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# THE NATURE AND EXTENT OF TRACE ELEMENT CONTAMINATION ASSOCIATED WITH FLY-ASH DISPOSAL SITES IN THE CHISMAN CREEK WATERSHED

A Report to:

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> > June, 1983





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### THE NATURE AND EXTENT OF TRACE ELEMENT CONTAMINATION ASSOCIATED WITH FLY-ASH DISPOSAL SITES IN THE CHISMAN CREEK WATERSHED

by

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June, 1983

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This study was conducted by the Virginia Institute of Marine Science (VIMS) and the Virginia Associated Research Campus (VARC), both branches of the College of William and Mary, to document the nature, extent, and severity of environmental contamination by trace elements from the landfill disposal of fly-ash within the Chisman Creek watershed. Previous work in the area demonstrated that some metals were apparently mobile in the groundwater, and that two nearby household wells were contaminated (Va. SWCB, 1981). These short term studies were limited to the testing of only a few selected contaminants in wells near the fly-ash pits. The goal of our study was to provide a more comprehensive sampling of the basin to delineate the geographical extent of trace element contamination, and to assess whether the levels found there pose a hazard to man or to the terrestrial and aquatic ecosystem. An important aspect of the program is the use of an analytical technique which provides simultaneous measurement of a large number of elements, thereby obviating the need to speculate which elements would be found before the field work was begun. Proton Induced X-ray Emmission (PIXE) is such a technique and provided data on 70 elements from each sample collected during this study.

Measurements made at control stations were used to establish 'background' concentrations of trace elements in soils, groundwater, surface water (streams), estuarine sediments, and oysters. The results from samples collected in and adjacent to the ash deposits were then compared to these background levels to determine if concentrations exceeded those normally expected. The results were also compared to existing water quality standards and criteria to assess the potential hazard posed by the trace element concentrations encountered in the various components (water, sediments, biota) of the Chisman Creek watershed and estuary.

The findings of the study are summarized in Table 1 for the important elements. An 'X' in the table represents observed concentrations exceeding the corresponding background concentrations. In the case of the composition of the fly-ash itself, concentrations

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	Fl	y-Ash		Groundwate		Surface Water Stream Below Pits	Estuary	
Element	Aqua Regia	HNO3 Leaches	Within Ash	Beneath Ash	Adjacent to Pits		Sediments	Oysters
Cadmium (Cd	) X		Х		X			
Nickel (Ni)	х	Х	х	X		X	x	х
Vanadium (V	) X	Х	X	Χ.	x	X	x	X
Manganese (Mn) X		X	X*	X*	X*	X*†		
Iron (Fe)	х		Χ*	X*		X*†		
Arsenic (As	) X	X	X*				x	
Aluminum (A	1) X	no data	х					
Chromium (C	r) X	no data	х	х				
Copper (Cu)	x	X	X.					
Selenium (S	e) X	X	Х*					
Zinc (Zn)	х	Х	х					
Silver (Ag)	х		х					
Lead (Pb)	х	X						
Molybdenum	х	Х						
(Mo) Mercury (Hg)	X	X						

Table 1. A Summary of Trace Element Contamination in the Chisman Creek Basin.

X denotes levels above background concentrations.

\* indicates concentrations exceeding drinking water standards (Va.Dept. of Health, 1982)

† indicates concentrations exceeding both drinking water standards and the criteria for the protection of marine aquatic life (NAS, 1973)

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were compared to the background found in natural soils. It can be seen that the groundwater residing directly within the ash contains elevated concentrations of many of the elements that are abundant in fly-ash. However, only a few of the elements (Cd, Ni, V, Mn, and Fe) were found at concentrations greater than background levels in groundwater outside of the pits and in the freshwater streams draining into the Chisman Creek estuary. Nickel, vanadium and arsenic levels were elevated in the surface sediments in the upper mile of the tidal estuary. That is. they were present at concentrations above background levels. Although nickel and vanadium have been shown to be harmful to many different organisms in bioassay studies, no drinking water quality standards have been established, and few published criteria on the environmental effects of Ni and V currently exist. A detailed discussion of the findings represented by the table follows.

#### Composition of Flyash

The fly-ash in question is different from most other ashes. because it resulted from the burning of both coal and delayed petroleum coke. Thus it contains trace elements typical of both coal and crude oil. The composition of the fly-ash within a single pit was variable, presumably an artifact of the heterogeneous sources of coal and oil. different mixes burned by the power plant, and varying combustion conditions. Vanadium was particularly abundant in the type of crude oil that was used and is found at high concentrations in the deposited ash. The characteristics of the groundwater withdrawn from that ash deposit vary as well, not only due to the ash composition, but also because different parcels of water will have unequal time of exposure to the ash, and because the acidity of the groundwater within the ash also varies The latter factor plays an important role in determining both greatly. the concentration of trace elements dissolved in the water and the chemical state of those elements.

#### Groundwater

Intensive sampling was focused on one of the three fly-ash pits (Pit C, Figure 1). The shallow groundwater residing directly in pit C was found to have elevated levels of most trace elements. Most notably, manganese, iron, arsenic, and selenium exceeded the established drinking

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water standards (Va. Dept. of Health, 1982). Also high were other elements for which no standards currently exist; in particular, nickel and vanadium levels were very high. Elevated concentrations of nickel, vanadium, manganese, iron and aluminum in groundwater residing directly below the pit suggest that ash-derived trace elements are in fact entering the natural aquifers.

Groundwater at the same depth as the ash deposit but 200 ft. to the south of the pit in natural soil deposits showed little evidence of contamination. None of the drinking water standards were exceeded. This is believed to be due to the nature of the groundwater flow, namely from the south, across the pit and towards Chisman Creek. Groundwater to the west of the pit (where contamination was first observed) was not sampled in this study because the household wells had been removed. Water from these wells was found to be contaminated by the SWCB in their 1981 survey. Again, it appears that the groundwater flow was important. Chisman Creek flows to the north behind these homes and then makes a sharp turn and flows to the east along the edge of pit C. Measurements of water levels in a number of wells suggest that groundwater from the western end of pit C flows under Wolftrap Road and toward the branch of stream that flows behind these homes. Thus it is not surprising that some near surface drinking water wells in the line of flow were affected.

Because the ash and the soils of the surface layer (the upper 20 ft., known as the Tabb formation) are light and relatively permeable, it is believed that groundwater movement is fairly rapid. The streams draining the watershed frequently and deeply incise this stratum and the near surface groundwater does not flow long distances before reaching a surface waterway. These factors appear to be at work in limiting the horizontal contamination of groundwater in this stratum. In other words, only those areas lying downslope between an ash deposit and a major surface stream are expected to be affected. The SWCB study showed that the impacts on shallow household wells in such a case can be severe.

Comparison of waters taken from shallow and deep wells at a number

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of locations near Pit C indicates that there is vertical migration of the surface groundwater into the deeper layer, known as the Yorktown formation. The concentrations of elements changes significantly because the fossil shells in the Yorktown formation produce slightly alkaline conditions, whereas groundwater in the Tabb formation was observed to be acidic to varying degrees. The patterns of groundwater transport in the Yorktown formation cannot be discerned in detail from the data collected in this study. However, it appears that adjacent to pit C a somewhat larger area in the deep groundwater is affected than in the shallow aquifer, with the contaminants being those elements soluble at higher pH levels. However, concentrations in the deeper formation did not exceed the drinking water standards.

#### Household Wells

It should be noted that numerous shallow and deep household wells exist in the basin. Of the seven residential wells tested in this study, none exhibited elevated trace element concentrations. Many more household wells exist within a half-mile radius of the fly-ash pits. It is recommended that a comprehensive inventory of groundwater users within at least a half-mile proximity of the fly-ash pits be compiled and their wells tested since no such comprehensive inventory of groundwater users currently exists. Patterns of groundwater flow could vary seasonally as a result of local water withdrawals, and further monitoring of groundwater movement in the area is also recommended.

Many of the wells in the area are not used for potable water supplies but rather are used to water lawns, gardens and shrubs. At least one report has demonstrated the accumulation of arsenic, selenium, boron, and manganese in vegetables grown on fly-ash amended soils (Furr, et al., 1978). Because the levels found in the deeper groundwater were well below the drinking water standards it is unlikely that there would be significant bioaccumulation of trace elements in vegetables grown using deep well water. Analysis of vegetables grown using local groundwater is recommended in order to evaluate this possibility.

#### Freshwater Streams

Water quality monitoring of the free flowing streams draining the

watershed indicates that concentrations of dissolved nickel and vanadium were elevated when compared to the control station, but did not exceed the drinking water standards. Levels of manganese and iron exceeded the drinking water standards and the criteria for the protection of marine aquatic life, but were present at comparable levels at the control site, suggesting that other sources in the study area are responsible for the high concentrations observed for these two elements. The concentrations of trace elements leaving the watershed were comparable to the concentrations measured by others in runoff from urbanized areas (cf. Randall, et al., 1981 for the Occoquan watershed). The bed sediments in the streams below the pits also were found to be rich in many elements that were found in the fly-ash. Given the disposal techniques that were used and the fact that fly-ash may have been used by local homeowners as fill and driveway material, one would expect the stream sediments to contain some fly-ash.

The dissolved concentrations of trace elements in the streams increased during runoff periods by as much as a factor of ten, indicating that storm events transport ash derived contaminants to the estuary. Since the particulate concentrations of trace elements are elevated too, we estimate that storms transport at least ten times more material through the streams to the estuary on an annual basis than continuous dry weather leaching of contaminants by groundwater. Also, stormwater runoff was more acid than baseflow. Quantitative particulate measurements and flow monitoring are recommended to more accurately estimate stream transport of contaminants to the estuary.

The linkage between the ash deposits and the streams cannot be proved conclusively using solely the trace element data gathered in this study because many of the elements found in the streams could have come from any of a multitude of commonplace activities occurring in the watershed. The fact that elements which are enriched in the stream below the pits are also elevated in the groundwaters in the Yorktown formation (Ni, V, Mn, Fe) suggests that the fly-ash is one source of the contaminants reaching the estuary. One method which is proposed to determine conclusively the hydraulic link between groundwater in the pits and the streams is to inject a conservative tracer into the groundwater and follow its dispersion and rate of transport.

#### Estuarine Sediments

Considerable anecdotal evidence indicates that the placement of fly-ash in the borrow pits occurred in ways that would be considered unacceptable today. When intense thundershowers occurred or when storm surges raised tidal levels, according to residents living in the area at the time, sizeable quantities of fly-ash were carried into the estuary. Analysis of estuarine sediments indicates that the zone of influence extends several miles downstream. Particularly, arsenic, vanadium and nickel were present at elevated levels. Goose Creek also showed high trace element concentrations in sediments, perhaps due to other sources but perhaps due to quiescent, backwater conditions which favor the deposition of fine particles. Comparison of concentrations at several depths in both Chisman Creek and Back Creek indicates that Chisman Creek sediments are enriched with trace elements down to about 10 inches.

#### Oysters

Oysters and other mollusks are excellent organisms for monitoring water quality conditions because they do not move about and they filter suspended matter from the water. Thus they tend to concentrate pollutants and provide an indication of conditions existing over the antecedent months. Levels of trace elements in oysters from Back Creek and Chisman Creek were generally similar and tended to be at the upper end of the range reported for "clean" waters and at the lower end of the range reported from "polluted" environments. It could not be interpreted from the data collected in this study whether the fly-ash deposits have had an impact on the oysters in Chisman Creek.

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