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CHESAPEAKE BAY RESEARCH CONFERENCE

**Effects of Upland and Shoreline Activities
on the Chesapeake Bay**

Proceedings of the Chesapeake Bay Research Conference

**EFFECTS OF UPLAND AND SHORELINE LAND USE ON
THE CHESAPEAKE BAY**

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TRACE ELEMENT CONTAMINATION FROM FLY ASH SITES NEAR CHISMAN CREEK VA.

by

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ABSTRACT

The safe disposal of fly ash from power plants remains a concern because of dwindling available disposal sites and potential or actual environmental consequences. During the period from 1957 to 1974, the Virginia Electric and Power Co. station at Yorktown used a mixture of coal and refinery coke for power generation. The fly ash and bottom ash byproducts were disposed of in borrow pits which drain into Chisman Creek, a small estuary near the York River. In 1980 a domestic well near the pits turned green and tests revealed high concentrations of V and Se in some wells. Subsequently, contaminated wells were capped and homes were connected to the municipal water supply.

In late 1981 with a small grant from the Virginia Environmental Endowment, we began a more detailed investigation of possible contamination from the pits. The sampling program included groundwater, surface water, estuarine water, flyash, soils near the pits, oysters and a variety of plants in the immediate vicinity. Most importantly, these samples were analyzed by PIXE (Proton-Induced X-Ray Emission), a sensitive and accurate multielemental technique which can simultaneously detect all elements from silicon to uranium without prior knowledge of the elements present.

Cores from monitoring wells drilled into one of the pits were analyzed to determine the spatial elemental composition within the fly ash and fly ash leachate. Analysis of shallow and deep well waters gave evidence for both vertical and lateral migration of leachate from the pit, although soil interactions apparently restrict groundwater concentrations outside the pits. Comparison of PIXE analyses of leaf tissues from woody upland, woody wetland, and wetland monocot species with controls demonstrated accumulation of several elements, especially selenium and nickel. Accumulation of several elements in wetland plants, as well as elevated Ni, V, and As concentrations in surface sediments for the upper mile of the estuary together indicate that some mobilization of trace elements into Chisman Creek is still occurring. Nickel and vanadium are unusually abundant in this fly ash due to the use of refinery coke in the fuel. Quantitative estimates of contamination would require a larger sampling program and greater resources than we had available for this work. In this regard analysis of oyster samples was inconclusive due to the limited number of available samples and tidal fluctuations in the estuary.

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EXPERIMENTAL SECTION

Sample Collection and Preparation. Each fly ash, soil and estuarine sediment sample was kept in a plastic bag until dried in a specially prepared, trace element free convection oven at 60 °C for at least 12 hours. All samples were dry sieved through a 3 mm polypropylene screen to remove large pieces of organic matter or pebbles and homogenized before selecting an aliquot for sample digestion.

Separate portions of the dried, homogenized samples were subjected to room temperature leaching with 5N nitric acid (in the ratio of 10 ml to 5g dry weight) for 2 hours. Soil or fly-ash was separated from the 5N nitric acid leachate and subsequent 2% nitric acid rinses by centrifugation. The leachate and rinses were combined, doped with indium as an internal standard, and spotted on targets for PIXE analysis. The HNO₃ mild chemical leaching procedure was tested previously for marine sediments collected on the mid-Atlantic outer continental shelf (Harris, et al., 1977).

Sediment bottom grabs were collected along the entire Chisman Creek estuary and in Goose Creek. Sediment cores were taken in the upstream reaches of Chisman Creek. A similar location in Back Creek was selected to serve as a control site. Estuarine sediments were wet sieved with the aid of deionized water and dried at 60 °C for approximately 48 hours. 5N HNO₃ leachates were prepared as described above.

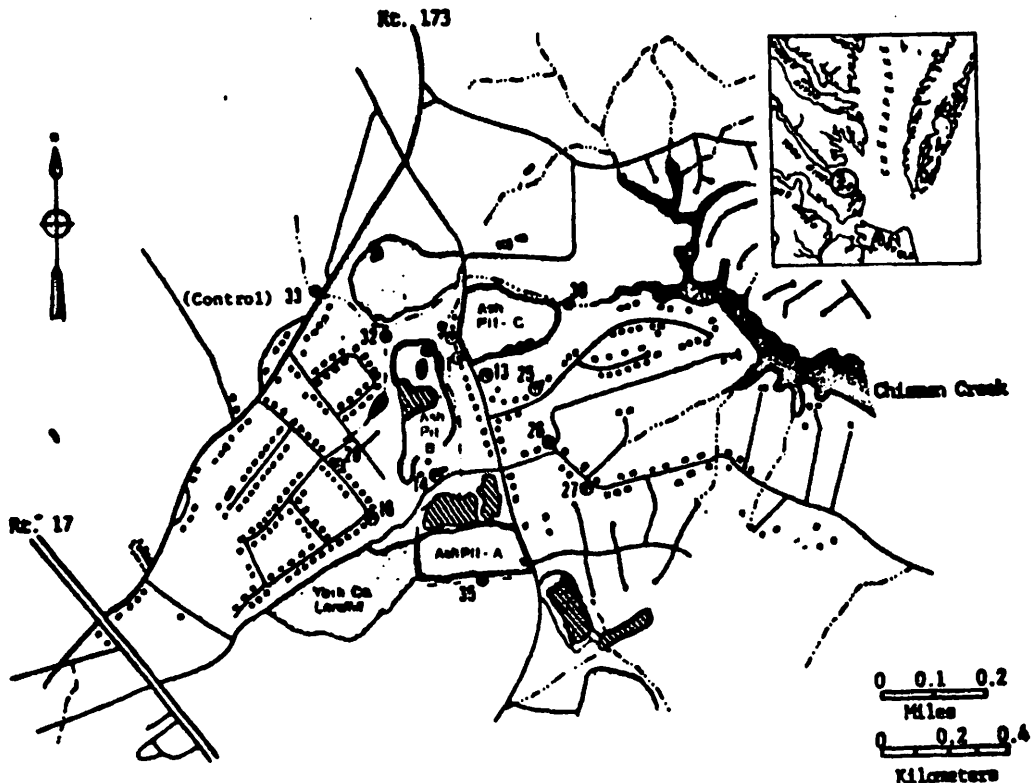


Figure 1. Fly ash disposal site near Chisman Creek in York County, VA

Water Samples

All water samples were collected in 1 liter polypropylene narrow-mouthed bottles, placed on ice and delivered to the laboratory within 4 hours of collection. The rapid and complete separation of particulates and dissolved fraction is essential to prevent any equilibration between the solution particles and container walls prior to analysis. pH readings were taken in the laboratory both before and after filtration through 0.4 nuclepore filters. The filtrate (dissolved fraction) was preserved using 0.05M HNO₃ until analysis (as recommended by the U.S. EPA (1979)). The filtrate was doped with indium as an internal standard and subjected to atomic absorption, PIXE or fluoride analysis. For some samples with relatively low dissolved solids the filtered water samples were preconcentrated to improve detection limits using an all plastic closed system (Grant, 1983).

A total of 66 plant samples, consisting of 24 separate species were collected on February 12, May 5, July 21 and October 15 1982. With the exception of perennial species collected on February 12 (grasses, rushes, goldenrod, etc.) all samples were living viable tissue. Upland species were collected near ash pits A, B, and C (figure 1) while wetland species were collected to the North and East of pit C.

Available species at sites located within the pit itself were sampled where possible in proximity to sampling piezometers where ground water was monitored. Control samples of the same species were collected where feasible at several sites upstream of the pit and in local marsh systems. Woody species were sampled by the removal of above ground growth (healthy branches and leaves) while the smaller herbaceous species were taken whole wherever possible (roots, rhizomes, stems). The samples were placed in plastic storage bags and transported immediately to the laboratory.

Upon receipt at the laboratory, plant parts were dissected immediately to remove dead tissue and to isolate subsamples from some species for separate analyses. These subsamples were then placed in pre-cleaned polyethylene bags in preparation for washing.

The wash procedure employed was designed to effectively remove site contaminants and dust, while still retaining those endogenous trace elements within plant tissues. Plants were agitated at least five times with several portions of deionized H₂O and rinsed until visible evidence of particles was absent from the rinse water. After washing all samples were rinsed (5X) with deionized water and dried in a trace metal free oven at 60 °C; for an average of 8 days to constant weight, as recommended by NBS for SRM 1575 (Pine Needles). After drying, each sample was then ground to #100 mesh using a SPEX 8000 grinder mill with acrylic beads or a SPEX 8500 shatterbox, using an alumina ceramic puck and dish.

Analytical Procedures.

Prepared samples were analyzed for trace element content using either Proton Induced X-ray Emission (PIXE), Atomic Absorption Spectrophotometry (AA), or both. PIXE is particularly useful for large scale environmental studies because of its rapid analysis of a large number of elements simultaneously from one sample (Harris, et al., 1977). AA requires more analytical time, but provides a lower detection limit for some elements. The PIXE data were analyzed for elemental composition using the comprehensive computer program described by Buckle, et al. (1976).

Powdered targets for PIXE analysis were prepared using standard laboratory procedures. The ground material was pushed on to a pre-tared polycarbonate film through a 100 mesh nylon screen. The powder was weighed and encapsulated on the blank with polystyrene film solution. The result is a uniform distribution of the material over a measurable area. External standards used in the analysis included NBS 1575 Pine Needles and NBS 1571 Orchard Leaves. Powdered targets of these materials were prepared using the identical procedure. Quality control procedures in routine use were as follows:

- (1) the use of highest purity reagents
- (2) in-house generation of high purity acids and water equivalent to NBS specifications
- (3) routine analysis of reagents used
- (4) rigorous cleaning of all labware before use according to established protocols
- (5) inclusion of procedural blanks with samples
- (6) analyses of standard reference materials of known composition similar to the samples analyzed
- (7) analyses of master mixes prepared from highest purity elements or compounds.

The pH of all water samples was measured in the laboratory within 2 hours of receipt using an Orion Model 801 pH meter with a Ross combination pH electrode (Model 815500). Fluoride measurements were made using an Orion Model 94-09 solid state fluoride electrode according to EPA method 340.2.

RESULTS AND DISCUSSION

In this study a variety of sample types was collected from different environments. The results of the analyses will be presented in a sequence more or less analogous to the presumed transfer of trace elements from the fly-ash through the environment: the composition of fly-ash and groundwater within the ash deposits, transport processes to the estuary, trace element accumulation in plants proximal to the disposal site, and possible contamination in estuarine sediments and oysters.

Fly ash and groundwater within the fly ash pits.

A relatively intensive sampling of one fly-ash deposit, Pit C, was conducted because this pit is very close to Chisman Creek and near the two homes where "green water" occurred. When wells were drilled to determine the stratigraphy, (Oakes, 1982) ash samples were collected from several depths. Soil samples from the Tabb formation and the underlying Yorktown formation were also collected.

It is important to remember that all of these trace elemental analyses were conducted on fly-ash which has weathered in the natural environment for a period of 10 to 20 years. Accordingly, a portion of the soluble elements probably has already leached from the fly-ash and some unknown amount of equilibration has already occurred between leached trace elements in the groundwater and soil particles in the surrounding area.

It is unlikely that more than a small fraction of the "total" trace elements in fly-ash would become available to the environment through chemical or biological action. Accordingly, a few chemical procedures for leaching trace elements from fly-ash were compared. Concentrations from the leaches generally decrease in the following order: total metals (aqua

regia digest slurry), aqua regia metals (without undigested particles), 5N HNO₃ digest (aqueous mineral acid digest). It should be noted that the pH of groundwaters within the pit was as low as 3.5. Thus the concentrations of those elements which are soluble at that pH, nickel for example, are a significant fraction of the total, whereas the solubility of other elements, such as titanium, which form hydroxides or hydrous oxides above pH 3, are extremely low.

The most useful chemical indicator of environmental availability used in this study is believed to be the mild HNO₃ digestion at room

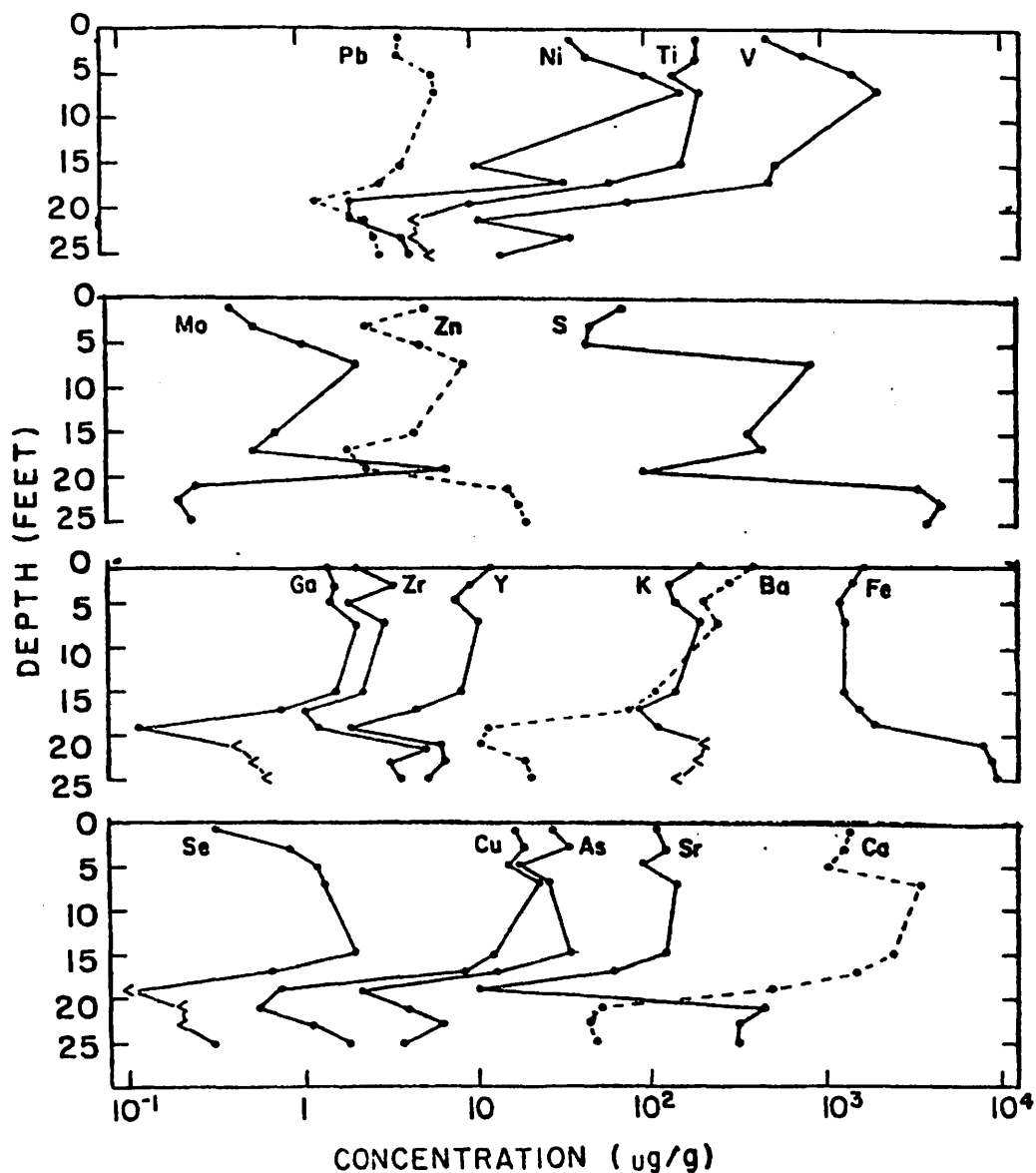


Figure 2. Trace element variation with depth in fly ash and soils from well 17D. PIXE results are from 5N HNO₃ leachates in ug/g (dry weight)

temperature (non-oxidizing conditions). The results of the acid digestions, expressed as percent of "total metal", were generally in the range of 40-90%. These percentages probably represent an upper bound on the portion of these elements which would be available to the environment under the natural conditions encountered. While the percentages for many elements are relatively small, it should be kept in mind that there is a very large volume of fly-ash in these pits.

The vertical distribution of trace elements within and below fly-ash Pit C is illustrated by Figure 2 for the drilling core from well 17. Physical examination of this vertical profile revealed fly ash down to a depth of approximately 18 feet, then approximately 2 feet of quartz sand remaining from the Tabb formation, followed by penetration into the Yorktown formation below. Arsenic, for example, can be seen at a concentration of approximately 50 ppm throughout the fly-ash, decreasing to 4 ppm in the Tabb formation and rising to a concentration of approximately 8 ppm in the underlying Yorktown formation. In general it can be seen that most elements are higher in concentration in the fly-ash than they are in the underlying Yorktown formation with notable exceptions of iron, zinc and sulphur. Molybdenum is apparently highest in the Tabb formation.

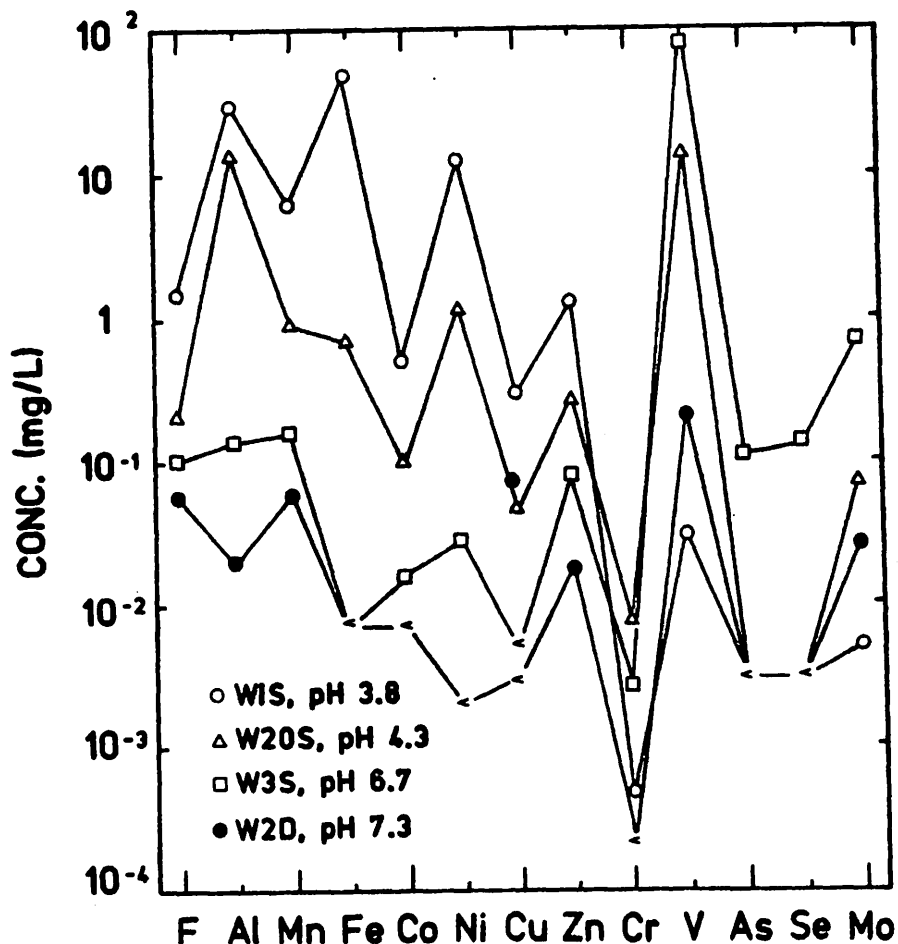


Figure 3. Dissolved trace element concentrations in groundwater residing in fly ash pit C.

Representative trace element data for water from monitoring wells in pit C are plotted in figure 3. The most highly contaminated water was found in wells 1S and 20S, near the bottom of the fly ash and to the downstream side of groundwater flow. Well 3S lies in the pit bottom on the upstream side and well 2D is adjacent to well 3S, but completely in the Yorktown formation underlying the fly ash. These analyses are included in a more complete spatial profile than possible from data reported previously (VA, SWCB, 1981), which shows that upon percolation through the fly ash of pit C, groundwater pH decreases to 3-4 while leaching trace elements before entering Chisman Creek.

Trace element transport to the estuary.

One goal of the groundwater monitoring was to determine if conditions varied seasonally. This was accomplished by repetitive sampling of most of the SWCB wells and some of the wells installed by Oakes (1982). Analysis of these data for most wells, within and outside the disposal sites, showed concentrations varied by less than a factor of 4 for the entire three year period. All of these samples were taken under quiescent conditions, at least several days after a storm event.

The primary purpose of the groundwater sampling was to ascertain the degree of contamination and the area affected. A necessary step towards that goal was the determination of groundwater characteristics within the fly ash deposit. Accordingly, initial groundwater samples were analyzed for a large number of elements. Outside fly ash pit C to the south (upstream), the concentrations of most elements in monitoring wells dropped rapidly to near detection limits, especially acid soluble ones such as Al, Fe, Mn, and Ni. In contrast, the concentrations of elements which can exist as anions near pH 7 (As, Se, V, Mo, etc.) persist at elevated concentrations, although at levels generally below Va Dept of Health limits.

Since there are many areas where exposed fly ash particles as well as dissolved contaminants may be dispersed further during storm events, surface water samples were analysed from a drainage ditch between pit A and new home sites and also from a drainage pond. Storm flow water (pH 7.0) had higher concentrations of most elements than controls which increased about an order of magnitude for most elements after 3 days standing (pH 6.4). Pond waters (pH 7.6) showed similar and often greater levels of contamination.

In order to assess the importance of particulates in storm runoff, PIXE analyses were conducted on suspended particulate matter from stream water, pond water and the drainage water in the construction ditch. All suspended particulates proved abundant in the major and trace elements relative to particulate matter in water from the control stream site. Especially enriched in storm water particulates were vanadium, manganese, nickel and arsenic. Comparing particulate trace to the dissolved fraction for the same water samples, it is evident that some trace elements, such as vanadium and nickel, are entering the estuary in both particulate and dissolved forms.

Minor and Trace Elements in Plant Tissues.

The concentrations of 28 selected trace elements were determined by PIXE from powder targets for 6 plant tissue controls. Excellent detection limits were obtained for several "difficult" elements to determine: arsenic, selenium, and molybdenum. Arsenic and selenium were generally below detection limits in control samples, but frequently elevated and precisely determined in plants grown on contaminated sites

in neutral soils. Vanadium, chromium and cadmium, three environmentally significant elements present in the fly ash, were below PIXE detection limits in most plant samples. However, the detection limits for these elements can be improved by approximately two orders of magnitude after digestion of the plant tissues followed by graphite furnace atomic absorption analyses, and these determinations should be done in future studies.

The concentrations of 21 trace elements found above PIXE detection limits in the wetland monocot, *Typha latifolia* (cattail) are compared in Figure 4 to control values. Both nickel and selenium are markedly elevated in this aquatic plant located near well 1 in the path of ground water draining from fly ash pit C. Interestingly, the concentrations of several other elements appeared to go in opposing directions - comparing cattail shoots to the inflorescence portion of this particular plant - most notably, potassium, barium, manganese and iron. The use of a "<" symbol at a relative concentration of 1.0 denotes that the trace element in both sample and control was below detection limits. A "<" symbol at a relative concentration less than 1.0 means that the control sample alone was found to be above detection limits, and a ">" symbol above a relative concentration of 1.0 means that the contaminated sample only was found to be above detection limits.

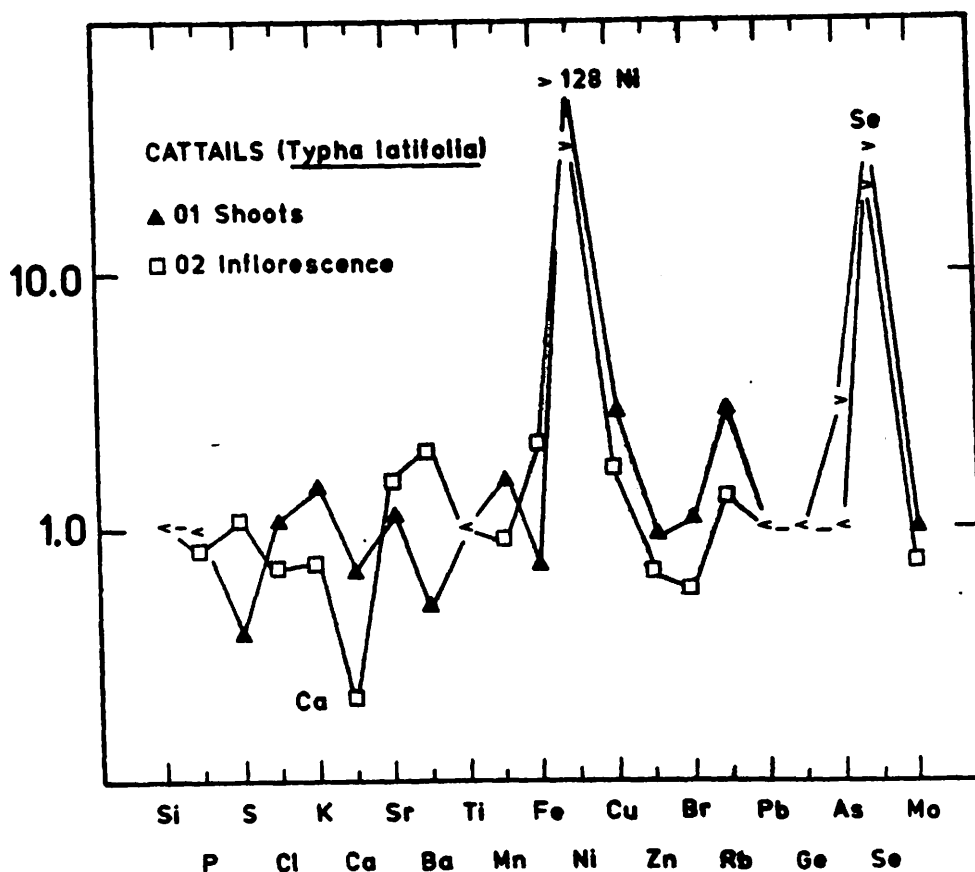


Figure 4. Trace elements in fly ash exposed cattails, relative to controls. PIXE analysis of powder targets.

The trace element composition of Pinus virginiana tissues taken from two different sites in fly ash pit A (pH neutral) show that concentrations of strontium and barium, two elements abundant in the fly ash, are elevated at the expense of calcium. Moreover, the concentrations of arsenic, selenium and molybdenum -- three elements present in fly ash and soluble under pH neutral conditions -- are markedly elevated. Similarly, for Pinus taeda, the concentrations of strontium, germanium, arsenic, selenium, and molybdenum are elevated in plants growing on neutral fly ash but much lower when located near well 1 (acidic conditions). This is undoubtedly related to the chemical solubility of the elements under these conditions, as well as bioavailability to plants. The concentrations of manganese, nickel and copper, three acid-soluble elements, are higher in P. taeda grown near well 1 than near well 4.

Trace elements for sweet gum tissues, also collected near wells 1 and 5, were compared to controls. Once again, for a plant grown on neutral fly ash, many trace elements are elevated in concentration, most conspicuously nickel and selenium. Interestingly, the concentrations of chlorine, manganese, bromine and lead are much lower in these tissues than in "controls".

As part of this preliminary survey, numerous other plant species were collected on or near fly ash pit sites, for which suitable controls of the same species were not available. For several of the plant species, the concentrations of Ni, As, Se, Rb, Sr, Mo, and Ba are elevated compared to other control plants of similar species. These elevated concentrations apparently reflect bioaccumulation by these species also from trace elements in the ground water.

A recent study of the mobility and bioavailability of elements in uranium mill tailings (Dreesen, et. al.) also reported the release of As, Mo, Se, and U from alkaline tailing leachates, which were readily assimilated by two western plant species, especially Mo and Se. Scanlon & Duggan (1979) have investigated trace element uptake in eight woody plant species from fly ash and reported that Ni and Se appeared to be especially available to plants. Our findings with well weathered fly ash appear consistent with these reports.

Trace elements in estuarine sediment and oysters.

Most trace elements are transported within a water system via particulate matter and, due to physical processes, are deposited as sediments. Thus they provide a record of prior conditions. Chisman Creek is a small (4 mile) subestuary fed by numerous small freshwater streams which are generally narrow (3 feet) and shallow (less than 2 feet). Goose Creek drains the northern portion of the basin. The main channel of the estuary is broad (0.5 mile) and river depths at Mean Low Water range from 12 feet at the mouth (confluence with the Poquoson River) to less than 3 feet adjacent to the ash disposal sites.

During the sampling period, seasonal runoff variations caused salinity in Chisman Creek to fluctuate; spring values ranged between 14-18 ppt throughout the main stem; in summer the creek was relatively homogeneous, and salinity was about 20-21 ppt. The pH in both Chisman and Back Creek estuaries ranged from 8 to 9. However, the upstream station in Chisman Creek, which was adjacent to an ash disposal site, was more acidic (pH of 6.4). Suspended solids ranged from 25-50 mg/l in both creeks.

Estuarine sediment samples were analyzed for 69 trace elements, many of which were below detection limits. Previous fly-ash studies in other estuaries have found arsenic, cadmium, chromium, lead, nickel, selenium and zinc at levels of 1 ppm or greater in fish tissues (Davison et al., 1974, Dreeson et al., 1977, Ray and Parker, 1977, Theis and Wirth, 1979). Because of the potential ecological and health concerns, the discussion of results has focused on these elements, as well as copper and vanadium.

Vanadium, arsenic and nickel exhibited a sharp increase in concentration with distance upstream. Of the 69 elements analyzed, vanadium in Chisman Creek sediment samples underwent the most dramatic increase. At the mouth of Chisman Creek, levels were 4.6 ppm. Four miles upstream, vanadium levels reached 541 ppm. Additionally, following a rain storm, stream sediments adjacent to Pit C (STR 30) contained vanadium concentrations of 605 ppm.

It is important to note that all sediment samples were passed through a 3mm mesh sieve to remove large particles and shells. However, no additional fractionation of the samples was done. Variations in particle size distributions undoubtedly affect the trace element distributions, and some portion of the observed decrease in concentration downstream is due to the increase in particle size that typically occurs in all estuaries (Luoma, 1983)

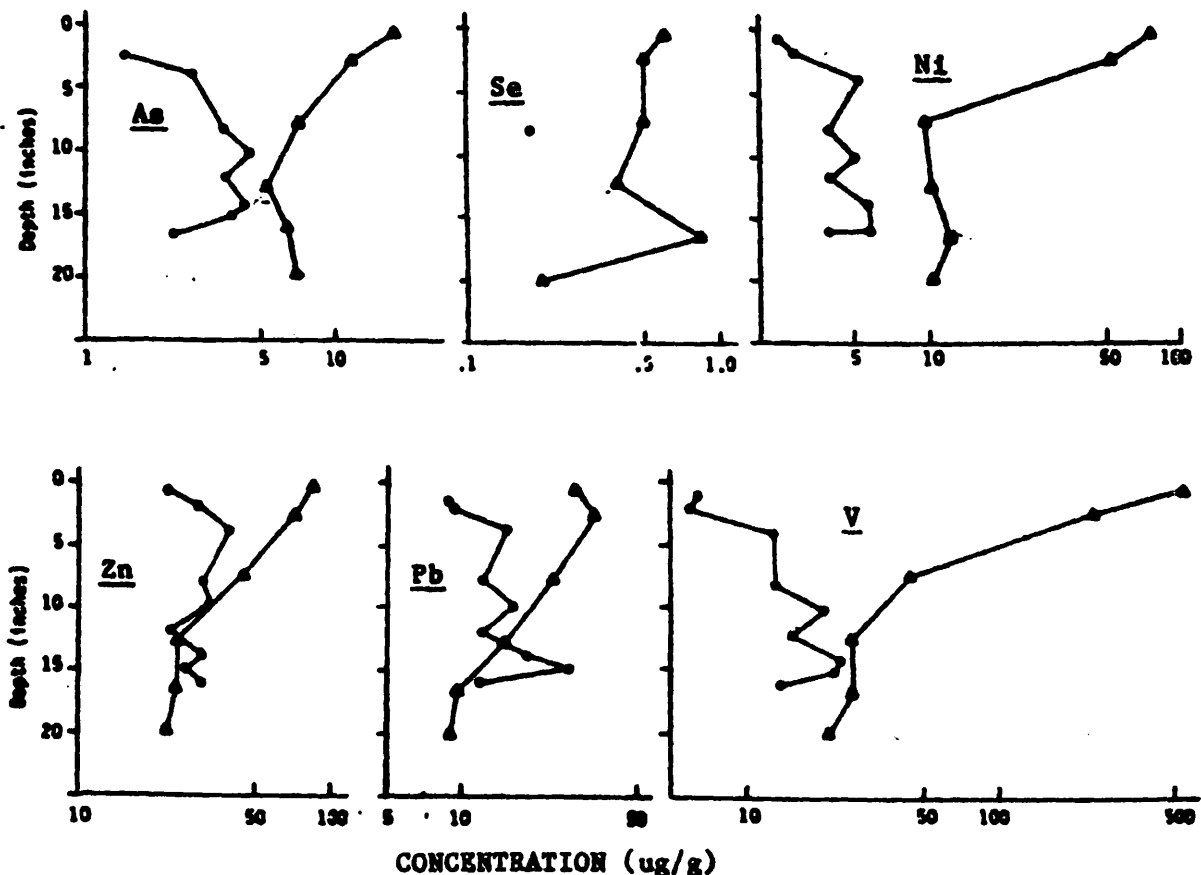


Figure 5. Trace elements in sediment cores from Chisman Creek () and Back Creek (), the control site. PIXE analyses of 5N HNO₃ leaches.

Analyses for 20 inch sediment cores are given in figure 5. For the elements vanadium, selenium, zinc, lead, arsenic, nickel and copper, concentrations were in all cases lower in the control core taken in Back Creek than in the core from Chisman Creek. Cadmium was not measurable in either creek and chromium was detected only at a depth of 12.5 inches in Chisman Creek (6 ppm). Concentrations of the trace elements in Chisman Creek were generally highest in the top 6 inches of sediment and, except for zinc and lead, these values were an order of magnitude greater than those present in Back Creek.

Vanadium, nickel and arsenic, elements which appear to be reasonable indicators of fly-ash impacts in the estuary, were greatly elevated in the Chisman Creek core to a depth of 6 inches when compared to the control core. Concentrations became more constant at depths greater than 10 to 12 inches, which may reflect background levels for the estuary. It also should be noted that at depths greater than 15 inches (75 years), trace element concentrations were similar in both creeks. A physical inspection of sediment texture indicated that the Chisman Creek core sediment was quite homogeneous with depth. The presence of uniform texture suggests that the observed elevated trace element concentrations in the upper 6 inches reflect contamination rather than the influence of a gradient in sediment particle size.

Trace element levels in oysters are difficult to interpret, primarily because of the low abundance in this estuary. Vanadium appeared to be the only element that showed a distinct increase in concentration with distance upstream. No trend was evident for most elements, although concentrations of copper, zinc, cadmium, nickel, chromium and lead were highest in oysters from Goose Creek.

Summary. The composition of fly ash and groundwaters in and near waste disposal sites in York County, VA have been investigated. Ten years after closing this site, the groundwaters outside the pits contain substantial concentrations of many trace elements present in the ash. Continuing dispersal of many trace elements through leachates and particulates during storm events was demonstrated. PIXE analyses revealed accumulation of several trace elements in terrestrial and aquatic plants and the top layers of estuarine sediments in Chisman Creek.

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