrichment factors (RE) for the same elements, indicating that they were not enriched in the bottom ash. The ESP's remove most of the elements of environmental interest as indicated by their high RE ratios of greater than > 0.7 . The rates of input of elements of environmental concern (As, Cd, Hg, Pb and Ni) for this station were 23.65, 1.24, 0.54, 98.2 and 95.2 kg/day, respectively, of which only 0.20, 0.02, 0.31, 0.48 and 0.36 kg/day were emitted from the stack. Thus only a small amount of these elements found in the milled coal was emitted while most were captured in the bottom and the ESP ashes. Nickel has the highest rate of emission (0.48 kg/day) within the elements of environmental concern group. However, the Ni emitted from this station does not belong to the toxic species. The element with the lowest rate of emission is Cd (0.02 kg/day). The total emission of elements of environmental concern is 1.37 kg/day, which is low as compared their ambient concentrations in either rural or urban air. The total rate of emission of B, Ba, Be, Co, Cr, Cu, Mn, Mo, Se, Th, U, V, and Zn is 56.51 kg/day and is mostly comprised of the total emission of Ba (21.73 kg/day) and Zn (19.14 kg/day).

Goodarzi, F., and Huggins, F.E. 2005. Speciation of chromium in feed coals and ash byproducts from Canadian power plants burning subbituminous and bituminous coals. Energy Fuels 19: 2500-2508.

Abstract: The chromium species in the feed coals and ash byproducts from seven Canadian coal-fired power plants that were burning local subbituminous or bituminous coals with sulfur contents in the range of 0.30-3.5 wt % have been examined using Cr X-ray absorption near-edge spectroscopy (XANES). Chromium in the Canadian feed coals is always found as Cr³⁺ but generally has a dual occurrence, as Cr³⁺ is distributed to varying degrees between the clay mineral illite (Cr³⁺/illite) and a poorly crystallized chromium oxyhydroxide (CrOOH) phase associated with the organic fraction. In two subbituminous feed coals from Alberta, chromium is present largely as Cr³⁺/illite, whereas in two other such coals, it is present predominantly as CrOOH. Chromium in a low-sulfur (0.50 wt %) bituminous feed coal from Alberta is found mostly as Cr³⁺/illite, whereas for feed coals from Nova Scotia with high sulfur contents (2.60-3.56 wt %), chromium is distributed between both Cr³⁺/illite and CrOOH. Very little chromium was found in the limestone used in a fluidized-bed combustor. The chromium species in most bottom ash samples from all seven combustion units is predominantly, if not entirely (>95%), Cr³⁺ associated with alumino-silicate phases. Chromium speciation for subbituminous electrostatic precipitator (ESP) fly ash is mostly Cr³⁺ (>95%), but in some cases, it is slightly less (>80%) and varies by sampling location at the plant. Chromium in fly ash from the combustion of bituminous feed coals is predominantly (>95%) Cr³⁺. A unique species of chromium found in one feed coal and an unrelated fly ash is metallic chromium (Cr⁰), similar to that in stainless steel. The occurrence of this form of chromium in these materials indicates contamination from machinery, such as the coal milling machine or possibly wearing down of stainless steel parts by the coal or ash. The observation of this unexpected contamination demonstrates the power and usefulness of X-ray absorption fine-structure (XAFS) spectroscopy for speciation determination.

Goodarzi, F., and Huggins, F.E. 2005. Speciation of arsenic in feed coals and their ash byproducts from Canadian power plants burning sub-bituminous and bituminous coals. Energy Fuels 19: 905-915.

Abstract: The arsenic species in the feed coals and ash byproducts from seven Canadian power plants (including one with a fluidized-bed combustor) that were burning local sub-bituminous and bituminous coals with sulfur contents in the range of 0.30-3.5 wt % have been examined using As X-ray absorption fine structure (XAFS) spectroscopy. The feed coals can be grouped based on their contents of arsenic associated with pyrite (As/ pyr) and as As³⁺ and As⁵⁺ (arsenate)

species. The arsenic species in sub-bituminous feed coals with low sulfur (0.22-0.38 wt %) and arsenic (1.6-2.2 mg/kg) contents consist of 50% As³⁺ and 50% As⁵⁺, whereas those with moderate sulfur (0.50 wt %) and arsenic (3.63 mg/kg) contents consist of 84% As/pyr, 7% As³⁺, and 9% As⁵⁺. In bituminous feed coal with low sulfur (0.40 wt %) and arsenic (4.39 mg/kg) contents, the arsenic speciation consists of 34% As/pyr, 12% As³⁺, and 54% As⁵⁺, and for those with high sulfur (2.60-3.56 wt %) and arsenic (54-84 mg/kg) contents, it consists of 77%-82% As/pyr and 18%-23% As⁵⁺. The bottom ash produced from sub-bituminous feed coals with low sulfur and arsenic contents consists of 10%-20% As³⁺ and 80%-90% As⁵⁺, and for moderate sulfur (0.50 wt %) and arsenic (3.63 mg/kg), the arsenic speciation consists of 5% As/pyr, 10% As³⁺, and 85% As⁵⁺ as arsenate. For bituminous feed coals with low sulfur and arsenic contents, the bottom ash is entirely As⁵⁺, whereas for coals with high sulfur and arsenic contents, the bottom ash consists of 10%-15% As³⁺ and 85%-90% As⁵⁺; and for the fluidized-bed combustor, the bottom ash is entirely As⁵⁺ arsenate. The species of arsenic in fly ash from sub-bituminous and bituminous coals are mostly arsenate (As⁵⁺), possibly in part incorporated in the glass matrix, and remains the same for coarse- and fine-grained electrostatic precipitator (ESP), baghouse, and stack-emitted ashes. The only difference between the ESP and baghouse fly ash is the higher amount of crystalline arsenates in the hopper fly ash. Neither the sulfur content nor the pyrite content of the feed coal seems to influence the speciation of arsenic, because virtually all of the arsenic in fly ash samples from high-sulfur coal is in the form of arsenate (As⁵⁺). However, arsenic (mostly as As⁵⁺) in these fly ashes is found to be very surface-enriched, because the amount measured by XPS decreases from >3 wt % to <0.8 wt % in the first few atomic layers. The presence of stable calcium or transition-metal iron hydroxyl arsenate hydrate [(M²⁺)₂Fe₃(AsO₄)₃(OH)₄+10 H₂O] complexes, as determined by X-ray diffractometry, in the fly ash produced from high-sulfur/pyrite feed coals indicates that some of the arsenic might be captured by calcium and iron compounds.

Guo, X., Zheng, C.G., and Xu, M.H. 2004. Characterization of arsenic emissions from a coal-fired power plant. *Energy Fuels* 18: 1822-1826.

Abstract: An emissions study for arsenic was conducted at a 300-MW coal-fired plant that was equipped with an electrostatic precipitator (ESP). The input and output streams, such as coal, slag, ESP ash, and flue gas that contained the post-ESP particulates, were collected. Gaseous arsenic was sampled using United States Environmental Protection Agency (USEPA) Method 29, and the arsenic concentrations in the samples were measured using inductively coupled plasma-atomic emission spectrometry. The mass balance recovery of arsenic estimated in this study was 87.2%. The arsenic concentration in the stack gas was 2.5 g/Nm³. Approximately 0.53% of the coal-derived arsenic was incorporated into slag, 84.6% of the arsenic was found on the fly ash that was collected by the ESPs, and 2.16% was found in the vapor phase. The relationship between arsenic concentration and ash particle size was also assessed, and arsenic was significantly concentrated in the small-sized particles. The modes of occurrence of arsenic in ash samples were studied using a modified sequential chemical extraction method. The extractable fraction was 13.78%-25.27% of the total arsenic in the fly ash particles, from the four ESP hopper samples. The arsenic concentrations found in the different extraction fractions were as follows: 74.73%-86.22% in the residue; 11%-19% in carbonate-bound, surface oxide-bound ions; 2.7%-6.0% in readily extractable ions; and 0.076-0.27% in water-extractable form. There were no appreciable differences in the arsenic solubility fractions between the different particle sizes of fly ash.

Huang, Y., B. Jin, Z. Zhong, R. Xiao, Z. Tang, and H. Ren. 2004. Trace elements (Mn, Cr, Pb, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler. *Fuel Processing Technology* 86:23-32.

Abstract: The concentrations of seven trace elements (Mn, Cr, Pb, Se, Zn, Cd, Hg) in raw coal, bottom ash and fly ash were measured quantitatively in a 220 tons/h pulverized coal boiler. Factors affecting distribution of trace elements were investigated, including fly ash diameter, furnace temperature, oxygen concentration and trace elements' characteristics. Modified enrichment factors show more directly element enrichment in combustion products. The studied elements may be classified into three groups according to their emission features: Group 1: Hg, which is very volatile. Group 2: Pb, Zn, Cd, which are partially volatile. Group 3: Mn, which is hardly volatile. Se may be located between groups 1 and 2. Cr has properties of both Groups 1 and 3. *The smaller the diameter of fly ash, the higher is the relative enrichment of trace elements (except Mn).* Fly ash shows different adsorption mechanisms of trace elements and the volatilization of trace elements rises with furnace temperature. Relative enrichments of trace elements (except Mn and Cr) in fly ash are larger than that in bottom ash. Low oxygen concentration will not always improve the volatilization of trace elements. Pb forms chloride more easily than Cd during coal combustion.

Huggins, F.E., Senior, C.L., Chu, P., Ladwig, K., and Huffman, G.P. 2007. Selenium and arsenic speciation in fly ash from full-scale coal-burning utility plants. Environmental Science & Technology 41: 3284-3289.

Abstract: X-ray absorption fine structure spectroscopy has been used to determine directly the oxidation states and speciation of selenium and arsenic in 10 fly ash samples collected from full-scale utility plants. Such information is needed to assess the health risk posed by these elements in fly ash and to understand their behavior during combustion and in fly ash disposal options, such as sequestration in tailings ponds. Selenium is found predominantly as Se(IV) in selenite (SeO_3^{2-}) species, whereas arsenic is found predominantly as As(V) in arsenate (AsO_4^{3-}) species. Two distinct types of selenite and arsenate spectra were observed depending upon whether the fly ash was derived from eastern U.S. bituminous (Fe-rich) coals or from western subbituminous or lignite (Ca-rich) coals. Similar spectral details were observed for both arsenic and selenium in the two different types of fly ash, suggesting that the post-combustion behavior and capture of both of these elements are likely controlled by the same dominant element or phase in each type of fly ash.

Ito, S., Yokoyama, T., and Asakura, K. 2006. Emissions of mercury and other trace elements from coal-fired power plants in Japan. Science of the Total Environment 368: 397-402.

Abstract: To evaluate trace element emissions from modern coal-fired power plants into the atmospheric environment in Japan, trace elements in the coal used in electric utility boilers, stack concentrations, emission rates and emission ratios of coal-fired power plants, and proportions of trace elements in coal-fired power plants were studied. The elements were As, B, Be, Cd, Co, Cr, F, Hg, Mn, Ni, Pb, Sb, Se and V, which are designated in the Law of Pollutant Release and Transfer Register. The particulate trace elements were collected in an electrostatic precipitator and a wet desulfurization scrubber. Emissions into the atmosphere were lower than 1% of the quantity in coal, but the volatile trace elements showed somewhat higher emission ratios. For mercury, the mean concentration in coal was 0.045 ppm, the mean emission rate was 4.4 g/kW h, and the mean emission ratio was 27%, the highest ratio among all elements in this study. The total annual emission of mercury from coal-fired power plants of the electric power industry in Japan was estimated to be 0.63 t/y. On the basis of these data, the atmospheric environment loads from a coal-fired power station were investigated. The calculation of stack gas dispersion showed that maximum annual mean ground level concentrations were in the order of 10^{-2} to 10^{-5} of the background concentrations, and that the adverse effect of the emissions from the coal-fired power station was small.

Keegan, T., B. Hong, I. Thornton, M. Farago, P. Jakubis, M. Jakubis, B. Pesch, U. Ranft, and M. Nieuwenhuijsen. 2002. Assessment of environmental arsenic levels in Prievidza district. *Journal of exposure analysis and environmental epidemiology* 12:179-185.

Abstract: A coal-burning power station in the Nitra Valley in central Slovakia annually emitted large quantities of arsenic (up to 200 tonnes) between 1953 and 1989. Since then, pollution-control measures have reduced arsenic emissions to less than 2 tonnes a year. However, the power station was still a source of airborne arsenic pollution. As part of an EU-funded study on exposure to arsenic and cancer risk in central and Eastern Europe we carried out a study of environmental levels of arsenic in the homes and gardens of residents of the district. Garden soil samples (n=210), house dust samples (n=210) and composite house dust samples (n=109) were collected and analysed using inductively coupled plasma atomic absorption spectroscopy (ICP-AES) at Imperial College. The mean arsenic content of coal and ash in samples taken from the plant was 519 µg/g (n=19) and 863 µg/g (n=22), respectively. The geometric mean (GM) arsenic concentration of garden soils was 26 µg/g (range 8.8-139.0 µg/g), for house dust 11.6 µg/g (range 2.1-170 µg/g) and for composite house dust 9.4 µg/g (range 2.3-61.5 µg/g). The correlation between the arsenic levels in soil and in house dust was 0.3 (P<0.01), in soil and composite house dust 0.4 and house dust and composite house dust 0.4 (P<0.01 for both), i.e., were moderate. Arsenic levels in both house dust and soil decreased with distance from the power station. Overall, levels in both fell by half 5 km from the point source. Weak correlations were seen between the total urinary arsenic concentrations and arsenic concentrations in composite house dust.

Keegan, T.J., Farago, M.E., Thornton, I., Hong, B., Colvile, R.N., Pesch, B., Jakubis, P., and Nieuwenhuijsen, M.J. 2006. Dispersion of As and selected heavy metals around a coal-burning power station in central Slovakia. *Science of the Total Environment* 358: 61-71.

Abstract: A power station in central Slovakia emitted arsenic (As) in large quantities for over 30 years as a result of burning As-rich brown coal. Nowadays emissions of As are low. Over the lifetime of the plant's operation over 3000 tonne of As have been emitted into the environment. This paper aims to examine the concentrations of As in the soil around the power station, and also to investigate whether the coal burnt in the plant, and consequently the emissions from it, contained raised levels of six further heavy metals. Soil concentrations were compared to ground level air As concentrations predicted by an air dispersion model. Coal samples were taken from the power station and analysed to determine concentrations of As, Zn, Pb, Cu, Cr, Ni and Cd. Soil samples (n = 113) were taken up to 12 km from the plant along a transect designed to follow the valley floor in which the power station is situated. Soil samples were analysed for concentrations of those elements for which coal was tested. Concentrations of As in coal were high (AM 518 µg/g). Those of other heavy metals were, in general, low. Concentrations of soil As were substantially raised in the near vicinity of the plant but decreased within 5 km to concentrations similar to those in the rest of the district. Overall, levels within 10 km of the plant were slightly above those recommended for residential levels in the UK. Soil concentrations of other heavy metals were higher in the vicinity of the plant but none, overall was raised. Comparison of results from a previous air dispersion model of ground level air arsenic concentrations showed a moderate correlation (r = 0.6) between modelled and measured values. Over its period of operation the power plant has contributed to raised levels of soil As in the local soils, though not substantially of other elements. Though now airborne As emissions are controlled, concern remains regarding soil arsenic concentrations and fugitive emissions from the plant that could be contributing to exposure of the local population and of the workforce.

Kingston, H.M., Cain, R., Huo, D., and Rahman, G.M.M. 2005. Determination and evaluation of hexavalent chromium in power plant coal combustion by-products and cost-effective environmental remediation solutions using acid mine drainage. Journal of Environmental Monitoring 7: 899-905.

Abstract: The chromium species leaching from a coal combustion fly ash landfill has been characterized as well as a novel approach to treat leachates rich in hexavalent chromium, Cr(VI), by using another natural waste by-product, acid mine drainage (AMD), has been investigated during this study. It is observed that as much as 8% (10 µg g⁻¹ in fly ash) of total chromium is converted to the Cr(vi) species during oxidative combustion of coal and remains in the resulting ash as a stable species, however, it is significantly mobile in water based leaching. Approximately 1.23 ± 0.01 µg g⁻¹ of Cr(VI) was found in the landfill leachate from permanent deposits of aged fly ash. This study also confirmed the use of AMD, which often is in close proximity to coal combustion by-product landfills, is an extremely effective and economical remediation option for the elimination of hexavalent chromium in fly ash generated leachate. Speciated isotope dilution mass spectrometry (SIDMS), as described in EPA Method 6800, was used to analytically evaluate and validate the field application of the ferrous iron and chromate chemistry in the remediation of Cr(VI) runoff.

Ladwig, K.J., Hensel, B.R., Hennings, B.G., Wallschlager, D., London, J., and Ferrarello, C.N. 2004. Arsenic and selenium in coal combustion products. Combined Power Plant Air Pollutant Control Mega Symposium, pp. 949-959.

Abstract: Arsenic and selenium are present in coal combustion products and can be mobile in the alkaline pH range. Knowledge of factors controlling their leachability and mobility in groundwater are critical to development of appropriate CCP management practices. Field leachate was sampled at 14 sites sampled in 2003 as part of a broad research effort to evaluate the leaching and attenuation of arsenic and selenium. Selenium concentrations ranged from non-detect to 2300 µg/L, with a median concentration of 15 µg/L. The highest selenium concentrations were observed in leachate from subbituminous coal ash. Arsenic concentrations ranged from non-detect to 240 µg/L, with a median concentration of 24 µg/L. Highest arsenic concentrations occurred at bituminous coal ash sites. Speciation was variable for both constituents, although the selenium appeared to be predominantly in the oxidized form. Preliminary data also suggest that additional research is needed on the role of ammonia-based NO_x controls and activated carbon for mercury control in the release of arsenic and selenium from fly ash.

Luo, K., Zhang, X., Chen, C., and Lu, Y. 2004. Estimate of arsenic emission amount from the coal power stations in China. Chinese Science Bulletin 49: 2183-2189.

Abstract: To study the amount of arsenic emission from the coal power stations (mainly Permo-Carboniferous coal) in China in different combustion conditions, the arsenic content of the coal, the fly ash and the cinder in high- temperature power stations as well as mid-low temperature power stations have been analyzed. This note provides a rough estimate of the total amount of arsenic emission as well as emission ratio from steam coal combustion in China. The results show that by combustion of 1 t of Permo-Carboniferous coal (containing roughly 5 mg/kg arsenic), high-temperature power stations emit roughly 0.40 g arsenic into the atmosphere and the arsenic emission rate is about 7.70%; mid-low power stations emit roughly 0.15 g arsenic into the atmosphere and the arsenic emission rate is about 2.97%. A total of 600 million tons coal is burnt annually in China power stations, and the coal comes mainly from PermoCarboniferous depositing in the North China Plate and northwest China coal mines. Taking the average arsenic content of the coal used at the value of 5 mg/kg, the total annual arsenic emission from steam coal combustion into the atmosphere is about 195.0 t. Most of the arsenic in coal can be released in the process of coal combustion, and the most of the released arsenic can be seized by the fly ash and

then both of them are seized by the dust catcher of power station, so the arsenic emission ratio to the atmosphere is declined; in addition, research on the arsenic emission amount and emission rules from the coal power stations in China should go on the coal power stations with the dry-process dust catchers by the experiments results. In the wet process of dust catcher, 20% of the arsenic in the fly ash is dissolved in the water of sedimentation tank in high-temperature power station; in the mid-low temperature power station there are 70% of the arsenic in the fly ash dissolved in the water of sedimentation tank, this is an important source of arsenic pollution in environment and should not be overlooked. The arsenic emission rate in the process of coal cination in the laboratory is higher than the actual arsenic emission rate of power station.

Luo, K., Wang, D., Tan, J., Wang, L., Feng, F., and Li, R. 2002. Lead emission amount from coal combustion and its environment effect in Xi'an City. *Huanjing Kexue* 23: 123-125.

Abstract: For study the lead emission amount from coal combustion and its environment effect, the lead content of coal, ash and cinder of power station and coal-fired boiler, the lead content of dusts in the period of heating time and the non-heating time in Xi'an City were studied in this paper. The results show that amount of lead emission from 1 ton coal combustion, which lead content in coal was 30 g, was 20 g in atmosphere. The rate of lead emission of coal combustion was about 66%. About 10 million tons of coal was straight burning every year in Xi'an City and suburb, those coal mainly come from Permo-Carboniferous coal in Weibei coal mine, Shaanxi, their average lead content was 30 mg/kg. So the total lead emission from coal combustion to atmosphere was about 200 t annually in Xi'an City.

Marrero, J., G. Polla, R. J. Rebagliati, R. Pla, D. Gomez, and P. Smichowski. 2007. Characterization and determination of 28 elements in fly ashes collected in a thermal power plant in Argentina using different instrumental techniques. *Spectrochimica Acta Part B-Atomic Spectroscopy* 62:101-108.

Abstract: Different techniques were selected for comprehensive characterization of seven samples of fly ashes collected from the electrostatic precipitator of the San Nicolas thermal power plant (Buenos Aires, Argentina). Particle size was measured using laser based particle size analyzer. X-ray diffraction powder (XRD) analysis and scanning electron microscopy (SEM) were used to characterize the mineral phase present in the matrix consisting basically of aluminosilicates and large amounts of amorphous material. The predominant crystalline phases were mullite and quartz. Major and minors elements (Al, Ca, Cl, Fe, K, Mg, Na, S, Si and Ti) were detected by energy dispersive X-ray analysis (EDAX). Trace elements (As, Cd, Co, Cr, Cu, Mn, Ni, Ph, Se, V and Zn) content was quantified by inductively coupled plasma optical emission spectrometry (ICP OES). Different acid mixtures and digestion procedures were compared for subsequent ICP OES measurements of the dissolved samples. The digestion procedures used were: i) a mixture of FH + HNO₃ + HClO₄ (open system digestion); ii) a mixture of FH + HNO₃ (MW-assisted digestion); iii) a mixture of HF and aqua regia (MW-assisted digestion). Instrumental neutron activation analysis (INAA) was employed for the determination of As, Ba, Co, Cr, Ce, Cs, Eu, Fe, Gd, Hf, La, Lu, Rb, Sb, Sc, Sm, Ta, Tb, Th, U and Yb. The validation of the procedure was performed by the analysis of two certified materials namely, i) NIST 1633b, coal fly ash and ii) GBW07105, rock. Mean elements content spanned from 41870 $\mu\text{g g}^{-1}$ for Fe to 1.14 $\mu\text{g g}^{-1}$ for Lu. The study showed that Fe (41870 $\mu\text{g g}^{-1}$) \gg V (1137 $\mu\text{g g}^{-1}$) $>$ Ni (269 $\mu\text{g g}^{-1}$) $>$ Mn (169 $\mu\text{g g}^{-1}$) are the main components. *An enrichment, with respect to crustal average, in many elements was observed especially for As, V and Sb that deserve particular interest from the environmental and human health point of view.*

Moreno, T., A. Alastuey, X. Querol, O. Font, and W. Gibbons. 2007. The identification of metallic elements in airborne particulate matter derived from fossil fuels at Puertollano, Spain. *International Journal of Coal Geology* 71:122-128.

Puertollano is the largest industrial centre in central Spain, and includes fossil fuel burning power plants as well as petrochemical and fertilizer complexes. The coal-fired power plants use locally mined coal from extensive coal deposits which continue to be exploited and used locally. The coal deposits have a distinctive geochemistry, being particularly enriched in Sb and Pb, as well as several other metals/metalloids that include Zn and As. ICP-AES and ICP-MS chemical analysis of particulate matter samples (both PM₁₀ and PM_{2.5}) collected at Puertollano over a 57-week period in 2004-2005 reveals enhanced levels of several metallic trace elements, especially in the finer (PM_{2.5}) aerosol fraction. Factor analysis applied to the data indicates that at least some of these metallic elements are likely to originate from hydrocarbon combustion: Sb and Pb are markers linked to the local coals, whereas V and Ni are, at least in the finer (PM_{2.5}) fraction, likely associated with other anthropogenic sources. Other factors measured are related to natural sources such as crustal/mineral and sea spray particles. Our study provides an example of how chemical analysis of large numbers of ambient PM samples, combined with statistical factor analysis and coal geochemistry, can reveal airborne emissions from the combustion of specifically identifiable fuels.

Narukawa, T., K. W. Riley, D. H. French, A. Takatsu, and K. Chiba. 2003. Investigation into the relationship between major and minor element contents and particle size and leachability of boron in fly ash from coal fuel thermal power plants. *Journal of Environmental Monitoring* 5:831-836.

A basic investigation of boron in discharged fly ash by coal fuel thermal power plants in several worldwide locations was carried out. Eight kinds of fly ash sample were prepared from eight coal fuel thermal power plants. Two of the fly ash samples were used to examine the relationship between the concentration of boron in fly ash and the particle size. When the particle size of fly ash is smaller, there is a possibility that it will be released into the air and spread over a wide area in the environment. However, it has become apparent that fly ash of smaller particle size has a higher concentration of boron and a higher enrichment factor. In other fly ash samples, the boron contents were examined and leaching tests were carried out. There is acidic fly ash as well as alkaline fly ash that contains larger amounts of acidic or basic salts. On alkaline fly ash, when the concentration of boron bound to Fe-Mn oxide is low; it has become apparent that leaching boron is increased in a solution with lower pH of approximately 4 which is nearly the pH of acid rain.

Narukawa, T., Takatsu, A., Chiba, K., Riley, K.W., and French, D.H. 2005. Investigation on chemical species of arsenic, selenium and antimony in fly ash from coal fuel thermal power stations. *Journal of Environmental Monitoring* 7: 1342-1348.

Abstract: Investigations of the existing chemical forms and the concentrations of arsenic (As), selenium (Se) and antimony (Sb) in samples of fly ash obtained from six coal-fired power stations in various countries were carried out. The concentration of As was found to vary from 5.4 to 22.3 mg kg⁻¹, and the most common mode of occurrence of As in the fly ashes is in association with carbonates or Fe-Mn oxides. The concentrations of Se and Sb ranged from 2.3-5.2 and 1.0-3.9 mg kg⁻¹, respectively. The dominant chemical forms of Se and Sb in the fly ashes were as extractable species. Also, water-soluble As, Se and Sb in the fly ashes were extracted, and the chemical species of As, Se and Sb in the extract determined using HPLC-ICP-MS. This was done as the potential release of soluble As, Se and Sb through leaching of fly ash is of environmental concern. The most abundant form of As in the extract was the low toxicity AS(V). The main species of Se was Se(IV), although it was found that the ratio of Se(VI) to Se(IV) in acidic fly ashes is higher than in alkaline fly ash samples. Antimony was mostly present as Sb(III).

Narukawa, T., Riley, K.W., French, D.H., and Chiba, K. 2007. Speciation of chromium in Australian fly ash. *Talanta* 73: 178-184.

Abstract: The concentrations of chromium (III) and (VI) in fly ash from nine Australian coal fired power stations were determined. Cr(VI) was completely leached by extraction with 0.01 M NaOH solution and the concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). This was confirmed by determining Cr(III) and Cr(VI) in the extracts of fly ash that had been spiked with chromium salts. These analytical measurements were done using a combination of ion-exchange chromatography and ICP-AES. The elutant was 0.05 M HNO₃ containing 0.5%-CH₃OH. When the column was operated at a flow rate of 1.2 ml min⁻¹ and samples were injected by use of a sample loop with a volume of 100 μ l, Cr(III) and Cr(VI) in sample solution was exclusively separated within approximately 10 min. The detection limits (3 σ) were 5 ng for Cr(III) (0.050 mg l⁻¹) and 9 ng for Cr(VI) (0.090 mg l⁻¹), respectively. A relative standard deviation of 1.9% (n = 6) was obtained for the determination by IC-ICP-AES of 0.25 mg l⁻¹ Cr(III) and Cr(VI).

Nelson, P. F. 2007. Trace metal emissions in fine particles from coal combustion. *Energy & Fuels* 21:477-484.

Fine-particle concentrations in the atmosphere and related human health impacts have been the subject of significant scientific research and regulatory development over the past couple of decades. Finer particles have been shown in epidemiological studies to be more strongly associated with adverse health outcomes than coarser particles, although the causal mechanisms responsible have not been definitively established. While the association between mortality and other health effects and particle mass show relatively consistent magnitudes of effects, there is considerably less agreement and consistency in the results from studies that have examined associations between health impacts and the composition of the fine particles. It has been known for more than 20 years that trace metals are enriched in the fine particles formed during coal combustion. Some of these metals are toxic at high concentrations, and reliable estimates of their emission rates in coal-fired plants are required to assist assessment of the relationships between fine-particle exposure and health impacts. In this paper, the current understanding of the health effects of fine particles, including the influence of composition, *and the factors that determine trace-element release and emission from full-scale plants, is reviewed.*

Noda, N., and Ito, S. 2008. The release and behavior of mercury, selenium, and boron in coal combustion. *Powder Technology* 180: 227-231.

Abstract: The release of mercury, selenium and boron from coal is investigated at high temperatures using a drop tube furnace and a coal combustion test facility. The results show that under combustion conditions, most of the mercury and selenium are released from the coal and did not remain in the fly ash at high temperatures, but some of the boron remains in the fly ash at high temperature. Under reducing conditions, all of the mercury is released from the coal, and some of the selenium and most of the boron remains in the coal char at 1473 K. This indicates that oxidation reaction contributes to the release of selenium and boron from coal. The transfer of these elements from gas to fly ash in coal combustion is tested as a function of temperature. The results show that mercury and selenium are captured on fly ash below 773 K, and the capture ratio increases as the temperature decreases. The transfer of boron from gas to fly ash is small between 393 K and 1273 K.

Pavageau, M.-P., C. Pecheyran, E. M. Krupp, A. Morin, and O. F. X. Donard. 2002. Volatile Metal Species in Coal Combustion Flue Gas. *Environmental Science & Technology* 36:1561-1573.

Abstract: Metals are released in effluents of most of combustion processes and are under intensive regulations. To improve our knowledge of combustion process and their resulting emission of metal to the atmosphere, we have developed an approach allowing us to distinguish between gaseous and particulate state of the elements emitted. This study was conducted on the emission of volatile metallic species emitted from a coal combustion plant where low/medium volatile coal (high-grade ash) was burnt. The occurrence of volatile metal species emission was investigated by cryofocusing sampling procedure and detection using low-temperature packed-column gas chromatography coupled with inductively coupled plasma-mass spectrometry as multielement detector [LT-GC/ICP-MS). Samples were collected in the stack through the routine heated sampling line of the plant downstream from the electrostatic precipitator. The gaseous samples were trapped with a cryogenic device and analyzed by LT-GC/ICP-MS. During the combustion process, seven volatile metal species were detected: three for Se, one for Sn, two for Hg, and one for Cu. Thermodynamic calculations and experimental metal species spiking experiments suggest that the following volatile metal species are present in the flue gas during the combustion process: COSe, CSSe, CSe sub(2), SeCl sub(2), Hg super(0), HgCl sub(2), CuO-CuSO sub(4) or CuSO sub(4). H sub(2)O, and SnO sub(2) or SnCl sub(2). The quantification of volatile species was compared to results traditionally obtained by standardized impinger-based sampling and analysis techniques recommended for flue gas combustion characterization. Results showed that concentrations obtained with the standard impinger approach are at least 10 times higher than obtained with cryogenic sampling, suggesting the trapping microaerosols in the traditional methods. Total metal concentrations in particles are also reported and discussed.

Reddy, M. S., S. B. Basha, H. V. Joshi, and B. Jha. 2005. Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion. Journal of Hazardous Materials 123:242-249.

Coal as well as fuel oil combustion generates emissions of potentially toxic trace pollutants including organic and inorganic chemical compounds besides major pollutants. A study on As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, and Zn emissions from a 220 MW coal-fired power plant equipped with a electrostatic precipitators (ESPs) and 6 MW oil fired-power plant was carried out, using stack monitoring kit, Envirotech APM 620, which is similar to EPA Method 29. Simultaneous sampling of coal, fuel oil, oil waste, bottom ash, fly ash, flue gases, and particles associated with the gas phase has been performed. This sampling method was used for trace metal sampling. The content of all these metals in coal, oil, oil waste, bottom ash, fly ash have been determined by XRF, whereas their contents in the flue gases, and particles associated with the gas phase has been analyzed with ICP-AES. The mass balances obtained for trace elements were satisfactory in case of fuel oil based power plant, whereas in case of coal fired power plant, the mass balance for all the trace elements were below 50% except for the As, Se, and Hg. The enrichment factors for all trace metals was < 1 in both cases. The above sampling method is moderately adequate method for trace element sampling in coal as well as oil fired power plants except for Hg. The results indicate that trace metals emissions were higher in coal-based power plant than the fuel oil-fired power plant.

Senior, C.L., Lignell, D.O., Sarofim, A.F., and Mehta, A. 2006. Modeling arsenic partitioning in coal-fired power plants. Combustion and Flame 147: 209-221.

Abstract: Vapor-phase arsenic in coal combustion flue gas causes deactivation of the catalysts used in selective catalytic reduction (SCR) systems for NO_x control. A one-dimensional model has been developed to predict the behavior of arsenic in the postcombustion region of a coal-fired boiler as a function of gas residence time. The purpose of the model is to calculate the partitioning of arsenic between the vapor phase from volatilization and arsenic on the ash particles due to surface reaction and/or condensation at temperatures characteristic of SCR

systems. The model accounts for heterogeneous condensation of arsenic on the fly ash, as well as surface reaction for two regimes: (1) the free molecular regime (submicrometer ash particles) and (2) the continuum regime (supermicrometer ash particles). All gas properties are computed as functions of gas temperature, pressure, and composition, which are allowed to vary. The arsenic model can be used to calculate the impact of coal composition on vapor-phase arsenic at SCR inlet temperatures, which will help utilities better manage coal quality and increase catalyst lifetimes on units operating with SCR. The arsenic model has been developed and implemented and was tested against experimental data for several coals.

Shah, P., Strezov, V., Stevanov, C., and Nelson, P.F. 2007. Speciation of arsenic and selenium in coal combustion products. *Energy Fuels* 21: 506-512.

Abstract: Coal combustion is one of the main anthropogenic sources of toxic trace element emissions to the environment. Various species and oxidation states of the trace elements released from power stations may determine their ultimate environmental fate and health impacts. This study focuses on speciation of arsenic and selenium present in the coal combustion products. Speciation analysis in representative coal, bottom ash, and fly ash obtained from four different Australian power stations was carried out in this work. Laboratory ash and char were also produced by carrying out combustion and pyrolysis experiments in a laboratory based drop tube furnace. The synchrotron based nondestructive speciation analysis method X-ray absorption fine structure spectrometry (XAFS) was applied for arsenic and selenium speciation analysis of the selected coal, ash, and char samples. The semiquantitative analysis of arsenic revealed variations in arsenic species in the coal samples indicating the presence of As/pyrite, arsenite (As³⁺), and arsenate (As⁵⁺) with the latter as a dominant form. Arsenic in power station fly ash samples was found to be mainly in an arsenate form with little presence of arsenite (As³⁺). Selenium speciation in coal samples indicated organic/reduced or elemental forms as dominant selenium species along with presence of selenite (Se⁴⁺)/selenate (Se⁶⁺). Selenium in fly ash was mainly found to be selenite with a minor presence of selenate. Char produced by pyrolysis indicated different speciation behavior of arsenic and selenium compared to coal and ash samples, which might be due to their further reactions with other volatilized species produced during pyrolysis and/or retained mineral matter.

Smolka-Danielowska, D. 2006. Heavy metals in fly ash from a coal-fired power station in Poland. *Polish Journal of Environmental Studies* 15:943-946.

The main subject of this study is fly ash created during coal combustion in Rybnik Power Station in Upper Silesia in the southern part of Poland. This is the biggest block power station in this region. Generated power is 1600 MW. Annual dust emission from professional energy in Upper Silesia is estimated at 32.8 thousand tons, which is about 22% of total national emissions. X-ray powder diffraction, Analytic Scanning Electron Microscopy (ASEM) and Induced Couple Mass Spectrometry (ICP-MS) methods have been applied extensively to heavy metals (Cu, Ni, Pb, Zn, Cr, Cd) content analysis and their host mineral phases identification. Concentrations of Cu, Ni, Pb, Zn, Cr and Cd as well as mineral composition of fly ash being their carriers have been specified. Average Zn concentrations in fly ash are 120 ppm, but for all other elements the average concentrations were 38 ppm for Cu, 41 ppm for Ni, 44 ppm for Pb, 64 ppm for Cr and 3 ppm for Cd. Amorphous aluminosilicate substances, oxides and sulphides are mineral phases containing heavy metals. The sizes of these particles are up to 12 μm .

Sun, J.M., Yao, Q., Liu, H.Y., Lu, J., Yin, G.X., and Zhao, C.M. 2004. Distribution of arsenic in PM₁₀ and PM_{2.5} caused by coal combustion and its enrichment mechanism. *Meitan Xuebao/Journal of the China Coal Society* 29: 78. (abstract not available)

Yudovich, Y. E., and M. P. Ketris. 2005. Arsenic in coal: a review. International Journal of Coal Geology 61:141-196.

The review presented covers: (a) historical introduction; (b) some analytical comments; (c) some peculiarities of the As geochemistry in environment; (d) an estimation of coal Clarke value of As; (e) some coals enriched in As; (f) mode of As Occurrence in coal; (g) factors influencing the As distribution in coal matter and coal bed; (h) genetic topics; (i) *some topics related to environmental impact of As by the coal combustion*. The World average As content in coals (coal Clarke of As) for the bituminous coals and lignites are, respectively, 9.0 +/- 0.8 and 7.4 +/- 1.4 ppm. On an ash basis, these contents are higher: 50 +/- 5 and 49+8 ppm, respectively. Therefore, As is a very coalphile element: it has strong affinity to coal matter - organic and (or) inorganic but obligatory authigenic. The coalphile affinity of As is like that for Ge or S. There is strong regional variability of As distribution due to geologic variability of the individual coal basins. For example, bituminous coals in Eastern Germany, Czech Republic and SE China are enriched in As, whereas the coals in South Africa or Australia are very depleted compared to coal Clarke of As. In general, some relationship exists between As content and its mode of occurrence in coals. Typically, at high As content, sulphide sites dominate (pyrite and other more rare sulphides), whereas at low As content, As-bio dominates, both being at-ithigenic. A contribution of the terrigenous As (in silicates) is usually minor and of the biogenic As-bio (derived from coal-forming plants) is poorly known. Both organic and inorganic As can exist not only as chemically bound form but also in the sorbed (acid leacheable) arsenate form. With increasing coal rank, sorbed exchangeable arsenate content decreases, with a minimum in the coking coals (German data: the Ruhr coals). Relations of As content in coal to ash yield (or its partitioning in sink-float fractions) and to coal petrographic composition are usually complicated. In most cases, these relations are controlled by main site (form) of As - As-py, or As-org. If As-pyr dominates, an As accumulation in heavy fractions (or in high-ash coals) is observed, and if As-org dominates, it is enriched in medium-density fractions (or low- and medium-ash coals). Arsenic is in part accumulated in the inertinite vs. vitrinite (As-org ?). There are four genetic types of As accumulation on coal: two epigenetic and two syngenetic: (1) Chinese type-hydrothermal As enrichment, sometimes similar to known Carlin type of As-bearing telethermal gold deposits; (2) Dakota type-hypergene enrichment from ground waters draining As-bearing tufa host rocks; (3) Bulgarian type-As enrichment resulting from As-bearing waters entered coal-forming peat bogs from sulphide deposit aureoles; (4) Turkish ope-volcanic input of As in coal-forming peat bog as exhalations, brines and volcanic ash. During coal combustion at power plants, most of the initial As in coal volatilizes into the gaseous phase. At the widely used combustion of pulverized coal, most of As-org, As-pyr and "shielded" As-bearing micromineral phases escape into gaseous and particulate phase and only minor part of As-clay remains in bottom ash. The dominant fraction of escaping As is in fly ash. ***Because 97-99% of the fly ash is collected by electrostatic precipitators, the atmospheric emission of As (solid phase and gaseous) is usually assumed as rather minor (10-30% from initial As in coal).*** However, fly ash disposal creates some difficult environmental problems because it is potentially toxic in natural waters and soils. The As leaching rate from ash disposal is greatly controlled by the ash chemistry. ***In natural environment, As can be readily leached from acid (SiO₂-rich) bituminous coal ashes but can be very difficult from alkali (CaO-rich) lignite ashes.*** If the As-pyr form dominates, conventional coal cleaning may be an efficient tool for the removing As from coal. However, organic-bound or micromineral arsenic ("shielded" grains of As-bearing sulphides) are not removed by this procedure. Some considerations show that "toxicity threshold" of As content in coal (permissible concentration for industrial utility) may be in the range 100-300 ppm As. However, for different coals (with different proportions of As-forms), and for different combustion procedures, this "threshold" varies

Yudovich, Y., and Ketris, M.P. 2006. Selenium in coal: A review. International Journal of Coal Geology 67: 112-126.

Abstract: The World average Se content in coals (coal Clarke of Se) for hard coals and brown coals are respectively 1.6 ± 0.1 and 1.0 ± 0.15 ppm. On an ash basis, these contents are greatly increased and are 9.9 ± 0.7 and 7.6 ± 0.6 ppm, respectively. Therefore, Se is a very coalphile element: it has strong affinity to coal matter - organic and (or) inorganic but is certainly authigenic. The "coal affinity" of Se is like that for Ge and S. Both organic (Seorg) and inorganic selenium (Semin) can exist in coal. In addition, Se can occur not only as a chemical-bound form, but also in sorbed (acid leachable) selenate form in the oxidized coals. The sulfidic form of Se is represented by isomorph Se in pyrite and some more rare sulfides, and the selenidic form by clauthalite PbSe. "Organic" Se may be present as both Se-organic compounds and elemental Se; disseminated through organic matter. There are some preliminary data that cleaning of high-sulfur coals, very effective for S, is less effective for Se due to enhanced contribution of the Seorg form (vs. Sorg). There are two genetic types of the Se-accumulations in coal: "reducing" and "oxidizing". In the first type, Se is enriched in high-sulfur coals, concentrating in sulfide phases. These accumulations are, in general, syngenetic, and may be epigenetic only if there are abundant hydrothermal sulfides of Fe, Cu, As, Pb. In coals of the second type, Se is enriched in the bed oxidation zones. Such coals are (or were) located in the areas with arid climate and enhanced Se content in water. Se concentrates in coal as a reduction or sorption geochemical barrier, probably, mostly as Se²⁻ in oxidized organic matter and partly pyrite. This type is characterized by oxidizing zonality and close paragenesis of Se with U, Fe, Mo, V, and Pb. These Se accumulations are mostly epigenetic. A study of Se in coal is evidently insufficient, and further detailed studies are needed, especially regarding Se forms (modes of occurrence).

Zhu, Z.J., Tan, Y., Zheng, J., Zhang, C.L., Li, Y.G., Zhang, D.L., and Wang, Q.J. 2003. Study on chromium existence and distribution in a 300 MW pulverized coal fired utility boiler. Zhongguo Dianji Gongcheng Xuebao/Proceedings of the Chinese Society of Electrical Engineering 23: 167-171.

Abstract: Through coal, slag, bottom and fly ashes sampling from a 300 MW utility boiler at the rated load and analysis of total and hexavalent chromium contents of those samples, the total chromium quantity distribution in coal and its combustion products was derived by means of mass balance methods. Characteristics of chromium transformation in a large-scale utility boiler is, therefore, analyzed and discussed. During coal combustion, the total chromium quantity in flue gas to raw coal is about 84%. The total chromium quantity in slag, bottom ash is about 1.1%, 0.6% respectively. The total chromium quantity in fly ashes can be distributed as 11.1% in No.1 ESP outlet, 1.2% in No.2 ESP outlet, 1.3% in No.3 ESP outlet. In combustion products the chromium in flue gas takes a very high ratio.

3.1.2 Polycyclic aromatic hydrocarbons (PAHs)

Arditsoglou, A., C. Petaloti, E. Terzi, M. Sofoniou, and C. Samara. 2004. Size distribution of trace elements and polycyclic aromatic hydrocarbons in fly ashes generated in Greek lignite-fired power plants. Science of the Total Environment 323:153-167.

Abstract: The fly ashes arrested by the electrostatic precipitators of four large lignite-fired Greek power stations (total installed capacity 4048 MW) were investigated regarding the distribution of 27 major, minor and trace elements and 13 polycyclic aromatic hydrocarbons (PAHs) in six size ranges from -40 to $> 105 \mu\text{m}$. An inverse relationship of concentration with particle size was observed for trace elements, such as As, Se, Zn, Pb, Cd, as well as for Ca, whereas the distribution of the matrix elements Al, Si, Ti, Fe, Mg was fairly flat up to $105 \mu\text{m}$ with relative enrichment or depletion in larger particle sizes. A reverse relationship of concentration with

particle size was also revealed for all PAHs, particularly the heavier compounds. The percent mass of all elements and PAH species in the suspendable fraction ($< 63 \mu\text{m}$) was between 25 and 30%. In all fly ashes, the PAH mixture was dominated by 4-ring species (48-62%) followed by 3-ring compounds (38-41%), whereas the carcinogenic 5- and 6-ring PAHs were less abundant (2-11%). Fly ash PAH concentrations were found to correlate strongly with the concentrations of certain trace elements either positively (e.g. Ba) or negatively (Mg, Cr, V, U) thus suggesting that some lignite elements might promote or prevent PAH formation during combustion. The suspendable fly ash fraction ($< 63 \mu\text{m}$) was found to contain 6-35% of the total mass of individual elements and 10-57% of the total mass of individual PAH components.

Cheng, J., Yuan, T., Wu, Q., Zhao, W., Xie, H., Ma, Y., Ma, J., and Wang, W. 2007. PM10-bound polycyclic aromatic hydrocarbons (PAHs) and cancer risk estimation in the atmosphere surrounding an industrial area of Shanghai, China. *Water Air Soil Pollut.* 183: 437-446.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the urban atmosphere. In particular, atmospheric pollution has increasingly become severe in China due to its rapid urbanization and industrialization. In recent years, a few studies have presented information about POPs (such as PAHs, PCBs, OCPs) in aerosols at a molecular level in a limited number of cities such as Beijing, Qingdao and Guangzhou, as well as Hong Kong. Whereas, these cities are located in northern and southern China, respectively, where characteristics of atmospheric pollution might be different from those in the eastern cities, such as Shanghai. Atmospheric particle pollution is a persistent problem in Shanghai, a typical metropolis of China, which has several huge industrial regions. In order to gain a comprehensive understanding of the present state, properties and sources of PAHs pollution in Shanghai, PM10 samples were collected at Coal-Fired Power Plant (CFP), Chlor-Alkali Chemical factory (CAC) and Coking and Chemical factory (CCF) in an industrial area, during the period, November 2004-September 2005. The concentrations of 16 PAHs were analyzed using the HPLC with UV visible detector. The results showed that the mean value of total PAHs in the industrial area was 64.85 ng m^{-3} ; 3-ring PAHs were found at low levels, while 4-, 5- and 6-ring PAHs were found at high levels. The levels of BaP were 3.07 and 7.16 ng m^{-3} at Chlor-Alkali Chemistry Factory and Coking and Chemistry Factory sites, respectively. PAHs levels exhibited distinct seasonal variation, with the highest level in autumn and the lowest in summer. The major source of PAHs at the industrial area was fossil fuel combustion, coal-burning, industrial furnaces including others. There was a very significant correlation of PAHs levels between CCF and CAC ($R^2=0.91$). The average concentration of BaP in the industrial area during the sampling period was 5.95 ng m^{-3} . It could be concluded the local population appears to be exposed to significantly high cancer risk (exceeding 2 ng m^{-3} in autumn and winter) as compared to the population of other areas.

Donahue, W.F., Allen, E.W., and Schindler, D.W. 2006. Impacts of coal-fired power plants on trace metals and polycyclic aromatic hydrocarbons (PAHs) in lake sediments in central Alberta, *Canadian Journal of Paleolimnology* 35: 111-128.

Abstract: Trace metals and polycyclic aromatic hydrocarbons (PAH) were analyzed in sediment cores from three central Alberta lakes to determine the contributions of local coal-fired power plants to contaminant loadings. In Wabamun Lake, with four power plants built since 1950 within a 35-km radius, sediment concentrations of mercury, copper, lead, arsenic and selenium have increased by 1.2- to 4-fold. Trace metal enrichments were less pronounced in Lac Ste. Anne and Pigeon Lake, situated 20 km north and 70 km south of Wabamun Lake, respectively. Total Hg flux to Wabamun Lake sediments ($21\text{-}32 \mu\text{g m}^{-2} \text{ yr}^{-1}$) has increased 6-fold since 1950, compared to 2- and 1.5-fold increases in Lac Ste. Anne and Pigeon Lake, respectively, since circa 1900. Total PAH flux to surface sediments was $730\text{-}1100 \mu\text{g m}^{-2} \text{ yr}^{-1}$ in Wabamun Lake, 290-

420 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ in Lac Ste. Anne, and 140-240 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ in Pigeon Lake. Without adoption of pollution-abatement technology that compensates for increases in generating capacity, continued expansion of coal-burning industry in Alberta will result in increased contaminant deposition, primarily from local sources.

Dyke, P.H., Foan, C., and Fiedler, H. 2003. PCB and PAH releases from power stations and waste incineration processes in the UK. *Chemosphere* 50: 469-480.

Abstract: This study focused on emissions of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) from incineration and power generation processes. Increased concern over human exposure to both classes of compounds has meant that environmental regulators need to assess the contribution made by emissions from regulated processes to human exposure. In the first part of an assessment in the UK we reviewed literature data on emissions of PCB, focusing on the dioxin-like PCB assigned toxic equivalency factors by the World Health Organization, and PAH. The literature study was supplemented by a series of plant tests to gather initial real plant data. Literature data were limited and the lack of standard protocols for measurement and reporting of both PCB and PAH meant that few data sets were comparable. Levels of dioxin-like PCB reported in the literature and measured in UK plant tests showed that well-controlled modern combustion plants with comprehensive pollution controls gave low emissions, typically about 5-10% of the toxic equivalent of the emissions of polychlorinated dibenzodioxins and dibenzofurans at the same plants and below the widely used standard of 0.1 ng TEQ/N m³.

Feng, C., Xia, X., Shen, Z., and Zhou, Z. 2007. Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China. *Environmental Monitoring and Assessment* 133: 447-458.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are important organic contaminants with great significance for China, where coal burning is the main source of energy. In this study, concentrations, distribution between different phases, possible sources and eco-toxicological effect of PAHs of the Yangtze River were assessed. PAHs in water, suspended particulate matters (SPM) and sediment samples at seven main river sites, 23 tributary and lake sites of the Yangtze River at the Wuhan section were analyzed. The total concentrations of PAHs in the studied area ranged from 0.242 to 6.235 $\mu\text{g/l}$ in waters and from 31 to 4,812 $\mu\text{g/kg}$ in sediment. The average concentration of PAHs in SPM was 4,677 $\mu\text{g/kg}$, higher than that in sediment. Benzo(a)pyrene was detected only at two stations, but the concentrations were above drinking water standard. The PAHs level of the Yangtze River was similar to that of some other rivers in China but higher than some rivers in foreign countries. There existed a positive relationship between PAHs concentrations and the TOC contents in sediment. The ratio of specific PAHs indicated that PAHs mainly came from combustion process, such as coal and wood burning. PAHs may cause potential toxic effect but will not cause acute biological effects in sedimentary environment of the Wuhan section of the Yangtze River.

Garcia, J.P., Beyne-Masclat, S., Mouvier, G., and Masclat, P. Emissions of volatile organic compounds by coal-fired power stations. *Atmospheric Environment Part A, General Topics* 1589-1597.

Abstract: This study concerns the emissions of volatile organic compounds (VOC) by coal-fired power stations. The most abundant compounds are aldehydes (formaldehyde and acetaldehyde), aliphatic and aromatic hydrocarbons (toluene, xylenes, ethylbenzene and benzene) and chlorinated hydrocarbons (tetrachloroethene). The relative importance of combustion parameters determining the level and the nature of emissions is described. The most important of these is the load of the station. A method is proposed to evaluate the combustion efficiency and to show the

relationship between the compounds emitted, the compounds formed during the combustion and those already present in the fuel. Mechanisms are proposed to explain the formation of chlorocompounds. Finally, a comparative study of the two sources of VOC-power stations and motor vehicle-indicates that the impact of the second on the environment is, by far, the most important.

Lee, R.G.M., Coleman, P., Jones, J.L., Jones, K.C., and Lohmann, R. 2005. Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM 10 from the domestic burning of coal and wood in the U.K. Environmental Science & Technology 39: 1436-1447.

Abstract: This paper presents emission factors (EFs) derived for a range of persistent organic pollutants (POPs) when coal and wood were subject to controlled burning experiments, designed to simulate domestic burning for space heating. A wide range of POPs were emitted, with emissions from coal being higher than those from wood. Highest EFs were obtained for particulate matter, PM10, (10 g/kg fuel) and polycyclic aromatic hydrocarbons (100 mg/ kg fuel for PAHs). For chlorinated compounds, EFs were highest for polychlorinated biphenyls (PCBs), with polychlorinated naphthalenes (PCNs), dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) being less abundant. EFs were on the order of 1000 ng/kg fuel for PCBs, 100s ng/ kg fuel for PCNs and 100 ng/kg fuel for PCDD/Fs. The study confirmed that mono- to trichlorinated dibenzofurans, C11,2,3DFs, were strong indicators of low temperature combustion processes, such as the domestic burning of coal and wood. It is concluded that numerous PCB and PCN congeners are routinely formed during the combustion of solid fuels. However, their combined emissions from the domestic burning of coal and wood would contribute only a few percent to annual U.K. emission estimates. Emissions of PAHs and PM 10 were major contributors to U.K. national emission inventories. Major emissions were found from the domestic burning for C11,2,3DFs, while the contribution of PCDD/F-TEQ to total U.K. emissions was minor.

Lee, J.H., Gigliotti, C.L., Offenberg, J.H., Eisenreich, S.J., and Turpin, B.J. 2004. Sources of polycyclic aromatic hydrocarbons to the Hudson River Airshed. Atmospheric Environment 38: 5971-5981.

Abstract: Sources of polycyclic aromatic hydrocarbons (PAHs) to the Hudson River Estuary Airshed were investigated using positive matrix factorization (PMF). A three-city dataset was used to obtain common factor profiles. The contributions of each factor on each sampling day and site were then determined, and a sensitivity analysis was conducted. A stable eight-factor solution was identified. PMF was able to identify a factor associated with air-surface exchange. This factor contains low-molecular weight PAHs and was a dominant contributor to the measured PAHs concentrations. Factors linked to motor vehicle use (diesel and gasoline vehicle emissions and evaporative/uncombusted petroleum) and natural gas combustion were also major contributors. Motor vehicle combustion and oil combustion factors were the predominant contributors to particle-phase PAHs, while natural gas combustion, air-surface exchange, and evaporative/uncombusted petroleum factors made substantial contributions to gas-phase PAH concentrations. In contrast to fine particulate matter (PM 2.5), which is dominated by regional transport, spatial variations in PAH concentrations suggest that PAH concentrations in the Hudson River Estuary Airshed are dominated by sources within the New York-New Jersey urban-industrial complex.

Li, X.D., Fu, G., You, X.F., and Yan, J.H. 2003. A study of the PAHs (polycyclic aromatic hydrocarbons) emissions resulting from the combustion of different ranks of coal. Reneng Dongli Gongcheng/Journal of Engineering for Thermal Energy and Power 18: 125-127.

Abstract: The organic pollutants generated by the combustion of coal, such as polycyclic aromatic hydrocarbons (PAHs), are carcinogenic, mutagenic and teratogenic. The authors studied

the generation of PAHs during the combustion of various kinds of coal and identified the relationship existing between the PAHs emissions during coal combustion and the content of PAHs in raw coal. Also researched is the influence of the constituent content of fixed carbon, volatile substance and ash in coal on PAHs emissions during the process of coal combustion.

Li, J., Zhang, G., Li, X.D., Qi, S.H., Liu, G.Q., and Peng, X.Z. 2006. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. Science of the Total Environment 355: 145-155.

Abstract: Mega-cities are large sources of air pollution on a regional base. Differences in energy structures, geographical settings and regional climate features lead to a large variety of air pollution sources from place to place. To understand the seasonality of air pollution sources is critical to precise emission inventories and a sound protection of human health. Based on a year-round dataset, the sources of PAHs in the air of Guangzhou were drawn by principal factor analysis (PCA) in combination with diagnostic ratios, and the seasonality of these sources were analyzed by PCA/MLR (multiple linear regressions) and discussed. The average total gaseous and particulate PAHs concentrations were 313 and 23.7 ng m⁻³, respectively, with a higher concentration of vapor PAHs in summer and particulate PAHs in winter. In addition to vehicle exhaust, which contributed 69% of the particulate PAHs, coal combustion was still an important source and contributed 31% of the particulate PAHs. Relatively constant contribution from coal combustion was found through the year, implying that coal combustion in power plants was not a seasonally dependent source. Evaporation from contaminated ground may be an important source of light PAHs in summer, providing an average contribution of 68% to the total PAHs in this study. By comparing the PAH concentrations and meteorological parameters, we found that higher concentrations of particulate PAHs in winter resulted from enhanced vehicle exhaust under low temperature and accumulation of pollutants under decreased boundary layer, slower wind speed, and long-term dryness conditions. It is suggested that the typical subtropical monsoon climate in South China, cool and dry in winter, hot and humid in summer, may play a key role in controlling the source seasonality (by enhancing vehicle exhaust in winter, ground evaporation in summer), and hence the ambient concentrations of PAHs in the air.

Liu G., Niu Z., Van Niekerk D., Xue J. & Zheng L. 2008. Polycyclic aromatic hydrocarbons (PAHs) from coal combustion: Emissions, analysis, and toxicology. in Reviews of Environmental Contamination and Toxicology. 192: 1-28.

Abstract: Coal is a complex heterogeneous mixture of organic and inorganic constituents of allothigenic or authigenic origin. Besides major (>1%) and minor (0.1%-1%) elements in coal, elements such as As, Se, and Hg occur commonly as trace elements (<1,000ppm) associated with both organic (e.g., polyaromatic hydrocarbons, PAHs) and inorganic matter (Swaine 2000; Liu et al. 1999; Finkelman 1995). PAHs in coal are the major source of organic pollution and may become easily accessible during combustion, coking, pyrolysis, and other coal preparation processes to make the coal consistent in quality and suitable for selling.

Liu, K., Heltsley, R., Zou, D., Pan, W.P., and Riley, J.T. 2002. Polyaromatic hydrocarbon emissions in fly ashes from an atmospheric fluidized bed combustor using thermal extraction coupled with GC/TOF-MS. Energy Fuels 16: 330-337.

Abstract: Over 120 polyaromatic hydrocarbons (PAHs) have been identified in urban pollution, of which 16 have been specified by the United States Environmental Protection Agency (EPA) as priority pollutants. Increased urban concentrations from anthropogenic sources are of particular concern because many of them show carcinogenic and/or mutagenic properties. In this study

thermal extraction (TE) coupled with GC/TOF-MS and solvent extraction coupled with GC/MS were utilized to determine the PAH concentrations in fly ash samples collected from a bench-scale 0.1 MWth fluidized bed combustor (FBC). In addition to the evaluation of the analysis procedures including conventional solvent extraction and thermal extraction, a comprehensive study of the effect of operating conditions on PAH emissions in fly ashes samples was conducted. The experimental results indicate the majority of PAHs (two and three fused-ring systems) found in the solid phase (fly ash) are derived from breakdown reactions during the combustion and/or pyrolysis processes in an FBC system. The results for PAH analysis obtained with the TE/GC/TOF-MS technique were comparable to or better than the conventional solvent extraction-GC/MS technique.

Meij, R., and te Winkel, H. 2007. The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations. *Atmospheric Environment* 41: 9262-9272.

Abstract: Extensive research for establishing the emissions of heavy metals from coal-fired power stations is performed in the Netherlands for the past 25 years. In the Netherlands coal is fired from all over the world. This means that the emissions are established for coal of various origins. In the eighties, the emissions of installations equipped with ESPs (electrostatic precipitators) were measured. In the nineties, the influence of wet FGD (flue gas desulphurisation) on the emissions was studied. The effect of co-combustion of biomass and other secondary fuels is the main item for the last 10 years. Fifty-five elements were measured in the solid state and eight elements in the gaseous phase. It appeared that at low particulate concentration the influence of calcium containing evaporated water droplets downstream the wet FGD on the emissions of heavy metals is bigger than the composition of the coal. Also it appeared that at modern coal-fired power stations the emissions are hardly influenced by co-combustion of biomass. All the results are used for modelling, resulting in the KEMA TRACE MODEL(R), by which the emissions can be predicted. The established emission factors are for most elements in good agreement with literature values for comparable modern installations. *Persistent organic pollutants (POPs) that were detected in the flue gases of coal-fired power stations are polycyclic aromatic hydrocarbons (PAH) and dioxins/furans. Measurements during full coal-firing and during co-firing of biomass have indicated that these emissions are negligible.*

Offenberg, J.H., and Baker, J.E. 2000. PCBs and PAHs in southern Lake Michigan in 1994 and 1995: Urban atmospheric influences and long-term declines. *Journal of Great Lakes Research* 26: 196-208.

Abstract: Surface water samples were collected in southern Lake Michigan off Chicago, IL to determine if elevated levels of urban atmospheric pollutants influence concentrations of organic contaminants in nearshore surface waters. Water was sampled every 12 hours for 2 to 12 days during May 1994, July 1994, and January 1995 sampling intensives. Total (dissolved + particulate; sum of 85 congeners) polychlorinated biphenyl (-PCB) concentrations ranged from 80 pg/L (26 July 1994) to 350 pg/L (18 January 1995), while total polycyclic aromatic hydrocarbon (24-PAH) concentrations during the same period ranged from 7 ng/L (18 May 1994) to 19 ng/L (17 January 1995). PCB concentrations in surface waters were higher when winds were from the S/SW, suggesting that the rate of direct atmospheric deposition of urban PCBs to the surface water may be fast relative to aquatic horizontal mixing and removal mechanisms. Additionally, PCB concentrations were higher during the winter than in the spring or summer, but PAH concentrations were not significantly different throughout the year. Lipid normalized PCB concentrations in zooplankton (> 202 µm) appear to be higher during the winter (780 vs. 14,200 ng -PCBs/g-lipid; July vs. January), but PAH levels in zooplankton were invariant with season

(21,000 vs. 21,200 ng -PAH/g lipid; July vs. January). The seasonal trend in surface water concentrations suggests relatively constant, elevated deposition of urban PAHs throughout the year, but net PCB exchange that varies seasonally. In spite of these elevated atmospheric deposition fluxes, the concentration of -PCB in Lake Michigan surface waters has declined ten fold over the past 14 years. The resulting pseudo-first order loss rate constant for Lake Michigan is $0.17 \pm 0.3/\text{yr}$ ($t(1/2) = 4.0$ years), which closely matches those found for the atmosphere and biota of Lake Michigan.

Ohura, T., T. Amagai, M. Fusaya, and H. Matsushita. 2004. Spatial distributions and profiles of atmospheric polycyclic aromatic hydrocarbons in two industrial cities in Japan. *Environmental Science & Technology* 38:49-55.

Abstract: The spatial distribution and concentration profiles of 39 vapor and particulate polycyclic aromatic hydrocarbons (PAHs) have been investigated in two Japanese industrial cities (Fuji and Shimizu; a summer and winter season in each). The concentrations of particulate PAHs in winter tended to be higher than those in the summer, but for vapor PAHs, this was not the case. Significant correlations ($p < 0.01$) were found between most of the PAH concentrations monitored in winter, suggesting the presence of common emission sources. To identify PAH spatial distributions and emission sources in the area, we created contour maps for PAHs monitored; this indicates that the distinctive local distributions correspond to the emission sources. PAH profiles based on benzo[e]pyrene (BeP) concentration, especially for certain relatively heavy molecular weight PAHs, showed differential behaviors among divided areas related to potential regional emission sources such as paper-making plants, power plants, and traffic. We conclude that the origins of atmospheric PAHs in the surveyed areas were dominated by not only traffic but also by stationary emission sources such as paper-making plants and power plants and that local distributions were dependent on the local wind direction.

Stracquadiano, M., and Trombini, C. 2006. Gas to particle (PM10) partitioning of polycyclic aromatic hydrocarbons (PAHs) in a typical urban environment of the Po Valley (Bologna, Italy). *Fresenius Environmental Bulletin* 15: 1276-1286.

Abstract: PM10 filter samples and polyurethane plugs, collected in the metropolitan area of Bologna (Italy) throughout 2002 and 2003, have been analysed for 9 polycyclic aromatic hydrocarbons (PAHs). Gas-particle partitioning coefficients K_P were determined for all PAHs at various temperatures, and good $\log K_P$ vs $1/T$ correlations were found, allowing us to estimate the heats of sorption of PAHs on PM10. Two linear log-log correlations were also checked; the former links K_P and the subcooled liquid vapour pressures (p_{Lo}) with $r^2 = 0.88$ and slope = -0.54. Slopes shallower than -0.6 indicate that absorption to the organic carbon (OC) microfilm coating particles is the prevailing sorption mechanism and that, by a molecular point of view, intermolecular interactions between PAHs and OC are smaller than intermolecular interactions in the pure liquid PAH. The second linear plot was found between K_P and the octanol-air partition coefficients (K_{OA}) with $r^2 = 0.89$ and slope = 0.56. The last good fitting again confirms absorption on OC as the most important process, and indicates that chemical composition of particulate matter in the days examined keeps quite constant, thus reinforcing the hypothesis that a main atmospheric pollution source (vehicular traffic) is responsible for the air quality in the area of Bologna.

Sun, C., Snape, C.E., McRae, C., and Fallick, A.E. 2003. Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints. *Fuel* 82 : 2017-2023.

Abstract: It has been established previously [Anal. Commun. 33 (1996) 331; Analyst 123 (1998) 1519; Org. Geochem. 30 (1999) 881; Environ. Sci. Technol. 34 (2000) 4684] that, for thermal conversion regimes where volatiles survive to a significant degree (e.g. low and high temperature carbonisation, domestic combustion), the stable carbon isotopic signatures of polycyclic aromatic hydrocarbons (PAHs) are similar to those of the parent coals (ca. -25‰, cf. -23.5‰ for the coals). This information has been used to unambiguously identify coal-derived PAHs in contaminated land sites. Aromatic hydrocarbons in a number of samples analysed from a former foundry site at Mansfield displayed variable compositions with those containing predominately alkylated benzenes and naphthalenes having carbon stable isotopic ratios in the range of -28 to -30‰, typical of transport fuels. The aliphatic hydrocarbon distributions confirmed the petroleum origin and indicated that the oil had also been biodegraded. Less negative (enriched in ¹³C, -25 to -26‰) isotopic profiles were obtained for the fractions rich in 3-6 ring parent PAHs, indicating a significant input from coal utilisation. Separating the aromatic by ring size enabled the coal-derived 3-6 ring PAHs to be identified in samples where petroleum-derived alkylated benzenes and naphthalenes dominated. A similar situation to this with only a small input from coal-derived PAHs was found for a soil heavily contaminated with diesel fuel from the Motherwell area. Carbon stable isotopic data taken in conjunction with PAH distributions indicate that the coal tar contaminating an area of Glasgow Green, which was believed to be dumped during the Second World War and was unearthed recently, probably originated from a high temperature coking plant as opposed to a gas works, as indicated by the isotopic signatures of the distributions of PAHs.

Yan, J.H., You, X.F., Li, X.D., Ni, M.J., Yin, X.F., and Cen, K.F. 2004. Performance of PAHs emission from bituminous coal combustion. Journal of Zhejiang University: Science 5: 1554-1564.

Abstract: Carcinogenic and mutagenic polycyclic aromatic hydrocarbons (PAHs) generated in coal combustion have caused great environmental health concern. Seventeen PAHs (16 high priority PAHs recommended by USEPA plus Benzo[e]pyrene) present in five raw bituminous coals and released during bituminous coal combustion were studied. The effects of combustion temperature, gas atmosphere, and chlorine content of raw coal on PAHs formation were investigated. Two additives (copper and cupric oxide) were added when the coal was burned. The results indicate that significant quantities of PAHs are produced from incomplete combustion of coal pyrolysis products at high temperature, and that temperature is an important causative factor of PAHs formation. PAHs concentrations decrease with the increase of chlorine content in oxygen or in nitrogen atmosphere. Copper and cupric oxide additives can promote PAHs formation (especially the multi-ring PAHs) during coal combustion.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., and Sylvestre, S. 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33: 489-515.

Abstract: Parent and alkyl PAHs (51 compounds and alkyl homologues) have been quantified in suspended particulates and sediments (345 samples) from the Fraser River system, British Columbia, Canada. The best potential to distinguish natural and anthropogenic sources is exhibited by ratios of the principal mass 178, 202, 228 and 276 parent PAHs, 1,7/2,6 + 1,7-DMP (dimethylphenanthrene), the phenanthrene/anthracene and fluoranthene/pyrene alkyl PAH series and several less commonly applied PAHs (e.g. acephenanthrylene and pentaphene). Using these ratios we infer sources of PAH to the Fraser basin and evaluate the consistency of these source assignments and the suitability of various commonly applied PAH ratios as indicators. PAH ratios and total concentration data reveal a basin lightly impacted by a variety of sources in its remote regions, especially near roads, but heavily impacted in urban areas, particularly near Vancouver. Contamination sources shift from biomass (e.g. wood and grass) burning to vehicle emissions

between remote and urban locations. Stormwater and wastewater discharges appear to collect PAH from urban areas and release them as point sources. In contaminated areas ratios are specific for combustion vs. petroleum sources, and some ratios (202 and 276) distinguish biomass or coal from liquid fossil fuel combustion. At lower concentrations multiple sources at times make interpretations based on a single ratio misleading and the higher mass ratios (228 and 276) may be most applicable to urban areas. In all cases the examination of a variety of PAH indicator ratios that encompass a range of masses is necessary for a robust interpretation.

3.1.3 Dioxins and furans

Choong Kwet Yive, N.S., and M. Tiroumalechetty *in press*. Dioxin levels in fly ash coming from the combustion of bagasse. *Journal of Hazardous Materials*.

Abstract: Levels of dioxins (PCDD/Fs) were determined in fly ash samples collected from a power plant burning bagasse for production of electricity. The concentrations ranged from 2.2 pgWHO-TEQ/g to 190 pg WHO-TEQ/g with samples collected after ESP containing significantly much higher (more than 12 times on average) levels than samples collected before ESP. Our results seem to indicate that both the de novo and the precursor mechanisms are significantly involved in the formation of dioxins the fly ash during combustion of bagasse.

Everaert, K., and Baeyens, J. 2002. The formation and emission of dioxins in large scale thermal processes. *Chemosphere* 46: 439-448.

Abstract: The paper assesses extensive data of PCDD/F measurements on flue gas emissions from thermal processes, including, e.g. municipal solid waste incinerators (MSWIs), combustors of wood and industrial waste, coal fired powerplants and boilers, ferro and non-ferro processes. Numerous investigators have conducted laboratory experiments to assess the formation mechanisms of PCDD/F. The results, obtained from fixed-bed experiments, have been critically evaluated and indicate that de novo synthesis is the dominant mechanism in actual thermal processes where conditions that favour the precursor formation are not experienced. The analysis of PCDD/F profiles from the large scale thermal processes in general, and MSWIs in particular, supports the dominant role of the de novo synthesis, irrespective of the type of thermal process considered. The PCDF/PCDD ratio exceeds 1 and the degree of chlorination points towards the dominant presence of HpCDD and OCDD within the dioxin group, and of PeCDF, HxCDF and HpCDF within the furan group. Since real-time measurement of PCDD/F is impossible, the correlation of PCDD/F emissions with operating parameters and/or emission levels of other more easily measured pollutants could be a tool in predicting the PCDD/F formation levels. Data of Flemish MSWIs were used to statistically assess such correlations. From an evaluation of the data at a given operating temperature, misleading conclusions can be drawn. Only the effect of temperature is evident. After converting all data at a reference temperature of, e.g. 230°C, PCDD/F concentrations achieve nearly constant values, irrespective of the values of other parameters, thus stressing that the major controlling parameter for the PCDD/F emission is the temperature of the ESP. The PCDD/F concentrations increase with temperature in the range up to 280°C. The ESP temperature should be kept preferably between 180°C and 200°C, where de novo synthesis is reduced and where PCDD/Fs are increasingly adsorbed on the fly ash, in line with the standard temperature dependence of adsorption isotherms.

Fernandez, M., pez, V., pez, M., Muniategui-Lorenzo, S., Prada, R., Abad, E., and Rivera, J. 2004. First assessment of dioxin emissions from coal-fired power stations in Spain. *Chemosphere* 57: 67-71.

Abstract: In this work, the findings of the first assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in emissions releases to the atmosphere from coal-fired power plants are given. A total of five plants were selected for the study located at different provinces in Spain. In all the cases, the results revealed very low levels, in the range of 0.41 pg I-TEQ/Nm³. The profile indicated in the majority of the cases predominance of highly chlorinated congeners being OCDD the most important contributor. The findings were also used to estimate contribution of PCDDs/PCDFs emitted from coal-fired power plants in Spain. Individual plant results revealed values below 0.02 g I-TEQ per year and plant. Nevertheless, considering the total coal consumption in Spain in 1997, the values are comparable to those reported in other countries in the range of 0.6-0.7 g I-TEQ per year. Moreover, emission factors were determined considering operating conditions of evaluated plants. In general, large variability was observed and values below 1-5 pg I-TEQ/kg coal were early reached.

Gulyurtlu, I., Crujeira, A.T., Abelha, P., and Cabrita, I. 2007. Measurements of dioxin emissions during co-firing in a fluidised bed. Fuel 86: 2090-2100.

Abstract: The emissions of dioxins could be considerable when fuels with high chlorine content are used, particularly in fluidised beds due to constraints to use temperatures in the range 800-900 °C for other considerations. However, mixing of fuels with different characteristics may lead to a reduction in dioxin emissions. Studies are currently being undertaken at the above-mentioned department in mixing fuels of varying chlorine and sulphur contents to monitor the emissions of dioxins both in the gas and solid phases. Furthermore, the influence of certain elements like Cu in the ash in the emissions of dioxins is also studied to verify the catalytic effect. The INETI pilot-scale test facility is used for the combustion work. Two different coals, namely Colombian and Polish, are used as the base fuel. The supplementary fuels for co-firing include MBM and straw pellets. The combustion temperature is maintained at about 800-830 °C range without any limestone addition. The residence time of over 2 s is respected. Results obtained by far suggest that the presence of sulphur in both fuels have a very strong effect on the eventual emissions of dioxins and the synergy regarding to reduce the dioxins below the levels permitted is possible by mixing fuels based on their characteristics. The paper reports the results obtained and evaluates the effect of fuel nature and operating conditions on the emissions of dioxins.

Li, X.D., Yin, X.F., Lu, S.Y., Gu, Y.L., Yan, J.H., Ni, M.J., and Cen, K.F. 2006. Correlation between PAHs and dioxins formation during coal and municipal solid waste co-incineration process. Kung Cheng Je Wu Li Hsueh Pao/Journal of Engineering Thermophysics 27: 691-694.

Abstract: In order to check the relation between PAHs and dioxins formation, the paper evaluated the possibility of dioxins formation from PAHs via precursor pathway, as well as the corresponding mechanism in municipal solid waste (MSW) incineration process. The incineration experiment mixed proportionally by municipal solid waste and coal on a fixed-bed had been done, then the PAHs and dioxins formation performance were studied. With the increase of S/Cl ratio, the total PAH emission decreases, and this trend is similar with that of dioxins emission. It shows that the correlation between PCDF and PAHs is obvious. Especially the correlation between Benzo(a) anthracene and PCDF is very obvious, so BaA may be one of typical PCDF indicators.

Lu, S.Y., Yan, J.H., Chen, T., Li, X.D., Chi, Y., Gu, Y.L., Ni, M.J., and Cen, K.F. 2003. Study on dioxin emission from plastic and coal co-combustion in a fluidized bed. Ranshao Kexue Yu Jishu/Journal of Combustion Science and Technology 9: 123-127.

Abstract: Dioxins were considered to be potential carcinogens and mutagens which are harmful to human health in environment. Plastics and plastics/coal mixed particles were combusted in a

lab-scale fluidized bed, and dioxin emission factor (EF) was investigated. Flue gas was sampled, pretreated and analyzed by HRGC/LRMS (high resolution gas chromatography/low resolution mass spectrometer). The results suggest that total and toxic EF for PVC combustion are 252.69 ng/g and 4.60 I-TEQ ng/g, for PVC combustion with coal are 79.72 ng/g and 2.41 I-TEQ ng/g, while the dioxin inhibition efficiencies for coal addition are 68.5% and 47.6% respectively. When PVC and PE are combusted, total and toxic EF are 1.76 ng/g and 0.11 I-TEQ ng/g, and when coal is added they become 2.57 ng/g and 0.03 I-TEQ ng/g, while the dioxin inhibition efficiencies are -46% and 72.7% respectively. The experimental results show that the co-combustion of plastics and coal makes the toxic EF a great decrease, but the inhibition of total EF is not clear.

Meyer Zu Reckendorf, R. 2003. Pattern change of several polycyclic aromatic furans and analogous thiophenes on oxidative pyrolysis of pitches in flue gases, and the relevance to their quantitative analysis. *Chromatographia* 58: 103-113.

Abstract: Coal tars, coal-tar pitches, and ring-furnace flue gases have been analyzed by GC-MS for several classes of polycyclic aromatic furans and thiophenes and concentration patterns were obtained for benzonaphthofurans, benzonaphthothiophenes, benzobisbenzofurans, and their isomers. During formation of tar in a coke oven battery non-peripheral and alternating polycyclic thiophenes are formed preferentially. Peripheral polycyclic furans were not found in any of the materials. During tar processing the concentrations of minor fractions of peripheral benzonaphthothiophene isomers are reduced substantially. A further reduction occurs during pitch carbonization under oxidative conditions in an annular baking furnace. This largely facilitates quantification of the non-peripheral compounds.

Roots, O. 2004. Polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in oil shale and fly ash from oil shale-fired power plant in Estonia. *Oil Shale* 21: 333-339.

Abstract: Estonian and Baltic Thermal Power Plants are the world largest thermal power plants burning low-grade local oil shale. During the European Dioxin Project the concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls were measured at Baltic Thermal Power Plant in oil shale and fly ash from electrostatic precipitators. The study of PCB and dioxin was carried out by Landesum-weltamt Nordrhein-Westfahlen, Germany. It was concluded that the power plants are probably not major sources of dioxins. It should be noted that the European Dioxin Inventory did not include any measurements of air emission from sources in Estonia.

Zhong, Z.P., Jin, B.S., Lan, J.X., Dong, C.Q., and Zhou, H.C. 2003. Dioxins emission and purification during co-combustion of municipal solid waste and coal mixture. *Zhongguo Dianji Gongcheng Xuebao/Proceedings of the Chinese Society of Electrical Engineering* 23: 184-188.

Abstract: This paper presents a flue gas purification technology of using fluidized absorption tower and fabric filter for flue gas of co-combustion municipal solid waste and coal in a fluidized bed. A fluidized absorption test rig for flue gas purification in MSW incineration is set up. It is composed of humidification and attemperation semi-system, absorption tower, demister, slurry-making pool, desilter, and measurement semi-system. The total height of the absorption tower is 6.5 m, diameter of reaction pool is 1.2 m and the flow rate of flue gas is about 150-2000 Nm³/h. The experimental results are as follows. When absorbent is limestone slurry, the concentration of slurry is 1%, the circulation ratio is 3, the jet rate is 5-15 m/s and the immersed depth of bubbling pipe under the slurry is 140 mm, the purification efficiency of dioxins in purification facility is 99.35%. The concentration of dioxins in flue gas is 0.1573 ng/Nm³ while the concentration of

oxygen is 11%. The emission concentration said above approaches the emission standard of the developed country.

Zhong, Z., Jin, B., Huang, Y., Zhou, H., and Lan, J. 2006. Experimental research on emission and removal of dioxins in flue gas from a co-combustion of MSW and coal incinerator. Waste Management 26: 580-586.

Abstract: This paper describes the experimental study of dioxins removal from flue gas from a co-combustion municipal solid waste and coal incinerator by means of a fluidized absorption tower and a fabric filter. A test rig has been set up. The flow rate of flue gas of the test rig is 150-2000 m³/h. The system was composed of a humidification and cooling system, an absorption tower, a demister, a slurry make-up tank, a desilter, a fabric filter and a measurement system. The total height of the absorption tower was 6.5 m, and the diameter of the reactor pool was 1.2 m. When the absorbent was 1% limestone slurry, the recirculation ratio was 3, the jet rate was 5-15 m/s and the submerged depth of the bubbling pipe under the slurry was 0.14 m, the removal efficiency for dioxins was 99.35%. The concentration of dioxins in the treated flue gas was 0.1573 + 10⁻¹³ kg/Nm³ and the concentration of oxygen was 11%. This concentration is comparable to the emission standards of other developed countries.

3.1.4 Fluoride

Liu, J., Qi, Q., Zhou, J., Cao, X., and Cen, K. 2003. Distribution of fluoride in the combustion products of coal. Huan jing ke xue= Huanjing kexue / [bian ji, Zhongguo ke xue yuan huan jing ke xue wei yuan hui 'Huan jing ke xue' bian ji wei yuan hui.] 24: 127-130.

Abstract: The static distribution characteristic of fluoride in the combustion products of coal was studied by ashing procedure of coal, and the dynamic distribution characteristics of fluorine in the combustion products of coal in pulverized-coal-fired boiler and layer-burning boiler were investigated. Experimental results identified that fluorine in coal belong to volatile elements, fluorine in fly ash and bottom ash were non-rich. About 94.5% of the fluorine in coal emitted as gaseous-fluorine during coal combustion in pulverized-coal-fired boiler, and about 80% of the fluorine in coal emitted as gaseous-fluorine during coal combustion in layer-burning boiler. 55%-60% of the fluorine in fly ash of pulverized-coal-fired boiler were distributed in fly ash particles with a diameter of 74 microns-104 microns.

Lopez-Vilarino, J. M., G. Fernandez-Martinez, I. Turnes-Carou, S. Muniategui-Lorenzo, P. Lopez-Mahia, and D. Prada-Rodriguez. 2003. Behavior of fluorine and chlorine in Spanish coal fired power plants with pulverized coal boilers and fluidized bed boiler. Environmental Technology 24:687-692.

Behavior and contents of fluorine and chlorine in coal feedstock, combustion wastes (slag and fly ash) and emissions were studied in five conventional coal fired power plants and in a fluidized bed coal power plant. The halide levels found in the used coal were quite low. Mass balances and emission factors were calculated. The volatility of these elements makes the gaseous emission the main target between the residues. The influence of combustion parameters is not clearly established. Several analytical techniques (ion selective electrodes, capillary electrophoresis and ion chromatography) are employed to determinate the halide concentration in the different samples taken in the power plants studied (coal, slag fly ash and flue gases).

Moufti, A., and Mountadar, M. 2004. Separating fluoride and metals to leave coal ash. Water Quality Research Journal of Canada 39: 113-118.

Abstract: Leaching of fluorides from fly ash has been studied at different conditions (ash/water distilled ratios, variable temperature and for one interval of the very precise pH). The contents of

the trace elements in the washed waters have also been evaluated. In this study, we demonstrated that the leaching depends on temperature and pH. To ambient temperature (22°C) and to pH greater than 4.5, one has less leaching of F⁻ and of trace metals. For acidic pH (pH <2.5), the fluoride content is influenced by complexation with Fe³⁺ and Al³⁺. This survey showed that the calcium is combined with carbonates and the majority of metals are under shapes of sulfates.

Mukherjee, A.K., Ravichandran, B., Bhattacharya, S.K., Ahmed, S., Roy, S.K., Thakur, S., Roychowdhury, A., and Saiyed, H.N. 2003. Environmental pollution in rural areas of Orissa state due to industrial emissions - With special reference to fluoride. Indian Journal of Environmental Health 45: 325-334.

Abstract: Angul - Talcher belt in Central Orissa, having a number of industries contributing to a great extent to deteriorate the air quality of the surrounding villages. Previous reports showed higher SPM, SO₂, NO_x levels in air and prevalence of respiratory illness, skin and teeth disorders among village population. Higher ground water fluoride, urine and serum fluoride among the cattle were also reported in some villages. Present study reports SPM, SO₂, NO_x and Fluorides (gaseous and Particulate) in ambient air around aluminium smelter during February and August 1996. High volume sampling technique for SPM and the standard colorimetric methods (BIS) for analyses of SO₂ and NO_x were adopted. Fluoride in air and water were estimated by standard fluoride ion selective electrode method. Higher SPM, SO₂ and NO_x values than prescribed CPCB standard were obtained in February. Gaseous fluoride in village air were varied between, 1.66-7.64 mg/m³ in February and 1.11-22.75 mg/m³ in August, whereas particulate fluoride ranged between, 0.054-19.61 mg/m³. Water sources of the villages near the smelter showed fluoride values above permissible limit. The study indicated higher fluoride pollution in air and water of the surrounding villages.

Qi, Q., Liu, J., Zhou, J., Cao, X., Cheng, J., Zhang, S., and Cen, K. 2003. Fluoride emission control by blending and injecting CaO and calcium-based sorbents during coal combustion. Huagong Xuebao/Journal of Chemical Industry and Engineering (China) 54: 226-231.

Abstract: The experimental and theoretical analysis about toxic fluoride removal during coal combustion are reported. It has been identified that CaO can restrain the emission of fluoride and fluoride retention ratios are between 12.2% and 61.0%, with mean value 39.5% by blending CaO with coal during coal combustion in tubular furnace at 900°C. Influence factors on fluoride retention by blending CaO with coal are studied such as type of coals, combustion temperature, retention time and Ca/S molar ratio. The optimum conditions for fluoride retention by blending CaO with coal are that combustion temperature in the range 800-1000°C retention time between 5-10 min and Ca/S ratio in the range 2.5-3.0. In chain-grate furnace combustion of coal, fluoride retention ratios are about 54.0%-64.8% with mean value 59.3% by blending calcium-based sorbents with coal and are about 72.5%-80.5% with mean value 75.5% by blending calcium-based sorbents with coal accompanied by injection of calcium-based sorbents.

3.1.5 Hydrogen chloride

Akosman, C., and Walters, J.K. 2003. Removal of hydrogen chloride from flue gases with calcined limestone particles in a fixed bed reactor. Fresenius Environmental Bulletin 12: 1530-1535.

Abstract: The sorption of hydrogen chloride gas (HCl) on fully calcined commercial limestone particles was experimentally investigated using a fixed bed reactor at temperatures between 400-650°C. The gas phase was a mixture of HCl and N₂ with an inlet HCl concentration of 0.5% mol. The limestone particles were diluted in inert mullite beads to obtain a proper gas-solid contact.

The experimental results showed that the conversion of solids increased with increasing temperature. Also HCl removal efficiency increased with increase in temperature and limestone quantity in the bed.

Tsubouchi, N., Ohtsuka, S., Nakazato, Y., and Ohtsuka, Y. 2005. Formation of hydrogen chloride during temperature-programmed pyrolysis of coals with different ranks. *Energy Fuels* 19: 554-560.

Abstract: The evolution of HCl during pyrolysis of 16 coals with different ranks at a heating rate of 10 °C/min has been studied with an online monitoring method. Approximately 50% - 95% of total chlorine is converted to HCl up to 800 °C, and the remainder is mostly retained in the char, which leads to a strong reverse correlation between the two. As the sum of Na and Ca naturally present in coal increases, the amount of HCl tends to decrease. The temperature dependence of the rate of HCl evolved differs with each coal and shows at least four peaks at 280, 360, 480, and 580 °C. The former two peaks are present for two coals alone, whereas the higher temperature HCl formation at >450 °C is common for almost all of the coals. The HCl peaks at 280 and 360 °C are considerably small by water washing. When model chlorine compounds added to activated carbon, such as hydrated NaCl, hydrated CaCl₂, and organic hydrochlorides, are pyrolyzed in the same manner as above, HCl formation occurs dominantly between 250 and 450 °C in every case. The pretreatment of a brown coal char with HCl at 500 °C and subsequent temperature-programmed desorption TPD measurement up to 950 °C suggest that HCl reacts with the nascent char upon pretreatment to form several types of Cl functional forms, from which the HCl desorption takes place at 450 - 750 °C upon TPD. The HCl evolved at <450 °C during pyrolysis may arise from water-soluble Cl functional groups in coal, whereas the HCl formation at >450 °C observed for almost all of the coals may proceed through a mechanism involving secondary reactions of HCl evolved at a lower temperature.

3.1.6 Radionuclides

Adrovic, F., Prokic, M., Ninkovic, M. M. and Glisic, R. (2004) Measurements of environmental background radiation at location of coal-fired power plants. *Radiat. Prot. Dosim.* 112, 439-442.

Abstract: Environmental radiation monitoring in the vicinity of coal-fired power plants which are used primarily to determine the variability in measured background exposures are presented in this article; this is in order to estimate the contribution due to the plants' operation. Measurements have been done using a multi-element, high sensitive dosimeter system composed of three solid, properly filtered, sintered CaSO₄:Dy thermoluminescent detectors, and one low-atomic number, MgB₄O₇:Dy,Na thermoluminescent detector produced at the Vinca Institute. The dosimeters were deployed quarterly 1 m above ground level at locations within 20 km of the power plants. Twenty urban and suburban measured stations were established. Measurements were carried out over one year period, from the beginning of the summer of 1995 to the end of the spring of 1996. The registered annual absorbed dose in air, from all of the 20 stations, vary from 0.91 to 1.46 mGy a⁻¹. One of the highest values of the annual absorbed dose was measured at the station near to the plant, i.e. at the place the most exposed to the lighter fly ash from the plant stack, as it was expected. The annual absorbed dose registered at the measuring stations that were selected as a control because they were situated practically away from possible influence of the plants were from 0.91 to 0.98 mGy a⁻¹. The above values of absorbed doses become very important, by concurrence of the circumstances, because they represent the zero background radiation level before the incidence of depleted uranium over former Yugoslav territory in the Kosovo region in the spring of 1999. These measured absorbed dose exposures have to be compared with corresponding absorbed dose rates from the natural sources, such as soil having an

exposure of 18–93 nGy h⁻¹ (average 35 nGy h⁻¹) according to the UNSCEAR 2000 Report. This investigation has been primarily done in order to check the impact of coal-fired power plants on the background radiation level in its vicinity. According to the experimental results, influence was confirmed both qualitatively and quantitatively.

Buke, T. 2003. Dose assessment around the Yatagan coal-fired power plant due to gross alpha-radioactivity levels in flying ash. Journal of Radioanalytical and Nuclear Chemistry 256:323-328.

The gross alpha-radioactivity levels in ash wastes from the Yatagan coal-fired power plant have been measured, and radiation dose calculations have been carried out, by the computer code CAP88-PC, around the plant environment by using the maximum measured gross alpha-activity in the flying ash samples as a radioactive source. The results obtained from the calculations are under the dose limits of International Commission of Radiation Protection (ICRP) and have not any risk for public health around the plant environment.

Chauhan, R. P., and S. K. Chakarvarti. 2002. Radon activity and exhalation rates in coal fired thermal power plants. Indian Journal of Pure & Applied Physics 40:242-245.

Abstract: The combustion of coal in various thermal power plants results in the release of some natural radioactivity to the atmosphere through formation of flyash and bottom ash or slag. This consequently increases the radioactivity in soil, water and atmosphere around thermal power plants, As the radon in the atmosphere (indoor and outdoor), soil, ground water, oil and gas deposits contributes the largest fraction of the natural radiation dose to populations, enhanced interest exhibited in tracking its concentration is thus fundamental for radiation protection, health and hygiene point of view. In the present study, measurements of radon emanation from coal, flyash, soil and water samples collected from five thermal power plants of north India have been made using SSNTDs. The average values of radon emanation at equilibrium in the air volume of Cans above different samples varied from 433+/-28 Bq m⁽⁻³⁾ to 2086+/-36 Bq m⁽⁻³⁾; mass exhalation rates from 13 mBq kg⁽⁻¹⁾ hr⁽⁻¹⁾ to 168 mBq kg⁽⁻¹⁾ hr⁽⁻¹⁾ and surface exhalation rates from 302 mBq m⁽⁻²⁾ hr⁽⁻¹⁾ to 1482 mBq m⁽⁻²⁾ hr⁽⁻¹⁾. The measured average radon concentration in the atmosphere of the thermal power plants have been found to vary from 558+/-40 Bq m⁽⁻³⁾ to 682+/-60 Bq m⁽⁻³⁾. Based upon these values, the average annual effective doses have also been calculated.

Dai, L. J., H. Y. Wei, and L. Q. Wang. 2007. Spatial distribution and risk assessment of radionuclides in soils around a coal-fired power plant: A case study from the city of Baoji, China. Environmental Research 104:201-208.

Coal burning may enhance human exposure to the natural radionuclides that occur around coal-fired power plants (CFPP). In this study, the spatial distribution and hazard assessment of radionuclides found in soils around a CFPP were investigated using statistics, geostatistics, and geographic information system (GIS) techniques. The concentrations of Ra-226, Th-232, and K-40 in soils range from 12.54 to 40.18, 38.02 to 72.55, and 498.02 to 1126.98 Bq kg⁽⁻¹⁾, respectively. Ordinary kriging was carried out to map the spatial patterns of radionuclides, and disjunctive kriging was used to quantify the probability of radium equivalent activity (Ra-eq) higher than the threshold. The maps show that the spatial variability of the natural radionuclide concentrations in soils was apparent. The results of this study could provide valuable information for risk assessment of environmental pollution and decision support.

Flues, M., I. M. C. Camargo, P. S. C. Silva, and B. P. Mazzilli. 2006. Radioactivity of coal and ashes from Figueira coal power plant in Brazil. Journal of Radioanalytical and Nuclear Chemistry 270:597-602.

The Figueira coal-fired power plant (CFPP) is among the Brazilian CFPP which presents higher uranium concentration. Gamma-ray spectrometry was used to determine U-238, Ra-226, Pb-210, Th-232 and K-40 contents in pulverized coal, furnace bottom ash and fly ash samples. The natural radionuclide concentrations in pulverized coal ranged from 813 to 2609 Bq(-)kg(-1) for U series and from 22 to 40 Bq(-)kg(-1) for Th-232. The fly ash fraction gave concentrations ranging from 1442 to 14641 Bq(-)kg(-1), for uranium series. The same enrichment factor was observed for U-238, Ra-226 and Th-232. Only Pb-210 and stable Pb presented a high enrichment factor for the last stage filter fly ash. The concentration of the uranium series found in the ashes is close to the limit adopted by the Brazilian guideline (CNEN-NN-4.01).(22) Therefore, it is advisable to evaluate the environmental impact of the installation.

Flues, M., V. Moraes, and B. P. Mazzilli. 2002. The influence of a coal-fired power plant operation on radionuclide concentrations in soil. Journal of Environmental Radioactivity 63:285-294.

Abstract: Fifty-two soil samples in the vicinity of a coal-fired power plant (CFPP) in Figueira (Brazil) were analyzed. The radionuclide concentration for the uranium and thorium series in soils ranged from <9 to 282 Bq kg(-1). The range of K-40 concentration in soils varied from <59 to 412 Bq kg(-1). The CFPP (10 MWe) has been operating for 35 years and caused a small increment in natural radionuclide concentration in the surroundings. This technologically enhanced natural radioactivity (TENR) was mainly due to the uranium series (Th-234, Ra-226 and Pb-210) and was observable within the first kilometer from the power plant. The CFPP influence was only observed in the 0-25 cm soil horizon. The soil properties prevent the radionuclides of the U-238-series from reaching deeper soil profiles. The same behavior was observed for K-40 as well. No influence was observed for Th-232, which was found in low concentrations in the coal.

Mandal, A., and D. Sengupta. 2003. Radioelemental study of Kolaghat, thermal power plant, West Bengal, India: possible environmental hazards. Environmental Geology 44:180-186.

Abstract: Coal combustion in power plants in India produces large quantities of coal-related wastes, e.g. fly ash and bottom ash. Indian coals used in power stations are of high ash content, thus resulting in the generation of large amounts of fly ash (similar to 100 million tons/year). Combustion of coal results in enhanced concentration of most radionuclides found in waste materials. In the present work, an attempt has been made to assess the radiological impact of the Kolaghat thermal power plant in West Bengal, India. The fly ashes and coal from the power plant were analysed for U-238, Th-232 and K-40 by a NaI (TI)-based gamma-ray spectrometer. The results show that Ra-226, and Th-232 range from 81.9-126 and 132-169 Bq/kg in fly ash and 25-50 and 39-55 Bq/kg in coal. These results are high compared to those of other thermal power plants of India. Hence, the Kolaghat fly ash has a significant amount of radioactivity which, if not, properly disposed, will be a serious threat to the ambient environment.

Papp, Z., Z. Dezso, and S. Daroczy. 2002. Significant radioactive contamination of soil around a coal-fired thermal power plant. Journal of Environmental Radioactivity 59:191-205.

Abstract: Soil samples were collected around a coal-fired power plant from 81 different locations. Brown coal, unusually rich in uranium, is burnt in this plant that lies inside the confines of a small industrial town and has been operational since 1943. Activity concentrations of the radionuclides U-238, Ra-226, Th-232, Cs-137 and K-40 were determined in the samples. Considerably elevated concentrations of U-238 and Ra-226 have been found in most samples collected within the inhabited area. Concentrations of U-238 and Ra-226 in soil decreased

regularly with increasing depth at many locations, which can be explained by fly-ash fallout. Concentrations of U-238 and Ra-226 in the top (0-5 cm depth) layer of soil in public areas inside the town are 4.7 times higher, on average, than those in the uncontaminated deeper layers, which means there is about 108 Bq kg⁻¹ surplus activity concentration above the geological background. A high emanation rate of Rn-222 from the contaminated soil layers and significant disequilibrium between U-238 and Ra-226 activities in some kinds of samples have been found.

Papp, Z., and Z. Dezso. 2003. Estimate of the dose-increment due to outdoor exposure to gamma rays from uranium progeny deposited on the soil around a coal-fired power plant in Ajka town, Hungary. *Health Physics* 84:709-717.

Abstract: Brown coal unusually rich in uranium is burnt in a coal-fired power plant that lies inside the confines of a small industrial town named Ajka, Hungary, and has been operational since 1943. The U-238 (Ra-226) activity discharged to the atmosphere per unit electrical energy produced was about 330-400 GBq (GW y)⁻¹, which is 66-80 times more than that was estimated by UNSCEAR (1988) as a characteristic value for old type coal-fired power plants [5 GBq (GW y)⁻¹]. The objective of this study was the experimentally established assessment of the artificial increment in the dose from external exposure to gamma rays of terrestrial radionuclides outdoors. Soil samples were collected in and near Ajka from 81 locations. The samples were investigated by Ge(Li) gamma spectrometry. Considerably elevated concentrations of uranium and its progeny have been measured in most of the samples that were collected near to the plant. Concentrations of U-238 and Ra-226 in the top (0-5 cm depth) layer of undisturbed soil at public areas inside town were 4.7 times higher, on average, than those in the uncontaminated deeper layers. Dose rate in air (air kerma) from external exposure to terrestrial gamma rays outdoors at a height of 1 m and effective doses were estimated from the measured activity concentrations using some relevant literature data. The estimated artificial increment in the dose rate in air was, on average, 32.8, 10.3, and 102.1 nGy h⁻¹ at public areas, vegetable gardens, and backyards, respectively. The mean artificial increment in the annual per caput effective dose from external exposure to terrestrial radionuclides outdoors is 21.8 μ Sv y⁻¹. The collective dose commitment per unit energy generated from outdoor exposure to the deposited uranium progeny is about 8.0-9.1 person Sv (GW y)⁻¹, which is 67-76 times more than that evaluated by UNSCEAR (1988) for a typical "old" coal-fired power plant [0.12 person Sv (GW y)⁻¹]. Ajka is a suitable place for studying the dosimetric consequences of the utilization of coal for energy production experimentally.

Zeevaert, T., L. Sweeck, and H. Vanmarcke. 2006. The radiological impact from airborne routine discharges of a modern coal-fired power plant. *Journal of Environmental Radioactivity* 85:1-22.

Abstract: In this paper the radiological impact from the airborne routine discharges of a modern coal-fired power plant at Langerlo (Belgium) is evaluated. Therefore, the natural radioactivity contents of the coal and the fly-ash discharged were measured. With a bi-Gaussian plume model the maximum annual values of the Ra-226 concentration in the air (4.5 nBq/m³) and of the total deposition (1.5 mBq/m²) were calculated. The transfer of the radionuclides from air and soil to the biospheric media, exposing man, were modelled and the annual, individual, effective dose to the critical group, after an assumed life span of the power plant of 70 years, was evaluated at 0.05 μ Sv/y. This is several orders of magnitude lower than the annual doses for most power plants reported in the literature. The flue gas purification system, extended with a denitrification unit and a desulphurisation unit, was found to be the basis for this low impact.

3.2 Environmental effects, ecotoxicity, and biomonitoring

3.2.1 Trace metals

Adriano, D.C., Weber, J., Bolan, N.S., Paramasivam, S., Koo, B.J., and Sajwan, K.S. 2002. Effects of high rates of coal fly ash on soil, turfgrass, and groundwater quality. *Water Air and Soil Pollution* 139: 365-385.

Abstract: A field study (1993-1996) assessed the effects of applying unusually high rates of coal fly ash as a soil additive for the turf culture of centipedegrass (*Eremochloa ophiroides*). In addition, the quality of the soil and the underlying groundwater was evaluated. A Latin Square plot design was employed to include 0 (control, no ash applied), 280, 560, and 1120 Mg ha⁻¹ (mega gram ha⁻¹, i.e., tonne ha⁻¹) application rates of unweathered precipitator fly ash. The once applied fly ash was rototilled and allowed to weather for 8 months before seeding. Ash application significantly increased the concentrations in plant tissue of B, Mo, As, Be, Se, and Ba while also significantly reducing the concentrations of Mg, Mn, and Zn. The other elements measured (i.e., N, K, Ca, Cu, Fe, Ag, Cd, Cr, Hg, Ni, Pb, Sb, Tl, Na, and Al) were not affected. Of these elements Mg, Cu, and Mo concentrations in plant tissue increased with time while B and Se decreased temporally. The diminution of B and Na appears to be related to the leaching of soluble salts from ash-treated soils. Of all the elements measured, only Mn produced significant correlation ($p = 0.0001$) between the tissue and soil extractable concentrations. Ash treatment elevated the soil pH to as high as 6.45 with the enhanced effect occurring primarily in the 0-15 cm depth. Soil salinity increased with the application rate with the largest increases occurring in the initial year of application. However, by the second year, most of the soluble salts had already leached from the treatment zone into deeper depths, and by the fourth year, these salts had completely disappeared from the profile. The chemical composition of the underlying groundwater was not adversely impacted by the ash application. Plant tissue and groundwater data however, indicate that much higher rates of fly ash can be used on this type of land use where the plant species is tolerant of soil salinity and does not appear to bioaccumulate potentially toxic trace elements.

Al-Alawi, M.M., Batarseh, M.I., Carreras, H., Alawi, M., Jiries, A., and Charlesworth, S.M. 2007. Aleppo Pine bark as a biomonitor of atmospheric pollution in the arid environment of Jordan. *Clean Soil, Air, and Water* 35: 438-443.

Abstract: Monitoring of atmospheric pollution using Aleppo bark as a bioindicator was carried out in the industrial area surrounding the Al-Hussein thermal power station and the oil refinery at Al-Hashimiyeh town, Jordan. The concentrations of heavy metals (copper, lead, cadmium, manganese, cobalt, nickel, zinc, iron, and chromium) were analyzed in bark samples collected from the study area during July 2004. The results showed that high levels of heavy metals were found in tree bark samples retrieved from all studied sites compared with the remote reference site. This is, essentially, due to the fact that the oil refinery and the thermal power plant still use low-quality fuel oil from the by-products of oil refining. Automobile emissions are another source of pollution since the study area is located along a major heavy-traffic highway. It was found that the area around the study sites (Al-Hashimiyeh town, Zarqa) is polluted with high levels of heavy metals. Pine bark was found to be a suitable bioindicator of aerial fallout of heavy metals in arid regions.

Bellis, D.J., Satake, K., Tsunoda, K., and McLeod, C.W. 2003. Environmental monitoring of historical change in arsenic deposition with tree bark pockets. *Journal of Environmental Monitoring* 5: 671-674.

Abstract: ICP-MS analysis recorded historical change (c. 1846 to 2002) in the arsenic concentration of bark included within the trunks (tree bark pockets) of two Japanese oak trees (*Quercus crispula*), collected at an elevated location approximately 10 km from the Ashio copper mine and smelter, Japan. The arsenic concentration of the bark pockets was $0.016 \pm 0.003 \text{ ?g cm}^{-2}$ c. 1846 (n = 5) and rose 50-fold from c. 1875 to c. 1925, from approximately 0.01 to 0.5 ?g cm^{-2} . The rise coincided with increased copper production in Ashio from local sulfide ores, from 46 tons per year in 1877 to 16,500 tons per year in 1929. Following a decline in arsenic concentration and copper production, in particular during the Second World War, a second peak was observed c. 1970, corresponding to high levels of production from both local (6,000 tons per year) and imported (30,000 tons per year) ores, smelted from 1954. Compared to the local ores, the contribution of arsenic from imported ores appeared relatively low. Arsenic concentrations declined from c. 1970 to the present following the closure of the mine in 1974 and smelter in 1989, recording $0.058 \pm 0.040 \text{ ?g cm}^{-2}$ arsenic (n = 5) in surface bark collected in 2002. ***The coincident trends in arsenic concentration and copper production indicated that the bark pockets provided an effective record of historical change in atmospheric arsenic deposition.***

Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., McLaughlin, M.J., Bundschuh, J., and Panaullah, G. 2007. Arsenic in the environment: Biology and Chemistry. Science of the Total Environment. 379: 109-120.

Abstract: Arsenic (As) distribution and toxicology in the environment is a serious issue, with millions of individuals worldwide being affected by As toxicosis. Sources of As contamination are both natural and anthropogenic and the scale of contamination ranges from local to regional. There are many areas of research that are being actively pursued to address the As contamination problem. These include new methods of screening for As in the field, determining the epidemiology of As in humans, and identifying the risk of As uptake in agriculture. Remediation of As-affected water supplies is important and research includes assessing natural remediation potential as well as phytoremediation. Another area of active research is on the microbially mediated biogeochemical interactions of As in the environment. In 2005, a conference was convened to bring together scientists involved in many of the different areas of As research. In this paper, we present a synthesis of the As issues in the light of long-standing research and with regards to the new findings presented at this conference. This contribution provides a backdrop to the issues raised at the conference together with an overview of contemporary and historical issues of As contamination and health impacts.

Boone, R., and R. Westwood. 2006. An assessment of tree health and trace element accumulation near a coal-fired generating station, Manitoba, Canada. Environmental monitoring and assessment 121:151-172.

Abstract: A forest health assessment was performed in stands dominated by bur oak and trembling aspen to study the potential effects of airborne emissions from a 132 MW coal-fired station. Forty-two stands were sampled within a 16-km radius of the station for both foliar stress symptoms and trace element toxicology. The concentrations of tracer elements (As, Ba, Sr, and V) in the leaf litter were not spatially congruent with airborne emission deposition models (except Ba, which showed elevated levels immediately SE of the station), nor were they at phytotoxic levels. Elemental concentrations were significantly related to soil parameters including organic matter and texture. No patterns were found in forest health along directional or distance gradients from the generating station. Trembling aspen stands demonstrated little decline in general, but three of the 19 bur oak plots, all located on thin sandy soils developed on calcareous till, demonstrated branch dieback. In addition to poor soil conditions, two of these sites also had high water tables, and exhibited tree mortality. The bur oak decline did not appear to be related to emissions from the station, but is suspected to be a result of poor site quality, with urban

development as a confounding factor.

Carballeira, A., and Fernandez, J.A. 2002. Bioconcentration of metals in the moss *Scleropodium purum* in the area surrounding a power plant: A geotopographical predictive model for mercury. *Chemosphere* 47: 1041-1048.

Abstract: Samples of the moss *Scleropodium purum* collected in 1995 and 1997 were used to biomonitor the deposition of metals in the area surrounding a thermal power plant. Significantly higher levels of Cu ($p < 0.05$), Fe ($p < 0.01$), As and Hg ($p < 0.001$) were found in the 1997 samples than in the 1995 samples, due to changes in atmospheric conditions. The influence on bioconcentration of the orientation of the sampling sites relative to the source of emission was studied. It was found that the increase recorded in 1997 generally occurred in the sampling sites in the south east of the study area. Analysis of the effect of distance from the source of emission revealed that the increase in metal levels in 1997 took place close to the power station (10-30 km). Finally, multiple regression analysis was used to construct a model that related different topographical variables to the concentrations of Hg in moss. The model, constructed using the data collected in both sampling periods, included the orientation of the sampling sites relative to the source of emission as well as the height of sampling sites in 1995 and the distance from the emission point in 1997. The model allowed us to determine the extent of the area affected by deposition and to establish the magnitude of deposition.

Fernandez, J.A., Ederra, A., Nunez, E., Martinez-Abaigar, J., Infante, M., Heras, P., Elias, M.J., Mazimpaka, V., and Carballeira, A. 2002. Biomonitoring of metal deposition in northern Spain by moss analysis. *Science of the Total Environment* 300: 115-127.

Abstract: The results of the first survey carried out in northern Spain to determine atmospheric deposition of metals by analysis of terrestrial mosses, are described. Samples of different mosses, mainly *Hypnum cupressiforme* and *Scleropodium purum*, were collected from 134 sampling sites, between 1995 and 1996. Levels of Al, As, Cr, Cu, Fe, Hg, Ni, Pb and Zn, were determined by flame atomic absorption or atomic fluorescence spectrophotometry. Regression analysis was used to compare the capacity of the selected moss species to accumulate the elements, and intercalibration of accumulation in these species was carried out where necessary. Distribution maps were prepared to allow the zones most affected by metal deposition to be identified and to relate this to known sources of contamination: electricity power stations and other industries (e.g. Hg and Ni), edaphic contamination (e.g. Al and Cr) and road traffic (Pb). Background levels of metals in each species were also determined for the study area.

Garty, J., S. Tomer, T. Levin, and H. Lehr. 2003. Lichens as biomonitors around a coal-fired power station in Israel. *Environmental Research* 91:186-198.

Abstract: In the present study epiphytic lichens were applied as biomonitors of air pollution to determine the environmental impact of a coal-fired power station. Thalli of the lichen *Ramalina lacera* (With.) J.R. Laund. growing on carob twigs (*Ceratonia siliqua* L.) were collected with their substrate in July 2000 in a relatively unpolluted forest near HaZorea, Ramoth Menashe, Northeast Israel, and transplanted to 10 biomonitoring sites in the vicinity of the coal-fired power station Oroth Rabin near the town of Hadera. The lichens were retrieved in January 2001. We examined the following parameters of lichen vitality: (a) potential quantum yield of photosynthesis expressed as fluorescence ratio Fv/Fm, (b) stress-ethylene production, and (c) electric conductivity expressing integrity of cell membranes. Following an exposure of 7 months, the lichens were retrieved and physiological parameters and data of elemental content were analyzed comparatively. Electric conductivity values correlated positively with B, Fe, Mg, Mn, Na, Pb, S, Sn, and Ti content. Concentrations of stress-ethylene correlated positively with Al, Ba, Pb, S, and V content and negatively with Cu and Sn. Fv/Fm ratios correlated negatively with S

content. Some of the heavy metals reached lower levels than those reported in the relevant literature despite a wind regime that should have blown pollutants toward the biomonitoring sites.

Hassler, C. S., R. D. Chafin, M. B. Klinger, and M. R. Twiss. 2007. Application of the Biotic Ligand Model to Explain Potassium Interaction with Thallium Uptake and Toxicity to Plankton. *Environmental Toxicology and Chemistry* 26:1139-1145.

Abstract: Competitive interaction between Tl(I) and K was successfully predicted by the biotic ligand model (BLM) for the microalga *Chlorella* sp. (Chlorophyta; University of Toronto Culture Collection strain 522) during 96-h toxicity tests. Because of a greater affinity of Tl(I) ($\log K = 7.3-7.4$) as compared to K ($\log K = 5.3-6.3$) for biologically sensitive sites, an excess of 40- to 160-fold of K is required to suppress Tl(I) toxic effects on *Chlorella* sp., regardless of [Tl(I)] in solution. Similar excess of K is required to suppress Tl(I) toxicity to *Synechococcus leopoliensis* (Cyanobacteria; University of Texas Culture Collection strain 625) and *Brachionus calyciflorus* (Rotifera; strain AB-R1F). The mechanism for the mitigating effect of K on Tl(I) toxicity was investigated by measuring super(204)Tl(I) cellular uptake flux and efflux in *Chlorella* sp. Potassium shows a competitive effect on Tl(I) uptake fluxes that could be modeled using the BLM-derived stability constants and a Michaelis-Menten relationship. A strong Tl efflux dependent only on the cellular Tl concentration was measured. Although Tl efflux does not explain the effect of K on Tl(I) toxicity and uptake, it is responsible for a high turnover of the cellular Tl pool (intracellular half-life = 12-13.5 min). No effect of Na super(+), Mg super(2+), or Ca super(2+) was observed on Tl super(+) uptake, whereas the absence of trace metals (Cu, Co, Mo, Mn, Fe, and Zn) significantly increased Tl uptake and decreased the mitigating effect of K super(+). *The importance of K super(+) in determining the aquatic toxicity of Tl super(+) underscores the use of ambient K super(+) concentration in the establishment of Tl water-quality guidelines and the need to consider K in predicting biogeochemical fates of Tl in the aquatic environment.*

Heim, M., O. Wappelhorst, and B. Markert. 2002. Thallium in Terrestrial Environments-- Occurrence and Effects. *Ecotoxicology* 11:369-377.

Abstract: In this investigation thallium contents in soil and plants in the EuroRegion Neisse were analysed and the distribution determined. The median top-soil content is 0.5 mg/kg in the area investigated. In this low-contaminated area the moss *Pleurozium schreberi* contains 0.04-0.13 $\mu\text{g/g}$ and the moss *Polytrichum formosum* between 0.01 and 0.05 $\mu\text{g/g}$ Tl. The effects of thallium on man and the terrestrial environment were examined. In an epidemiological study a significant positive correlation was found between the thallium content of the two mosses and the incidence of disease of the circulatory system. The LOEC for thallium in bioassays with terrestrial invertebrates and plants in artificial soil ranged from 1 to 500 mg/kg, which indicates a toxicity of thallium up to 100 times higher than that of Cadmium.

Hopkins, W.A., DuRant, S.E., Staub, B.P., Rowe, C.L., and Jackson, B.P. 2006. Reproduction, embryonic development, and maternal transfer of contaminants in the amphibian *Gastrophryne carolinensis*. *Environmental Health Perspectives* 114: 661-666.

Abstract: Although many amphibian populations around the world are declining at alarming rates, the cause of most declines remains unknown. Environmental contamination is one of several factors implicated in declines and may have particularly important effects on sensitive developmental stages. Despite the severe effects of maternal transfer of contaminants on early development in other vertebrate lineages, no studies have examined the effects of maternal transfer of contaminants on reproduction or development in amphibians. *We examined maternal transfer of contaminants in eastern narrow-mouth toads (*Gastrophryne carolinensis*) collected from a reference site and near a coal-burning power plant. Adult toads inhabiting the*

industrial area transferred significant quantities of selenium and strontium to their eggs, but Se concentrations were most notable (up to 100 ug/g dry mass). Compared with the reference site, hatching success was reduced by 11% in clutches from the contaminated site. In surviving larvae, the frequency of developmental abnormalities and abnormal swimming was 55-58% higher in the contaminated site relative to the reference site. Craniofacial abnormalities were nearly an order of magnitude more prevalent in hatchlings from the contaminated site. When all developmental criteria were considered collectively, offspring from the contaminated site experienced 19% lower viability. Although there was no statistical relationship between the concentration of Se or Sr transferred to eggs and any measure of offspring viability, our study demonstrates that maternal transfer may be an important route of contaminant exposure in amphibians that has been overlooked.

Hsieh, C.-Y., M.-H. Tsai, D. K. Ryan, and O. C. Pancorbo. 2004. Toxicity of the 13 priority pollutant metals to *Vibrio fischeri* in the Microtox® chronic toxicity test. Science of the Total Environment 320:37-50.

Abstract: The Microtox® Acute Toxicity Test has been successfully used to measure the toxicity of metals and other pollutants at high concentrations (ppm) in selected environmental samples. However, metals and other toxicants are often found in much lower concentrations (ppb) in many municipal wastewaters and receiving waters. In order to assess the toxicity of these pollutants in these samples, a more sensitive toxicity assay is needed. *The Microtox® chronic toxicity test has been developed to measure the sublethal effect of toxicants over multiple generations of the test species, *Vibrio fischeri*. In this study, the toxicity of the 13 priority pollutant metals [i.e. As, Se, Cd, Cr (III and VI), Cu, Pb, Sb, Ag, Tl, Zn, Be, Hg and Ni] to *V. fischeri* was evaluated using the Microtox super([registered]) chronic toxicity test.* In this test, the inhibitory concentration (IC), lowest observable effect concentration (LOEC), and no observable effect concentration (NOEC) were obtained after 22-h of incubation at 27±1 not equal to , by comparing the light output of the control to that of the test sample. *Among the 13 priority pollutant metals, beryllium (Be) was found to be the most toxic in the test (LOEC=0.742-1.49 µg/l) while thallium (Tl) was the least toxic (LOEC=3840-15 300 µg/l).* The LOECs for copper (as Cu) and lead (Pb) in reagent (ASTM Type I) water were 6.78-13.6 µg/l and 626-1251 µg/l, respectively. The toxicity of copper sulfate (as Cu) in reagent water was shown and significantly reduced with the addition of natural organic matter (fulvic acid) or EDTA to the sample. *The LOEC values for the 13 priority pollutant metals in this test were comparable to or lower than those reported for commonly used aquatic toxicity tests, such as the *Ceriodaphnia dubia* assay.*

Kuzmick, D.M., Mitchelmore, C.L., Hopkins, W.A., and Rowe, C.L. 2007. Effects of coal combustion residues on survival, antioxidant potential, and genotoxicity resulting from full-lifecycle exposure of grass shrimp (*Palaemonetes pugio* Holthius). Science of the Total Environment 373: 420-430.

Abstract: Coal combustion residues (CCRs), largely derived from coal-fired electrical generation, are rich in numerous trace elements that have the potential to induce sublethal effects including oxidative stress, alterations in antioxidant status and DNA single strand breaks (SSB). CCRs are frequently discharged into natural and man-made aquatic systems. As the effects of CCRs have received relatively little attention in estuarine systems, the estuarine grass shrimp, *Palaemonetes pugio*, was chosen for this study. Grass shrimp were exposed in the laboratory to CCR-enriched sediments and food over a full life cycle. Survival to metamorphosis was significantly reduced in CCR-exposed larvae (17 ± 4 versus 70 ± 13% in the controls) but not in the juveniles or adults. The COMET assay, a general but sensitive assay for genotoxicity, was used to quantify DNA SSB in the adults. Total antioxidant potential was examined to assess the overall

antioxidant scavenging capacity of CCR-exposed and non-exposed adult grass shrimp. Grass shrimp exposed to CCR significantly accumulated selenium and cadmium compared to unexposed shrimp, although an inverse relationship was seen for mercury accumulation. Chronic CCR exposure caused DNA SSB in hepatopancreas cells, as evidenced by the significantly increased percent tail DNA, tail moment, and tail length as compared to reference shrimp. However, no significant difference was observed in total antioxidant potential. Our findings suggest that genotoxicity may be an important mode of toxicity of CCR, and that DNA SSB may serve as a useful biomarker of exposure and effect of this very common, complex waste stream.

Lan, C.-H., and T.-S. Lin. 2005. Acute toxicity of trivalent thallium compounds to *Daphnia magna*. *Ecotoxicology and environmental safety* 61:432-435.

Abstract: *Daphnia magna* was used to evaluate the aquatic toxicity of Tl(III) compounds including Tl(III) nitrate, Tl(III) chloride, and Tl(III) acetate. The results clearly show that Tl(III) is extremely toxic to daphnids. The 48-h LC₅₀ values for Tl(III) nitrate, Tl(III) chloride, and Tl(III) acetate are 24, 61, and 203 µg/L, respectively. Tl(III) is much more toxic than Tl(I) and many other metals such as Cd(II), Cu(II), and Ni(II); it is similar to the toxicity that of Hg(II). The formation of Tl(III)-complexes would significantly reduce Tl(III) toxicity.

Lin, T.-S., P. Meier, and J. Nriagu. 2005. Acute Toxicity of Thallium to *Daphnia magna* and *Ceriodaphnia dubia*. *Bulletin of environmental contamination and toxicology* 75: 350-355. Abstract not available.

Liu, G., Zhang, Y., Qi, C., Zheng, L., Chen, Y., and Peng, Z. 2007. Comparative on causes and accumulation of selenium in the tree-rings ambient high-selenium coal combustion area from Yutangba, Hubei, China. *Environmental Monitoring and Assessment* 133: 99-103.

Abstract: Toxic trace elements emitted during coal combustion are the main sources of air pollution. They are released into the atmosphere mainly in the forms of fine ash, smoke and flue, and thus adversely affect plant, animal and human health. Selenium is one of toxic and the most volatile in coal. Large amount of atmospheric emission of selenium, as well as selenium present and scrubber stockpiles in ash may create serious environmental problems. In the paper, on the basis of investigating the abundance and distribution of selenium in plant-rings during recent 20 years, the bioaccumulation of selenium is explained that selenium in plant, which were collected from the village of selenium-rich coal combustion, is much higher than that in plants collected away from the village of selenium-rich coal combustion. The main origins of selenium are selenium-rich coal combustion and high-selenium rock weathered. The selenium recycle by food chain and selenium will accumulate and redistribute in environments.

Palace, V.P., Baron, C., Evans, R.E., Holm, J., Kollar, S., Wautier, K., Werner, J., Siwik, P., Sterling, G., and Johnson, C.F. 2004. An assessment of the potential for selenium to impair reproduction in bull trout, *Salvelinus confluentus*, from an area of active coal mining. *Environmental Biology of Fishes* 70: 169-174.

Abstract: Selenium (Se) is an essential nutrient, but in higher concentrations can reduce recruitment in fish populations by increasing rates of deformities during early development. Recent work has identified elevated levels of Se in water and biota collected downstream from coal mining activity in Alberta's northeast slopes region. We also recently identified increased incidence of terata and edema in rainbow trout and brook trout with elevated tissue Se from this area. However, there is currently no information regarding the potential for Se to contribute to declining stocks of bull trout, a species of concern in the area. The present study provides an assessment of the potential for Se to contribute to low recruitment in bull trout downstream from coal mining activity. Non-destructive muscle biopsy sampling and a sensitive atomic fluorescence

analysis technique are used to determine Se. Results indicate that most bull trout (>90%) captured immediately downstream from coal mining activity in the region have concentrations of Se that would be expected to impair recruitment. Additional work is required to determine the extent of Se's contribution to low recruitment in bull trout.

Peter, A.L.J., and Viraraghavan, T. 2005. Thallium: A review of public health and environmental concerns. Environ. Int. 31: 493-501.

Abstract: Thallium (Tl) is a rare but widely dispersed element. All forms of thallium are soluble enough to be toxic to living organisms. Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc and has been responsible for many accidental, occupational, deliberate, and therapeutic poisonings since its discovery in 1861. Its chemical behavior resembles the heavy metals (lead, gold and silver) on the one hand and the alkali metals (K, Rb, Cs) on the other. It occurs almost exclusively in natural waters as monovalent thallos cation. The solubility of thallos compounds is relatively high so that monovalent thallium is readily transported through aqueous routes into the environment. *Tl can be transferred from soils to crops readily and accrues in food crops. The fascinating chemistry and high toxicity potential make thallium and its compounds of particular scientific interest and environmental concern.* Thallium was detected in base-metal mining effluents. The conventional removal of heavy metals from wastewater has little effect on thallium. In this review, various treatment options and removal technologies are enumerated in order to protect the environment from thallium toxicity.

Pinochet, H., I. De Gregori, and M. F. Cavieres. 2002. Selenium Concentration in Compartments of Aquatic Ecosystems in Central Chile. Bulletin of environmental contamination and toxicology 69:139-146.

Abstract: Selenium (Se) toxicity in aquatic ecosystems has been the subject of extensive studies during the last decade. Atmospheric emissions from coal power plants and copper refineries may lead to Se deposition into aquatic systems. Congenital malformations as well as cancer in birds and fish have been detected in lakes contaminated by Se (Ohlendorf et al. 1988 and 1990; Saiki et al. 1993; Welsh and Maughan 1994; Lemly 1995; Schultz and Hermanutz 1990; Hermanutz 1992; Lemly 1993). The fact that Se can bioaccumulate and biomagnify further increases the risk of ecotoxicity (Maier and Knight 1994).

Pokorny, B., A. Glinsek, and C. Ribaric-Lasnik. 2004. Roe deer antlers as a historical bioindicator of lead pollution in the Salek Valley, Slovenia. Journal of Atmospheric Chemistry 49:175-189.

Abstract: Antlers of different deer species are of particular importance for assessing temporal and/or spatial variations in environmental pollution with bone-seeking pollutants, such as Pb. Since antlers have a well-defined annual growth cycle, they accumulate Pb during a seasonally fixed time span, which provides natural standardisation of samples. Moreover, they are kept as trophies in well-dated collections enabling their use in historical studies. Considering these benefits, Pb levels were determined (by inductively coupled plasma mass spectrometry after the wet digestion of samples) in 116 antlers of roe deer (*Capreolus capreolus* L.), shot in the period 1961-2002 in the vicinity of the largest Slovene thermal power plant of Sostanj (STPP). Irrespective of the year of antler growth and the age of the animal analysed (no age-dependent influences were revealed), Pb levels ranged from 0.20 to 7.28 mg kg⁻¹ (mean: 1.32 +/- 10.19 mg kg⁻¹), with the highest contents in the oldest and the lowest contents in the most recent samples. Since the mid-1960s, lead pollution has continuously decreased in the study area; three very evident drops (after 1975, 1985 and 1995, respectively) indicate the combined effect of three different remediation measures as follows: construction of a remote heating system in the seventies; introduction of unleaded petrol in the late-1980s, and construction of clean-up devices

at the STPP in the late-1990s. The high positive correlation between the annual emissions from the STPP and the mean yearly Pb levels in antlers showed that roe deer antlers may be an useful tool for assessing temporal trends of ambient Pb pollution.

Policnik, H., F. Batic, and C. Ribaric Lasnik. 2004. Monitoring of short-term heavy metal deposition by accumulation in epiphytic lichens (*Hypogymnia physodes* (L.) Nyl.). *Journal of Atmospheric Chemistry* 49:223-230.

Many lichens are very sensitive to air pollution due to their symbiotic nature. However, they are generally less sensitive to toxic effects of trace elements; therefore they can be used as accumulator organisms for estimating concentrations of these elements in the environment. Heavy metal accumulation in lichens is a commonly used bioindication method for assessing heavy metal ambient levels. An active biomonitoring method was used for the determination of short-term accumulation of zinc, lead, arsenic and cadmium by epiphytic lichens transplanted at different localities in Slovenia polluted by heavy metals. The atomic absorption spectrophotometry method was used for the determination of heavy metal content in lichen thalli. The content of heavy metals in lichens collected in the background area with clean air (Rogla, Pohorje Mountains) was used as the reference value. Lichens were transplanted from Rogla using the branch transplantation technique for a period of 6 months in the surroundings of Slovenian thermal power plants (Velenje, Sostanj, Zavodnje, Veliki Vrh, Vnajarje, and Dobovec) and close to the lead and zinc ore smelter at Zerjav. The monthly accumulation of heavy metals was comparable within years at selected locations. Heavy metal pollution was the highest at Zerjav despite of remediation of lead and zinc ore smelter. The monthly accumulation of all four heavy metals was statistically significantly higher in lichens exposed at Zerjav than at other localities.

Ramamurthy, N., and K. Thillaivelavan. 2005. Determination of Trace Elements in Dairy Milk Collected from the Environment of Coal-fired power plant. *Journal of Environmental Science & Engineering* 47:53-58.

Abstract: In the present study the environmental effects on herbivores mammals in and around Coal-fired power plant were studied by collecting the various milk samples of Cow and Buffalo in clean polyethylene bottles. Milk samples collected at five different locations along the banks of the Paravanaru river in and around Neyveli area. These samples were prepared for trace metal determination. The concentration of trace metals (Cu, Zn, Ni, Cd, Cr, Mn, Co and Hg) were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Cold Vapour Atomic Absorption Spectrometry (CVAAS). It is observed that the samples contain greater amounts of trace metals than that in the unexposed areas. Obviously the milk samples are contaminated with these metals due to fly ash released in such environment.

Roe, J.H., Hopkins, W.A., Baionno, J.A., Staub, B.P., Rowe, C.L., and Jackson, B.P. 2004. Maternal transfer of selenium in Alligator mississippiensis nesting downstream from a coal-burning power plant. *Environmental Toxicology and Chemistry* 23: 1969-1972.

Abstract: Selenium (Se) is embryotoxic in many oviparous vertebrates, but little is known about maternal transfer of Se and its impact in reptiles. Over a four-year period, we collected three clutches of eggs of the American alligator (*Alligator mississippiensis*) from a single nest at a site contaminated with Se and compared egg and hatchling Se concentrations and clutch viability from this nest to nests downstream from the contaminated site (two clutches from two nests) and at a reference site (two clutches from two nests). Eggs and hatchlings from the nest at the Se-contaminated site and downstream nests had elevated Se concentrations (2.1-7.8 ppm) and lower viability (30-54%) compared to reference nests (1.4-2.3 ppm and 67-74% viability), but Se concentrations did not exceed reproductive toxicity thresholds established for other oviparous vertebrates. Selenium concentrations were higher in chorioallantoic membranes of eggs from Se-

contaminated sites, suggesting that this tissue may be useful as a nondestructive index of Se exposure for embryos of *A. mississippiensis*. Examination of these data suggests that further studies on uptake, accumulation, and reproductive success of crocodilian embryos exposed to excessive Se are warranted

Sharma, A. P., and B. D. Tripathi. 2008. Magnetic mapping of fly-ash pollution and heavy metals from soil samples around a point source in a dry tropical environment. *Environmental Monitoring and Assessment* 138:31-39.

Abstract: The Singrauli region in the southeastern part of Uttar Pradesh, India is one of the most polluted industrial sites of Asia. It encompasses 11 open cast coalmines and six thermal power stations that generate about 7,500 MW (about 10% of India's installed generation capacity) electricity. Thermal power plants represent the main source of pollution in this region, emitting six million tonnes of fly-ash per annum. Fly-ash is deposited on soils over a large area surrounding thermal power plants. Fly-ashes have high surface concentrations of several toxic elements (heavy metals) and high atmospheric mobility. Fly ash is produced through high-temperature combustion of fossil fuel rich in ferromagnetic minerals. These contaminants can be identified using rock-magnetic methods. Magnetic susceptibility is directly linked to the concentration of ferromagnetic minerals, primarily high values of magnetite. In this study, magnetic susceptibility of top soil samples collected from surrounding areas of a bituminous-coal-fired power plant were measured to identify areas of high emission levels and to chart the spatial distribution of airborne solid particles. Sites close to the power plant have shown higher values of susceptibility that decreases with increasing distance from the source. A significant correlation between magnetic susceptibility and heavy metal content in soils is found. A comparison of the spatial distribution of magnetic susceptibility with heavy-metal concentrations in soil samples suggests that magnetic measurements can be used as a rapid and inexpensive method for proxy mapping of air borne pollution due to industrial activity.

Stepanauskas, R., Glenn, T.C., Jagoe, C.H., Tuckfield, R.C., Lindell, A.H., and McArthur, J.V. 2005. Elevated microbial tolerance to metals and antibiotics in metal-contaminated industrial environments. *Environmental Science and Technology* 39: 3671-3678.

Abstract: To test the hypothesis that industrial metal contaminants select for microorganisms tolerant to unrelated agents, such as antibiotics, we analyzed metal and antibiotic tolerance patterns in microbial communities in the intake and discharge of ash settling basins (ASBs) of three coal-fired power plants. High-throughput flow-cytometric analyses using cell viability probes were employed to determine tolerances of entire bacterioplankton communities, avoiding bias toward culturable versus nonculturable bacteria. We found that bacterioplankton collected in ASB discharges were significantly more tolerant to metal and antibiotic exposures than bacterioplankton collected in ASB intakes. Optical properties of microorganisms collected in ASB discharges indicated no defensive physiological adaptations such as formation of resting stages or excessive production of exopolymers. Thus, it is likely that the elevated frequency of metal and antibiotic tolerances in bacterioplankton in ASB discharges were caused by shifts in microbial community composition, resulting from the selective pressure imposed by elevated metal concentrations or organic toxicants present in ASBs.

Taylor, T.P., Ding, M., Ehler, D.S., Foreman, T.M., Kaszuba, J.P., and Sauer, N.N. 2003. Beryllium in the environment: A review. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 38: 439-469.

Abstract: Beryllium is an important industrial metal because of its unusual material properties: it is lighter than aluminum and six times stronger than steel. Often alloyed with other metals such as copper, beryllium is a key component of materials used in the aerospace and electronics

industries. Beryllium has a small neutron cross-section, which makes it useful in the production of nuclear weapons and in sealed neutron sources. Unfortunately, beryllium is one of the most toxic elements in the periodic table. It is responsible for the often-fatal lung disease, Chronic Beryllium Disease (CBD) or berylliosis, and is listed as a Class A EPA carcinogen. ***Coal-fired power plants***, industrial manufacturing and nuclear weapons production and disposal operations have released beryllium to the environment. This contamination has the potential to expose workers and the public to beryllium. ***Despite the increasing use of beryllium in industry, there is surprisingly little published information about beryllium fate and transport in the environment. This information is crucial for the development of strategies that limit worker and public exposure. This review summarizes the current understanding of beryllium health hazards, current regulatory mandates, environmental chemistry, geochemistry and environmental contamination.***

Uyar, G., M. Oren, Y. Yildirim, and M. Ince. 2007. Mosses as indicators of atmospheric heavy metal deposition around a coal-fired power plant in Turkey. *Fresenius Environmental Bulletin* 16:182-192.

Abstract: This study was carried out from May 2003 to October 2004 in the vicinity of Catalagzi coal-fired power plant (CATES) located in Zonguldak, North-West Turkey, in order to investigate atmospheric heavy metal depositions by sampling and analysing Pleurocarp mosses as biomonitoring plants. Initially, ISC-ST (Industrial Source Complex-Short Term) dispersion models were used to determine theoretically the most polluted sites of CATES. After the modelling, sampling was performed in these theoretically determined grids. Samples were analyzed using graphite-furnace atomic absorption spectrometry (AAS) after wet digestion. In the region, the general order of heavy metal content in samples of mosses was determined to be as follows: Fe>Pb>Ni>Cr>Cu>Co>As. Background mean levels of the metals studied, except Cu, were determined and found to be higher than that of European background. The results are also presented in the form of thematic maps using the Geographic Information System (GIS).

Wayland, M., Kneteman, J., and Crosley, R. 2006. The American dipper as a bioindicator of selenium contamination in a coal mine-affected stream in West-Central Alberta, Canada. *Environmental Monitoring and Assessment* 123: 285-298.

Abstract: Elevated levels of selenium have been found in water and aquatic biota downstream from two open-pit coal mines in the Rocky Mountain foothills of Alberta. Birds are particularly sensitive to excessive dietary selenium. However, there is relatively little information on selenium accumulation in birds' eggs on fast-flowing mountain streams. We determined levels of selenium in water samples, caddisfly larvae and eggs of American dippers (*Cinclus mexicanus*) nesting on the Gregg River, downstream from the mines, and on reference streams in the same general vicinity. Selenium levels (mean, 95% confidence limits) in water samples and caddisflies collected from sites near dipper nests on the Gregg River (water: 4.26, 1.90-9.56 $\mu\text{g L}^{-1}$; caddisflies: 8.43, 7.51-9.46 $\mu\text{g g dry wt}^{-1}$) were greater than those collected from sites near nests on reference rivers (water: 0.38, 0.21-0.71 $\mu\text{g L}^{-1}$; caddisflies: 4.65, 4.35-4.97 $\mu\text{g g dry wt}^{-1}$). The mean (\pm 1SE) selenium level in dipper eggs from the Gregg River (6.3 \pm 0.2 $\mu\text{g g}^{-1}$ dry wt) was significantly higher than it was in eggs from reference streams (4.9 \pm 0.2 $\mu\text{g g}^{-1}$ dry wt). Concentrations of selenium in eggs were significantly correlated with those in water samples ($r = 0.45$). The maximum selenium level in eggs from the Gregg River (9.0 $\mu\text{g g}^{-1}$) may have been high enough to warrant concern from an ecotoxicological perspective. The American dipper can serve as a useful bioindicator of selenium contamination in mountainous, lotic ecosystems.

Xu, W.D., Zeng, R.S., Ye, D.N., and Querol, X. 2005. Distributions and environmental impacts of selenium in wastes of coal from a power plant. *Huanjing Kexue* 26: 64-68.

Abstract: Samples of coals, fly ashes, slags and tiny fly ashes with different sizes, collected from a large power plant, were studied. It shows that Se tends not to be enriched in coarse fly ash and slag, but to be enriched in fine fly ashes especially in fine fly ash with size >19.0 µm. This kind of distribution is shaped by: (1) volatility and organic-occurrence of Se in coal; (2) residence time in flue gases; (3) morphology of particles [holes on the surface of particles (> 19.0 µm) may adsorb more Se]. Sequence leaching test shows that Se is mainly organic-bonded (69.7%) in coal. Mass balance calculation of burned coal indicates that 16.5% of Se in coal may be disposed into air directly. The environmental impacts of Se in fine fly ashes can be ignored because of its small proportion and distributional character (mainly in particles with sizes >19.0 µm). Se in slag may cause little environmental impacts. Se in coarse fly ash is partially mobile and may be used to benefit the soil which is lack of Se.

Yenisoy-Karakas, S., and S. G. Tuncel. 2006. Geographic patterns of elemental deposition in the Aegean region of Turkey indicated by the lichen, *Xanthoria parietina* (L.) Th. Fr. *Science of the Total Environment* 329:43-60.

Abstract: Lichen samples from different parts of the world have been known to accumulate elements to a greater degree than higher plants, if they are exposed to these elements from the atmosphere or from water and sediments. It has been hypothesized that lichens can be used to monitor air pollution around point and area emission sources. Local variation (variation in substrate, age and morphology of lichen samples) of element concentrations would not be large enough to affect the concentration patterns in large areas. We tested this hypothesis in the Aegean region of Turkey, which is very urbanized and industrialized. No such study has been conducted before in this part of the country. A total of 234 samples of the lichen *Xanthoria parietina* were collected from a 51 800-km² area. Samples were washed and analyzed by INAA and ICP-AES for 35 elements. The range of the concentrations for most of the elements on a local scale was an order of magnitude lower than for the element concentrations on a regional scale. The mean local coefficient of variance (CV) was found to be 15, providing that the local variation did not affect the concentration of elements in the sampling region. According to cluster analysis, 8 (As, Hg, Pb, Sb, Fe, Mn, Na and K) elements are indicative of important local pollution locations and their zone of impact in the region. By mapping the concentrations of eight indicative elements in lichen *Xanthoria parietina* of the Aegean region, it was possible to relate deposition to the existence of known sources of pollution in certain areas. Location of pollution sources such as iron-steel plants, and coal burning in the cities, industrial activity and two important coal-fired power plants generally corresponded with locations of highest element accumulations in the lichens.

3.2.2 Polycyclic aromatic hydrocarbons

Gourlay, C., C. Miede, A. Noir, C. Ravelet, J. Garric, and J.-M. Mouchel. 2005. How accurately do semi-permeable membrane devices measure the bioavailability of polycyclic aromatic hydrocarbons to *Daphnia magna*? *Chemosphere* 61:1734-1739.

Abstract: Semi-permeable membrane devices (SPMDs) are passive samplers that have been designed to sample the bioavailable fractions of hydrophobic organic compounds in aquatic ecosystems. This study aims at evaluating the ability for SPMD to sample polycyclic aromatic hydrocarbons (fluoranthene, pyrene and benzo[a]pyrene) that are actually bioavailable to *Daphnia magna*. For that purpose, the SPMD-available fraction and the bioavailable fraction to *D. magna* are compared in controlled media with Dissolved Organic Matters (DOMs) from various origins and at different concentrations. The presence of all but one DOM reduces the accumulation of PAHs in SPMD or in *D. magna*. Moreover, this comparative laboratory study shows that in 10 cases on 13, the SPMD-available fraction is close to the available fraction to *D. magna*. When significant differences are observed between SPMD-available and bioavailable fractions, they

remain less than 50% at DOM concentrations below 10mg/l DOC, which corresponds to a maximum DOC concentration usually found in temperate rivers. This study confirms the suitability of the SPMD technique to monitor readily bioavailable hydrophobic contaminants in aquatic environments containing DOM from various origins and characteristics.

Lampi, M. A., J. Gurska, K. I. C. McDonald, F. Xie, X.-D. Huang, D. G. Dixon, and B. M. Greenberg. 2006. Photoinduced Toxicity of Polycyclic Aromatic Hydrocarbons to *Daphnia Magna*: Ultraviolet-Mediated Effects and the Toxicity of Polycyclic Aromatic Hydrocarbon Photoproducts. *Environmental Toxicology and Chemistry* 25:1079-1087.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants known for their photoinduced toxicity. This toxicity may occur through two mechanisms: Photosensitization, and photomodification. Photosensitization generally leads to the production of singlet oxygen, a reactive oxygen species that is highly damaging to biological molecules. Photomodification of PAHs, usually via oxidation, results in the formation of new compounds and can occur under environmentally relevant levels of actinic radiation. The toxicities of 16 intact PAHs to *Daphnia magna* were assessed under two ultraviolet radiation conditions. The toxicity of intact PAHs generally increased in the presence of full-spectrum simulated solar radiation relative to that in the presence of visible light plus ultraviolet A only. Despite the knowledge of a bipartite mechanism of phototoxicity that includes photosensitization and photomodification, few studies have examined the effects of PAH photoproducts on animals. To expand the existing data, 14 PAH photoproducts (oxy-PAHs) also were assayed, most of which were highly toxic without further photomodification. Two photoproducts of benzo[a]pyrene, 1,6- and 3,6-benzo[a]pyrenequinone, were the most toxic compounds tested, followed closely by benz[a]anthraquinone. Each of these three compounds had a median effective concentration in the low nanomolar range. The data presented highlight the effects of ultraviolet radiation on mediating PAH toxicity and the need to analyze absorption spectra of contaminants in the prediction of photoinduced toxicity. *The importance of the role of photomodification also is stressed, because several oxy-PAHs, an unregulated group of contaminants, were highly toxic to D. magna, a key bioindicator species in aquatic ecosystems.*

Landrum, P.F., Robinson, S.D., Gossiaux, D.C., You, J., Lydy, M.J., Mitra, S., and Ten Hulscher, T.E.M. 2007. Predicting bioavailability of sediment-associated organic contaminants for *Diporeia* spp. and oligochaetes. *Environ. Sci. Technol.* 41: 6442-6447.

Abstract: Biota-sediment accumulation factors (BSAF) were calculated for *Diporeia* spp. and oligochaete worms exposed to polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) from field-collected sediment. These data were compared to the contaminant fraction extracted from sediment with Tenax resin using a 24 h extraction. A previous laboratory study suggested a linear relationship between log BSAF and the contaminant fraction rapidly desorbed from sediment. However, the BSAF data in our study did not fit this relationship. Better predictive regressions for both PCBs and PAHs were found when the log of the lipid-normalized organism contaminant concentrations were plotted against the log of the Tenax-extracted organic carbon-normalized sediment contaminant concentration. Regression lines for the two species had the same slope, but the *Diporeia* intercept was 2.3 times larger. When adjusted for a 6 h Tenax extraction, based on a regression between 6 and 24 h Tenax extractions, data from this study and two other studies that included multiple oligochaete species fit a single predictive regression. The exception included some PAHs that fell below the regression line. Thus, a single relationship generally predicted bioaccumulation across sediments, compound classes, oligochaete species, and among laboratories.

Lehndorff, E., and L. Schwark. 2004. Biomonitoring of air quality in the Cologne

Conurbation using pine needles as a passive sampler; Part II: polycyclic aromatic hydrocarbons (PAH). Atmospheric Environment 38:3793-3808.

Abstract: Emissions from fossil fuel combustion pose a serious threat to public health and impose the need for an improved monitoring of polycyclic aromatic hydrocarbons (PAH), a major class of persistent organic pollutants. For this purpose, utilization of evergreen conifers offers significant biomonitoring potential. In part I of this series we inspected the load of combustion derived magnetic particles in pine needles from 43 locations of the Cologne Conurbation, Germany; we here report the corresponding PAH concentrations and distribution patterns. Concentrations (dry weight) of summed 3-6-ring PAH range between 51 and 410 ng g super(-1) with a median of 123.8 ng g super(-1); thus being in agreement with other urban studies. Phenanthrene was the dominating PAH with median concentrations of 47 ng g super(-1) followed by fluoranthene and pyrene at 22 and 13 ng g super(-1), respectively. The major proportion of PAH was attributed to traffic sources, with minor contribution from power plant, domestic heating, industrial, and vegetation burn emissions. Significant differences between major and minor roads were not observed indicating a thorough mixing of PAH-loaded air masses in the Cologne Conurbation. Needles in inner city parks gave much higher PAH concentrations than those in suburban green areas. Although distribution patterns of PAH were variable a PAH source reconciliation based on isomer compositions is difficult, due to thorough mixing of air masses and associated loss of source specificity. Ambient air monitoring in urban areas based on persistent organic pollutant load of vegetation is a feasible and cost effective way of controlling environmental quality.

Mastral, A.M., Callen, M.S., Garcia, T., pez, J.M., and Maranon, E. 2002. Relationship between ecotoxicity and PAH content in coal combustion waste samples. Polycyclic Aromatic Compounds 22: 571-578.

Abstract: Three different series of combustion samples (from the ash pan, samples C; from the particulate matter trapped on cyclone, samples PM; and from the finest particulate matter, samples M) have been analyzed looking for any relationship between their PAH content and their ecotoxicity. PAH content was analyzed by synchronous fluorescence spectroscopy. Ecotoxicity of the combustion samples was determined by using the Photobacterium phosphoreum test to assess their toxicity through an ecotoxicity assay. Results obtained are shown and discussed in relation to the PAH content of the samples.

Moermond, C. T. A., I. Roessink, M. T. O. Jonker, T. Meijer, and A. A. Koelmans. 2007. Impact of Polychlorinated Biphenyl and Polycyclic Aromatic Hydrocarbon Sequestration in Sediment On Bioaccumulation in Aquatic Food Webs. Environmental Toxicology and Chemistry 26:607-615.

Abstract: It is not clear whether sequestration or aging of organic chemicals like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) limits accumulation in higher levels of aquatic food chains. Therefore, the effect of aging on accumulation was studied in 1-m super(3) model ecosystems that mimicked fish-dominated, macrophyte-dominated, and fish- and macrophyte- dominated shallow lakes. Also treatments without fish and macrophytes were included. General characteristics, biomasses, total (Soxhlet-extractable), and labile (6-h Tenax-extractable) PCB and PAH concentrations in sediment and biota were monitored over time. Accumulation data for PCB 28, PCB 149, and fluoranthene (native to the sediment taken from the field) were compared to those for spiked analogues PCB 29, PCB 155, and fluoranthene-d sub(10). Labile fractions for spiked compounds were higher than for their native analogues and decreased over time, suggesting sequestration in the sediment. In the majority of cases, 6-h Tenax-extractable concentrations correlated better with concentrations in biota than Soxhlet-extractable concentrations. Ecosystem structure affected food web accumulation, but replicate

variability was too high to detect clear treatment effects. *Differences in accumulation between spiked compounds and their native analogues indicated an effect of aging for invertebrates, macrophytes, and benthivorous fish. Thus, aging may translate directly into reduced uptake at higher trophic levels.*

Shailaja, M. S., R. Rajamanickam, and S. Wahidulla. 2006. Formation of Genotoxic Nitro-PAH Compounds in Fish Exposed to Ambient Nitrite and PAH. Toxicological Sciences 91:440-447.

Abstract: Mutagenic nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) have been known to arise in the environment through direct emissions from combustion sources and nitration of PAHs, primarily in the atmosphere. Here, we report the formation of nitro-PAH compounds in fish contaminated with PAH and exposed to nitrite [Formula: see text] in the ambient water. Electrospray ionization mass spectrometric analysis of the bile of the euryhaline fish *Oreochromis mossambicus* exposed simultaneously to field-relevant, sublethal concentrations of phenanthrene (1 μ g/g) and [Formula: see text] (1 μ M) and collision-induced dissociation of selected ions revealed the presence of two strongly genotoxic nitro-PAH metabolites, namely phenanthrene-6-nitro-1,2-dihydrodiol-3,4-epoxide (mass/charge [m/z] 273) and dihydrodihydroxy acetylaminophenanthrene (m/z 359). These two metabolite peaks present only in the bile of fish exposed simultaneously to phenanthrene and [Formula: see text] constituted, respectively, about 3.1 and 2.7% of the highest peak among the putative unconjugated phenanthrene metabolites in the mass spectrum. The presence of the oxidized phenanthrene metabolite dihydroxyphenanthrene (m/z 233) in fish exposed to phenanthrene alone as well as phenanthrene plus [Formula: see text] suggested that oxidation of phenanthrene precedes nitration in the sequence of reactions leading to the formation of the observed nitrophenanthrene metabolites. However, the route of PAH administration seems to determine the nature of metabolites formed. Nearly 92% of the hepatic cells of the fish exposed to phenanthrene in the presence of [Formula: see text] were found to have suffered extensive DNA fragmentation on comet assay.

Simcik M.F. & Offenberg J.H. 2006. Polycyclic aromatic hydrocarbons in the Great Lakes. In Handbook of Environmental Chemistry, Volume 5: Water Pollution, p. 307-353.

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are produced during the incomplete combustion of organic material. They can also be produced through natural, non-combustion processes, and may be present in uncombusted petroleum. Uncombusted petroleum can be a direct source to the waters of the Great Lakes, but combustion sources discharge PAHs into the coastal atmosphere. Atmospheric deposition of combustion related PAHs seems to be the dominant source to the Great Lakes, except in nearshore areas where point sources can be significant. Once airborne, PAHs partition in the atmosphere between the gas and particle phases and can undergo long-range transport. During transport, PAHs can be degraded or modified by photochemical reactions. Both the original PAH species and their degradation products can be washed out of the atmosphere by wet and dry deposition, air-water exchange and air-terrestrial exchange. Once in an aquatic system, PAHs partition between the dissolved and particle phases. In general, PAHs are particle reactive and settle out in sediments. PAH contamination of Great Lakes sediments are higher in the nearshore regions where ports, harbors, and urban/industrial areas are the densest. In the open lake area, sediment concentrations are rather uniform, with Lake Superior having slightly less PAHs in its surficial sediments. That portion of the PAHs that does not partition to particles can bioaccumulate in the lipid reserves of organisms. PAHs accumulated in an organism may be metabolized to more toxic by-products or exert toxicity in its original form. When combined with ultraviolet radiation this toxicity is greatly enhanced. In coastal areas where concentrations can be quite high, PAHs can be toxic to all forms of aquatic life during at least part of their life cycle. PAHs are expected to remain an ecological threat to the Great Lakes

well into the future. The threat may even increase with the increasing combustion needed for the increasing population centers and greater transportation needs. Of particular concern is the short-term increase in PAH concentrations that can result from the dredging of ports and harbors where highly contaminated sediments have been buried.

Stabenau, E. K., D. T. Giczewski, and K. Y. Maillacheruvu. 2006. Uptake and Elimination of Naphthalene from Liver, Lung, and Muscle Tissue in the Leopard frog (*Rana pipiens*). *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering* 41:1449-1461.

Abstract: The effects of a 0-12-hour naphthalene exposure on pulmonary CO sub(2) excretion and bioaccumulation in the leopard frog, *Rana pipiens*, were investigated. The data showed that naphthalene transport occurred from the aqueous phase into the frog tissue. The first-order rate constant (k in day super(-1)) for the entry of naphthalene from the water into the frog was 0.079 plus or minus 0.007 (k plus or minus 95% C.I.). Bioaccumulation of naphthalene was measured in liver, lung, and thigh muscle tissue. Exposure to naphthalene caused a significant reduction in pulmonary CO sub(2) excretion, particularly following the first 30 minutes of exposure. Pulmonary CO sub(2) excretion returned to baseline levels after 8 hours of exposure, indicating that some degree of acclimation had occurred. Depuration experiments were used to monitor recovery from naphthalene exposure. Recovery of CO sub(2) excretion was evident following 2 hours of depuration and complete elimination of naphthalene from tissues occurred after 3 hours. The data indicate that accumulated polycyclic aromatic hydrocarbons (PAHs) may alter normal physiologic functions such as gas exchange. *Since amphibians, such as frogs, are one of the first organisms to come into contact with contaminated water and sediments, the information in this study suggests that this species may be used to assess bioaccumulation and toxicity of PAHs in ecosystems.*

Verrhiest, G. J., B. Clement, B. Volat, B. Montuelle, and Y. Perrodin. 2002. Interactions between a polycyclic aromatic hydrocarbon mixture and the microbial communities in a natural freshwater sediment. *Chemosphere* 46:187-196.

The toxicity of a polycyclic aromatic hydrocarbon (PAH) mixture was assessed on the indigenous microbial communities of a natural freshwater sediment. The fate and effects of the PAH mixture (phenanthrene, fluoranthene and benzo(k)fluoranthene) were studied over 28 days. Bacterial communities were described by bacterial counts (total bacterial and viable bacteria), and by some hydrolytic enzyme activities (beta -glucosidase and leucine-aminopeptidase), PAH concentrations were measured in the overlying waters and in the sediments. No effect of PAH was detected at 30 mg/kg for all bacterial parameters. At 300 mg/kg, the quantity of total bacteria and the proportion of viable bacteria markedly decreased, compared to the control (0 mg PAH/kg). At 300 mg/kg, an increase of the beta -glucosidase activity and a decrease of the leucine-aminopeptidase activity were observed. For all treatments, the benzo(k)fluoranthene concentration in the sediment was stable over 28 days whereas, in the same time, only 3-6% of the initial concentrations of phenanthrene and fluoranthene remained. This study shows that (1) PAH induce perturbations of sediment microbial communities in terms of density and metabolism (but not always as an inhibition), (2) indigenous bacteria of sediments might be used for toxicity assessment of specific organic pollutants, (3) native microorganisms of sediment seem to have a high capacity for PAH degradation, depending on the physico-chemical properties and the bioavailability of the substance encountered.

Zhang, H.Y., Liu, G.J., Xue, J., and Wang, X.M. 2005. Study of polycyclic aromatic hydrocarbons (PAHs) and its environmental impact in coal and coal combusting products. *Meitan Xuebao/Journal of the China Coal Society* 30: 97-101.

Abstract: The relationship of the content, species and forming mechanism of polycyclic aromatic hydrocarbons in raw coal and the coal forming environment, coal rank and ingredient were studied. The species, rule of occurrence, change of distribution of polycyclic aromatic hydrocarbons and their relation to ingredient and combustion conditions were particular discussed. The conditions of combustion to the total amount of PAHs and its releasing characters were analyzed. The release of low ring PAHs and its environmental impact were discussed. On the basis of research, the problems of the research of PAHs in coal and directions of future research were analyzed.

3.2.3 Dioxins and furans

Bochentin, I., Hanari, N., Orlikowska, A., Wyrzykowska, B., Horii, Y., Yamashita, N., and Falandysz, J. 2007. Polychlorinated dibenzo-p-dioxins (PCDDs) and -furans (PCDFs) in pine needles of Poland. Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering 42: 1969-1978.

Abstract: There is scarcity of data on sources, environmental diffusion and concentrations of PCDD/Fs and dioxin-like compounds in the Eastern and Central Europe. A study has been conducted using pine needles as passive matrix on diffusion of airborne 17 highly toxic PCDD/Fs in Poland. The target compounds were quantified using isotope dilution and HRGC/HRMS. One-year-old pine needles collected from 25 spatially distant sites in October 2002 revealed a relatively very low aerial emission and degree of pollution with PCDD/Fs. The most toxic 2,3,7,8-TCDD was absent (< 0.44 pg/g) in fresh pine needles sampled and absent at all sites were also 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD and 1,2,3,7,8,9-HxCDF (< 0.27 pg/g). OCDD at concentration range from 1.4 to 34 pg/g and OCDF at range from 1.5 to 41 pg/g were the only among 17 compounds found at each site, and next in prevalence was 1,2,3,4,7,8,9-HpCDF (total range from < 0.41 to 8.1 pg/g), which was found at 24 off 25 sites. The I-TEQ transformed concentrations of PCDD/Fs of pine needles of Poland ranged from < 0.01 to 1.28 pg/g ww or from 0.01 to 3.18 pg/g dw. The CDD/F homologue groups and congeners profiles of pine needles with highly dominant HpCDD/F and OCDD/F found in this survey suggest on lack of significant other than coal/lignite/wood combustion sources of PCDD/Fs diffusion to ambient air in Poland.

3.2.4 Fluoride

Franzaring, J., Hrenn, H., Schumm, C., Klumpp, A., and Fangmeier, A. 2006. Environmental monitoring of fluoride emissions using precipitation, dust, plant and soil samples. Environmental Pollution 144: 158-165.

Abstract: A pollution gradient was observed in precipitation, plants and soils sampled at different locations around a fluoride producing chemical plant in Germany. In all samples the influence of emissions was discernible up to a distance of 500 m from the plant. *However, fluoride concentrations in plant bioindicators (leaves of birch and black berry) and in bulk precipitation showed a more pronounced relationship with the distance from the source than fluoride concentrations in soil.* Vegetables sampled in the vicinity of the plant also had elevated concentrations of fluoride, but only the consumption of larger quantities of this material would lead to exceedances of recommended daily F-intake. The present study did not indicate the existence of low phytotoxicity thresholds for fluoride in the plant species used in the study. *Even at very high fluoride concentrations in leaf tissue (963 ppm) plants did not show injury due to HF.* Dust sampling downwind of the chemical plant confirmed that particulate fluoride was of minor importance in the study area.

Kierdorf, U., and H. Kierdorf. 2002. Assessing Regional Variation of Environmental Fluoride Concentrations in Western Germany by Analysis of Antler Fluoride Content in Roe Deer (*Capreolus capreolus*). Archives of Environmental Contamination and Toxicology 42:99-104.

Abstract: To assess regional variation in ambient fluoride levels, we analyzed the fluoride content of 188 antlers of roe deer (*Capreolus capreolus*) killed between 1990 and 1999 in 14 areas of the federal state of North Rhine-Westphalia, Germany. Individual antler fluoride concentrations ranged between 113 and 11,995 mg F super(-)/kg bone ash, and sample means differed significantly ($p < 0.0001$) among the study areas. Low average concentrations (geometric means of 262 and 277 mg F super(-)/kg bone ash, respectively) were found in antler samples from two control areas, located quite remote to major fluoride emission sources. The highest geometric mean fluoride content (1,677 mg F super(-)/kg bone ash) was recorded for an antler sample from a study area exposed to fluoride emissions from an aluminium smelter and two mineral coal-fired power stations. In eight antlers obtained from roe deer living in the direct vicinity of the aluminium smelter, fluoride values ranged between 2,067 and 11,995 mg F super(-)/kg bone ash, thereby demonstrating the strong impact of this emission source on its surroundings. The study showed that by analyzing antler fluoride concentrations, large-scale surveys of environmental contamination by fluoride can be performed in a standardized and cost-effective way in areas inhabited by deer. Due to its rather narrow home range, abundance, and high adaptability, the roe deer is particularly suited for such studies.

Kierdorf, U., and Kierdorf, H. 2005. Antlers as biomonitors of environmental pollution by lead and fluoride: A review. European Journal of Wildlife Research 51: 137-150.

Abstract: Antlers are periodically cast and re-grown cranial appendages of deer. Both endochondral and intramembranous ossification are involved in the formation of antler bone. After velvet shedding, antlers are completely bony structures which are referred to as hard antlers. Growing antlers accumulate substances with an affinity to mineralized tissues. Among these substances are lead and fluoride. Due to the seasonally limited life span of antlers, the concentrations of lead and fluoride in hard antlers reflect uptake by the forming bone during a defined, species-specific period of some months. Antlers can thus be viewed as "naturally standardized" environmental samples that are well suited as biomonitors of environmental pollution by bone-seeking contaminants. Because hard antlers are collected by hunters as trophies and kept in private or public collections, material for study can be obtained rather easily. So far, lead concentrations in hard antlers have been reported only from Europe, whereas data for fluoride are available from both Europe and North America. Some studies compared contaminant concentrations in antlers from different regions, while others analyzed time-trends in contaminant levels in antlers from a single region. Using the latter approach, a pronounced drop of lead concentrations during recent decades has been reported for antlers from various European countries. This indicates a marked decline of environmental lead levels that can be attributed mainly to the phase-out of leaded gasoline and, in addition, to a reduction of lead emissions also from stationary sources. In Germany, a corresponding drop has also been recorded for fluoride concentrations in antlers, which is attributed to a decline of fluoride emissions from stationary sources due to improved emission-control measures. There is some evidence that exposure to higher levels of fluoride may lead to an impaired antler mineralization. Using antlers as biomonitors has been shown to be an efficient method for assessing environmental pollution by lead and fluoride at low cost. Further studies using this now well established approach are therefore encouraged.

Liteplo, R., Howe, P., Malcolm, H., Aggett, P., Belmar, R., Bucher, J., Camargo, J., Cauley, J., Ekstrand, J., Howe, P., Karthikeyan, G., Kierdorf, U., Kurttio, P., Liteplo, R.,

Nishikawa, A., Stevens, D., Vineis, P., and Yinlong, J. 2002. Environmental health criteria 227: Fluorides. <http://www.inchem.org/documents/ehc/ehc/ehc227.htm>

Abstract: This document focuses on environmental exposure to fluoride derived mostly from inorganic sources and its effects on humans, animals and other biota. Data on hydrogen fluoride, calcium fluoride, sodium fluoride, sulfur hexafluoride and silicofluorides are covered, as these compounds are considered to be the most relevant of the inorganic fluorides on the basis of quantities released to the environment, environmental concentrations and toxicological effects on living organisms.

Vairagade, D.M., Juneja, H.D., Jadhav, R.T., and Paliwal, L.J. 2003. Impact of ash bund of thermal power station on fluorides in ground water. Indian Journal of Environmental Protection 23: 1223-1229.

Abstract: In Koradi Thermal Power Station, 21000MT of coal is burnt everyday, producing 9100MT of coal ash which pollutes the environment. Out of the total ash generated, 910MT (containing 2204.5 mg/L fluoride), is released into the atmosphere as flyash daily. The remaining 8190 MT ash containing on an average of 1746 mg/L fluoride is dispersed on land surface in the form of slurry. The slurry containing 8190 MT ash and 17,571mL water is finally stored in ash bunds. The supernatant water is charged into the local drainage system. Koradi Thermal Power Station, thus, pollutes the atmosphere everyday with 910 MT flyash containing 1443kg fluoride. 17,571mL effluent from ash bunds pollutes local surface water with 13,148kg fluoride/day. The Ca²⁺ and SO₄²⁻ rich ash bund water fortunately critically decreases CaF₂ solubility. Possibility of significantly high fluoride content due to coal ash pollution of similar composition in water, poor in Ca²⁺ and SO₄²⁻ content is strongly indicated. Ground water samples were collected and analysed for fluoride content and other quality parameters. Fluoride content (0.4 to 2.8 mg/L) was found to be higher than that of the permissible levels recommended by World Health Organisation (0.5mg/L) and ICMR (1.0mg/L).

Zakrzewska, H., ska, M., Orowicz, W., Samujo, D., jcik, A., and Kolanus, A. 2004. Content of fluoride in hair and hoofs of wild boars and deer from Western Pomerania as a bioindicator of environmental pollution. Annales Academiae Medicae Stetinensis. 50 Suppl 1: 100-103.

Abstract: The aim of this study was to assess the fluoride content in hair and hoofs of wild boars and deer from Western Pomerania (Poland). Fluoride content was determined with the Orion 96-09 fluoroselective electrode. The highest content of fluoride (13.39 microg/g d.m.) was found in hair of wild boars from the city of Stargard Szczecinski. The lowest fluoride content was in the control group of boars from the city of Pyrzyce (8.41 microg/g d.m.) and Mysliborz (6.11 microg/g d.m.). It was concluded that biomonitoring of fluoride accumulation in hair and hoofs may be useful for the assessment of environmental pollution with fluorine compounds.

Zemek, F., M. Herman, H. Kierdorf, U. Kierdorf, and F. Sedlacek. 2006. Spatial distribution of dental fluorosis in roe deer (*Capreolus capreolus*) from North Bohemia (Czech Republic) and its relationships with environmental factors. Science of the Total Environment 360:491-505.

Abstract: We assessed the spatial variation of fluoride load on the local ecosystem in the Czech part of the Ore Mountains region and its southern foothills - a heavily polluted part of Europe's 'Black Triangle' region. Dental fluorosis in roe deer (*Capreolus capreolus*) served as a biomarker of fluoride exposure and thus as an indicator of environmental pollution by fluoride. The mean dental lesion index of fluorosis (DLI) calculated from the analyzed mandibles of wild roe deer (>=2years of age) was assigned to the hunting ground from which the specimens originated and classified into one of the eight fluorosis categories. Environmental factors potentially related to

dental fluorosis (atmospheric deposition of sulfur, concentration of fluoride in and pH of surface waters, geomorphologic features, bedrock and soil type, and vegetation cover), which were represented in the study by GIS layers, were examined to explain the distribution pattern and severity of fluorosis in the roe deer. The study revealed that 75.5% of 616 analyzed mandibles showed dental fluorosis to different extent, with individual DLIs ranging from 0 to 21. The spatial pattern of marked fluorosis on the Czech side continues that found in a previous study on the German side of the Ore Mountains. Together they create a landscape island around several thermal power plants in the region. General Linear Model (GLM) analyses revealed significant relationships between degree of forest damage, soil type, and atmospheric sulfur deposition from air pollution and dental fluorosis, expressed as mean DLI in the roe deer.

3.2.5 Radionuclides

Ugur, A., B. Ozden, M. M. Sac, and G. Yener. 2003. Biomonitoring of Po-210 and Pb-210 using lichens and mosses around a uraniumiferous coal-fired power plant in western Turkey. Atmospheric Environment 37:2237-2245.

Abstract: In Gokova region where Yatagan is located there are three major uraniumiferous coal-fired power plants (CPPs) and they cause some pollution in the surroundings. Studies were realized over a wide area around the coal-fired power station located at Yatagan to evaluate the possible increase of natural radioactivity level due to the operation of the plant. The lichens *Rhizoplaca melanophthalma*, *Cladonia convoluta*, *Cladonia pyxidata* and the mosses *Grimmia pulvinata*, *Hypnum cupressiforme* were investigated for potential use as bioindicators for Po-210 and Pb-210 deposition. The maximum Po-210 and Pb-210 activities were observed around the hill close to ash stacks. The capture efficiency was the highest in one of the moss species, *G. pulvinata* with the activity concentration ranges of 600 +/- 19-1228 +/- 36 and 446 +/- 15-650 +/- 21 Bq kg(-1) for Po-210 and Pb-210, respectively. Soil samples were also collected and analysed in order to investigate any possible contamination in soil profiles due to CPPs and to determine unsupported Pb-210 flux. The Pb-210 and Ra-226 concentrations in uncultivated soil profiles varied between 58 +/- 2 and 258 +/- 6 Bq kg(-1), 50 +/- 5 and 58 +/- 5 Bq kg(-1), respectively. The unsupported Pb-210 inventory in the core was calculated to be 3312 Bq m(2). The corresponding annual Pb-210 flux of 103 Bq m(-2) yr(-1) is high with compare to estimates of the atmospheric flux given in literature for the same region.

3.3 Regulations, policies, and abatement technologies

Hamilton, S. J. 2002. Rationale for a tissue-based selenium criterion for aquatic life. *Aquatic Toxicology* 57:85-100.

Abstract: This paper proposes a national tissue-based criterion for the protection of aquatic life in the United States based on the growing body of selenium literature, but may be of international importance due to the raising global awareness of selenium contamination. A recent peer consultation workshop was undertaken by the US Environmental Protection Agency to address the technical issues underlying the freshwater aquatic life chronic criterion for selenium. The workshop participants discussed concerns associated with three possibilities for a new criterion: a water-based criterion, a tissue-based criterion, and a sediment-based criterion. Since the current national water quality criterion was established in 1987, several publications have reported adverse effects in fish from dietary selenium exposure with waterborne concentrations below the current criterion of 5 $\mu\text{g/l}$. Based on this literature, a water-based criterion seems unsuitable because of the propensity for selenium to bioaccumulate through the food chain to toxic dietary concentrations. There is little information to support a sediment-based criterion. A tissue-based criterion accounts for selenium's biogeochemical pathways because it integrates the route, duration, and magnitude of exposure, chemical form, metabolic transformations, and modifying biotic and abiotic factors. The convergence of laboratory and field data shows 4 $\mu\text{g/g}$ to be a conservative value for a national tissue-based criterion for selenium.

Hamilton, S. J. 2003. Review of residue-based selenium toxicity thresholds for freshwater fish. *Ecotoxicology and environmental safety* 56:201-210.

Abstract: A variety of guidelines have been proposed in recent years for linking selenium concentrations in the whole body of fish or in diet with adverse effects in fish. Diverging viewpoints seem to be forming separating groups supporting either the low-selenium guidelines proposed by the government and academic researchers or the high-selenium guidelines proposed by other researchers. Recently, an article was published that reviewed selected studies and recommended guidelines for selenium concentrations in the whole body of fish and in diet that were higher than those proposed by other researchers (4 $\mu\text{g/g}$ in whole body and 3-4 $\mu\text{g/g}$ in diet). That article also recommended separating guidelines for coldwater fish (6 $\mu\text{g/g}$ in whole body and 11 $\mu\text{g/g}$ in diet) and warmwater fish (9 $\mu\text{g/g}$ in whole body and 10 $\mu\text{g/g}$ in diet). The approaches, information, and guidelines presented in the article are reviewed and problems in their interpretation and conclusions are discussed. The majority of the selenium literature supports a whole-body threshold of 4 $\mu\text{g/g}$ in fish and 3 $\mu\text{g/g}$ in diet.

Menkedick, J. R. 2002. Energy and the Emerging PBT Focus. *Environmental Protection* 13:30.

Abstract: When President George W. Bush announced his Clear Skies Initiative in February 2002, the White House hailed it as the most aggressive initiative in American history to cut power plant emissions, as well as a bold new strategy for addressing global climate change. The president spoke of expected reductions of billions of pounds of emissions of sulfur dioxide, nitrogen oxides and greenhouse gases. In light of the quantities, it may seem surprising that both the Clear Skies Initiative, as well as other national programs, have given an equal amount of attention to releases of pollutants that are only one-millionth of that amount, that are more appropriately measured in pounds, or in some cases, even grams. Yet there are a group of pollutants, recently classified as Persistent Bioaccumulative Toxics (PBTs), that have gained national attention as a significant component of the risk equation when assessing the

environmental and health impacts of energy emissions. PBT chemicals are those that partition primarily to water, sediment or soil and are not removed at rates adequate to prevent their bioaccumulation in aquatic or terrestrial species.

Rogers, M. D. 2003. Risk analysis under uncertainty, the Precautionary Principle, and the new EU chemicals strategy. *Regulatory Toxicology and Pharmacology* 37:370-381.

Abstract: Three categories of uncertainty in relation to risk assessment are defined; uncertainty in effect, uncertainty in cause, and uncertainty in the relationship between a hypothesised cause and effect. The Precautionary Principle (PP) relates to the third type of uncertainty. Three broad descriptions of the PP are set out, uncertainty justifies action, uncertainty requires action, and uncertainty requires a reversal of the burden of proof for risk assessments. The application of the PP is controversial but what matters in practice is the precautionary action (PA) that follows. The criteria by which the PAs should be judged are detailed. This framework for risk assessment and management under uncertainty is then applied to the envisaged European system for the regulation of chemicals. A new EU regulatory system has been proposed which shifts the burden of proof concerning risk assessments from the regulator to the producer, and embodies the PP in all three of its main regulatory stages. The proposals are critically discussed in relation to three chemicals, namely, atrazine (an endocrine disrupter), cadmium (toxic and possibly carcinogenic), and hydrogen fluoride (a toxic, high-production-volume chemical). Reversing the burden of proof will speed up the regulatory process but the examples demonstrate that applying the PP appropriately, and balancing the countervailing risks and the socio-economic benefits, will continue to be a difficult task for the regulator. The paper concludes with a discussion of the role of precaution in the management of change and of the importance of trust in the effective regulation of uncertain risks.

Sloss, L. L. 2002. Trace elements - controlling emissions from coal combustion. *International Journal of Environment and Pollution* 17:110-125.

International and national legislation is increasingly being applied to trace element emissions. Although emissions have decreased for a variety of reasons in many developed countries, continued use of coal and more successful control strategies in other sectors mean that coal combustion is still a relatively important source of some trace elements, especially mercury. Existing pollution control equipment for other emissions is also effective in reducing most trace element emissions. However, the more volatile trace elements are captured to a much lower extent in coal-fired power stations. These species are still relatively poorly understood and this is reflected in the confusion over the best approach to control emissions.

4 Additional references on emissions

4.1 Primary publications

Ahn, Y. C., and J. K. Lee. 2006. Physical, chemical, and electrical analysis of aerosol particles generated from industrial plants. *Journal of Aerosol Science* 37:187-202.

The physical, chemical, and electrical characteristics of industrial aerosol particles generated from a steel sintering plant, a cement plant, a coal power plant, and a foundry plant were investigated experimentally to improve the performance of electrostatic precipitators. The major constituents of sinter particles from the steel plant and of cement particles from the cement plant are Fe₂O₃ (39.6-74.5%) and CaO (41.8-65.5%), respectively; the coal fly ash generated from the coal power plant and the foundry particles from the foundry plant consist mainly of SiO₂ (53.3-80.6%) The resistivities of sinter and cement particles are in the high range of 10(10)-10(15) Omega/cm due to high components of Fe₂O₃ and CaO. Coal fly ash and foundry aerosols do precipitate well in the electrostatic precipitator since, given their operational temperature and moisture content, their electrical resistivity is below 10(10) Omega/cm, a representative resistivity range for collecting airborne particles in ESP operation.

Backreedy, R. I., J. M. Jones, L. Ma, M. Pourkashanian, A. Williams, A. Arenillas, B. Arias, J. J. Pis, and F. Rubiera. 2005. Prediction of unburned carbon and NO_x in a tangentially fired power station using single coals and blends. *Fuel* 84:2196-2203.

Abstract: Coal blends are now widely used by the power generation industry and the general characteristics are well known. Attention is still directed to the emission of NO_x, which is subject to more stringent regulation, and to the amount of carbon in ash. The latter is increased when low NO_x burners are employed, which is the norm now. It is also increased as a result of additional air staging when over-fire air is added in furnaces, especially tangential fired systems. Such a furnace is studied here. Two approaches can be employed for prediction of NO_x and unburned carbon. The first approach uses global models such as the 'slice' model which requires the combustor reaction conditions as an input but which has a detailed coal combustion mechanism. The second involves a computational fluid dynamic model that in principle can give detailed information about all aspects of combustion, but usually is restricted in the detail of the combustion model because of the heavy computational demands. The slice model approach can be seen to be complimentary to the CFD approach since the NO_x and carbon burnout is computed using the slice model as a post-processor to the CFD model computation. The slice model that has been used previously by our group is applied to a commercial tangentially fired combustor operated in Spain and using a range of Spanish coals and imported coals, some of which are fired as blends. The computed results are compared with experimental measurements, and the accuracy of the approach assessed. The CFD model applied to this case is one of the commercial codes modified to use a number of coal combustion sub-models developed by our group. In particular it can use two independent streams of coal and as such it can be used for the combustion of coal blends. The results show that both model approaches can give good predictions of the NO_x and carbon in ash despite the fact that certain parts of the coal combustion models are not exactly the same. However, if a detailed insight into the combustor behaviour is required then the CFD model must be used.

Baba, A. 2003. Geochemical assessment of environmental effects of ash from Yatagan (Mugla-Turkey) Thermal Power Plant. *Water Air and Soil Pollution* 144:3-18.

Abstract: Yatagan thermal power plant consumes annually 5.4 million tons of coal and the annual production capacity of the plant is 3.78 billion KWh. The thermal power plant uses 15000 tons of coal and discharges 5000 tons of fly and bottom ash daily to the disposal site. The waste is dumped using conveyer belts and pipes into a dam founded on metamorphic rocks. However, as the waste hills formed, the water level reached the karstic marbles that over lay schist. Water leaches through dried waste hills and karstic marbles, ultimately adversely affecting the quality of ground and surface waters. The concentrations of major and minor ions were determined on water samples taken at 2 points in the dam, 5 points in surface water and at 21 points in groundwater located in the vicinity of the waste disposal site, total of 28 samples, for three years. The chemical analyses revealed that the concentrations of Ca²⁺, Cd²⁺, Pb²⁺, Sb²⁺ and SO₄²⁻ in some samples exceed the Turkish Drinking Water, the U.S. EPA and WHO limits. Isotope analyses were carried out to determine the origins of waters, which showed that contamination is taking place in the vicinity of the waste disposal site.

Baba, A. 2003. Geochemical assessment of environmental effects of ash from Yatagan (Mugla-Turkey) Thermal Power Plant. Water Air and Soil Pollution 144:3-18.

Abstract: Yatagan Thermal Power Plant consumes low-quality lignite produced from the Yatagan Basin, located in the western part of the Aegean region nearby Mugla City. The basin is aligned in a northwest-southeast direction. The dominant wind direction is also northwest-southeast, which controls the boundary of the waste at the disposal site. In this study, the concentration of 30 volatile elements was analyzed in coal, bottom ash, fly ash and background soil. The study area was divided into grids. The size of the grids was 1 km² for the background soil and 50-100 m for the ash in the vicinity of the waste disposal site. 15 fly and bottom ash, six coal and nine-background soil samples were analyzed according to a sequential technique using ICP-AES. The results reveal that heavy metal concentrations in the coal are below the world averages for coal whereas those of bottom ash and fly ash are within the world averages for the respective ashes, indicating heavy metal enrichment. It is recommended that extra care should be taken to prevent subsurface contamination in the study area.

Baba, A., and A. Kaya. 2004. Leaching characteristics of solid wastes from thermal power plants of western Turkey and comparison of toxicity methodologies. Journal of Environmental Management 73:199-207.

Abstract: Use of lignite in power generation has led to increasing environmental problems associated not only with gaseous emissions, but also with the disposal of ash residues. In particular, use of low quality coals with high ash content results in huge quantities of both fly and bottom ashes to be disposed of. A main problem related to coal ash disposal is the heavy metal content of the residue. In this regard, experimental results of numerous studies indicate that toxic trace metals may leach when fly and bottom ashes are in contact with water. In this study, fly and bottom ash samples obtained from thermal power plants, namely Yenikoy, Kemerkooy and Yatagan, located at the southwestern coast of Turkey, were subjected to toxicity tests such as the extraction (EP) and toxicity characteristic leaching (TCLP) procedures of the US Environmental Protection Agency (USEPA) and the so-called 'Method A' extraction procedure of the American Society of Testing and Material (ASTM). The geochemical composition of ash samples showed variations depending on the coal burned in the plants. Furthermore, the EP, TCLP and ASTM toxicity tests showed variations such that the ash samples were classified as 'toxic waste' based on EP and TCLP results whereas they were classified as 'non-toxic' based on ASTM results, indicating test results are pH dependent. When the extraction results were compared with the chemical composition of water samples obtained in the vicinity of the thermal power plants, it was found that the results obtained using the ASTM procedure cannot be used to predict subsurface contamination whereas the EP and TCLP procedures can be used.

Baba, A., and A. Kaya. 2004. Leaching characteristics of fly ash from thermal power plants of Soma and Tuncbilek, Turkey. *Environmental Monitoring and Assessment* 91:171-181.

Abstract: Use of lignite in power generation has led to increasing environmental problems associated not only with gaseous emissions but also with the disposal of ash residues. In particular, use of low quality coal with high ash content results in huge quantities of fly ash to be disposed of. The main problem related to fly ash disposal is the heavy metal content of the residue. In this regard, experimental results of numerous studies indicate that toxic trace metals may leach when fly ash contacts water. In this study, fly ash samples obtained from thermal power plants, namely Soma and Tuncbilek, located at the west part of Turkey, were subjected to toxicity tests such as European Committee for standardization (CEN) and toxicity characteristic leaching (TCLP) procedures of the U. S. Environmental Protection Agency (U. S. EPA). The geochemical composition of the tested ash samples from the power plant show variations depending on the coal burned in the plants. Furthermore, the CEN and TCLP extraction results showed variations such that the ash samples were classified as 'toxic waste' based on TCLP result whereas they were classified as 'non-toxic' wastes based on CEN results, indicating test results are pH dependent.

Chatzimouratidis, A. I., and P. A. Pilavachi. 2007. Objective and subjective evaluation of power plants and their non-radioactive emissions using the analytic hierarchy process. *Energy Policy* 35:4027-4038.

Abstract: Non-nuclear power plant emissions are of great concern to the public and to scientists alike. As energy demand tends to rise rapidly, especially in the developing countries, the negative effects to human health and to the environment from gaseous emissions together with hazardous particulate matter released by power plants can no longer be ignored. In this study, the impact of non-radioactive emissions is evaluated with the Analytic Hierarchy Process (AHP) by synthesizing objective and subjective criteria. There are five main emissions to be evaluated, non-methane volatile organic compounds (NMVOC), carbon dioxide equivalent (CO₂-eq), nitrogen oxides (NO_x), sulphur dioxide (SO₂) and particulates or particulate matter (PM). Objective evaluation is achieved by expressing the impact of each emission released in monetary terms following generally accepted market rules, international agreements and protocols. That is, the Euro per kilogram of each emission exceeding a specific limit that should be paid as a penalty for environmental pollution and human health damage. Subjective assessment requires an intuitive expression of the percentage of damage to human health and to the ecosystem that each emission causes. Sensitivity analysis is then used in order to examine how change of input data affects final results. Finally, 10 main types of power plant are evaluated according to the level and kind of emissions they release. These types are coal/lignite, oil, natural gas turbine, natural gas combined cycle (NGCC), nuclear, hydro, wind, photovoltaic, biomass and geothermal.

Chun, S. K., and S. C. Yi. 2003. The contribution rate of coal-fired power plant analyzed by CMB modeling with component analysis data of PM₁₀. *Journal of Industrial and Engineering Chemistry* 9:629-634.

Abstract: The purpose of this study is to analyze the contribution rate of air pollutants from Taean coal-fired power plants of four measuring points. For this purpose, total mass analysis, metal component analysis, ion component analysis, and carbon analysis were performed on particulate matter 10 (PM₁₀) samples, collected over 24 h. In addition, to perform comparative analysis, data measured by the Ministry of Environment at Pado-ri, Taean-gun was also used. As a result of the analysis, at Pado-ri point, 15km away from the plant, Na⁺ and SO₄²⁻ accounted for 12%, respectively, occupying the biggest portion, while at the four neighboring points around the plant, organic carbon (OC) and elemental carbon (EC) accounted for up to 34.8%. The result of

factor analysis performed by using SPSS 6 statistical package revealed that four measuring points around the plants have a correlation coefficient greater than 0.9. As a result of chemical mass balance (CMB) modeling, a receptor model, it was found to be the contribution rate of the power plants' four measuring points and standard error within 24% similar to 52% and 0.38 similar to 0.89 mg/m³, respectively. In detail, a-1 point (Hakam-po) showed the highest contribution ratio, while at a-2 point (Bangal-ri) contribution ratio of biomass burning (27%) was greater than that of emissions from the power plant (24%). In the next study, performing dispersion modeling on air pollutants from power plants and comparing this data with CMB 8 Modeling should be required, to locate pollutant sources and to establish an effective method of converting contribution ratio.

Demirak, A. 2007. The influence of a coal-fired power plant in Turkey on the chemical composition of rain water in a certain region. Environmental Monitoring and Assessment 129:189-196.

Abstract: In this study, the chemical composition of the rainwater in Yatagan, which is a region surrounding a coal power plant was investigated from February to April 2002. Rainwater samples were obtained from Yatagan, located northwest of Mugla City in Turkey. pH values and concentrations of major ions (Ca²⁺, Na⁺, K⁺, SO₄²⁻, NO₃⁻, NH₄⁺) in the rainwater samples were analyzed. The pH varied from 5.1 to 7.9 with an average of 6.7 which was in alkaline range considering 5.6 as the neutral pH of cloud water in equilibrium with atmospheric CO₂. In the total of 30 rain events, only three events were observed with water in the acidic range (< 5.6), which occurred after continuous rains. The equivalent concentration of components followed the order: Ca²⁺ > SO₄²⁻ > Na⁺ > NH₄⁺ > NO₃⁻ > K⁺ > H⁺. The anion and cation concentrations in the rainwater samples showed a high sulphate concentration (131 µEq/l), as well as high sodium (40 µEq/l) and calcium (298 µEq/l) concentrations. These values indicate that one probable source of the high sodium concentration is fly ash, after the coal burning process SO₄²⁻ and the power plant can be effective on level 4 concentrations in rainwater. In addition, the dust-rich local and surrounding limestone environment might have caused the high concentration of Ca (2+) in rainwater of the Yatagan Basin. Due to a large contribution of these cations to the sulphate neutralization action, the rainwater of this region displays only a moderate acidity, which does not cause significant environmental impact.

Dutkiewicz, V. A., S. Qureshi, L. Husain, J. J. Schwab, and K. L. Demerjian. 2006. Elemental composition of PM_{2.5} aerosols in Queens, New York: Evaluation of sources of fine-particle mass. Atmospheric Environment 40:S347-S359.

Abstract: As a part of the PM_{2.5} Technology Assessment and Characterization Study-New York (PMTACS-NY) daily aerosol samples were collected from July 2001 to December 2004 at three NY sites: urban Queens, and rural Pinnacle State Park, and Whiteface Mountain lodge. Sulfate was determined on all samples while the 2001 and 2002 samples also had 15 metals determined: Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd, Sb, and Pb. This is the second of a set of papers that deals with the composition of fine particulate matter at the urban site in Queens, NY. We use the large daily elemental database to explore the inter-elemental relationships with statistical methods and air trajectories on a seasonal basis to glean insight into the regional and local area sources impacting Metropolitan NY.

England, G. C., J. G. Watson, J. C. Chow, B. Zielinska, M. C. O. Chang, K. R. Loos, and G. M. Hidy. 2007. Dilution-based emissions sampling from stationary sources: Part 2 - Gas-fired combustors compared with other fuel-fired systems. Journal of the Air & Waste Management Association 57:79-93.

With the recent focus on fine particle matter (PM_{2.5}), new, self-consistent data are needed to characterize emissions from combustion sources. Such data are necessary for health assessment and air quality modeling. To address this need, emissions data for gas-fired combustors are presented here, using dilution sampling as the reference. The dilution method allows for collection of emitted particles under conditions simulating cooling and dilution during entry from the stack into the air. The sampling and analysis of the collected particles in the presence of precursor gases, SO₂, nitrogen oxide, volatile organic compound, and NH₃ is discussed; the results include data from eight gas fired units, including a dual-fuel institutional boiler and a diesel engine powered electricity generator. These data are compared with results in the literature for heavy-duty diesel vehicles and stationary sources using coal or wood as fuels. The results show that the gas-fired combustors have very low PM_{2.5} mass emission rates in the range of similar to 10⁻⁴ lb/million Btu (MMBTU) compared with the diesel backup generator with particle filter, with similar to 5 x 10⁻³ lb/MMBTU. Even higher mass emission rates are found in coal-fired systems, with rates of similar to 0.07 lb/MMBTU for a bag-filter-controlled pilot unit burning eastern bituminous coal. The characterization of PM_{2.5} chemical composition from the gas-fired units indicates that much of the measured primary particle mass in PM_{2.5} samples is organic or elemental carbon and, to a much less extent, sulfate. Metal emissions are quite low compared with the diesel engines and the coal- or wood-fueled combustors. The metals found in the gas-fired combustor particles are low in concentration, similar in concentration to ambient particles. The interpretation of the particulate carbon emissions is complicated by the fact that an approximately equal amount of particulate carbon (mainly organic carbon) is found on the particle collector and a backup filter. It is likely that measurement artifacts, mostly adsorption of volatile organic compounds on quartz filters, are positively biasing "true" particulate carbon emission results.

Evans, J. S., S. K. Wolff, K. Phonboon, J. I. Levy, and K. R. Smith. 2002. Exposure efficiency: an idea whose time has come? *Chemosphere* 49:1075-1091.

Abstract: Exposure efficiency, the fraction of material released from a source that is eventually inhaled or ingested, is arguably the simplest of all possible descriptions of the link between pollutant emissions and population exposures. This paper, prepared in late 1999 for the SGOMSEC Workshop, notes that several groups of researchers independently developed the concept of exposure efficiency in the late 1980s and early 1990s but argues that the potential importance of exposure efficiency in risk analysis and life cycle assessment has only recently been appreciated. The paper reviews the history of the concept; discusses and summarizes previous estimates of exposure efficiency for particulate matter and other air pollutants; presents new values for fine particulate matter emitted from power plants and mobile sources in the United States; and illustrates how preliminary estimates of exposure efficiency might be developed. The authors assert that in order for the concept of exposure efficiency to achieve its full potential exposure efficiency estimates for a wide variety of pollutants and sources must be developed and that both the results and methods must be made widely available and accessible to the community of risk assessors and life cycle analysts

Gaffney, J. S., N. A. Marley, and M. M. Cunningham. 2004. Natural radionuclides in fine aerosols in the Pittsburgh area. *Atmospheric Environment* 38:3191-3200.

Abstract: Natural radionuclides have been proposed for use as tracers in assessing the transport of ozone and aerosols in the troposphere. Beryllium-7 is produced in the upper troposphere and lower stratosphere and after formation rapidly attaches itself to fine aerosol particles. Measurements of Be-7 at ground level can therefore be used as a tracer of stratospheric/tropospheric folding events, leading to injection of ozone and upper atmospheric aerosols into the lower atmosphere. Since its concentration varies little on regional scales it can

also be used to detect and correct for sampling problems in particulate monitoring networks. Lead-210 and its progeny, Bi-201, and Po-210 can also be used to determine the apparent tropospheric residence times for fine aerosols by looking at the Bi-210/Pb-210 and Po-210/Pb-210 activity ratios. Reported here are measurements of the natural radionuclides Be-7 and Pb-210, taken at two sites near Pittsburgh, PA in the summer of 2001 and at a site near Centerton, New Jersey in 1999 during the NEOPS field campaign. Beryllium-7 results show no evidence of upper atmospheric input during the sampling period. Apparent residence times as calculated from Po-210/Pb-210 ratios are shorter for Pittsburgh than for Centerton, and shorter for both sites than those obtained previously in other areas, indicating a local aerosol source as well as a higher loading of water-soluble species such as sulfate and nitrate. A comparison of fine and coarse aerosol lifetimes shows no contribution of excess Po-210 from wind-blown soil or from coal-fired power plants.

Galbreath, K. C., R. L. Schulz, D. L. Toman, C. M. Nyberg, F. E. Huggins, G. P. Huffman, and E. J. Zillioux. 2005. Nickel and sulfur speciation of residual oil fly ashes from two electric utility steam-generating units. *Journal of the Air & Waste Management Association* 55:309-318.

Abstract: Representative duplicate fly ash samples were obtained from the stacks of 400- and 385-MW utility boilers (Unit A and Unit B, respectively) using a modified U.S. Environmental Protection Agency (EPA) Method 17 sampling train assembly as they burned 0.9 and 0.3 wt% S residual (No. 6 fuel) oils, respectively, during routine power plant operations. Residual oil fly ash (ROFA) samples were analyzed for Ni concentrations and speciation using inductively coupled plasma-atomic emission spectroscopy, X-ray absorption fine structure (XAFS) spectroscopy, and X-ray diffraction (XRD). ROFA deionized H₂O extraction residues were also analyzed for Ni speciation using XAFS and XRD. Total Ni concentrations in the ROFAs were similar, ranging from 1.3-1.5 wt%; however, stack gas Ni concentrations in the Unit A were 0.990 µg/Nm³ compared with 0.620 µg/Nm³ for Unit B because of the greater residual oil feed rates employed at Unit A to attain higher 400-MW load conditions with a lower heating value oil. Ni speciation analysis results indicated that ROFAs from Unit A contain similar to 3 wt% NiSO₄ (x)H₂O (where x is assumed to be 6 for calculation purposes) and similar to 4.5 wt% of a Ni-containing spinel compound, similar in composition to (Mg,Ni)(Al,Fe)₂O₄. ROFAs from Unit B contain on average 2 wt% NiSO₄ (x)H₂O and 1.1 wt% NiO. XAFS and XRD analyses did not detect any nickel sulfide compounds, including carcinogenic nickel subsulfide (Ni₃S₂) (XAFS detection limit is 5% of the total Ni concentration). In addition, XAFS measurements indicated that inorganic sulfate and organic thiophene species accounted for >97% of the total S in the ROFAs. Unit A ROFAs contained much lower thiophene proportions because cyclone-separated ROFA reinjection is employed on this unit to collect and reburn the larger carbonaceous particles.

Giere, R., L. E. Carleton, and G. R. Lumpkin. 2003. Micro- and nanochemistry of fly ash from a coal-fired power plant. *American Mineralogist* 88:1853-1865.

Abstract: Fly ash from a coal-fired power plant was investigated to obtain detailed information on its physical and chemical properties, and to gain an understanding of potential environmental and health impacts associated with its disposal in landfills. The studied material was produced through combustion of Illinois Basin coal and trapped within the power plant by an electrostatic precipitator. It is a fine-grained, low-Ca fly ash containing primarily SiO₂, Al₂O₃, and Fe₂O₃, and is enriched in many toxic elements (e.g., Be, Zn, As, Cd, Tl, Pb, and U) by a factor of up to 30 relative to coal. The ash consists of mainly hematite, magnetite, mullite, quartz, and amorphous material. These constituents occur mostly as spherical particles with diameters of less than 13 µm. We examined the physical, chemical, and structural characteristics of individual fly

ash particles by scanning and transmission electron microscopy and electron probe microanalysis. The results demonstrate that, with the exception of complex plerospheres, individual particles are chemically fairly homogeneous, but a pronounced compositional variation exists among particles with similar physical and structural attributes. Electron microprobe data document that several trace elements, including U, are partitioned into the Fe-rich particles. Transmission electron microscopy revealed that various types of small (<1 µm) crystalline Ca-rich phases, including lime, are attached to the glass spheres, particularly the nonmagnetic glass. These crystals may contain substantial amounts of S. Even though only a few of these crystals were analyzed quantitatively, our data indicate that the Ca-rich and S-rich phases may be important hosts for trace elements such as V and Zn. The observed element partitioning and the existence of surface-attached crystals enriched in certain trace elements suggest that fly ash from coal-fired power plants might have a more deleterious environmental impact than is inferred from bulk analytical data.

Goodarzi, F. (2002) Concentration of metals and polynuclear aromatics in drinking water in the vicinity of the Lake Wabamun area, Alberta, Canada. Retrieved Jan 8, 2008 from <http://geoscan.ess.nrcan.gc.ca/cgi-bin/starfinder/0?path=geoscan.fl&id=fastlink&pass=&search=R%3D213260&format=FULL>.

Graney, J. R., and T. M. Eriksen. 2004. Metals in pond sediments as archives of anthropogenic activities: a study in response to health concerns. *Applied Geochemistry* 19:1177-1188.

Abstract: An environmental geochemistry approach was applied in response to health concerns about present day and past exposure to pollutants within Broome County, New York by determining historical records of anthropogenic activities as preserved in sediment cores. Sediment was collected from a stormwater retention pond adjacent to a warehouse complex in the urban community of Hillcrest as well as from 3 other ponds in rural locations in Broome County. Metal concentrations and decay products of Pb-210 and Cs-137 were measured to determine the timing of source specific differences in the distribution of metals in the sediment cores. Concentrations of Zn, Pb, Ni, Cu, Cr, Cd and As were elevated in the retention pond sediments when compared to sediment from other locations. Topography influenced atmospheric transport and deposition of pollutants within incised river valleys and enhanced runoff from impervious surfaces within an urban watershed contributed to the elevated metal concentrations at Hillcrest. Temporal changes in Pb deposition within retention pond sediment mimic the rise and fall in use of leaded gasoline. Arsenic concentrations decreased following placement of emission controls on nearby coal-fired power plant sources. Superimposed over the temporal trends of Pb and As are co-varying Zn, Ni, Cu, Cr and Cd concentrations; a suite of metals commonly used in metal plating processes by local industries. Analysis of sediment in stormwater retention ponds in other urban areas may provide opportunities for detailed records of pollution history to be obtained in many communities. Residents in urban communities located in incised river valley locations similar to Hillcrest may be particularly prone to enhanced exposure to metals from anthropogenic sources.

Hagreen, L. A., and B. A. Lourie. 2004. Canadian mercury inventories: the missing pieces. *Environmental Research* 95:272-281.

Abstract: Research was conducted to determine the significance of the deliberate use of mercury in products in Canada and the associated releases from these sources. Through a combination of literature review and new calculations, the reservoir, flux, and releases of mercury from eight product sources were calculated, and these results compared to historical Canadian inventories.

Mercury contributions from the waste sector were also assessed and compared to total Canadian mercury releases and to mercury releases from coal-fired generating stations. Results suggest the use and release of mercury associated with release of mercury associated with its use in products is 4.5 times what previous inventories indicate. Including dental amalgam and sewage sludge, the total releases of mercury to all environmental compartments in Canada totals 20 tonnes per year. This accounts for less than one-half of the 44 tonnes per year of mercury released from mercury waste disposal each year in Canada. Waste mercury contributions from hazardous waste imports, unknown product sources, and incomplete information on the use of mercury in known products may account for this discrepancy. Waste-related mercury releases and transfers for disposal and recycling are 11 times greater than that of electricity generation in Canada. Results indicate that Canadian inventories have underestimated the significance of mercury use and release associated with products, calling into question the current priorities for mercury management. This paper was developed as part of a panel session at the International Joint Commission "Mercury in the Ecosystem" workshop, February 26-27, 2003, Windsor, ON, Canada, as a complement to the information on Canadian Inventories presented by Luke Trip (Senes Consulting, Ottawa, ON, Canada).

He, B., Y. Cao, C. E. Romero, H. Bilirgen, N. Sarunac, H. Agarwal, and W. P. Pan. 2007. Comparison and validation of OHM and SCEM measurements for a full-scale coal-fired power plant. *Chemical Engineering Communications* 194:1596-1607.

Abstract: Mercury emission measurements were performed at a 250 M W coal-fired power plant using the Ontario Hydro method (OHM) and semi-continuous emission monitors (SCEM). Flue gas sampling was performed at the inlet of the air preheater and at the outlet of the electrostatic precipitator. The results indicated that there is some agreement between the OHM and SCEM measurements on the total mercury species. However, the SCEM results were not always in good agreement with the OHM measurements on the elemental mercury species. These discrepancies in elemental mercury concentrations are probably the result of the differences in the location of the SCEM and OHM probes, the temperature difference between the SCEM sampling probe and the flue gas, and the nonuniformities in mercury concentration over the flue gas duct cross section. The other factor that contributed to the deviation between the SCEM and OHM measurement results is the sampling method the SCEM measurements were performed at a single point while the OHM probe was traversed over multiple points over the duct cross section and the results were averaged. The effect of the SCEM sampling probe temperature was investigated by designing a sampling probe that could be heated to the sampled flue gas temperatures. This resulted in improvements in the accuracy of the elemental mercury measurements by the SCEM system.

Hicks, J., and J. Yager. 2006. Airborne crystalline silica concentrations at coal-fired power plants associated with coal fly ash. *Journal of Occupational and Environmental Hygiene* 3:448-455.

Abstract: This study presents measurements of airborne concentrations of respirable crystalline silica in the breathing zone of workers who were anticipated to encounter coal fly ash. Six plants were studied; two were fired with lignite coal, and the remaining four plants used bituminous and subbituminous coals. A total of 108 personal breathing zone respirable dust air samples were collected. Bulk samples were also collected from each plant site and subjected to crystalline silica analysis. Airborne dust particle size analysis was measured where fly ash was routinely encountered. The results from bituminous and subbituminous fired plants revealed that the highest airborne fly ash concentrations are encountered during maintenance activities: 0.008 mg/m³ to 96 mg/m³ (mean of 1.8 mg/m³). This group exceeded the threshold limit values (TLV (R)) in 60% of the air samples. During normal production activities, airborne

concentrations of crystalline silica ranged from nondetectable to 0.18 mg/m³ (mean value of 0.048 mg/m³). Air samples collected during these activities exceeded the current and proposed TLVs in approximately 54% and 65% of samples, respectively. Limited amounts of crystalline silica were detected in samples collected from lignite-fired plants, and approximately 20% of these air samples exceeded the current TLV. Particle size analysis in areas where breathing zone air samples were collected revealed mass median diameters typically between 3 μ m and 8 μ m. Bulk and air samples were analyzed for all of the common crystalline silica polymorphs, and only alpha quartz was detected. As compared with air samples, bulk samples from the same work areas consistently yielded lower relative amounts of quartz. Controls to limit coal fly ash exposures are indicated during some normal plant operations and during episodes of short term, but high concentrations of dust that may be encountered during maintenance activities, especially in areas where ash accumulations are present.

Horvat, M., N. Nolde, V. Fajon, V. Jereb, M. Logar, S. Lojen, R. Jacimovic, I. Falnoga, L. Y. Qu, J. Faganeli, and D. Drobne. 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Science of the Total Environment* 304:231-256.

Abstract: The province of Guizhou in Southwestern China is currently one of the world's most important mercury production areas. Emissions of mercury from the province to the global atmosphere have been estimated to be approximately 12% of the world total anthropogenic emissions. The main objective of this study was to assess the level of contamination with Hg in two geographical areas of Guizhou province. Mercury pollution in the areas concerned originates from mercury mining and ore processing in the area of Wanshan, while in the area of Quingzhen mercury pollution originates from the chemical industry discharging Hg through wastewaters and emissions to the atmosphere due to coal burning for electricity production. The results of this study confirmed high contamination with Hg in soil, sediments and rice in the Hg mining area in Wanshan. High levels of Hg in soil and rice were also found in the vicinity of the chemical plant in Quingzhen. The concentrations of Hg decreased with distance from the main sources of pollution considerably. The general conclusion is that Hg contamination in Wanshan is geographically more widespread, due to deposition and scavenging of Hg from contaminated air and deposition on land. In Quingzhen Hg contamination of soil is very high close to the chemical plant but the levels reach background concentrations at a distance of several km. Even though the major source of Hg in both areas is inorganic Hg, it was observed that active transformation of inorganic Hg to organic Hg species (MeHg) takes place in water, sediments and soils. The concentration of Hg in rice grains can reach up to 569 μ g/kg of total Hg of which 145 μ g/kg was in MeHg form. The percentage of Hg as MeHg varied from 5 to 83%. The concentrations of selenium can reach up to 16 mg/kg in soil and up to 1 mg/g in rice. A correlation exists between the concentration of Se in soil and rice, indicating that a portion of Se is bioavailable to plants. No correlation between Hg and Se in rice was found. Exposure of the local population to Hg may occur due to inhalation of Hg present in air (in particular in Hg mining area) and consumption of Hg contaminated food (in particular rice and fish) and water. Comparison of intake through these different routes showed that the values of Hg considerably exceed the USA EPA Reference Concentration (RfC) for chronic Hg exposure (RfC is 0.0004 mg/m³) close to the emission sources. Intake of Hg through food consumption, particularly rice and fish, is also an important route of Hg exposure in study area. In general, it can be concluded that the population mostly at risk is located in the vicinity of smelting facilities, mining activities and close to the waste disposal sites in the wider area of Wanshan. In order to assess the real level of contamination in the local population, it is recommended that biomonitoring should be performed, including Hg and MeHg measurements in hair, blood and urine samples.

Izquierdo, M., O. Font, N. Moreno, X. Querol, F. E. Huggins, E. Alvarez, S. Diez, P. Otero, J. C. Ballesteros, and A. Gimenez. 2007. Influence of a modification of the petcoke/coal ratio on the leachability of fly ash and slag produced from a large PCC power plant. *Environmental Science & Technology* 41:5330-5335.

Abstract: Co-firing of coal with inexpensive secondary fuels such as petroleum coke is expected to increase in the near future in the EU given that it may provide certain economic and environmental benefits with respect to coal combustion. However, changes in the feed fuel composition of power plants may modify the bulk content and the speciation of a number of elements in fly ash and slag. Consequently, leachability of these byproducts also can be modified. This study is focused on identifying the changes in the environmental quality of co-fired fly ash and slag induced by a modification of the petcoke/coal ratio. Petcoke was found to increase the leachable content of V and Mo and to enhance the mobility of S and As. However, with the exception of these elements, the addition of this secondary fuel did not drastically modify the bulk composition or the overall leachability of the resulting fly ash and slag.

Katsoyiannis, A. 2006. Occurrence of polychlorinated biphenyls (PCBs) in the Soulou stream in the power generation area of Eordea, northwestern Greece. *Chemosphere* 65:1551-1561.

Abstract: The occurrence of polychlorinated biphenyls (PCBs) was investigated in the Soulou stream in the area of Eordea, northwestern Greece, receiving the effluents of two lignite burning power plants. The study was carried out after an accidental fire in one of the power plants during which losses of an amount of Aroclor 1232 were recorded. PCBs were determined in water and sediment samples collected from the wastewater treatment unit of the power plant and various points across the stream. Concentrations of PCBs were in the same order of magnitude as in other surface waters and sediments previously found in the Greek territory. The sum concentrations of seven PCBs (#28, #52, #101, #118, #138, #153, #180) varied between 94 and 206 ng l⁻¹ in waters, and between 67 and 500 ng g⁻¹ in sediments. Profile analysis of PCB congeners revealed large differences between waters and sediments, showing also significant dissimilarity with the profile of Aroclor 1232.

Lee, Y. E. 2005. Life cycle Assessment(Lca) of the power generation system for the establishment of environmental management system in Korea. Pages 667-673 in *On the Convergence of Bio-Information-, Environmental-, Energy-, Space- and Nano-Technologies, Pts 1 and 2.*

Abstract: The development of electricity technology from the environmental aspect has become the key factor for competitiveness, i.e., environmental friendliness is one of the most important considerations for technology development. Under the monopolised electric industry of the past, there was little motivation for individual companies to actually manage their company. However, because of the increasing demand for energy and the concerns for the environment, energy policies are shifting towards a sustainable development, which considers both the economics and environmental protection. According to the paradigm shift of the energy policy, it is necessary to compare two major electricity sources from the view of environmental management issues. It is effective with the common dimensionless unit concerning the various environmental categories including the radiological and non-radiological points of view, which can be realized by the new environmental impact assessment methodology such as the Life Cycle Assessment (LCA). This study aims at a comparison of the environmental impacts of the nuclear and coal power generation systems using the LCA methodology. These results are very preliminary ones, however, this study will be helpful in making a decision on a long term electricity plan and the energy mix optimization when considering the environmental aspect in Korea and also the power

generation companies could enhance their images by showing off their willingness to improve the environmental quality.

Lewerissa, K. B., and J. Boman. 2007. Study of trace elements and soot in aerosols from a coal-fired power plant in northern Vietnam. *Environmental Monitoring and Assessment* 130:301-309.

Abstract: Two measurement campaigns were conducted in two sampling sites, An Think and Duy Minh, in northern Vietnam during the months of November-December 2000 and November 2001-February 2002 in order to investigate the extend of the particulate air pollution from the Pha Lai coal fired power plant. Fine particle samples were analyzed by Energy Dispersive X-Ray Fluorescence spectrometry and soot samples were analyzed by reflectometer. The result showed that high concentration of soot and elements mostly coincided with the air masses originating from the power plant. Sea spray aerosol was found to be the major source of chlorine at both sites. Ratios of specific elements and principal component analysis (PCA) revealed that coal combustion was the main contributor to the air pollution at both sites. PCA also indicated that there were other sources responsible for the elements emission, probably the influence of long distance transport and Asian Brown Cloud.

Li, J., X. B. Gao, B. Goeckner, D. Kollakowsky, and B. Ramme. 2005. A pilot study of mercury liberation and capture from coal-fired power plant fly ash. *Journal of the Air & Waste Management Association* 55:258-264.

Abstract: The coal-fired electric utility generation industry has been identified as the largest anthropogenic source of mercury (Hg) emissions in the United States. One of the promising techniques for Hg removal from flue gas is activated carbon injection (ACI). The aim of this project was to liberate Hg bound to fly ash and activated carbon after ACI and provide high-quality coal combustion products for use in construction materials. Both bench- and pilot-scale tests were conducted to liberate Hg using a thermal desorption process. The results indicated that up to 90% of the Hg could be liberated from the fly ash or fly-ash-and-activated-carbon mixture using a pilot-scale apparatus (air slide) at 538 C with a very short retention time (less than 1 min). Scanning electron microscope (SEM) evaluation indicated no significant change in fly ash carbon particle morphology following the thermal treatment. Fly ash particles collected in the baghouse of the pilot-scale apparatus were smaller in size than those collected at the exit of the air slide. A similar trend was observed in carbon particles separated from the fly ash using froth flotation. The results of this study suggest a means for power plants to reduce the level of Hg in coal-combustion products and potentially recycle activated carbon while maintaining the resale value of fly ash. This technology is in the process of being patented.

Lu, Z. Q., Y. Liu, V. Barreto, C. Pohl, N. Avdalovic, R. Joyce, and B. Newton. 2002. Determination of anions at trace levels in power plant water samples by ion chromatography with electrolytic eluent generation and suppression. *Journal of Chromatography A* 956:129-138.

Abstract: An ion chromatographic method was developed for the determination of nine inorganic and organic acid anions at sub- to low-mug/l levels in power plant water samples. In this method, samples were injected using a large-volume direct injection technique, the analyte anions were separated on a hydroxide-selective anion-exchange column using high-purity hydroxide eluents generated by an on-line electrolytic eluent generator and detected using the suppressed conductivity detection method. The method performance was evaluated by analyzing synthetic water samples containing additives encountered in the power plant water samples and four water samples from a fossil fuel power plant. The relative standard deviations of retention times of analyte ions separated on the hydroxide-selective anion-exchange column were less than 0.4%.

The recoveries of analyte ions spiked into the synthetic water samples at concentrations of 0.13-1.0 mug/l were in the range of 70-120%. The method detection limits for analyte ions in deionized water were 0.0099, 0.0056, 0.019, 0.057, 0.0084, 0.023, 0.067, 0.037, and 0.079 mug/l for fluoride, acetate, formate, chloride, nitrite, sulfate, bromide, nitrate, and phosphate, respectively.

Mandal, A., and D. Sengupta. 2006. An assessment of soil contamination due to heavy metals around a coal-fired thermal power plant in India. Environmental Geology 51:409-420.

Abstract: Combustion of coals in thermal power plants is one of the major Sources of environmental pollution due to generation of huge amounts of ashes, which are disposed off in large ponds in the vicinity of the thermal power plants. This problem is of particular significance in India, which utilizes coals of very high ash content (similar to 55 wt%). Since the thermal power plants and the ash ponds are located in densely populated areas, there is potential chance for contamination of soil and groundwater of the surrounding areas from the toxic trace elements in the ash. An attempt has been made to study the extent of soil contamination around one of the largest thermal power plants of India located at Kolaghat, West Bengal India. Chemical analysis of the top soils and the soils collected from the different depth profiles surrounding the ash ponds, show that the top soils are enriched in the trace elements Mo, As, Cr, Mn, Cu, Ni, Co, Pb, Be, V, Zn, which show maximum enrichment (2-5) in the top soils collected from all the soil profiles. These elements are also enriched in the pond ash. Since there are no other sources of industrial effluents, it can be said that the enrichment of the trace elements (Mn, Co, Mo, Cr, Cu, Pb, Zn, As, Ni, Be, V) is attributed to their input from ash from the disposal pond. The study has been further strengthened by log-normal distribution pattern of the elements.

Marovic, G., J. Sencar, J. Kovac, and I. Prlic. 2004. Improvement of the radiological environmental situation due to remedial actions at a coal-fired power plant. Journal of Radioanalytical and Nuclear Chemistry 261:451-455.

Abstract: An assessment of the radiological situation in the area of a coal-fired power plant is made in order to determine their possible impact of a waste landfill located close to the sea and to a rather populated area. The studies carried out over the past decades and repeated radioactivity measurements of slag and ash have shown that the concentration of U-238 and Th-212 decay series cannot be considered negligible. The aim of this paper was to analyse data collected in the period prior the restoration plan and compare them with the most recent data when in situ restoration measures are in progress.

Ogulei, D., P. K. Hopke, L. M. Zhou, J. P. Pancras, N. Nair, and J. M. Ondov. 2006. Source apportionment of Baltimore aerosol from combined size distribution and chemical composition data. Atmospheric Environment 40:S396-S410.

Abstract: Several multivariate data analysis methods have been applied to a combination of particle size and composition measurements made at the Baltimore Supersite. Partial least squares (PLS) was used to investigate the relationship (linearity) between number concentrations and the measured PM_{2.5} mass concentrations of chemical species. The data were obtained at the Ponca Street site and consisted of six days' measurements: 6, 7, 8, 18, 19 July, and 21 August 2002. The PLS analysis showed that the covariance between the data could be explained by 10 latent variables (LVs), but only the first four of these were sufficient to establish the linear relationship between the two data sets. More LVs could not make the model better. The four LVs were found to better explain the covariance between the large sized particles and the chemical species. A bilinear receptor model, PMF₂, was then used to simultaneously analyze the size distribution and chemical composition data sets. The resolved sources were identified using information from

number and mass contributions from each source (source profiles) as well as meteorological data. Twelve sources were identified: oil-fired power plant emissions, secondary nitrate I, local gasoline traffic, coal-fired power plant, secondary nitrate II, secondary sulfate, diesel emissions/bus maintenance, Quebec wildfire episode, nucleation, incinerator, airborne soil/roadway dust, and steel plant emissions. Local sources were mostly characterized by bi-modal number distributions. Regional sources were characterized by transport mode particles (0.2-0.5 μm).

Osman, A., and R. Ries. 2007. Life cycle assessment of electrical and thermal energy systems for commercial buildings. *International Journal of Life Cycle Assessment* 12:308-316.

Abstract: Background, Aim and Scope. The objective of this life cycle assessment (LCA) study is to develop LCA models for energy systems in order to assess the potential environmental impacts that might result from meeting energy demands in buildings. The scope of the study includes LCA models of the average electricity generation mix in the USA, a natural gas combined cycle (NGCC) power plant, a solid oxide fuel cell (SOFC) cogeneration system; a microturbine (MT) cogeneration system; an internal combustion engine (ICE) cogeneration system; and a gas boiler. Methods. LCA is used to model energy systems and obtain the life cycle environmental indicators that might result when these systems are used to generate a unit energy output. The intended use of the LCA analysis is to investigate the operational characteristics of these systems while considering their potential environmental impacts to improve building design using a mixed integer linear programming (MILP) optimization model. Results. The environmental impact categories chosen to assess the performance of the energy systems are global warming potential (GWP), acidification potential (AP), tropospheric ozone precursor potential (TOPP), and primary energy consumption (PE). These factors are obtained for the average electricity generation mix, the NGCC, the gas boiler, as well as for the cogeneration systems at different part load operation. The contribution of the major emissions to the emission factors is discussed. Discussion. The analysis of the life cycle impact categories indicates that the electrical to thermal energy production ratio has a direct influence on the value of the life cycle PE consumption factors. Energy systems with high electrical to thermal ratios (such as the SOFC cogeneration systems and the NGCC power plant) have low PE consumption factors, whereas those with low electrical to thermal ratios (such as the MT cogeneration system) have high PE consumption factors. In the case of GWP, the values of the life cycle GWP obtained from the energy systems do not only depend on the efficiencies of the systems but also on the origins of emissions contributing to GWP. When evaluating the life cycle AP and TOPP, the types of fuel as well as the combustion characteristics of the energy systems are the main factors that influence the values of AP and TOPP. Conclusions. An LCA study is performed to evaluate the life cycle emission factors of energy systems that can be used to meet the energy demand of buildings. Cogeneration systems produce utilizable thermal energy when used to meet a certain electrical demand which can make them an attractive alternative to conventional systems. The life cycle GWP, AP, TOPP and PE consumption factors are obtained for utility systems as well as cogeneration systems at different part load operation levels for the production of one kWh of energy output. Recommendations and Perspectives. Although the emission factors vary for the different energy systems, they are not the only factors that influence the selection of the optimal system for building operations. The total efficiencies of the system play a significant part in the selection of the desirable technology. Other factors, such as the demand characteristics of a particular building, influence the selection of energy systems. The emission factors obtained from this LCA study are used as coefficients of decision variables in the formulation of an MILP to optimize the selection of energy systems based on environmental criteria by taking into consideration the system efficiencies, emission characteristics, part load operation, and building

energy demands. Therefore, the emission factors should not be regarded as the only criteria for choosing the technology that could result in lower environmental impacts, but rather one of several factors that determine the selection of the optimum energy system.

Ozturk, N., and Z. S. Ozdogan. 2004. Preliminary analyses of natural radionuclides in selected Turkish power plant lignites. *Journal of Radioanalytical and Nuclear Chemistry* 259:233-237.

Abstract: This preliminary study describes the concentration of radionuclides U-238, Th-232, K-40, and Ra-226 in Afsin-Elbistan lignite samples which are primarily used for power generation in the Afsin-Elbistan Coal-Fired Power Plant. The results show that the concentration of U-238 is higher in the Afsin-Elbistan lignite compared to various world coals whereas the opposite is observed with Th-232 and K-40.

Pacca, S., and A. Horvath. 2002. Greenhouse gas emissions from building and operating electric power plants in the upper Colorado River Basin. *Environmental Science & Technology* 36:3194-3200.

Abstract: As demand for electricity increases, investments into new generation capacity from renewable and nonrenewable sources should include assessment of global (climate) change consequences not just of the operational phase of the power plants but construction effects as well. In this paper, the global warming effect (GWE) associated with construction and operation of comparable hydroelectric, wind, solar, coal, and natural gas power plants is estimated for four time periods after construction. The assessment includes greenhouse gas emissions from construction, burning of fuels, flooded biomass decay in the reservoir, loss of net ecosystem production, and land USE. The results indicate that a wind farm and a hydroelectric plant in an arid zone (such as the Glen Canyon in the Upper Colorado River Basin) appear to have lower GWE than other power plants. For the Glen Canyon hydroelectric plant, the upgrade 20 yr after the beginning of operation increased power capacity by 39% but resulted in a mere 1% of the CO₂ emissions from the initial construction and came with no additional emissions from the reservoir, which accounts for the majority of the GWE.

Peiu, N. 2007. Life Cycle Inventory Study of the electrical energy production in Romania. *International Journal of Life Cycle Assessment* 12:225-229.

Abstract: Aim, Scope and Background. The paper proposes the assessment of the environmental interventions resulting from the electrical energy production in Romania, a Central East European country, using the LCA technique limited to a Life Cycle Inventory study (an LCA without the Life Cycle Impact Assessment phase). Main Features. The following life cycles of the energy carriers employed in the production of the electrical energy are analysed according to their provenance: lignite (domestic) 31.2%, brown coal (domestic) 3.4%, brown coal (import) 0.4%, heavy oil (domestic, land) 4.2%, heavy oil (domestic, continental platform of the Black Sea) 0.4%, heavy oil (import) 3.6%, natural gas (domestic) 12.4%, natural gas (import) 6.1%, hydropower 27.8%, and nuclear energy 10.5% from the total of the electrical energy produced in Romania. The unit processes of the life cycles of these energy carriers are aggregated in two main stages: Pre-combustion (extraction, processing, transport and achievement of infrastructure) and Combustion (the production of electricity). The functional unit of the study is represented by 1 kwh. The spatial limits of the analysed system are extended as far as CIS countries for coal, Western Siberia (Russian Federation) for natural gas and the OPEC countries for oil. The temporal limits are included in the year 2000. Results and Discussion. The LCI study enabled us to quantify the interventions on the environment, which result from the electricity production in Romania, the independent use of different energy carriers and the different life cycle stages of the system. The use of the LCA technique in a prospective way shows the reduction of these

interventions that could be achieved through the adoption of specific scenarios for the development of electrical energy production in the country. Conclusions. The main findings of this Life Cycle Inventory study, the first for Romania, are: the emissions of pollutant substances are prevailing in the combustion stage; for different energy carriers, the magnitude of environmental interventions decrease in the following order: coal, oil, natural gas, hydropower and nuclear energy. By comparison with other countries, the environment is more affected by the production of electricity in the case of Romania and only the promotion of alternative, renewable resources such as hydropower could substantially improve these interventions. Recommendations and Perspectives. Some important interactions with the environment, like land use or the risks of the nuclear energy, are not taken into consideration in the study because of the lack of particular data for Romania. We would like to continue the investigation in order to surpass the limits of the study, on the one hand by collecting data concerning the risk of nuclear power or land use at the national level for different energy carriers or, on the other hand, by taking into account some other renewable resources like wind or solar energy.

Qin, Y. J., E. Kim, and P. K. Hopke. 2006. The concentrations and sources of PM_{2.5} in metropolitan New York city. *Atmospheric Environment* 40:S312-S332.

Abstract: The concentration time series of chemical species measured in PM_{2.5} samples from four speciation trend network (STN) sites in the New York City metropolitan area and a upwind background site were explored. PM_{2.5} concentrations and chemical compositions measured in metropolitan area of New York City are uniform. About 69-82% Of PM_{2.5} mass derives from transport. The most important constituents of the PM_{2.5} were SO₄²⁻, NH₄⁺ and NO₃⁻ and account 54-67% of PM_{2.5} mass. More than 93% of SO₄²⁻ and about 54-65% of NO₃⁻ are likely to have been transported into the NYC area based on the concentrations observed at the background site. Backward air parcel trajectories indicate that coal-fired power plants in the border area among West Virginia, Ohio and Pennsylvania are related to typical high PM_{2.5} events having peak secondary pollutant concentrations in New York City. Positive matrix factorization (PMF) was applied to identify the PM_{2.5} sources and estimate the source contributions. Sources common to all five sites included secondary sulfate, secondary nitrate, soil and aged sea salt. Oil combustion was identified at four of the sites. At the Elizabeth site, the oil combustion source appears to show an influence from ship emissions. Motor vehicles were apportioned into two sources (gasoline and diesel) at three site and three sources at the Elizabeth site, probably because of its proximity to a major interstate highway. At the Queens College site, only a combined motor vehicle factor could be resolved. The source profiles, source contributions and seasonal or weekday variations derived by PMF are compared to source inventories for the area. It appears that there were more vehicle exhausts and less dust and wood smoke than are indicated by the source inventories.

Stout, S. A., and T. N. Wasielewski. 2004. Historical and chemical assessment of the sources of PAHs in soils at a former coal-burning power plant, New Haven, Connecticut. *Environmental Forensics* 5:195-211.

Abstract: Soils from the manmade island in the Mill River (New Haven, CT) where a former power plant (English Station) operated for nearly 100 years had been previously shown to contain polycyclic aromatic hydrocarbons (PAHs) at concentrations that exceed the state's Department of Environmental Protection (DEP) Remediation Standard Regulations (RSRs) numerical cleanup criteria for industrial/commercial properties. Understanding the source(s) of these PAHs was important for property development and environmental management decisions. This study was designed to assess the industrial use history of the study area and conduct detailed chemical and organic petrographic characterization of the organic matter in the site's soils, particularly the PAHs, in order to determine their likely source or sources.

Historical documents revealed that the English Station property is a largely manmade island and consists of sediments dredged from the Mill River, on various occasions from the late 1800s to at least 1936, to improve navigability. Throughout this time period, and as early as 1861, a manufactured gas plant (MGP) operated immediately downriver from the English Station site. The land use in the vicinity of the site and along the Mill River historically was industrial. In 1886, the English Station property was filled sufficiently to support operations of coal and wood storage yards. In 1901, and until the 1960s, the site was used for electric power generation via separate coal-fired power plants. In the 1960s, the boilers were converted to burn residual fuel oil rather than coal and operated until they were decommissioned in 1992.

Swisher, J. N., and M. C. McAlpin. 2006. Environmental impact of electricity deregulation. *Energy* 31:1067-1083.

Abstract: Restructuring of electric utilities affects environmental quality primarily through its effect on airborne emissions. We examine emissions from 1993 to 2002 and discuss possible explanatory factors. Annual NO_x and SO₂ emissions fell nationally, mostly due to decreases in emission limits driven by state and Federal regulations. CO₂ emissions have increased almost proportionately with increased generation. Generation increased more than it would have, partly due to energy efficiency spending reductions that accompanied deregulation. The fuel mix shifted slightly from coal to gas, offsetting some CO₂ emissions increases and contributing to SO₂, and NO_x emissions decreases. While the percentage share of generation from renewable sources remained at about 2%, recent and expected future increases in wind generating capacity promise future emissions reductions. Although deregulation lacks clear environmental advantages, the deregulation process creates an opportunity for implementation of state policies to reduce emissions. Regulated and deregulated states with renewable portfolio standards (RPS) have a higher average percent of generation from renewable sources. Average energy efficiency savings are higher in regulated states, but slightly higher in deregulated states with a system benefits charge (SBC) than in regulated states without a SBC.

Teinemaa, E., U. Kirso, M. R. Strommen, and R. M. Kamens. 2003. Deposition flux and atmospheric behavior of oil shale combustion aerosols. *Oil Shale* 20:429-440.

Abstract: The atmospheric behavior of oil shale combustion fly ash aerosol was studied under simulated conditions. The fine (respirable) fraction of fly ash particles, which contributes most to the health effects of the aerosol, significantly increased (from 25 to 65% by mass) in time scale. The toxic elements and carcinogenic PAH adsorbed on the fine particles of fly ash could represent a health hazard for human. The bulk and trace elements in emissions (flue gases) and integrated deposition samples were also investigated based on original measurements and literature data.

van Zyl, H. D. and Heath, R. G. (2007) Assessment of point and non-point pollution associated with the power generation sector in South Africa. *Water Science and Technology* 55, 143-149.

Abstract: Access to water and water availability remains a key factor in ensuring the sustainability of development in Southern Africa. The need for guidelines to improve management of this valuable resource, and to regulate pollutant discharge, is therefore of national interest. A new and growing threat to our natural water resources is non-point source (NPS) pollution. The important distinction between point pollution and NPS pollution is that the latter is difficult to identify and the entry point of contamination to resources is diffuse and not limited to a single location. NPS pollution associated with power generation includes, but is not limited to, atmospheric deposition resulting from emissions (air and water), leachate from coal storage piles and runoff from impervious areas which are covered with dust fallout from coal and ash handling operations. Emissions of primary concern are sulfur, nitrogen and mercury.

Weber, R. 2003. Short-term temporal variation in PM2.5 mass and chemical composition during the Atlanta supersite experiment, 1999. Journal of the Air & Waste Management Association 53:84-91.

Abstract: Measurements in urban Atlanta of transient aerosol events in which PM2.5 mass concentrations rapidly rise and fall over a period of 3-6 hr are reported. The data are based on new measurement techniques demonstrated at the U.S. Environmental Protection Agency (EPA) Atlanta Supersite Experiment in August 1999. These independent instruments for aerosol chemical speciation of NO3-, SO42-, NH4+, and organic and elemental carbon (OC and EC), reconstructed the observed hourly dry PM2.5 mass to within 20% or better. Data from the experiment indicated that transient PM2.5 events were ubiquitous in Atlanta and were typically characterized by a sudden increase of EC (soot) and OC in the early morning or SO42- in the late afternoon. The frequent temporal decoupling of these events provides insights into their origins, suggesting mobile sources in metro Atlanta as the main contributor to early morning PM2.5 and more regionally located point SO2 sources for afternoon PM2.5 events. The transient events may also have health implications. New data suggest that short-term PM2.5 exposures may lead to adverse health effects. Standard integrated filter-based techniques used in PM2.5 compliance monitoring networks and in most past PM2.5 epidemiologic studies collect samples over 24-hr periods and thus are unable to capture these transient events. Moreover, health-effects studies that focus on daily PM2.5 mass alone cannot evaluate the health implications of the unique and variable chemical properties of these episodes.

Yang, Y. H., S. J. Lin, and C. Lewis. 2007. Life cycle assessment of fuel selection for power generation, in Taiwan. Journal of the Air & Waste Management Association 57:1387-1395.

Abstract: Life cycle assessment (LCA) was applied to performance data from 1997-2002 to evaluate the environmental impacts of the energy input, airborne emission, waterborne emission, and solid waste inventories for Taiwan's electric power plants. Eco-indicator 95 was used to compare the differences among the generation processes and fuel purification. To better understand the environmental trends related to Taiwan's electric power industry, three fuel scenarios were selected for LCA system analysis. Results indicate that there are differences in characteristic environmental impact among the 13 power plants. Scenario simulation provided a basis for minimizing environmental impacts from fuel selection targets. Fuel selection priority should be a gas-fired combined cycle substituted for a coal-fired steam turbine to be more environmentally friendly, particularly in the areas of the greenhouse effect, acidification, winter smog, and solid waste. Furthermore, based purely on economic and environmental criteria, it is recommended that the gas-fired combined cycle be substituted for the oil-fired steam turbine.

4.2 Grey literature

Agency for Toxic Substances and Disease Registry (ATSDR). (2002) Health Consultation, Gavin Power Plant, Cheshire, Gallia County, Ohio. Retrieved Dec 18, 2007 from http://www.atsdr.cdc.gov/HAC/pha/gavinpower/gpp_p1.html#back.

Agency for Toxic Substances and Disease Registry (ATSDR). (2003a) Public Health Assessment, Fort Wainwright, Fairbanks North Star Borough, Alaska. Retrieved Dec 18, 2007 from http://www.atsdr.cdc.gov/HAC/pha/fortwainwright/wai_toc.html.

Agency for Toxic Substances and Disease Registry (ATSDR). (2003b) Public Health Assessment, Select PCB Exposure Pathways, Agana Power Plant, Mongmong, Guam. Retrieved Dec 18, 2007 from http://www.atsdr.cdc.gov/HAC/pha/aganapowerplant/app_toc.html.

Agency for Toxic Substances and Disease Registry (ATSDR). (2004) Public Health Assessment, Air and Groundwater Pathways Analyses, Agana Power Plant, Mongmong, Guam. Retrieved Dec 18, 2007 from <http://www.atsdr.cdc.gov/HAC/pha/AganaPower/aganapower-toc.html>.

Alberta Environment. (2003) An overview of recent studies on Wabamun Lake. Retrieved Dec 30, 2007 from <http://environment.gov.ab.ca/info/library/6138.pdf>.

Alberta Environment. (2006) Coal Mines. Retrieved Jan 13, 2008 from <http://www3.gov.ab.ca/env/land/quality/html/use/coal.html>.

Electric Power Research Institute (EPRI). (2007) Assessment of PISCES Wastewater Characterization Reports. Retrieved Jan 13, 2008 from <http://my.epri.com/portal/server.pt?>

New Hampshire Department of Health and Human Services. (2003) Health Consultation, Merrimack Station Power Plant, Bow, Merrimack County, New Hampshire. Retrieved Dec 18, 2007 from http://www.atsdr.cdc.gov/HAC/pha/merrimack/msp_p1.html#purp.

Ontario Power Generation. (2007) Sustainable Development 2006 Report. Retrieved Jan 14, 2008 from <http://www.opg.com/pdf/sustainable%20development%20reports/sustainable%20development%20Report%202006.pdf>.

Sullivan, T. M., Lipfert, F. D. and Morris, S. M. (2003) The Local Impacts of Mercury Emissions from Coal Fired Power Plants on Human Health Risk Progress Report for the Period of Mar 2002 – Mar 2003. Retrieved Dec 6, 2007 from <http://www.bnl.gov/des/ertd/TechDevelApp/files/pdf/71554-Local-Impacts-of-Mercury-Emissions-from-Coal-Fired-Power-Plants-on-Human-Health-Risk-Progress-Report-3-02-to-3-03.pdf>, BNL-71554-2003.

West Virginia Department of Health and Human Resources. (2004) Health Consultation, Chauncey, Logan County, West Virginia. Retrieved Dec 18, 2007 from <http://www.atsdr.cdc.gov/HAC/pha/ChaunceyPCB030804-WV/ChaunceyPCB030804HC.pdf>.