

TRACE METAL CONCENTRATIONS IN A STREAM-SWAMP SYSTEM RECEIVING COAL ASH EFFLUENT

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INTRODUCTION

Coal combustion for electrical energy generation produces vast quantities of ash materials. Approximately 32×10^6 tons yr^{-1} of fly ash is produced (Rohman 1971) which must be disposed of in an environmentally sound manner. More stringent air quality control regulations have dictated that fine particulate fly ash be removed from stack emissions (Davison et al. 1974). Therefore, fly ash removed by stack mechanical collectors and electrostatic precipitators must be disposed of on land (Brown et al. 1976). Because this ash contains concentrations of trace elements elevated over the general lithosphere (Furr et al. 1977, Bowen 1966), including some potentially toxic trace heavy metals (Anon. 1973), there exists the possibility of polluting aquatic systems receiving drainage from ash disposal sites.

Our studies have sought to detect elevated trace metal concentrations in biotic and abiotic components of a stream-swamp complex on the Department of Energy's Savannah River Plant (SRP) in South Carolina. The SRP is located on the upper coastal plain, and the surface waters are characteristically acidic and have low inorganic ligand concentrations. Thus, inorganic complexation equilibrium chemistry predicts that trace metals introduced into these waters would exist in solution mainly as free divalent cations or oxyanions. Therefore, in the absence of significant organic complexation, trace metals introduced into southeastern surface waters may be more available to biota and thus more toxic than in harder waters.

STUDY AREA

Fly ash is introduced into the Beaver Dam Creek stream-swamp system from the routine operations of a four unit, 396×106 btu hr^{-1} coal burning steam plant that has been operating since 1952. In 1975 the plant burned 333,500 tons of coal averaging 1.39% sulfur. The ash content of the coal is currently 11.9%, a rise from 9% during early operations. Prior to 1976, about two-thirds (28,600 tons yr^{-1}) of the ash was collected by mechanical cyclone collectors (60%) or as bottom ash (40%). The remaining ash (10,600 tons yr^{-1}) went up the stacks. Since the beginning of 1976, electrostatic precipitators have operated to remove fly ash from stack emissions with greater than 99% efficiency.

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The ash particulates collected by the electrostatic precipitators are smaller in size than those trapped by the cyclone collectors and contain higher concentrations of many of the trace metals with which we are concerned (Florton et al. 1977).

Until recently, the combined bottom and fly ash has been sluiced into one of two 50 m x 100 m settling basins where many of the ash particulates sediment out. About 4.9×10^9 l yr^{-1} of sluice water is used. An unknown fraction of the sluice water, along with elements leached from the ash, percolates into the underlying water table. These two basins have recently been filled with ash, and a new larger basin to the east is currently receiving the sluiced ash. Overflow water from these basins, along with the smaller sized or less dense fly ash particulates in suspension, drain through a single channel into a 2.5 km² swamp. This connects in turn with Beaver Dam Creek, and the combined flow passes through a small 1,000 m x 25 m lake and into a second swamp before entering the Savannah River. Periodic flooding caused by flow regulation of the Savannah River can back up Savannah River water as far as the junction of Beaver Dam Creek and the first swamp. Upstream from here, Beaver Dam Creek is formed from branches originating as process water from the steam plant and heavy water (D_2O) enrichment facility.

Most of the water flowing down Beaver Dam Creek is not local surface runoff, but has been pumped from the Savannah River. The flow ranges from 35 to 65×10^9 l yr^{-1} . This water has been treated with alum and lime as flocculants, chlorine as a biocide, sodium sulfite, and phosphates. Annual additions to Beaver Dam Creek from the power plant and heavy water plant also include 3,800 liters of 30% silicone solution, 1,800 kg detergents, 450 kg concrete cleaner, 11,200 kg Na_3PO_4 , 2,200 kg H_3PO_4 , 675 kg mixed $\text{KMnO}_4 + \text{MnO}_2$, 9,000 kg H_2S , and heated water. Periodic regeneration of the ion exchanger in the power plant at one to two day intervals utilizes 25 kg or larger additions of H_2SO_4 and NaOH which are added in alternate pulses to Beaver Dam Creek. Resultant pH transgressions range from as low as 4 to as high as 11.

Steel Creek, an adjacent stream similar to Beaver Dam Creek but not receiving ash effluent, was sampled for comparative purposes. It drains approximately 9,000 ha of pine forests on the SRP, and has a narrow valley bounded by 45 m high clay cliffs in some areas. Steel Creek received production reactor cooling water and purge water from reactor fuel and target disassembly basins until 1967. A thorough discussion of ^{137}Cs cycling in Steel Creek is given by Brisbin et al. (1972), while trace metal transport is discussed in detail by Giesy and Briese (1978). The normal pH, alkalinity, and hardness regimes for Steel and Beaver Dam Creeks are similar with mean values of 6.4 and 6.6, 26 and 25 mg l^{-1} CaCO_3 , and 15 and 23 mg l^{-1} CaCO_3 , respectively.

METHODS

Samples of water, suspended particulate matter, periphyton, and aquatic and semi-aquatic plants were collected from both creeks during a fifteen month period in 1976 and 1977 in order to compare concentrations of Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn between the two creeks. Samples of water and suspended particulates were collected from the ash slurry entering the settling basin and in the effluent from the basin entering the Beaver Dam Creek drainage. Samples of precipitator ash from the power plant were subjected to leaching in order to predict how readily the associated trace metals might be dissolved and thus enter Beaver Dam Creek in solution.

Water samples were collected directly in acid-washed polyethylene bottles. Suspended particulates were separated by continuous flow centrifugation with a Sorvall SS-1 centrifuge

which the effluent flows before entering the creek. (5) Organic matter at relatively higher levels in Beaver Dam Creek may complex dissolved metals and reduce their availability to plants and other biota as has been shown for Cd (Giesy et al. 1977). (6) The ability of organisms to regulate their metal content against external concentration fluctuations may also limit the impact of the effluent on Beaver Dam Creek plants. Terrestrial plants grown in soils amended with fly ash accumulate certain trace elements such as As, B, Se, and Mo to levels greater than plants from non-amended soils (Furr et al. 1977). Aquatic plants, rooted in sediments containing coal ash, might also be expected to show elevated concentrations. However, elements which are essential to plants and whose concentrations are therefore regulated would not be expected to show elevated concentrations reflecting elevated sediment concentrations. This may explain why Zn, Mo, Fe, and Co, all essential elements, are no more concentrated in plants in Beaver Dam Creek than in Steel Creek, whereas the non-essential elements, Cd, Cr, and Pb, are more concentrated in the creek with higher environmental concentrations. Manganese, an essential plant nutrient, and Ni, not known to be essential, do not fit this pattern, and Cu is ambiguous. The location of *Salix nigra* on higher ground and thus less exposure to coal ash in stream deposits may explain its poor reflection of elevated metal levels in Beaver Dam Creek.

Although we observed only minor elevations in metal concentrations in Beaver Dam Creek that seem attributable to the ash basin, that does not mean that other aquatic systems might not experience more extensive impact of this sort. There are other systems of less dilution capacity, greater coal and ash metal content, and different water chemistry in ash basin and receiving waters. Helmke et al. (1977) have reported increases by factors of 5 to 20 in concentrations of Ba and Cr in water, suspended particulates, and aquatic invertebrates of a channel receiving ash basin effluents, with lesser elevations of Sb and Se. Metal problems are likely to be greatest in areas where dilution water is limited, as in the arid west, where high sulfur coal results in acidic basin effluents or where the natural waters have lower pH, causing the greater solubility of many metals from ash particulates (Theis and Wirth 1977).

Even in the absence of extensive metal pollution in the Beaver Dam Creek system, the effluent has had an influence on biota, with a reduction in biological diversity observed in the drainage between the basin exit and its entrance into Beaver Dam Creek (Guthrie et al. 1974). Magnuson et al. (1977) observed changes in the composition and abundance of aquatic invertebrates in a drainage stream receiving ash basin effluents. Skogerboe et al. (1977) and Birge (1978) have both observed toxic effects of coal ash aqueous leachates on aquatic biota. Although toxicity could not be definitively attributed to trace metals in the leachate, Cu, Al, Ni, Zn, and Cd (among others) were at concentrations in the leachate and in some ash basin effluents sufficient to be toxic if applied singly in flowing bioassay experiments. Whether such effluents would remain toxic after dilution in receiving waters is uncertain and argues for consideration of both the chemistry and ecology of receiving waters where ash disposal effluents enter.

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Water, suspended particulates, periphyton, and emergent plants were analyzed for the trace metals, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn in a stream-swamp system receiving effluents from a coal ash disposal basin, and in a comparison stream on the Savannah River Plant, South Carolina. The effluent-receiving system showed small (less than four times) elevations in metal concentrations in biotic and abiotic components relative to the comparison stream. Factors limiting the impact of the effluents on metal concentrations to such minor levels include metal concentrations in ash materials, particle retention in the basin, sorptive phenomena, dilution, and homeostatic regulation of essential elements by plants.

REFERENCES

- Andren, A., M. Anderson and N. Loux. 1977. Documentation of Environmental Change Related to the Columbia Electric Generating Station. Tenth Semi-annual Rpt. Winter-Spring 1977. IES Report 82, June 1977, Institute for Environmental Studies, Univ. Wisconsin, Madison.
- Anonymous. 1973. Trace metals: unseen pollution threat. Chem. and Eng. News 19:29, 30, 33.
- Birge, W.J. 1978. Aquatic toxicology of trace elements of coal and fly ash. In J.H. Thorp and J.W. Gibbons (eds.), Energy and Environmental Stress in Aquatic Systems. U.S. Dept. Energy Symp. Series (CONF-771114), (in press).
- Bloom, H. and G.M. Ayling. 1977. Heavy metals in the Derwent estuary. Environ. Geol. 2:3-22.
- Bowen, H.J.M. 1966. Trace Elements in Biochemistry. Academic Press, London, 241 p.
- Briese, L.A. and J.P. Giesy. 1975. Determination of lead and cadmium associated with naturally occurring organics extracted from surface waters, using flameless atomic absorption. Atomic Abs. Newsletter. 14(6):133-136.
- Britsin, I.I., Jr., R.J. Beyers, R.W. Dapson, R.A. Geiger, J.B. Gentry, J.W. Gibbons, M.H. Smith and S.K. Woods. 1972. Patterns of radiocesium in the sediments of a stream channel contaminated by production reactor effluents. Health Phys. 27:19-27.
- Brown, J., N.J. Ray and M. Ball. 1976. The disposal of pulverized fuel ash in water supply catchment areas. Water Res. 10:1115-1121.
- Bryan, G.W. and L.G. Hummerstone. 1977. Indicators of heavy-metal contamination in the Looe estuary (Cornwall) with particular regard to silver and lead. J. Mar. Biol. Assoc. U.K. 57:75-92.
- Davison, R.L., D.F.S. Natusch, J.R. Wallace and C.A. Evans, Jr. 1974. Trace elements in flyash: Dependence of concentration on particle size. Environ. Sci. Technol. 8:1107-1113.
- Dreesen, D.R., E.S. Gladney, J.W. Owens, B.L. Ikerkin, C.L. Wienke and L.E. Wangen. 1977. Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal-fired power plant. Environ. Sci. Technol. 11:1017-1019.
- Furr, A.K., T.F. Parkinson, R.A. Hinrichs, D.R. Van Campen, C.A. Beche, W.H. Gutenmann, L.E. St. John, Jr., I.S. Pakkala and D.J. Lisk. 1977. National survey of elements and radioactivity in fly ashes: Absorption of elements by cabbage grown in fly ash-soil mixtures. Environ. Sci. Technol. 11:1194-1201.

Table 2 Trace metal concentrations in suspended particulates and periphyton collected from Beaver Dam (BD) and Steel (S) Creeks. Mean concentrations are reported as $\mu\text{g}\cdot\text{l}^{-1}$ dry weight with ± 2 standard error confidence limits. Sample size is reported in parenthesis.

| Element | Beaver Dam (BD) | | Steel (S) | | Periphyton | | | | | |
|---------|-----------------|-------|-----------|-------|--------------|---------------|---------------|---------|---------|----------|
| | Mean | SE | Mean | SE | Particulates | Mn | Ni | Pb | Zn | |
| Cd | 1.9 + 0.6 | (26) | 70 + 9 | (26) | 149 + 24 | 58000 + 8000 | 2900 + 900 | 39 + 18 | 80 + 17 | 290 + 53 |
| | 0.4 + 0.2 | (3) | 53 + 36 | (3) | 94 + 33 | 64000 | 7600 + 9100 | 14 + 11 | 48 + 34 | 154 + 33 |
| Cr | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Cu | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Fe | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Mn | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Ni | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Pb | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |
| Zn | 1.7 + 0.4 | (102) | 28 + 5 | (103) | 144 + 14 | 61000 + 5000 | 12500 + 4800 | 79 + 16 | 33 + 3 | 240 + 24 |
| | 1.4 + 0.8 | (10) | 31 + 12 | (10) | 46 + 20 | 64000 + 16000 | 25000 + 18000 | 31 + 11 | 29 + 11 | 170 + 51 |

Table 3 Metal concentration ratios to that of iron in Beaver Dam and Steel Creek suspended particulate matter and in nitric acid extracts of precipitator ash.

| Source | Metal/Fe X 1000 | | | | | | |
|------------------|-----------------|-----|-----|----|-----|-----|-----|
| | Cd | Cr | Cu | Mn | Ni | Pb | Zn |
| Beaver Dam | .04 | 1.3 | 2.8 | 48 | .8 | 1.5 | 5.3 |
| Steel | .01 | 1.0 | 1.8 | 75 | .07 | 1.3 | 2.7 |
| Precipitator Ash | .07 | 5.4 | 3.7 | 5 | 1.8 | 2.8 | 11 |

background sediment materials (represented by Steel Creek samples) and coal ash, as evidenced by the intermediate ratios found.

Metal concentrations in periphyton are quite similar to those of suspended particulate matter, with the exception of Mn. It seems likely that metals analyzed in these samples are derived predominantly from suspended particulate matter passively entrapped in the open meshed or fibrous structure or on the mucilaginous surface of the periphyton community. Beaver Dam Creek shows higher concentrations of Cd, Cu, Ni, and Zn in periphyton than does Steel Creek, as was the case for suspended particulate matter. Neither Mn nor Co was analyzed in these samples.

Among aquatic and semi-aquatic plants, the cattail, *Typha latifolia*, most consistently showed differences in metal concentration between Beaver Dam and Steel Creek sites. Significantly higher concentrations ($P < .05$) of Cd, Cr, Cu, and Pb were found in the former (Table 4). These elements also tended to be higher in the arrowhead plant, *Sagittaria latifolia*, but less consistently so in the willow *Salix nigra*, collected from Beaver Dam Creek. Conversely, Mn was lower in Beaver Dam Creek plants, paralleling its behavior in water, particulate matter, and periphyton. In contrast, Zn and Ni, which were higher in Beaver Dam Creek water, particulates, and periphyton, showed no significant differences between plants of the two creeks.

DISCUSSION

Overall, the trace metal contamination of Beaver Dam Creek resulting from coal ash effluents is minor. Concentrations of Cd, Cr, Co, Cu, Ni, Pb, and Zn in ecosystem components of Beaver Dam Creek are generally no more than 2 to 4 times those in a similar stream receiving no ash effluent, and they are frequently indistinguishable in their trace

Table 4 Metal concentrations in emergent plants from Beaver Dam (BD) and Steel (S) Creeks. Mean concentrations are reported as $\mu\text{g}\cdot\text{g}^{-1}$ dry weight with ± 2 standard error confidence limits. N = 80 for BD and 20 for S.

| Element | <i>Salix nigra</i> (Leaves) | | <i>Salix nigra</i> (Stems) | |
|---------|-----------------------------|-------------|----------------------------|-------------|
| | BD | S | BD | S |
| Cd | 0.36 + 0.14 | 0.28 + 0.14 | 0.35 + 0.11 | 0.73 + 0.71 |
| | 0.78 + 0.11 | 1.05 + 0.32 | 0.13 + 0.04 | 0.29 + 0.09 |
| Cr | 0.55 + 0.20 | 0.31 + 0.24 | 0.24 + 0.07 | 0.10 + 0.03 |
| | 6.0 + 0.6 | 6.4 + 1.6 | 5.4 + 0.9 | 11.6 + 2.8 |
| Cu | 175 + 41 | 529 + 257 | 56 + 9 | 92 + 50 |
| | 1120 + 190 | 1500 + 360 | 390 + 90 | 450 + 120 |
| Mn | 0.19 + 0.03 | 0.19 + 0.11 | 0.48 + 0.31 | 0.46 + 0.24 |
| | 0.76 + 0.26 | 0.74 + 0.19 | 2.6 + 0.5 | 1.5 + 0.9 |
| Ni | 1.9 + 0.4 | 2.2 + 0.6 | 4.1 + 1.8 | 4.5 + 1.1 |
| | 76 + 11 | 82 + 30 | | |
| Pb | | | | |
| | | | | |
| Zn | | | | |
| | | | | |

metal concentrations. This contrasts with the marked elevation of metal concentrations in aquatic systems receiving metal inputs from other industrial activities such as mining or metal refining (Bryan and Hummerstone 1977, Bloom and Ayling 1977).

Several reasons can be suggested why greater trace metal contamination was not observed. (1) Although containing trace metal concentrations elevated above those of average soils and sediments, this coal precipitator ash contains no more than three to five times the metal levels found in fine-grained Steel Creek sediments (Table 1). Thus, in the absence of solution or precipitation reactions, one would not expect suspended particulate materials in Beaver Dam Creek to contain more than three to five times the trace metal concentrations in Steel Creek, which was what we observed. (2) Although the trace metal solubility of many trace metals from precipitator ash is greater than from natural sediments in Steel Creek (Evans, unpublished data), solubility is less at the near neutral pH of these ash basin waters than at lower pH, and for some metals such as Cr, Mo, and Fe, solubility is less than at pH > 11 (Theis and Wirth 1977, Dreesen et al. 1977, Andren et al. 1977). Thus, the solubilities of many of the metals are lower than they would be in more acidic or alkaline ash disposal basins, and the flux of metals from the basin in solution to Beaver Dam Creek is, therefore, reduced. (3) Many of the metals initially dissolved from ash particles are subsequently removed from solution during passage through the ash basin. This can be seen by comparing concentrations in the incoming ash slurry and ash basin effluent in Table 1. Many of metals existing in solution as cations could be removed by adsorption on negatively charged ash particles or on secondary minerals such as zeolites formed within the ash basin as reported by Andren et al. (1977) in a Wisconsin ash basin. The observation that Mo (thought to exist as the molybdate anion) is not appreciably removed from solution during passage through the basin would support this mechanism. (4) Dilution of the effluent by a factor of 10 by Beaver Dam Creek water further reduces metal concentrations, as does periodic flooding of lower Beaver Dam Creek by the Savannah River. Basin effluent averages 74 $\mu\text{g}\cdot\text{ml}^{-1}$ Mo in solution, but Beaver Dam Creek water has but 0.6 $\mu\text{g}\cdot\text{ml}^{-1}$ Mo, which emphasizes the magnitude of dilution and of removal processes in the swamp area through

with titanium rotor at 7,000 rpm and a flow rate of 242 ml min⁻¹. These conditions should separate particles of greater than 0.15 µm diameter and 2.65 g cm⁻³ density (Periac 1972). The supernatant water was acidified to 1% with redistilled HNO₃ and stored at 4 °C until analyzed. Particulates were digested for four hours at 70 °C with HNO₃ and diluted for analysis.

Periphyton samples were collected on glass microscope slides placed in the creeks for one to two months in modified Cathwood diatometers. Oven-dried at 55 °C, they were digested in ceramic crucibles with redistilled HNO₃ followed by 30% H₂O₂. Vascular plants were collected by hand into clean plastic bags, lyophilized to constant weight, and digested as were the periphyton. Species studied were the blackwillow, *Salix nigra* (separate leaves and stems), arrowhead, *Sagittaria latifolia* (combined leaves and stems), and cattail, *Typha latifolia* (combined leaves and stems).

Precipitator ash samples were equilibrated with 1N ammonium acetate solution for one week at a 1:10 weight-volume ratio. The ash and extract solution were separated by filtration (Gelman Type A/E glass fiber).

Trace metal concentrations were determined using flame and graphite furnace atomization atomic absorption spectrophotometry. Dilutions, matrix modification, and background correction were made as necessary using instrument optimization and other adjustments as described by Briese and Giesy (1975) and Giesy and Briese (1977). Technique blanks were determined to assess possible contamination.

RESULTS

Coal ash settling basins are generally efficient retainers of ash particulates sluiced into them. The basin at the 484-D power plant receives a sluiced coal ash slurry averaging 7,400 mg l⁻¹ suspended solids and delivers to Beaver Dam Creek drainage water containing less than 50 mg l⁻¹ suspended solids. The impact of the basin in elevating trace metal concentrations in Beaver Dam Creek will therefore depend heavily on how readily metals are dissolved from the coal ash and can exit the basin in solution. Moreover, dissolved metals will probably be more readily available to biota in the receiving waters than particulate metals.

The solubility of trace metals associated with coal ash will depend on many factors, especially pH. The ash slurry entering the 484-D disposal basin has had pH values of less than 4 to more than 10, but generally varies around neutrality, as does the water exiting the basin. Extraction of precipitator ash with neutral 1N ammonium acetate solution might then simulate trace metal dissolution from slurried ash particulates. This will probably be an overestimate of metal solubility because precipitator ash comprises only a fraction of the slurried ash, and bottom and other ashes tend to have both lower trace metal concentrations and extractabilities than precipitator ash. Table 1 shows metal concentrations of Steel Creek sediments (A) and precipitator ash (B), percentage extractable by ammonium acetate solution from this ash (C), the predicted concentrations of dissolved metals in the ash pond based on this extraction (D), and predicted changes in Beaver Dam Creek, assuming a further 10 to 1 dilution of (D) with creek water (E). These predictions can be compared to the dissolved concentrations actually measured in the ash slurry (G), the ash basin effluents (H), the receiving waters of Beaver Dam Creek (I), and in a comparison stream, Steel Creek (J). Metals for which the predicted augmentations are comparable to or greater than measured concentrations in Steel Creek would be expected to show up as differences in the mean metal concentrations between Steel and Beaver Dam Creeks, assuming the

Table 1. Metal concentrations in coal precipitator ash, in waters impacted by coal ash and concentrations changes predicted by ash extraction with 1N ammonium acetate. Measured concentrations are means ± 1 standard deviation.

| | A | B | C | D | E | F | G | H | I | J |
|----|-------|-------|--------|------|-----|-----|-----|-----|-----|-----|
| Cd | 4 | 71 | 48 | 2.5 | 25 | 30 | 24 | 28 | 36 | 17 |
| Co | 24 | 67 | <1.5 | <7 | <7 | 8 | 8 | 2.8 | 2.7 | 1.2 |
| Cu | 55 | 171 | 3 | 2 | 7.4 | 1.4 | 4 | 15 | 18 | 2.5 |
| Cr | 31 | 130 | 2.3 | 2.2 | 14 | 12 | 11 | 20 | 6.7 | 7.9 |
| Fe | 28000 | 51000 | <0.004 | <1.5 | <15 | 420 | 200 | 220 | 140 | 60 |
| Mn | 920 | 352 | 3.1 | 8.0 | 45 | 19 | 36 | 24 | 18 | 15 |
| Mo | --- | 18 | 56 | 73 | 7.3 | 1 | 5 | 130 | 140 | 74 |
| Ni | 62 | 89 | 11.2 | 74 | 7.4 | 1.3 | 1.2 | 9.0 | 9.8 | 4.3 |
| Pb | 75 | 60 | <7 | 43 | 4.3 | 2.5 | 6.5 | 6.7 | 9.5 | 6.7 |
| Zn | 73 | 280 | 6.4 | 240 | 24 | 7.1 | 5.4 | 11 | 10 | 15 |

A. µg g⁻¹ in fine grain Steel Creek sediments.
 B. µg g⁻¹ in precipitator ash.
 C. % extractable from precipitator ash with neutral 1N ammonium acetate.
 D. Change in dissolved metals (µg l⁻¹) in ash basin predicted from extraction (C).
 E. Change in dissolved metals (µg l⁻¹) in Beaver Dam Creek assuming 1:10 dilution of (D).
 F. Measured dissolved metal concentrations (µg l⁻¹) in water used to sluice ash.
 G. Measured dissolved metal concentrations (µg l⁻¹) in ash slurry.
 H. Measured dissolved metal concentrations (µg l⁻¹) in ash basin effluent.
 I. Measured dissolved metal concentrations (µg l⁻¹) in Beaver Dam Creek.
 J. Measured dissolved metal concentrations (µg l⁻¹) in Steel Creek.

differences are due to inputs from the ash basin. On this basis, Cd, Cr, Cu, Zn, and especially Ni and Mo should have measurably higher concentrations in Beaver Dam than Steel Creek. We do indeed observe higher dissolved concentrations of these metals in Beaver Dam Creek than Steel Creek (Table 1), but positive concentrations differences are also seen for Fe, Mn, and Pb, elements for which we predicted little or no difference due to dissolutions from coal ash. The wide variability of dissolved metal concentrations makes the determination of statistically significant differences difficult.

When the predicted dissolution of metals from precipitator ash with ammonium acetate solution (D) is compared with measured mean dissolved concentrations in the ash slurry (G) and in the ash basin effluents (H), the agreement, except for Mo, is poor. The observed mean dissolved concentrations in the ash slurry are less than the extractions would predict for all elements except Fe, Cr, and Mo, and much or all of their dissolved concentrations could be due to the content in the sluicing water prior to its mixing with ash. Moreover, dissolved metal concentrations are generally less in the ash basin effluent than in the ash slurry input, indicating adsorptive or precipitative losses from solution during water transit through the basin. Thus, although we observed higher dissolved metal concentrations in Beaver Dam Creek which received ash basin effluents than a similar stream which did not, the differences cannot be convincingly attributed to coal ash.

Physical evidence of coal ash is found in the Beaver Dam Creek drainage as ash deposits in slack water areas, apparently the result of less efficient retention of ash particulates in the basins in the past or erosion of ash used in road fill. As a result, we might expect to find ash-derived metals in Beaver Dam Creek particulate matter. Table 2 shows metal concentrations in suspended particulate matter collected from both Beaver Dam and Steel Creeks. With the exception of Fe and Mn, metal concentrations are greater in Beaver Dam Creek, although observed variability again makes it difficult to conclude that the differences are statistically different. Cadmium, nickel, and zinc seem to be the metals most clearly elevated in Beaver Dam Creek, by about a factor of two to four. If metal concentration ratios to that of iron are calculated (iron being a major natural component of soils and sediments not enriched in coal ash) it is seen that these ratios are greater in Beaver Dam Creek than Steel Creek and less than that of nitric acid extracts of precipitator ash (Table 3). Suspended particulate matter would appear to be a mixture of natural

- Giesy, J.P. and L.A. Briese. 1977. Metals associated with organic carbon extracted from Okfenokee swamp water. *Chem. Geol.* 20:109-120.
- Giesy, J.P. and L.A. Briese. 1978. Trace metal transport by particulates and organic carbon in two South Carolina streams. *Intl. Verein. Limnol. Verhandlungen* (in press).
- Giesy, J.P., Jr., G.J. Leverage and D.R. Williams. 1977. Effects of naturally occurring aquatic organic fractions on cadmium toxicity to *Simonephalus serrulatus* (Daphniidae) and *Gambusia affinis* (Poeciliidae). *Water Res.* 11:1013-1020.
- Guthrie, R.K., D.S. Cherry and J.H. Rodgers. 1974. The impact of ash basin effluent on biota in the drainage system. pp. 17-43, In *Proc. 7th Mid-Atlantic Ind. Waste Conf.* Nov. 12-14, Drexel Univ., Philadelphia, PA.
- Helinke, P., W. Robarge, M. Schoenfeld and J. Thresher. 1977. Trace elements. In *Documentation of Environmental Change Related to the Columbia Electric Generating Station. Tenth Semi-Annual Report Winter-Spring 1977*, IES Rpt. 82, June 1977, Institute for Environmental Studies, Univ. Wisconsin, Madison.
- Horton, J.H., R.S. Dorsett and R.E. Cooper. 1977. Trace elements in the terrestrial environment of a coal-fired powerhouse. DOE Report DP-1475. E.I. DuPont de Nemours and Company, Savannah River Laboratory, Aiken, SC, 49 p.
- Magnuson, J., A. Forbes, J. Schwarzmeier and D. Harrell. 1977. Aquatic invertebrates. In *Documentation of Environmental Change Related to the Columbia Electric Generating Station. Tenth Semi-annual Rpt. Winter-Spring 1977*. IES Rpt. 82, June 1977, Institute for Environmental Studies, Univ. Wisconsin, Madison.
- Perhac, R.M. 1972. Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in dissolved and particulate solids from two streams in Tennessee. *J. Hydrobiol.* 15:177-186.
- Rohman, F.A. 1971. Analyzing the effect of fly ash on water pollution. *Power* 115:76-77.
- Skogerboe, R.K., D.F.S. Natusch, R.C. Russo and R.V. Thurston. 1977. Chemical characterization and aquatic bioassays of energy development process effluents. *Energy/environment II*. pp. 503-508, In *Second National Conf. on the Interagency R & D Program*. June 6 and 7, 1977, Sponsored by the Office of Energy, Minerals and Industry, Office of Research and Development, Environmental Protection Agency.
- Theis, T.L. and J.L. Wirth. 1977. Sorptive behavior of trace metals on fly ash in aqueous systems. *Environ. Sci. Technol.* 11:1096-1100.