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Project Summary

Impacts of Coal Combustion on Trace Elements in the Environment: Wisconsin Power Plant Impact Study

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This report describes the influence of the Columbia Generating Station on trace elements in the environment surrounding the plant. It is part of a larger study which documents a broad spectrum of environmental impacts stemming from construction and operation of a 1050 MW coal-fired power plant in south central Wisconsin.

Samples of coal, fly ash, aerosolic dust, material from the ash pit, and organisms living in the vicinity of the power plant were analyzed to determine the partitioning of elements during combustion; the distribution of fly ash particles according to size; the composition of aerosolic dust; the distribution of fly ash from the Columbia power plant in the environment surrounding the generating station; the processes of devitrification and recrystallization taking place in the ash pit; the effects of fly ash effluent on concentrations of elements in aquatic organisms living in the drainage system of the ash pit; the effects of aerosolic dust on oak leaves, including possible injury and the trace element composition of the leaves.

Analytical methods included electron microscopy, x-ray fluorescence, x-ray diffraction, and neutron activation.

During combustion, a marked fractionation of elements takes place, which results in the enrichment of volatile elements on the surface of fly ash particles. This fractionation is related to factors such as the size and resistivity of fly ash particles. Concentrations of Fe decrease in the last stages of the electrostatic precipitators, but those of Hf, K, and Se remain about the same, and all others increase. The potential effects of reactive trace elements concentrated on particle surfaces may be overlooked if only the bulk elemental composition of the particles is considered.

In terms of bulk composition, only boron potentially poses an obvious problem in agricultural uses of fly ash. There was no significant evidence of damage to oak leaves from aerosolic dust in general or from Columbia fly ash in particular or of any effect of fly ash or dust on the elemental composition of oak leaves. In the studies of aquatic invertebrates, concentrations of Ba, Cr, Se, and possibly Sb were significantly higher in animals taken from the drainage system of the ash pit than in controls. Guidelines were established for selecting test species and procedures developed for estimating the contribution of contamination from sediments and gut contents to the analytical results.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The full report is one of a series on the environmental effects of the Columbia Generating Station, a 1050 MW coal-fired power plant in south central Wisconsin The first unit of the plant began operation in April, 1975, and the second, in June, 1978. Each unit burns about 4535 metric tons/day of pulverized, low sulfur, subbituminous western coal, which has an ash content of 7 to 8%.

The broad goal of the project was to document environmental change resulting from construction and operation of the power plant Within that framework, the goal of this study was to determine the influence of the power plant on trace elements in the environment surrounding the plant. The goal suggested three specific objectives.

- To measure the distribution and elemental composition of fly ash and possible volatile materials in the vicinity of the generating station
- To elucidate the reactions and fate of fly ash in the environment.
- To assess the availability of trace elements in fly ash to the biota

Methods

Coal, Fly Ash, and Aerosolic Dust

The purpose of these analyses was to determine the partitioning of elements during combustion, the distribution of fly ash particles according to size, the composition of aerosolic dust, the distribution of fly ash from the Columbia Generating Station in the environment surrounding the station, and the processes of devitrification and recrystallization taking place in the ash pit. For these studies, samples were obtained as follows

1. The Wisconsin Power and Light Company (WPL) provided samples of coal burned at Columbia on various dates in 1975 and 1978. For comparison, samples of an eastern coal from Illinois were also analyzed.
2. WPL collected fly ash from each of the stages of the electrostatic precipitators and from the base of the stack. They also provided one sample of bottom slag.
3. Samples were dug from the upper 60 cm of material in the ash pit
4. Water was collected from the ash pit and its drainage system. The water was filtered through 0.45 μm Millipore filters to separate particulate material, and both filtrate and residue were analyzed
5. Aerosolic dust was collected in fallout buckets at eight sites around the power plant, up to a distance of 19 km. In the laboratory, contents of the buckets were washed onto 0 45 or 0.1 μm Millipore or Nucleopore filters. After filtration, the filters were dried at 60 °C and the weight of the collected particles was determined

All samples were analyzed by neutron activation procedures to determine their content of trace elements. For some samples, major elements were determined by x-ray fluorescence. In selected cases, determinations were made of both total composition and surface composition of fly ash particles. Mineral species in samples from the ash pit were identified by x-ray diffraction and electron microscopy.

Aquatic Invertebrates

The primary objective of this part of the study was to determine the effects of ash effluent on the concentration of elements in aquatic organisms living in the drainage system of the ash pit. Experimental animals represented three genera of crustaceans and seven genera of insects (Table 1) These organisms were usually abundant in the study area, they are near the base of ecologically important food chains, and they represent a variety of types of feeders.

The general approach for determining the impact of the generating station was to compare elemental concentrations in animals collected before and after the station went into operation After the station began operating, additional control specimens were taken from nearby sites not affected by the ash effluent.

Specimens were collected with a nylon dip net or in artificial substrate samplers. They were washed in distilled-deionized water, blotted dry, counted, weighed, and frozen. For analysis by nondestructive neutron activation, samples were freeze-dried, weighed, and irradiated in the University of Wisconsin nuclear reactor Samples and standards were radioassayed at various times after irradiaton, by methods described in the literature.

Oak Leaves

The small percentage of fly ash that escapes the electrostatic precipitators and leaves the stack of modern coal-fired power plants is dispersed widely in the environment. This fly ash, together with other anthropogenic and natural dusts, forms the aerosolic dust that is continuously removed from the atmosphere by various processes. Part of it is deposited on vegetation, where certain elements theoretically could dissolve and cause injury or be taken up by the plant. Oak leaves were chosen for determining whether such injury or uptake does occur, because oaks are common in the study area and their deep and extensive root systems should minimize variations in the uptake of elements from the soil.

The objectives of this part of the study were to establish baseline data for oak leaves as a foundation for future studies and to determine the effect, if any, of fly ash from the Columbia Generating Station on oak leaves.

Leaves from white oak (*Quercus alba*), black oak (*Q. velutina*), and red oak (*Q. rubra*) were collected at four sites up to 12 km from the power plant. Leaves were sampled four times during each growing season.

Electron microscopy with x-ray fluorescence revealed the types of inorganic particles on the leaf surface. These particles could not be removed effectively by washing. Elements such as Sc, Ga, and Hf, which do not accumulate significantly in leaves but occur at relatively high concentrations in inorganic dusts, were used to indicate the extent of inorganic contamination. Leaf samples were analyzed by nondestructive and radiochemical neutron activation.

Table 1. *Taxonomic Information for Invertebrates Analyzes*

Class	Order	Family	Genus and species
Crustacea	Amphipoda	Gamaridae	*Gammarus*
		Talitridae	*Hyallela azteca*
	Isopoda	Asellidae	*Asellus racovitzai*
Insecta	Coleoptera	Gyrinidae	*Dineutus*
	Hemiptera	Corixidae	*Hesperocorixa*
			Sigara
	Odonata	Aeshnidae	*Anax*
		Corulidae	*Tetragoneuria*
		Libellulidae	*Libellula*
			Sympetrium

Findings and Recommendations

Coal, Fly Ash, and Aerosolic Dust

Table 2 presents results of some analyses of coal and fly ash, including one sample of bottom slag. Although the bulk composition of coal burned at the power plant varies slightly from batch to batch and the bulk composition of fly ash also varies, these results are typical.

The major portion of each element in the coal is associated with silicates or other inorganic constituents rather than with the carbon The high concentrations of Ca in coals from Wyoming and Montana result from their high content of $CaCO_3$, which is usually accompanied by low concentrations of other elements except for Mg, Sr, and Ba. By comparison, samples of eastern coal from Illinois had relatively high levels of such elements as As, Cr, Fe, Rb, Se, and Zn.

During the gaseous phase of combustion, particles of fly ash form a highly reactive surface on which elements that are volatile at the temperature of the flame condense as heat is extracted from the flue gas The fractionation of the elements is related to various factors, including size and resistivity of particles as well as condensation of volatile elements. Thus, concentrations of Fe decrease in the last stages of the precipitator, those of Hf, K, and Se remain about the same, and all others increase

The surface enrichment of certain elements, many of which are toxic, represents one of the potentially harmful environmental impacts of fly ash Previous assessments of the possible impacts of fly ash have underestimated the potential availability of those elements concentrated on the surface. A comparison of surface analysis and bulk analysis shows surface·bulk ratios of 33:1 for Th, 3 5 1 for Cr, 11.7.1 for Zn, and 2 5·1 for As. Disposal or use of fly ash must be carefully evaluated with this surface enrichment in mind To add to the complexity of the problem, some particles of ash are hollow and contain smaller particles, presenting the theoretical potential for timed-release effects which may not be observable until some future date.

Fly ash from the Columbia power plant has some of the highest concentrations of Ca and Ba reported, and its reaction when mixed with water is strongly basic Because of the high content of Ca, the fly ash has potential as a liming agent on agricultural soils Ability to control fugitive dust during application and to retard the availability of free lime so that larger, less frequent applications could be made would enhance the usefulness of fly ash in agriculture. Again, the possible toxicity of readily available surface constituents should be considered. In bulk analyses, Hg is found in uniformly low concentrations in all samples Levels of B, which ranged from 500 to 800 $\mu g/g$, are high enough to cause symptoms of severe boron toxicity in plants if large amounts of fly ash were applied to the soil. Bulk concentrations of B, Ba, Ca, Na, Sb, and Se are greater in Columbia fly ash than in most soils, but only B potentially poses an obvious problem in the use of fly ash as a soil amendment

The mean size of fly ash particles decreases from stage to stage of the electrostatic precipitators It is primarily the smallest particles, along with gases, that escape from the stack Particles of fly ash can be distinguised from other dust by their shape, as revealed through electron microscopy Dust particles are angular, while fly ash particles are spherical

Fly ash from the Columbia plant can be further differentiated by its chemical composition and by the smooth, glassy surface of its particles Particles of fly ash that have come from sources at greater distances have a pitted surface. X-ray fluorescence analysis showed that background fly ash had concentrations of Si>Al, K>Ca, and detectable concentrations of S, Cr, Mn, Co, and Na Columbia fly ash had concentrations of Si≃Al and Ca>K, and the other elements were present at very low or undetectable levels

The flux of fly ash deposited in fallout buckets was a few tenths of a $mg/m^2/day$ over a period of one month Ash from Columbia generally made up less than 10% of the total, except when a fumigation occurred Samples collected in fallout buckets had bulk concentrations of most trace elements similar to those in local soil, although Br, Hg, Sb, Se, and to a lesser extent U, Th, and Zn were at significantly higher levels in the dust. Fly

Table 2. *Elemental Composition (µg/g) of Coal and Ash Samples, as Determined by Neutron Activation Analysis*

Element	*Coal*[1]	*Bottom slag*[2]	*Stage 1*[3]	*Stage 2*[3]	*Stage 3*[3]	*Ash pit particles*[4]
As	1 0	1 7	8.0	21	24	13
Ba	640	4,500	7,200	8,200	10,000	17,000
Ca	11,500	94,000	9.1	12	13	11,000
Cd	-	-	0.9	1 6	1 5	-
Ce	6 2	59	70	96	99	14
Co	0.46	6 6	7.8	11	11	2.5
Cr	3.8	36	38	64	68	130
Cs	0 12	0 87	1'2	1.5	1 4	1 4
Cu	7.0	-	60	90	100	-
Eu	0.09	1 1	0.97	1 3	1 4	0 20
Fe	2,600	9,400	7,900	6 9	3 4	2.8
Ga	-	-	24	52	61	-
Hf	0 76	10	8 8	8 6	8 8	0 77
Hg	0.03	-	<0 002	<0 002	<0 003	-
K	228	3,100	0.35	0 44	0 36	1,700
La	3.7	35	37	52	54	7 7
Lu	0 04	0 46	0 48	0 62	0.64	0 17
Mn	116	-	860	1,100	1,100	-
Na	170	2,200	1,900	2,400	2,400	820
Nd	2 9	30	29	40	42	13
Rb	1.4	-	16	24	18	5
Sb	0.76	1 5	4 2	9 1	11	5 0
Sc	1.0	8 9	9 8	14	14	1 7
Se	0.08	2 2	2 8	2 6	3 1	-
Sm	0.52	5 2	5 7	8.1	8 5	1 4
Tb	0 01	0 77	1.2	1 6	1.6	0 15
Th	2.2	21	22	29	30	3 1
U	0 56	3 5	7	10	12	2 4
Yb	0 24	3 1	2 9	3 5	3 4	0 36
Zn	4 9	-	50	79	83	38

[1]*Average values for four samples burned in May 1975*
[2]*Sample taken September 5, 1975.*
[3]*Samples taken September 5, 1975, from electrostatic precipitators. Stage 1 represents material closest to combustion chamber, Stage 3, material closest to stack.*
[4]*Suspended material from ash pit water as it enters the drainage ditch and is diluted with water from outside the system*

ash may be the source of the excess Sb, Se, Th, and U, but it is definitely not the source of excess Hg. It is also possible that the same processes that result in enrichment of fly ash in certain elements are responsible for the high concentrations of these elements in other aerosolic dusts as well.

Fresh fly ash consists mostly of glassy, amorphous material. Small amounts of quartz, anhydrite, magnetite, hematite, periclase, and CaO are in the fly ash from Columbia. Several new minerals form after the ash is mixed with water and slurried to the ash pond, the most important being the calcium aluminate sulfates and calcium aluminate silicates These minerals contribute to the strength and properties of Portland cement and, undoubtedly, to the hardness of the fly ash in the ash pond. Further research should explore the pozzolanic reactions of fly ash so that new uses for the ash can be developed. Similar reactions may reduce SO_4 pollution in other wastes, because calcium aluminate sulfates are much less soluble than gypsum.

Concentrations of dissolved Al, Ba, Ca, and Cr as CrO_4^{2-} are much higher in water from the ash pit and its drainage system than in unaffected waters. Some of the CrO_4^{2-} is reduced to Cr^{3+} in the lower portions of the drainage system, where it precipitates as $Cr(OH)_3$. $Al(OH)_3$ also precipitates as the pH decreases. The system is saturated with $BaSO_4$, which precipitates as water from the ash pit is diluted with less basic water. All these materials coat the substrate of the drainage system and may disrupt the habitat and life cycles of organisms living in the water

Aquatic Invertebrates

To be useful in the monitoring of trace elements in ecosystems, an organism should be relatively common and be distributed throughout the study area, be amendable to collection and analysis, and have been present long enough to reflect conditions at the site of collection. It should also be able to survive in a wide range of conditions, have concentrations of trace elements that are high enough to be correlated with environmental conditions and high enough for accurate and precise analysis Of the organisms listed in Table 1, *Asellus racovitzai* and Odonata meet these criteria best.

One of the difficulties in measuring the uptake of trace elements by aquatic organisms is eliminating contamination by sediments and ingested food. After mixed success in attempts to wash the animals and keep them alive in clean water until their guts were empty, Sc was chosen as the best indicator of inorganic contamination, and the effects of extraneous material on the elemental composition samples of organisms was estimated from interelement ratios and a mass balance for each element. The degree of contamination was related to the habitat and feeding patterns of the organism Benthic detritus-feeders such as *A. racovitzae* were the most contaminated, the herbivorous Corixidae and *Gammarus* species had an intermediate level of contamination; and the surface feeding *Dineutus* species were least contaminated. Carnivores may be contaminated by the gut contents of their prey.

Of the elements studied, the concentrations of Ba, Cr, Se, and possibly Sb were significantly higher in aquatic invertebrates taken from the drainage system of the ash pit than in controls. The differences were most easily measured in *A. racovitzai*, but they were also evident in *Hyallela azteca* and Odonata. Data for *A. racovitzai*, corrected for contamination, show Se 10 to 20 times higher than in controls, Cr$<1 \mu g/g$ in controls but up to 7 $\mu g/g$ in affected samples, and Ba from 2 to 10 times higher than in controls. In addition to providing information on the bioavailability of elements in the ash effluent, these results can form a base for future studies of the effects of trace elements on organisms.

Oak Leaves

Aerosolic dust is deposited on leaf surfaces and a significant portion of this is fly ash. The amount of fly ash increases throughout the growing season, indicating that wind and rain do not remove fly ash from leaves very efficiently

Tracer studies showed that oak leaves do not bioaccumulate Sc. Assuming that all the Sc found in the analysis of oak leaves represented contamination by aerosolic dust, the proportion of other elements contributed by dust can be calculated by a method similar to that used for aquatic invertebrates Results indicate that most of the Ba, Br, Ca, Cs, Cu, Hg, K, Rb, and Zn found in the leaves was indigenous; most of the La, Sb, Sc, and Sm was from aerosolic contamination; and the content of As, Co, and Fe was derived from both sources. Levels of As, Sb, Se, Hg, Th, and U (toxic elements of concern in this study) were consistently low or below detection limits.

Concentrations of various elements in oak leaves change rapidly during development of leaves in May and June but remain relatively constant thereafter. The elemental composition of oak leaves is similar from year to year and from site to site for any given stage of the growing season.

Although no effects of fly ash from the Columbia power plant were detected in this study, future studies should search for possible physical effects of alkaline or acid particles of fly ash on leaves. Data presented in the full report serve as a baseline for future studies evaluating the additional loading of the atmosphere with aerosolic dust as new facilities come into operation

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***Gary E. Glass** is the EPA Project Officer (see below).*

The complete report, entitled "Impacts of Coal Combustion on Trace Elements in the Environment: Wisconsin Power Plant Impact Study," (Order No. PB 84-207 638; Cost: $13.00, subject to change) will be available only from:

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