

ELEMENTAL ANALYSIS OF WATER AND SEDIMENTS  
IN THE MAHONING RIVER BY  
NAA, AA, AND ICP SPECTROSCOPY

by

James P. White III

Submitted in Partial Fulfillment of the Requirements  
for the Degree of  
Master of Science  
in the  
Chemistry  
Program

<u>                    Inally Mahadeviak                    </u>	<u>                    8/16/85                    </u>
Adviser	Date
<u>                    Sally M. Hotchkiss                    </u>	<u>                    August 21, 1985                    </u>
Dean of Graduate School	Date

Youngstown State University

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<u>Inally Mahadeviah</u>	<u>Aug 14, 1985</u>
Adviser	Date
<u>R. C. Phillips</u>	<u>August 15, 1985</u>
Adviser	Date
<u>Steven M. Schilderout</u>	<u>Aug. 14, 1985</u>
Adviser	Date
<u>Edward Mooney, Jr.</u>	<u>August 15, 1985</u>
Adviser	Date
<u>Sally M. Hotchkiss</u>	<u>August 21, 1985</u>
Dean of Graduate School	Date

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ABSTRACT

ELEMENTAL ANALYSIS OF WATER AND SEDIMENTS IN THE  
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JAMES P. WHITE III

MASTER OF SCIENCE IN CHEMISTRY

YOUNGSTOWN STATE UNIVERSITY, 1985

The **Mahoning** River runs from Trumbull and **Mahoning** Counties in Ohio to Lawrence County in Pennsylvania where it empties into the Beaver River. From the turn of the century, the iron and steel industries in the area have used the river as a source of process water for manufacturing. Since the late 1970's, however, economic hardships have forced drastic cutbacks in steelmaking and related industrial production in the area. Curtailment of industrial production has greatly lessened active pollution of the river, but the impact of years of steel making on the river system is not known.

Elemental analysis of river water and sediment samples were performed to determine residual elemental pollution of the river system by the metal industries. Water and sediment samples from **18** sites along the entire length of the river, plus **5** samples from entering streams were analyzed. Elemental concentrations in the samples located upstream from the major industrialized areas

and from entering streams (pre-industrial sites) were averaged and taken as background levels for the elements detected. Elemental concentrations in the samples downstream from the major industrial areas (industrial sites) were then compared to the background concentrations. Elements that are significantly higher than two standard deviations above the average concentrations of elements for pre-industrial sites are classified as pollutants. Using this criterion, nine elements (Al, Sc, Cr, Mn, Fe, Co, Zn, Sb, Cs) were identified as pollutants in river sediments and two of these elements (Fe, Zn) were found as water pollutants.

Sediment samples were analyzed by neutron activation analysis (NAA) at the Ohio State University Nuclear Reactor Laboratory in Columbus, Ohio. Water samples were analyzed by atomic absorption (AA), atomic emission (AE), and inductively coupled plasma (ICP) spectroscopy. An Instruments Laboratory Video 11 Atomic Absorption Spectrophotometer, and an Instruments Laboratory Plasma 200 ICP Spectrometer were used at Youngstown State for the analysis. Two samples of water were also analyzed by NAA.

In the Sediment samples, twenty-eight elements (Na, Al, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Rb, Zr, Sn, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Hf, Ta, Th, Pa, U) were detected, with concentration data obtained for all but Tb, Yb, Hf, and Pa.

Analysis of the water samples resulted in detection of twenty-two elements (K, Fe, Zn, Mn, Na, Ca, Mg, Sr, Ba, Si, P, Al, Cu, Sc, Au, U, Cr, Co, Cs, Rb, Br, Cl). Concentration values were obtained in all sites for 10 elements (K, Fe, Zn, Na, Ca, Mg, Sr, Ba, Si, Mn).

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## CHAPTER I

### INTRODUCTION

The **Mahoning** River, located in Northeastern Ohio and Western Pennsylvania, is 108 miles long and encompasses a total drainage area of 1,131 square miles. It has, since the turn of the century, served the basic iron and steel works and their related industries in the area. In part, due to its extensive use by these manufacturers, it has become highly polluted. Most evident is the thermal pollution, since the river, which is not particularly fast flowing, does not freeze even in the coldest winters.

In recent years, beginning in 1977, the basic steelmaking industry has sharply curtailed production in the **Mahoning** Valley through which the river flows. From 1974 to 1982, over 56% of the employees of the primary metal industries in the **Mahoning** Valley were laid off, nearly all of whom were from three large basic steelmaking mills.<sup>1,2</sup> The closing of the blast furnaces in these mills greatly lessened the thermal and chemical pollution being introduced into the river system, but residual contamination from these processes still remains. Since steelmaking as a process uses mainly pure elements or their common ores, an elemental

analysis of the river waters and sediments could reveal the extent of this residual pollution. An elemental analysis of river waters could indicate any active pollution of the river system.

Previous investigators have performed elemental analyses on the **Mahoning** River System. Cordon, Hazari, Muntean, and Kline et al. analyzed water and sediment samples from selected portions of the river from 1972 to 1974, a period when steel production was at its peak.<sup>3,4,5,6</sup> The analyses were made primarily using neutron activation analysis (NAA) with the Youngstown State University Californium-252 neutron source and detector facilities. Both sediment and water samples were analyzed by NAA, with atomic absorption (AA) and wet chemical methods used to a limited extent in some of the water analyses.<sup>5,6</sup> Up to ten elements were detected in the sediments (Na, Mg, Al, Cl, K, Ca, V, Mn, Cu, Br), with these and four additional elements (Fe, Ni, Zn, Pb) found in some water samples.

The Cf-252 neutron source used in these earlier studies produced at best a rather low neutron flux of  $10^9 \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . Gamma detectors used in these analyses were of relatively low resolution and were not shielded to reduce background radiations. Also, instrumentation at this time was not computerized, and gamma spectra had to be analyzed manually. These factors limited the detectability of elements with small thermal neutron

cross sections or those low in concentration. Most noticeably absent in these findings were any indications of iron, chromium, cobalt, or zinc in the river sediments. Iron and zinc were, however, detected in water samples by other methods, and found to be in relatively high concentrations. A more thorough study with better detection limits is needed to discover the full extent of pollution in the river system.

In the present study we will determine active and residual elemental pollution in the **Mahoning** river system, now that the majority of the heavy industries using the river have ceased operations. Samples of water and sediments were collected along the entire length of the river, and from five streams that feed into the river. Elemental analysis of the samples was performed using NAA, AA and inductively coupled plasma (ICP) spectroscopy. Elemental concentrations in the river sites upstream from industrialized areas and from entering streams are used as background levels for the river. Samples from industrialized areas or downstream from them are compared to the pre-industrial upstream sites. Elements showing concentrations significantly higher than the background levels will be considered pollutants.

Sediment samples were analyzed by NAA at the Ohio State University Nuclear Reactor Laboratory (OSU-NRL) in Columbus, Ohio. This facility offered a higher neutron flux and a higher resolution shielded detector, which

allowed much lower detection limits and thus identification of more elements. Water samples were analyzed by AA and ICP at Youngstown State University. In addition, two water samples were analyzed using neutron activation at OSU-NRL.

Particular emphasis is placed on the sediment analysis, since, now that most of the steel manufacturing facilities are closed, pollution attributed to them would be residual and show up mostly in the river bed. Detection of first row transition elements was most important in the sediments, since they are the main constituents in steel making. Appropriate decay schemes for NAA of the sediments were chosen to determine V, Cr, Mn, Fe, Co, and Zn in particular.

Water analysis was done to determine residual pollution of the river, such as leaching of elements from the sediments, and to find any active pollution sources.

## CHAPTER II

### HISTORY AND THEORY OF THE ANALYTICAL METHODS:

#### NAA, AA, AND ICP SPECTROSCOPY

##### Neutron Activation Analysis

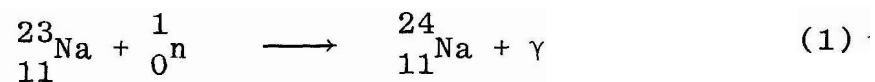
The first neutron activation analysis experiment was made in 1936 by Hevesy and Levi to analyze impure yttrium for traces of dysprosium.<sup>7</sup> Other experiments using neutron activation were made during the late 1930's, but neutron fluxes and detector sensitivities remained low, limiting its use as an analytical method. The real development of neutron activation came as a result of wartime research in nuclear physics. By the late 1940's, research reactors and cyclotrons came into use and with them ample neutron fluxes for activation analysis. Neutron fluxes as high as  $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  were available at this time.

Neutron activation developed rapidly throughout the 50's and 60's, being used to determine trace elements from  $10^{-6}$  to  $10^{-12}$  grams in samples such as water, biological tissue, and high purity silicon.<sup>8</sup> The advent of Ge(Li) detectors and computers in the 1970's greatly enhanced the speed and resolution of activation analysis, allowing determinations of many elements simultaneously. Today, higher efficiency intrinsic germanium and HgI<sub>2</sub>

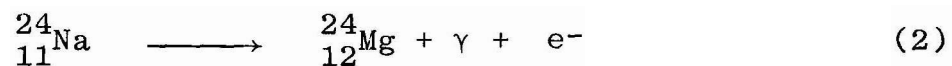


detectors are being used, plus greater computer assisted analysis for better and faster results. Neutron fluxes up to  $10^{15} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  are currently available.

Neutron activation can be induced by either fast or thermal neutrons. For most elements heavier than neon, thermal neutron activation is the method of choice since the reaction probability or cross section for thermal neutron reactions is usually higher than that for high energy neutrons. The typical thermal neutron activation experiment is as follows: neutrons from a reactor or radioisotope source are passed thru a moderator, usually water, which slows them to thermal energies. A sample is then placed in the thermal neutron source, where various nuclei ( $^{23}_{11}\text{Na}$  for example) absorb neutrons releasing a prompt gamma-ray



The neutron rich isotopes produced are commonly unstable. They decay according to their half-life, by beta (electron and gamma-emission (B-decay) to a stable element one higher in atomic number (Eqn. 2). The gamma-rays emitted have specific energies,



characteristic of the individual nucleus. Using gamma spectroscopy, the  $\gamma$  radiation energy from the B-decay can be measured, identifying the element present.

The general equation for measuring the activity of the radiation produced by thermal neutron bombardment is equation 3.<sup>9</sup>

$$A = N \phi \epsilon \alpha mG \left( 1 - \exp \left( -\frac{0.6934t}{t_{\frac{1}{2}}} \right) \right) \quad (3)$$

where

A = activity measured by the detector

N = number of target nuclei

$\phi$  = flux of neutrons,  $n \cdot cm^{-2} \cdot s^{-1}$

$\alpha$  = reaction cross section in  $cm^2$

$\epsilon$  = detector efficiency

m = isotopic abundance of nuclei

G = detector geometric factor

t = irradiation time

$t_{\frac{1}{2}}$  = half life of the nucleus.

Generally neutron activation is not done on an absolute basis, but on a comparative basis. A sample of known concentration (standard) is irradiated along with the unknown sample to be determined. This eliminates any errors due to changes in the neutron flux with time. If the same detector and geometry are then used to measure both samples, assuming isotopic abundancies are the same, equation 3 for the standard and unknown can be reduced to

$$A_{\text{unknown}} = N_{\text{unknown}} \cdot \text{constant} \quad (4)$$

$$A_{\text{standard}} = N_{\text{standard}} \cdot \text{constant} \quad (5)$$

since both activities are measured and  $N_{\text{standard}}$  is known, by the following equation.

$$N_{\text{unknown}} = \left( \frac{A_{\text{unknown}}}{A_{\text{standard}}} \right) \cdot N_{\text{standard}} \quad (6)$$

### Inductively Coupled Plasma Spectroscopy

The ICP, first described and used by Reed in 1961, was developed by Greenfield, Wendt, and Fassel in the mid-1960's mainly as an analytical technique.<sup>10</sup> Greenfield devised the first laminar flow argon plasma torch specifically designed for analytical purposes in 1964. This design was later modified by Fassel in 1965 and became known as the Fassel torch. Using an argon flow gas, it was found that stable plasmas of 10,000 K were possible. Analytical work showed the argon plasmas to be remarkably free of matrix effects. By 1969, detection limits with ICP were shown to be equal to that of other techniques, such as Flame Atomic Emission. Improvements in instrumentation in the early 1970's led to the first complete commercially available ICP spectrometer in 1974. Recent improvements in nebulizers, generators, and monochromator systems have greatly increased resolution and detection limits in ICP spectroscopy.

In a typical ICP spectrometer, argon flow gas through a Fassel type torch is ignited by inductive heating from a two or three turn induction coil. A pilot spark from a tesla coil is necessary initially to make the

argon gas a conductor. Once ignited, a stable plasma will form within a few minutes. Analytical solutions are then aspirated by peristaltic pump into a nebulizer to form an aerosol, then injected into the base of the plasma. Elements within the sample form excited atoms or ions in the torch, which give rise to atomic or ionic emissions. The emitted photons then enter a monochromator system for analysis. Diffraction gratings are used in ICP monochromators for wavelength separation. The photons resolved by wavelength enter a photomultiplier tube (PMT) connected to small capacitor. Signals from the PMT are collected over a given time interval, usually 0.5 to 10 seconds. The charge built up on the capacitor is proportional to the amount of light striking the PMT, and thus proportional to the amount of analyte emitting the light. In this sense the light is said to be "integrated". The integrated signals are then fed to a computer for data processing.

#### Atomic Absorption and Emission Spectroscopy

Atomic spectroscopy has its roots in observations by Wollaston (1802) and later more thorough studies by Fraunhofer (1814) of dark lines appearing in the solar spectrum. By 1859, Kirchoff and Bunsen presented an explanation for the dark lines, showing that they arise from atomic absorption in the solar atmosphere. Application of this idea to elemental analysis in the

laboratory came after work by Saha (1929) on thermal ionization and later theories on line absorption coefficients. A mercury atomic absorption instrument was built in the early 1930's, but AA analysis of other elements was hindered by problems in producing free gaseous atoms. Walsh in 1953 and Alkemade and Milatz, soon after proposed the use of AA as an analytical method. A simple flame AA was demonstrated at the Physical Institute of Melbourne in 1954, and the first papers dealing with analytical applications of AA appeared in 1958.<sup>11</sup> From this slow beginning, AA has developed into one of the most sensitive and widely used modern analytical techniques. Currently flame excitation sources are the most common, but new furnace excitation sources can now achieve sub-part per billion measurements of certain elements.

Atomic absorption is based on the principle that atoms absorb light at the wavelength at which they emit. Samples to be analyzed are aspirated into an atomization source, a flame for example, where free atoms of the element are formed. For elements of low volatility, most of the atoms remain in the ground electronic state. A hollow cathode lamp made of the element to be tested emits light at frequency from the excited atoms within the lamp. This light is passed through the flame where the ground state atoms absorb it. Theoretically, absorption follows the Beer - Lambert Law.<sup>12</sup>

$$A = 2.303 \chi n \ell \quad (7)$$

where A is defined as absorbance and

$\chi$  = effective cross section for atomic absorption  
at frequency

n = number of atoms present

$\ell$  = path length the incident light travels through  
the sample.

Measuring light intensity (I) of the sample at the resonance frequency  $\nu$  absorption is given by

$$A = \log(I_0/I) \quad (8)$$

where  $I_0$  is the light intensity with no analyte present.

In an AA experiment  $\chi$  and  $\ell$  are both constant, so absorption is dependent only on the amount (concentration) of analyte atoms present.

In AA measurements, standards of known concentrations are analyzed and a standard curve of absorbance vs. concentration is made. Absorbances of unknown samples are measured, and concentrations deduced from the plot.

In an atomic emission experiment, the flame provides enough thermal energy to excite a large number of the analyte atoms present. The excited atoms emit light at a resonance frequency  $\nu$  of intensity I which is measured. Analogous to the absorption experiment, the intensity difference between signals in the absence and presence of analyte is measured. This signal constitutes light emission from the analyte, which is directly

proportional to the analyte concentration. Plots of emission signal vs. concentration are made for standards, from which the concentrations of unknown samples can be inferred.

## CHAPTER III

### EXPERIMENTAL PROCEDURES AND INSTRUMENTAL PARAMETERS

#### Sample Collection

Water and sediment samples were collected at 23 locations from August 9, 1984 to October 6, 1984. At each site, the temperature and pH of the water was measured. All samples were taken along the riverbank, usually by a bridge for easier access to the river. A list of sample sites is shown in Table 1, and their locations shown in figure 1.

Water samples were collected in a polyethylene bucket with a nylon rope attached. The bucket was thrown into the middle of the river and pulled carefully to shore so as not to include any stirred up sediment. The temperature and pH were then immediately recorded. New one liter polyethylene sample bottles were rinsed 3 times with the water before being filled to the mark (1 - liter). The first 10 samples were acidified on site with Baker Ultrex Instra-Analyzed Nitric Acid, added drop-wise until sample pH was less than 2. This proved difficult due to leaks in the nitric acid container, so subsequent samples were acidified in the laboratory within 3 hours of collection. The addition of acid was to prevent dissolved minerals from depositing on the surface of the container.



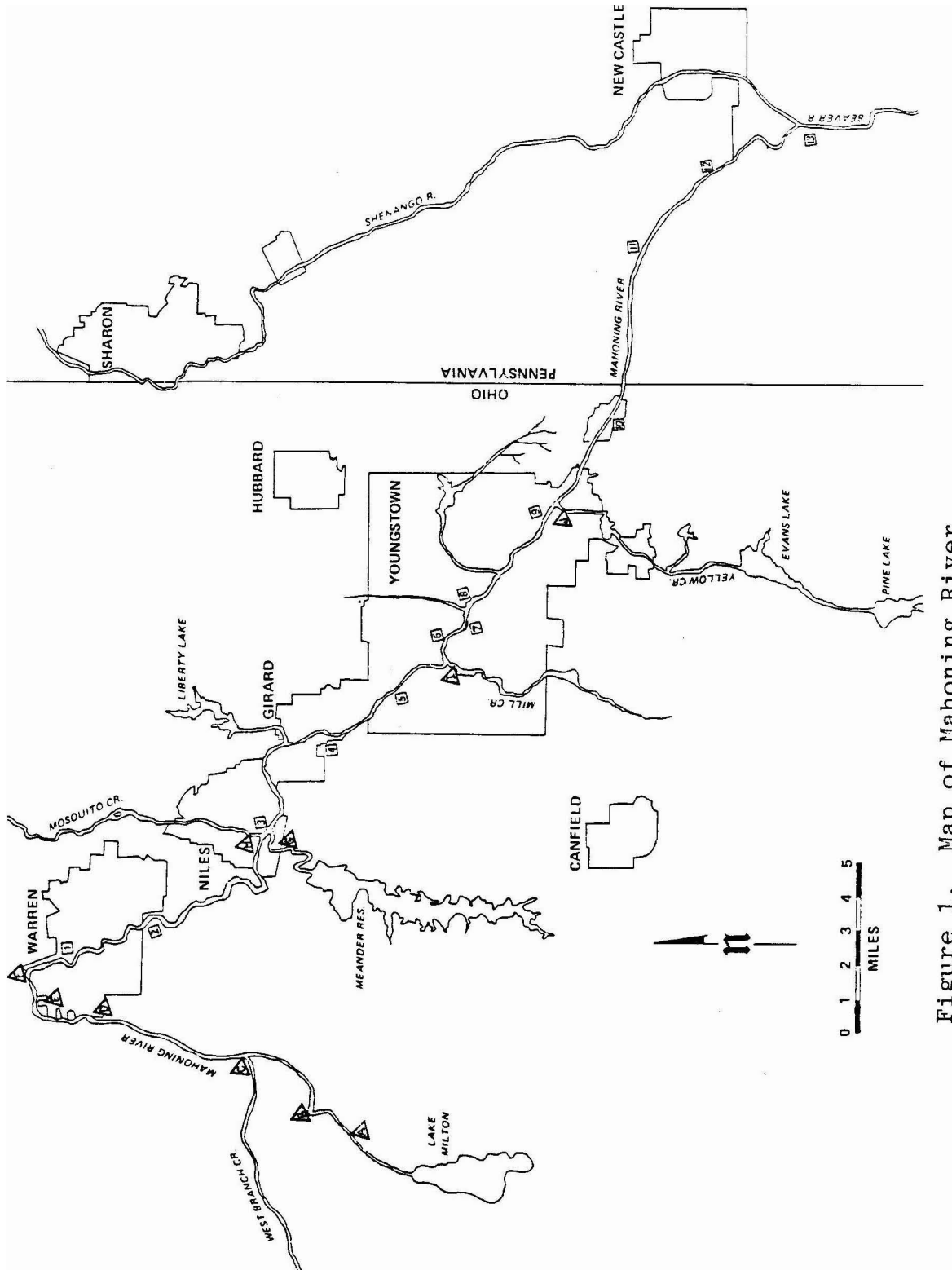


Figure 1. Map of Mahoning River

TABLE 1

LIST OF SAMPLE SITES IN ORDER OF COLLECTION<sup>a</sup>

<u>SITE</u>	<u>LOCATION</u>	<u>WATER</u>		<u>COLLECTION</u> <u>DATE</u>
		<u>TEMP, °C</u>	<u>pH</u>	
A	Mahoning-Trumbull Rd. Bridge	24.0	5.9	8-9-84
B	West River Rd.	24.5	5.6-5.9	8-9-84
C	West Branch Creek Bridge	23.5	5.6	8-9-84
D	Rt. 5 Bridge	25.0	5.6-5.9	8-9-84
E	Levitt's Rd. Bridge	25.0	5.6-5.9	8-9-84
F	<b>Parkman</b> Rd. (Rt. <b>422</b> ) Bridge	26.0	5.6-5.9	8-9-84
1.	Rt. <b>45</b> just north of Packard Park	26.8	5.6-5.9	8-9-84
2.	West Park Rd. Bridge	27.3	6-7	8-9-84
G	Meander Creek Rt. <b>46</b> Bridge	21.0	5.6	8-9-84
H	Mosquito Creek Rt. <b>46</b> Bridge	24.5	5.6-5.9	8-10-84
3.	Belmont Ave. Bridge, Niles	25.6	5.6-5.9	8-11-84
4.	Liberty St. Bridge, Girard	25.8	5.9-6.2	8-11-84
5.	Salt Springs Rd. Bridge I-680 and Rt. <b>422</b> Mill Creek	24.5	5.6	8-11-84
6.	<b>Mahoning</b> Ave. Bridge <b>Mahoning</b> Ave. Oak Hill Bridge	25.3	5.6	8-11-84
7.	Market St. Bridge, Youngstown	22.0	5.6	9-21-84
8.	South Ave. Bridge	22.2	5.6-5.9	9-21-84
9.	Bridge St. Bridge, Struthers	23.1	5.6-5.9	9-21-84
J	Yellow Creek, Struthers	14.0	5.6	10-6-84
10.	Rt. <b>289</b> Bridge, <b>Lowellville</b>	17.7	5.9-6.2	10-6-84
11.	Rt. <b>224</b> Bridge	17.2	5.6-5.9	10-6-84
12.	Rt. <b>108</b> Bridge, Pennsylvania	17.4	5.9	10-6-84
13.	Beaver River, Rt. <b>168</b> Bridge	19.4	5.6-5.9	10-6-84

<sup>a</sup>Letters denote pre-industrial sites.  
Numbers indicate industrial river sites.

The volume of acid added was approximately 1 ml for all samples.

Sediment samples were scooped from the river bed using a polyethylene cup attached to a one meter stick. Sediment was taken from 3 to 5 feet from the river's edge as near as possible to the location where the water sample was obtained. The sediment was then drained by funnel into a 200 ml polyethylene sample bottle, pre-washed with river water. This procedure, used for the first 15 samples, tended to include some small rocks, sticks, etc., in the sediments. To prevent this, the last 8 sediment samples were also strained through a fiberglass screen. All samples, both water and sediments, were tightly capped, labeled, and stored at room temperature until needed.

### Sediment Analysis By NAA

#### Sample Preparation

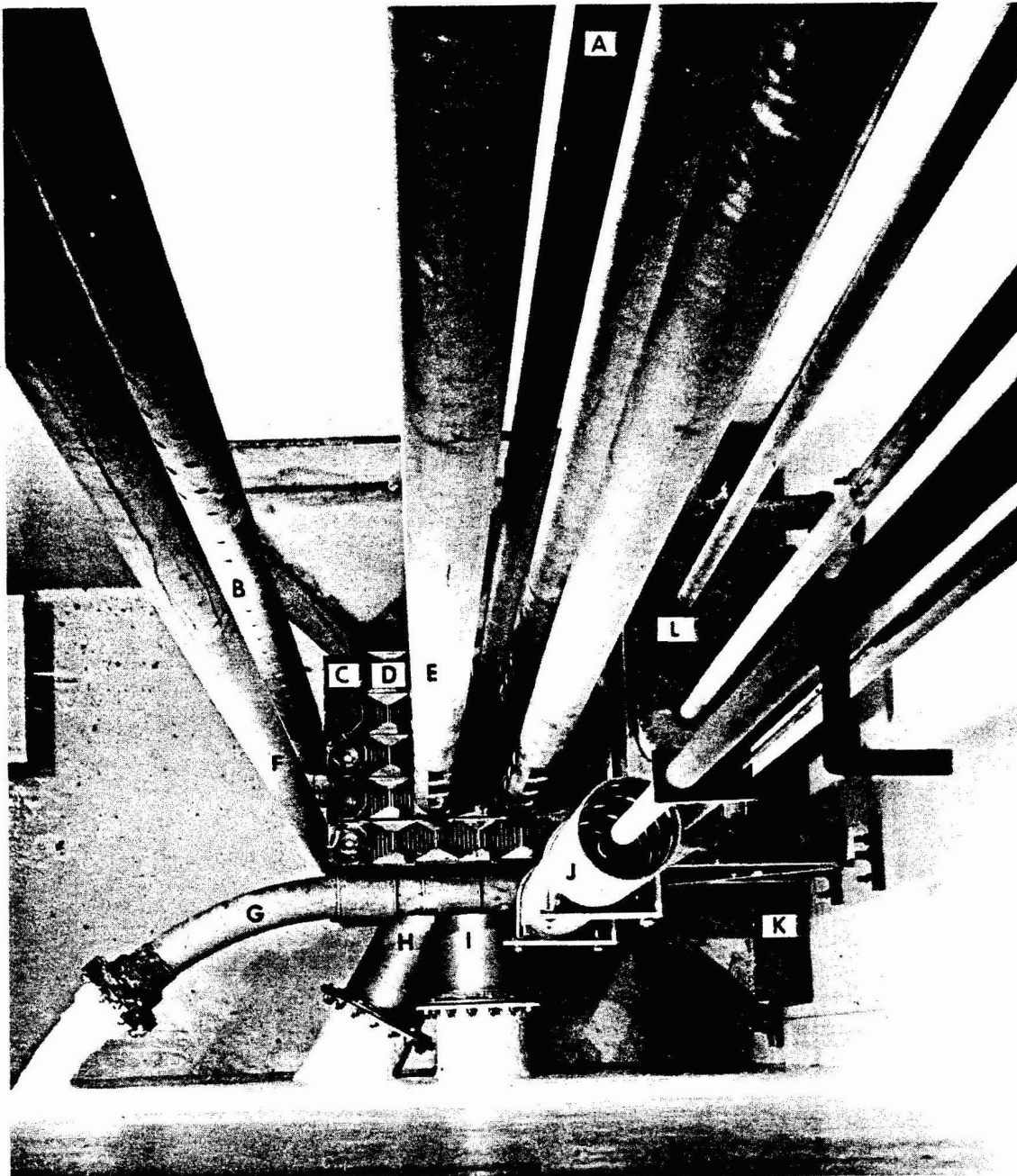
Sediment samples were collected on Whatman No. 42 filter paper and dried under an infra-red heat lamp. Any large rocks or organic matter were removed, then the remaining solid was ground to a fine powder in a pyrex mortar and pestle, which was pre-cleaned by soaking with dilute nitric acid and rinsing with glass distilled water. The powdered solids were mixed thoroughly to insure a homogeneous sample. The prepared sediments were then transferred to weighed 0.3 ml polyethylene irradiation

vials. The vials were pre-cleaned using absolute ethanol, allowed to air dry, and handled only with gloves once cleaned. The filled vials, containing approximately 200 mg of solid, were again weighed, then marked with a sharp knife for identification with a sharp knife.

#### The Ohio State University Nuclear Reactor Laboratory

All neutron activation analysis work was performed at The Ohio State University Nuclear Reactor Laboratory. The OSU-NRL building is located on Kinnear Rd. in Columbus, Ohio. The Ohio State University Research Reactor (OSURR) is a pool type reactor licensed to operate at a maximum power level of 10 kilowatts. The reactor core contains 93% enriched uranium-235 fuel, and is surrounded by light water for cooling, radiation shielding, and neutron moderation. Access to the core for this experiment was gained using the Central Irradiation Facility (CIF) and Rabbit System, both shown in Figure 2. Thermal neutron fluxes for the access ports are given in Table 2.

Irradiated samples were measured with the Gamma-ray Spectroscopy System (GRSS) at the OSU-NRL. The GRSS consists of a Princeton Gamma-Tech lithium-drifted germanium [Ge(Li)] detector with an active volume of 60 cm<sup>3</sup>. The detector has a 14% efficiency, a peak-to-Compton ratio of 46:1, and an energy resolution of 733 eV full-width at half-maximum at 121.9 KeV. The entire detector is surrounded by a graded shielding of lead, copper, and



A - CIF  
 B - SOURCE DRIVE  
 C - GRAPHITE ELEMENT  
 D - FUEL ELEMENT  
 E - CONTROL ROD DRIVE  
 F - DRY TUBE  
 G - RABBIT TUBE  
 H - BEAM PORT NO.2  
 EXTENSION

I - BEAM PORT NO. 1  
 EXTENSION  
 J - FISSION CHAMBER  
 DRIVE  
 K - THERMAL COLUMN  
 EXTENSION  
 L - IONIZATION CHAMBER  
 HOUSING

Figure 2. Reactor Core of the Ohio State University Research Reactor

TABLE 2

## NEUTRON FLUX VALUES FOR THE OHIO STATE UNIVERSITY RESEARCH REACTOR

	Beam Port #1	Beam Port #2	Thermal Column	Central Irradia. Facility	Rabbit
Integrated Flux ( $n \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ )					
Total	$2.17 \times 10^{11}$	$1.54 \times 10^{11}$	$1.88 \times 10^{10}$	$3.97 \times 10^{11}$	$6.42 \times 10^{10}$
Maxwellian	$1.22 \times 10^{11}$	$9.47 \times 10^{10}$	$1.29 \times 10^{10}$	$1.94 \times 10^{11}$	$4.47 \times 10^{10}$
1/E	$5.46 \times 10^{10}$	$3.26 \times 10^{10}$	$5.42 \times 10^9$	$1.20 \times 10^{11}$	$1.44 \times 10^{10}$
Fission	$4.08 \times 10^{10}$	$2.67 \times 10^{10}$	$4.96 \times 10^8$	$8.40 \times 10^{10}$	$5.11 \times 10^9$
Thermal	$1.27 \times 10^{11}$	$9.74 \times 10^{10}$	$1.33 \times 10^{10}$	$2.02 \times 10^{11}$	$4.58 \times 10^{10}$
Epithermal	$9.08 \times 10^{10}$	$5.67 \times 10^{10}$	$5.52 \times 10^9$	$1.95 \times 10^{11}$	$1.84 \times 10^{10}$

cadmium to reduce background radiations. The Ge(Li) detector is connected to a Canberra 8180 Multichannel Analyzer (MCA). The MCA has a 4096 channel memory, and is interfaced with a PDP-11/05 mini-computer. The computer has a hard disk for spectrum storage, and contains a comparison analysis program which calculates elemental concentrations according to equation 6.

### Irradiation Standards

Standards for sediment analysis were provided by the OSU-NRL. The standard used in the computer comparison was the International Atomic Energy Agency (IAEA) certified soil-5 reference material.<sup>13</sup> Also used, but only for comparison (these standards were analyzed as unknowns) were IAEA soil-7 and National Bureau of Standards standard reference material 1645 river sediment. Standards were prepared at the OSU-NRL the same as were the river sediment samples.

### Irradiation and Measurement

To analyze for elements which have relatively long half-life isotopes ( $t_{\frac{1}{2}} \geq 12$  hours) produced by thermal neutron bombardment, samples and standards were irradiated together in the CIF for 3-4 hours. At the end of the irradiation period (0-Day Decay), the samples were measured with the GRSS. Subsequent measurements were also made after a decay period of 1 day, 7 days, and 40 days.

Elements with shorter half-life isotopes (Na-24, K-42, As-76, Mn-56) were determined in the zero or one day measurements. Elements with moderate to long half-life isotopes (La-140, Sm-153, U-238, Ce-141, Cs-134, Sc-46, Fe-59, Th-232, Cr-51, Eu-152, Co-60, Sb-122, Sb-124, <sup>m</sup>Sn-117, Ba-131, Zn-65, Zr-95, Rb-86, Ta-182) were determined in the 7 or 40 day measurements. For isotopes that were measured in multiple analyses, the concentration value having the smallest error was used.

Elements with very short half-life isotopes (Al-28, V-52) were determined using the OSU-NRL rabbit facility.

Samples were irradiated two at a time for five minutes, then measured within two minutes using the GRSS.

## WATER ANALYSIS

### Sample Preparation

Approximately 150 ml of each water sample was gravity filtered through Whatman No. 42 filter paper to remove any solids. To each 150 ml sample, two drops of Triton X-100 (Fischer) surfactant was added to aid in aspiration in ICP and AA nebulizers.

### Inductively Coupled Plasma Analysis

ICP analysis was conducted at Youngstown State using an Instruments Laboratory Plasma-200 ICP Spectrometer. This instrument has a 2 kW radio frequency generator



operating at a frequency of 27.12 MHz. The torch consists of 3 concentric quartz tubes, the largest being 20 mm O.D. and the innermost 1.5 mm I.D. A double monochromator of Ebert-Fastie design provides second order resolution of 0.02 nm and stray light exclusion of  $1:10^6$ . Instrument functions are controlled by an Intel 80/16 singleboard computer, interfaced with an IBM-PC for data and program storage. Software available includes a multiquant program used for all analyses.

The multiquant program, supplied by Allied Analytical Systems, allows rapid calibration and quantitative analysis of up to 30 emission lines. The provided program was modified to analyze 22 emission lines for 21 elements (Table 3). The program uses a blank and a 3 element standard of Zn and Cu at 10 ppm and Ba at 5 ppm (called header elements) for calibration. All other emission lines in the program are referenced to the nearest header element emission line, and calibrated with a predetermined emission ratio. Torch conditions, observation height and integration times were optimized for each emission line.

#### ANALYTICAL STANDARDS

Concentration standards for ICP analysis were prepared from 1000 ppm aqueous elemental standard solutions from Fischer, GFS, and Spex Industries. Using deionized glass distilled water, the elemental standards were diluted

TABLE 3

## EMISSION LINES FOR ELEMENTS ANALYZED BY ICP MULTIQUANT

<u>Element</u>	<u>Emission Line (nm)</u>
Zn	213.86
Pb	220.35
Ba	233.53
Ba*	455.40
Mn	257.61
Mg	285.21
V	292.40
Cu	324.75
Na	589.59
Al	237.32
Ca	315.89
Cr	205.55
Li	670.78
Ni	231.60
P	213.62
Sr	421.55
Fe	259.94
Co	238.89
Si	251.61
Ti	323.45
Mo	202.02
B	208.96

\* Line used for Ba concentration values.

to the 1 to 10 ppm range in a 1-liter volumetric flask containing 0.05 ml Triton X-100 and 1 ml of Fischer Ultrex Spectranalyzed nitric acid. Seventeen of the elements could be prepared as one stable solution, but four others (Mo, Ti, B, Si) had to be made separately because the solutions required special conditions or were unstable upon standing. A solution of 1 ml Ultrex HNO<sub>3</sub> and 0.05 ml Triton X-100 in 1-liter of glass distilled water was used as a blank. The prepared solutions were used to set emission ratios in the multiquant program.

#### Atomic Absorption/Emission Analysis

Atomic absorption and emission measurements were also performed at YSU using an Instruments Laboratory Video 11 AA/AE Spectrophotometer. This instrument uses an air/acetylene flame or a graphite oven for atomization of samples. A Smith-Hieftje Background Correction System is also available. Resolution of the instrument is 0.01 nm. Data and analytical parameters are stored within the system computer and can be recalled on screen or printed hardcopy at an external printer. All measurements were made using the air/acetylene flame.

Both iron and copper were determined in water samples by AA. Standards were made for each analysis by dilution of Fischer 1000 ppm elemental standards. Three dilutions were made for each element, matching the acid and Triton surfactant levels of the samples and blank. A standard

curve of absorbance vs. concentration was made for both Fe and Cu, and sample concentrations were determined from this curve. The 248.3 nm line was used for Fe, and the 324.7 nm resonance line used for Cu.

Atomic emission was used to determine potassium levels in the river water. A potassium standard of 993.1 ppm was prepared from Aldrich gold lable KBr in a 1-liter flask containing 1 ml Ultrex  $\text{HNO}_3$  and 0.05 ml Triton X-100, diluted to the mark with glass distilled water. Three dilutions of this standard plus an acid blank were used to make a standard emission vs. concentration curve, from which concentrations of river samples were deduced. The K emission line at 766.5 nm was used for the analysis.

#### Neutron Activation Analysis

Two river water samples (10 and 11, see Table 1) were analyzed by NAA as a cross reference for ICP and as a check on detection limits of various elements. Five ml aliquots of each sample, measured by class A transfer pipet, were placed in 7 ml polyethylene irradiation vials. A multi-element aqueous standard (Table 4) containing 21 elements was prepared in a 2-liter volumetric flask by diluting Fischer, GFS, and Spex aqueous elemental standards with glass distilled water. Two ml of Ultrex  $\text{HNO}_3$  and 20 drops ( $\sim 0.1$  ml) of Triton X-100 were added to the standard solution before diluting to the mark. A 5 ml aliquot of this multi-element standard was also put in a 7 ml irradiation vial by transfer pipet.

TABLE 4

## MULTI-ELEMENT STANDARD FOR NAA WATER

<u>ELEMENT</u>	<u>CONCENTRATION</u> <u>PPM OR mg/l</u>
Co	0.500
Cr	0.500
Fe	1.000
Sc	0.497
Mn	0.500
Cu	0.500
Ni	0.500
Zn	0.500
Au	0.500
U	0.505
Th	0.499
Sr	0.500
Ba	0.500
Rb	0.500
Cs	0.500
K	4.965
Mg	10.00
Na	25.00
Ca	25.00
Br	10.15
Cl	NOT DETERMINED

The water samples were irradiated together in the Central Irradiation Facility at OSU-NRL for three hours. Gamma spectra were measured using the multi-element standard as a reference after zero and ten days decay.

## CHAPTER IV

### RESULTS

#### Sediment Analysis

Data from NAA of the river sediments are listed in Tables 5 to 28. Standard deviations for pre-industrial site averages were calculated using

$$\left(\frac{\delta u}{U}\right)^2 = \left(\frac{\delta x_1}{X_1}\right)^2 + \left(\frac{\delta x_2}{X_2}\right)^2 + \dots + \left(\frac{\delta x_n}{X_n}\right)^2 \quad (9)$$

where  $\delta u$  is the standard deviation of the average value  $U$ ,  $\delta x_1$  is the error in measurement  $X_1$ ,  $\delta x_2$  is the error in measurement  $X_2$ , etc. The energies from the gamma spectra of the sediment samples are given in Table 29. For elements with multiple gamma peaks, concentration values were determined for each peak, and an average of these values serves as the reported concentration. Each concentration value has an error from gamma counting statistics shown in the tables, plus an additional error due to discrepancies between reported and measured concentrations for NBS-1645 and IAEA soil-7 standards. Tables 30 and 31 show the results of analysis of these standards, and the variance in percent.

To determine if an element was a residual pollutant, sediment concentrations in samples taken

TABLE 5

ANTIMONY SEDIMENT CONCENTRATIONS FROM Sb-122 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (µg/g)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	1.79	0.31
B	2.20	0.36
C	0.72	0.16
D	0.40	0.10
E	0.93	0.16
F	0.98	0.19
G	0.96	0.17
H	3.21	0.52
I	1.61	0.27
J	1.00	0.18
<b>AVERAGE</b>	<b>1.38</b>	<b>0.82</b>
<b>Industrial</b>		
1	1.64	0.31
2	12.57	1.98
3	4.11	0.68
4	5.07	0.82
5	5.56	0.88
6	7.29	1.16
7	4.98	0.82
8	10.64	1.67
9	3.87	0.61
10	8.01	1.25
11	14.14	2.22
12	2.84	0.48
13	2.78	0.46
<b>AVERAGE</b>	<b>6.42</b>	<b>_____</b>

CONCENTRATION RANGE: 0.40-14.14 ppm

<sup>a</sup> µg ELEMENT/g SAMPLE



Table 6

ARSENIC SEDIMENT CONCENTRATIONS FROM As-76 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (µg/g)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	26.8	6.6
B	15.4	3.6
C	13.3	3.7
D	9.0	2.6
E	10.5	2.5
F	10.9	2.0
G	8.6	2.4
H	34.5	4.7
I	9.6	1.9
J	15.4	1.9
<b>AVERAGE</b>	15.4	11.1
<b>Industrial</b>		
1	17.4	4.0
2	23.5	3.5
3	28.2	4.4
4	25.2	4.1
5	15.8	2.4
6	25.8	4.1
7	30.3	3.9
8	35.4	4.4
9	28.9	2.7
10	16.5	2.7
11	62.6	6.7
12	14.4	3.1
13	13.0	2.5
<b>AVERAGE</b>	25.9	—

CONCENTRATION RANGE: 8.6 - 62.6 ppm

<sup>a</sup>µg ELEMENT/g SAMPLE

TABLE 7

## CHROMIUM SEDIMENT CONCENTRATIONS FROM Cr-51 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup></u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	49.6	5.6
B	43.0	4.9
C	67.9	7.2
D	69.1	7.0
E	87.8	8.4
F	113.	11.
G	106.	10.
H	117.	12.
I	107.	10.
J	290.	46.
<b>AVERAGE</b>	<b>105.</b>	<b>36.</b>
<b>Industrial</b>		
1	376.	36.
2	420.	41.
3	480.	47.
4	507.	49.
5	221.	22.
6	402.	39.
7	379.	60.
8	447.	71.
9	360.	57.
10	304.	48.
11	268.	43.
12	584.	92.
13	80.4	13.1
<b>AVERAGE</b>	<b>371.</b>	<b>—</b>

CONCENTRATION RANGE: 43.0 - 584 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 8

## ZINC SEDIMENT CONCENTRATIONS FROM Zn-65 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	148	17
B	1,350	140
C	126	15
D	82	10
E	122	12
F	203	22
G	156	17
H	546	56
I	453	45
J	253	11
<b>AVERAGE</b>	<b>344</b>	<b>113</b>
<b>Industrial</b>		
1	327	36
2	1,590	160
3	2,240	230
4	2,750	280
5	735	75
6	3,300	330
7	2,883	84
8	2,662	77
9	2,191	65
10	1,109	31
11	742	24
12	2,807	82
13	771	26
<b>AVERAGE</b>	<b>1,850</b>	<b>—</b>

CONCENTRATION RANGE: 82-3,300 ppm

<sup>a</sup>  $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 9

## IRON SEDIMENT CONCENTRATIONS FROM Fe-59 DATA

<u>SITE</u>	<u>CONCENTRATION IN WEIGHT %</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	2.93	0.32
B	1.83	0.20
C	2.19	0.24
D	1.38	0.32
E	2.62	0.28
F	2.95	0.32
G	2.96	0.32
H	4.18	0.45
I	7.94	0.85
J	5.53	0.28
<b>AVERAGE</b>	<b>3.45</b>	<b>1.34</b>
<b>Industrial</b>		
1	6.67	0.72
2	11.9	1.3
3	9.36	1.0
4	13.9	1.5
5	11.0	1.2
6	11.1	1.2
7	10.0	0.54
8	14.2	0.72
9	7.85	0.39
10	27.9	1.4
11	27.9	1.4
12	22.1	1.1
13	9.13	0.46
<b>AVERAGE</b>	<b>14.1</b>	<b>_____</b>

CONCENTRATION RANGE: 1.38-27.9 Wt. %

TABLE 10

## COBALT SEDIMENT CONCENTRATIONS FROM Co-60 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	12.0	0.76
B	7.09	0.48
C	7.78	0.53
D	5.29	0.36
E	7.86	0.44
F	8.78	0.56
G	6.17	0.40
H	11.7	0.72
I	6.47	0.36
J	9.79	1.0
<b>AVERAGE</b>	<b>8.29</b>	<b>1.8</b>
<b>Industrial</b>		
1	16.0	1.0
2	18.3	1.1
3	16.6	1.1
4	17.1	1.1
5	9.62	0.60
6	17.8	2.7
7	20.1	1.9
8	16.0	1.4
9	15.1	1.7
10	17.2	2.0
11	17.4	1.8
12	16.2	1.2
13	9.38	—
<b>AVERAGE</b>	<b>16.0</b>	

CONCENTRATION RANGE: 5.29-20.1 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 11

## CESIUM SEDIMENT CONCENTRATIONS FROM Cs-134 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
Pre-Industrial		
A	2.86	0.38
B	2.21	0.32
C	2.55	0.35
D	1.52	0.22
E	1.50	0.12
F	2.51	0.32
G	1.39	0.22
H	4.09	0.43
I	1.10	0.11
J	2.79	0.38
<b>AVERAGE</b>	<b>2.25</b>	<b>0.92</b>
Industrial		
1	4.01	0.53
2	3.87	0.61
3	6.16	0.76
4	5.87	0.72
5	2.06	0.36
6	5.97	0.55
7	7.09	0.80
8	8.55	0.86
9	5.49	0.71
10	2.92	0.51
11	7.02	0.92
12	2.78	0.59
13	2.36	0.39
<b>AVERAGE</b>	<b>4.93</b>	<b>—</b>

CONCENTRATION RANGE: 1.10-8.55 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 12

RUBIDIUM SEDIMENT CONCENTRATIONS FROM Rb-86 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (µg/g)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	82.0	17.0
B	84.0	14.0
C	92.0	15.0
D	49.9	9.9
E	42.7	4.7
F	61.0	14.0
G	58.0	12.0
H	78.0	18.0
I	45.9	5.6
J	86.0	19.0
<b>AVERAGE</b>	<b>67.8</b>	<b>41.0</b>
<b>Industrial</b>		
1	148	26
2	104	31
3	146	34
4	128	35
5	66	20
6	134	23
7	175	35
8	102	35
9	159	32
10	65	31
11	164	50
12	87	36
13	70	22
<b>AVERAGE</b>	<b>119</b>	<b>—</b>

CONCENTRATION RANGE: 42.7-175 ppm

<sup>a</sup>µg ELEMENT/g SAMPLE

TABLE 13  
SODIUM SEDIMENT CONCENTRATIONS FROM Na-24 ISOTOPE DATA

<u>SITE</u>	<u>CONCENTRATION IN WEIGHT %</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	0.301	0.018
B	0.436	0.026
C	0.555	0.033
D	0.436	0.026
E	0.286	0.017
F	0.456	0.027
G	0.356	0.021
H	0.596	0.036
I	0.216	0.013
J	0.238	0.013
<b>AVERAGE</b>	<b>0.388</b>	<b>0.073</b>
<b>Industrial</b>		
1	0.539	0.032
2	0.260	0.016
3	0.402	0.024
4	0.358	0.022
5	0.219	0.013
6	0.215	0.018
7	0.316	0.019
8	0.281	0.017
9	0.279	0.017
10	0.154	0.009
11	0.134	0.008
12	0.229	0.014
13	0.278	0.017
<b>AVERAGE</b>	<b>0.282</b>	<b>—————</b>

CONCENTRATION RANGE:           .134-.596 wt. %



TABLE 14

## POTASSIUM SEDIMENT CONCENTRATIONS FROM K-42 DATA

<u>SITE</u>	<u>CONCENTRATION IN WEIGHT %</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	0.90	0.11
B	1.04	0.10
C	1.25	0.12
D	0.91	0.09
E	0.79	0.08
F	1.02	0.09
G	0.69	0.07
H	1.08	0.11
I	0.39	0.04
J	0.75	0.08
<b>AVERAGE</b>	<b>0.88</b>	<b>0.29</b>
<b>Industrial</b>		
1	1.34	0.14
2	1.01	0.10
3	1.54	0.15
4	1.14	0.12
5	0.61	0.06
6	1.36	0.14
7	1.58	0.16
8	1.23	0.12
9	1.50	0.15
10	0.53	0.05
11	0.74	0.07
12	0.54	0.05
13	0.73	0.07
<b>AVERAGE</b>	<b>1.07</b>	<b>—</b>

**CONCENTRATION RANGE: 0.39-1.58 Wt. %**

TABLE 15

## MANGANESE SEDIMENT CONCENTRATIONS FROM Mn-56 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup></u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	13,660	650
B	2,021	99
C	882	45
D	536	28
E	2,167	106
F	1,704	85
G	1,297	65
H	1,663	83
I	1,478	72
J	2,963	148
<b>AVERAGE</b>	<b>1,635:</b> <b>2,837</b>	<b>245</b>
<b>Industrial</b>		
1	1,087	57
2	1,592	80
3	1,332	69
4	1,210	63
5	662	33
6	3,715	184
7	2,573	129
8	1,809	90
9	2,382	119
10	2,544	127
11	2,116	106
12	2,175	109
13	964	48
<b>AVERAGE</b>	<b>1,859</b>	<b>—</b>

CONCENTRATION RANGE: 536-13,660 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

<sup>b</sup>EXCLUDING SITE A

<sup>c</sup>WITH SITE A

TABLE 16  
TIN SEDIMENT CONCENTRATIONS FROM Sn-117 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	1.91	0.28
B	0.44	0.15
C	0.33	0.16
D	1.06	0.17
E	4.63	0.53
F	3.40	0.42
G	5.15	0.60
H	3.11	0.41
I	4.42	0.52
J	5.79	0.62
<b>AVERAGE</b>	<b>3.02</b>	<b>2.10</b>
<b>Industrial</b>		
1	2.83	0.40
2	3.09	0.42
3	3.51	0.48
4	4.04	0.54
5	4.64	0.55
6	3.83	0.53
7	3.78	0.49
8	2.88	0.37
9	3.42	0.37
10	2.15	0.25
11	3.22	0.40
12	3.69	0.42
13	1.91	0.23
<b>AVERAGE</b>	<b>3.31</b>	<b>—</b>

CONCENTRATION RANGE: 0.33-5.79 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 17

## URANIUM SEDIMENT CONCENTRATIONS FROM U-238 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	2.70	0.72
B	1.69	0.51
C	2.16	0.62
D	1.55	0.55
E	2.25	0.53
F	2.22	0.63
G	1.84	0.51
H	3.66	0.94
I	1.56	0.46
J	4.04	0.88
<b>AVERAGE</b>	<b>2.10</b>	<b>1.86</b>
<b>Industrial</b>		
1	3.22	0.91
2	2.10	0.73
3	4.09	1.12
4	3.30	0.99
5	2.51	0.68
6	3.67	1.10
7	3.54	1.17
8	3.59	1.07
9	4.23	0.91
10	2.45	0.71
11	4.56	1.30
12	2.91	0.87
13	2.40	0.68
<b>AVERAGE</b>	<b>3.27</b>	<b>_____</b>

CONCENTRATION RANGE: 1.55-4.56 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 18

## THORIUM SEDIMENT CONCENTRATIONS FROM Th-232 DATA

<u>SITE</u>	CONCENTRATION <sup>a</sup> <u>IN PPM</u> ( $\mu\text{g/g}$ ).	STANDARD DEVIATION
<b>Pre-Industrial</b>		
A	5.44	0.56
B	5.35	0.52
C	7.56	0.70
D	3.96	0.39
E	6.85	0.56
F	6.10	0.58
G	3.65	0.38
H	8.95	0.81
I	3.70	0.38
J	6.79	0.54
<b>AVERAGE</b>	<b>5.84</b>	<b>1.75</b>
<b>Industrial</b>		
1	8.82	0.84
2	5.93	0.65
3	9.86	0.95
4	8.23	0.84
5	5.69	0.54
6	8.50	0.89
7	10.38	1.01
8	8.61	0.79
9	8.48	0.67
10	3.53	0.38
11	6.02	0.67
12	4.98	0.51
13	4.52	0.44
<b>AVERAGE</b>	<b>7.22</b>	<b>—————</b>

CONCENTRATION RANGE: 3.53-10.38 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 19

## TANTALUM SEDIMENT CONCENTRATIONS FROM Ta-182 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup></u> <u>IN PPB ng/g</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	755	230
B	699	190
C	1,266	240
D	640	140
E	465	73
F	867	190
G	557	140
H	951	240
I	299	56
J	652	170
<b>AVERAGE</b>	<b>715</b>	<b>532</b>
<b>Industrial</b>		
1	1,361	320
2	1,211	310
3	1,024	370
4	1,571	360
5	572	33
6	907	250
7	957	280
8	1,534	310
9	1,309	300
10	806	220
11	1,380	360
12	1,043	250
13	884	170
<b>AVERAGE</b>	<b>1,120</b>	<b>—</b>

CONCENTRATION RANGE: 299-1,571 ppb

<sup>a</sup>ng ELEMENT/g SAMPLE

TABLE 20

## ZIRCONIUM SEDIMENT CONCENTRATIONS FROM Zr-95 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	262	100
B	348	96
C	465	110
D	265	68
E	195	37
F	387	98
G	416	87
H	375	14
I	137	31
J	375	110
<b>AVERAGE</b>	<b>313</b>	<b>248</b>
<b>Industrial</b>		
1	420	140
2	320	160
3	387	190
4	307	180
5	213	97
6	385	130
7	403	190
8	328	180
9	591	180
10	72	57
11	179	130
12	441	220
13	444	120
<b>AVERAGE</b>	<b>345</b>	<b>—</b>

CONCENTRATION RANGE: 72-591 ppm

<sup>a</sup>  $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 21

ALUMINUM SEDIMENT CONCENTRATIONS FROM A1-28 DATA

<u>SITE</u>	<u>CONCENTRATION IN WEIGHT %</u>	<u>STANDARD DEVIATION</u>
Pre-Industrial		
A	4.62	0.19
B	6.07	0.23
C	7.12	0.29
D	4.90	0.19
E	6.06	0.24
F	6.97	0.27
G	4.24	0.17
H	9.13	0.35
I	4.27	0.16
J	4.65	0.18
<b>AVERAGE</b>	<b>5.80</b>	<b>0.72</b>
Industrial		
1	9.24	0.36
2	6.76	0.26
3	11.06	0.43
4	9.54	0.37
5	6.19	0.24
6	9.94	0.40
7	6.95	0.26
8	6.24	0.24
9	7.08	0.27
10	2.83	0.11
11	4.15	0.17
12	3.17	0.12
13	3.28	0.13
<b>AVERAGE</b>	<b>6.65</b>	<b>—</b>

CONCENTRATION RANGE: 2.83-11.06 Wt. %



TABLE 22

## VANADIUM SEDIMENT CONCENTRATIONS FROM V-52 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup></u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
Pre-Industrial		
A	80.6	18
B	66.1	13
C	74.7	16
D	53.6	10
E	62.6	13
F	84.5	14
G	64.9	12
H	122.4	19
I	44.8	8.6
J	95.1	14
<b>AVERAGE</b>	74.9	45
Industrial		
1	105.0	20
2	85.1	15
3	167.7	27
4	154.0	24
5	78.2	14
6	128.5	25
7	108.1	18
8	129.1	20
9	124.0	18
10	55.4	8.3
11	107.5	17
12	62.4	9.4
13	47.8	8.6
<b>AVERAGE</b>	104.1	—

CONCENTRATION RANGE: 44.8-167.7 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 23

## BARIUM SEDIMENT CONCENTRATIONS FROM Ba-131 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	467	120
B	436	100
C	413	110
D	316	73
E	333	45
F	605	110
G	274	78
H	511	130
I	317	43
J	586	130
<b>AVERAGE</b>	<b>426</b>	<b>304</b>
<b>Industrial</b>		
1	602	160
2	512	170
3	737	220
4	820	210
5	332	110
6	627	150
7	937	220
8	630	200
9	658	210
10	679	160
11	849	260
12	630	190
13	518	130
<b>AVERAGE</b>	<b>656</b>	<b>—</b>

CONCENTRATION RANGE: 274-937 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 24

SCANDIUM SEDIMENT CONCENTRATIONS FROM Sc-46 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (µg/g)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	6.28	0.30
B	5.01	0.24
C	6.13	0.29
D	3.55	0.17
E	6.15	0.29
F	6.79	0.32
G	3.69	0.18
H	9.47	0.45
I	4.53	0.21
J	9.21	0.44
<b>AVERAGE</b>	6.08	0.91
<b>Industrial</b>		
1	8.41	0.40
2	6.65	0.32
3	10.98	0.53
4	8.96	0.43
5	6.18	0.30
6	10.33	0.49
7	12.27	0.59
8	10.03	0.48
9	11.32	0.54
10	4.77	0.23
11	7.19	0.35
12	5.80	0.28
13	5.35	0.26
<b>AVERAGE</b>	8.33	_____

CONCENTRATION RANGE: 3.55-12.27 ppm

<sup>a</sup>µg ELEMENT/g SAMPLE

TABLE 25

## LANTHANUM SEDIMENT CONCENTRATIONS FROM La-140 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	22.0	1.5
B	18.9	1.3
C	23.4	1.6
D	14.6	1.0
E	26.1	1.6
F	21.0	1.4
G	13.4	0.9
H	31.0	2.0
I	14.2	0.9
J	24.9	1.5
<b>AVERAGE</b>	<b>21.0</b>	<b>4.4</b>
<b>Industrial</b>		
1	29.9	2.0
2	21.1	1.4
3	33.1	2.2
4	29.1	2.0
5	19.3	1.3
6	30.9	2.1
7	34.6	2.2
8	28.9	2.0
9	31.8	1.9
10	13.5	1.0
11	24.9	1.8
12	18.0	1.2
13	19.7	1.3
<b>AVERAGE</b>	<b>25.8</b>	—

CONCENTRATION RANGE: 13.4-34.6 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 26

## EUROPIUM SEDIMENT CONCENTRATIONS FROM Eu-152 DATA

<u>SITE</u>	<u>CONCENTRATION"</u> <u>IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD</u> <u>DEVIATION</u>
<b>Pre-Industrial</b>		
A	0.82	0.12
B	0.72	0.10
C	0.73	0.11
D	0.54	0.08
E	0.76	0.09
F	0.91	0.12
G	0.51	0.08
H	1.14	0.15
I	0.58	0.08
J	1.09	0.11
<b>AVERAGE</b>	<b>0.78</b>	<b>0.19</b>
<b>Industrial</b>		
1	1.12	0.16
2	0.75	0.13
3	1.27	0.19
4	1.06	0.17
5	0.72	0.10
6	1.16	0.19
7	1.38	0.22
8	1.15	0.15
9	1.15	0.12
10	0.58	0.08
11	1.20	0.16
12	0.68	0.10
13	0.76	0.10
<b>AVERAGE</b>	<b>1.00</b>	<b>—</b>

CONCENTRATION RANGE: 0.51-1.38 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 27

## SAMARIUM SEDIMENT CONCENTRATIONS FROM Sm-153 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup></u> <u>IN PPM (µg/g)</u>	<u>STANDARD</u> <u>DEVIATION</u>
Pre-Industrial		
A	4.40	0.33
B	3.65	0.27
C	4.78	0.36
D	2.92	0.22
E	4.55	0.34
F	4.39	0.33
G	2.78	0.21
H	6.01	0.45
I	2.80	0.21
J	5.26	0.39
<b>AVERAGE</b>	<b>4.15</b>	<b>0.98</b>
Industrial		
1	5.96	0.44
2	4.19	0.31
3	6.63	0.49
4	5.75	0.43
5	3.68	0.27
6	6.21	0.46
7	7.05	0.53
8	5.71	0.43
9	6.64	0.49
10	2.71	0.20
11	4.82	0.36
12	3.71	0.28
13	3.90	0.29
<b>AVERAGE</b>	<b>5.15</b>	—

CONCENTRATION RANGE: 2.71-7.05 ppm

<sup>a</sup>µg ELEMENT/g SAMPLE

TABLE 28

## CERIUM SEDIMENT CONCENTRATIONS FROM Ce-141 DATA

<u>SITE</u>	<u>CONCENTRATION<sup>a</sup> IN PPM (<math>\mu\text{g/g}</math>)</u>	<u>STANDARD DEVIATION</u>
<b>Pre-Industrial</b>		
A	50.2	4.2
B	42.4	3.5
C	53.2	4.3
D	35.7	2.8
E	60.0	4.2
F	50.6	4.1
G	31.0	2.7
H	68.6	5.4
I	36.1	2.9
J	55.7	3.6
<b>AVERAGE</b>	<b>48.4</b>	<b>12.1</b>
<b>Industrial</b>		
1	63.8	5.3
2	49.2	4.4
3	79.8	6.6
4	69.2	5.9
5	54.8	3.7
6	77.5	6.6
7	86.9	7.3
8	69.3	5.1
9	74.3	4.6
10	33.7	2.6
11	64.1	4.9
12	41.8	3.3
13	43.4	3.1
<b>AVERAGE</b>	<b>62.1</b>	<b>—</b>

CONCENTRATION RANGE: 31.0-86.9 ppm

<sup>a</sup> $\mu\text{g}$  ELEMENT/g SAMPLE

TABLE 29

## GAMMA ENERGIES FOR SEDIMENT ANALYSIS

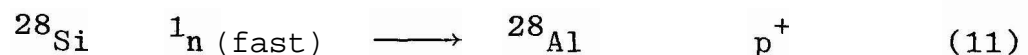
<u>ISOTOPE</u>	<u>ENERGY (KeV)</u>
Al-28	1,779.00
V-52	1,433.60
Na-24	1,368.60
Mn-56	846.75
	1,810.66
K-42	1,524.66
La-140	487.01
	1,596.17
Sm-153	103.18
U-238	228.14
Ce-141	145.44
	569.35
Cs-134	604.73
	795.84
Sc-46	889.26
	1,120.52
Fe-59	1,099.22
	1,291.56
Th-232	311.90
Cr-51	420.08
Sb-122	564.09
SB-124	1,690.94
Eu-152	121.78
	344.20
Co-60	1,173.21
	1,332.49
As-76	559.07
Sn-117m	158.56
Ba-131	216.08
	373.24
	496.36
Zn-65	1,115.50
Zr-95	756.72
Ta-182	222.11
	1,221.38
Rb-86	1,076.77
Pa-233	94.50
	398.51
Yb-169	62.93
	177.24
Hf-181	482.19
Tb-160	879.24



downstream from the first heavy industry (Copperweld Steel in Warren, Ohio) were compared to the average concentration of all the pre-industrial sites (which includes 5 samples from streams). Considering the errors stated above, elements whose errors did not overlap (were greater) two standard deviations above the pre-industrial average were classified as residual pollutants. Nine such pollutants were discovered (Al, Sc, Cr, Mn, Fe, Co, Zn, Sb, Cs) and plots of concentration vs. sample site for them are shown in figures 3-11.

#### Aluminum

Aluminum concentrations are well above the average at four locations (fig. 3). Even considering a 13.4% variance in the IAEA soil-7 standard, these 4 locations still are higher than two standard deviations (SD). It must be noted, however, that Al measurement of soils by NAA is inherently inaccurate, since the Al-28 isotope formed from thermal neutron bombardment also is formed from Si-28 by an (n,p) reaction with fast neutrons. Since irradiations



using the rabbit facility at OSU-NRL are exposed to a total flux containing 29% fast neutrons (Table 2), contributions from the (n, p) reaction are bound to occur. Thus, although high, the Al concentrations will be misleading if the silicate matrix of the sediment changes, since both reactions form the isotope from which the gamma energy is measured.

#### Scandium

Scandium levels are above 2 SD in 7 seven different locations. Statistical errors are very low for Sc-46, because it is a strong gamma emitter. Considering an additional error of 2.15% from the IAEA soil-7 standard, all 7 concentrations still lie above the 2 SD level.

#### Manganese

In the first pre-industrial site, the manganese concentration is the highest of any site, more than 4 times the level of any other upstream location. By Q test this is a valid data point and should be included in the average. Doing so, only the highest industrial site is above the 2 SD level.

This site was also sampled by Muntean, and was also found to be the highest in Mn concentration.<sup>14</sup> This indicates the location is naturally high in manganese, and is probably not a good reference for calculating a general background concentration. On these grounds,

the site A manganese concentration was not used in calculation of the pre-industrial average. By using this average, and considering an additional 11.9% error from the NBS-1645 river standard, three sites are above the 2 SD level.

#### Chromium

Chromium concentrations are above the 2 SD level for all but one site, even when a 9.43% error from NBS-1645 is considered.

#### Iron

Iron concentrations, considering a 2 . 1 error from the NBS standard, are above the 2 SD level for all but the first industrial site.

#### Cobalt

Cobalt concentrations show all but two locations above the 2 SD level. This includes an additional 7.2% error from the NBS river sediment measurement.

#### Zinc

IAEA soil-7 had no zinc value listed, so the 48% error from the NBS standard must be used. Even so, eight of thirteen locations (2, 3, 4, 5, 6, 7, 8, 9, and 12) still have levels above the 2 SD cutoff.

### Antimons

Because the NBS-1645 antimony value for Sb is not certified, the IAEA error of 3.49% is used. Thus, all but sites 1, 12 and 13 have concentrations above the 2 SD level.

### Cesium

The Cs values for NBS-1645 are not listed, and the IAEA standard has a high error variance of 24%. Within the limit of this error, 3 locations (7, 8, and 11) have concentrations above the 2 SD level.

### Other Elements

Some elements, though not quite above the 2 SD level when error overlap is applied, still show elevated levels in the industrial river sites. These elements (Th, Rb, V, As, La, Sm, and Ce) may have one value near the cutoff value, but all other measurements fall below the two standard deviation level.

The other elements detected show only random scatter, or have errors too large to show any significant trend. One interesting observation is that the concentration of the lanthanides in the sediments appear to be correlated, as shown by a plot of concentration vs. sample site (for all samples, in order of collection) in figure 12. The lanthanides vary by their relative abundances.

TABLE 30

ANALYSIS OF NBS -1645 RIVER SEDIMENT STANDARD BY NAA

<u>ELEMENT</u>	<u>UNIT</u>	<u>EXPERIMENTAL CONCENTRATION</u>	<u>LITERATURE CONCENTRATION</u>	<u>% VARIANCE</u> <sup>b</sup>
Na	PPM	5,540	5,500 <sup>a</sup>	0.71
K	PPM	12,500	1,200	3.8
AS	PPM	68.3	66 <sup>a</sup>	3.4
Mn	PPM	692	785	11.9
La	PPM	7.96	9 <sup>a</sup>	12
Sm	PPM	1.42	-	-
U	PPM	2.21	1.11	98.8
Ce	PPM	27.1	-	-
Cs	PPM	23.9	-	-
Sc	PPM	2.01	2 <sup>a</sup>	0.4
Fe	wt. %	9.93	11.3	12.1
Th	PPM	11.8	1.62	630
Cr	wt. %	2.68	2.96	9.4
Eu	PPM	0.55	-	-
Co	PPM	8.58	8 <sup>a</sup>	7
Sb	PPM	37.6	51 <sup>a</sup>	26
Sn	PPM	3.6	-	-
Ba	PPM	470	-	-
Zn	PPM	1.160	1,720	48
Zr	PPM	88	-	-
Rb	PPM	88	-	-
Ta	PPB	440	-	-
Al	wt. %	2.9	2 <sup>a</sup>	31
V	PPM	34.9	23.5	33

<sup>a</sup>Value not certified

- Value not listed

<sup>b</sup>(Experimental Conc. - Literature Conc.) x100/  
Literature Conc.

TABLE 31

## ANALYSIS OF IAEA SOIL -7 STANDARD BY NAA

<u>ELEMENT</u>	<u>UNIT</u>	<u>EXPERIMENTAL CONCENTRATION</u>	<u>LITERATURE CONCENTRATION</u>	<u>% VARIANCE<sup>a</sup></u>
Na	PPM	2,380	2,370	0.42
K	PPM	11,100	12,100	8.10
AS	PPM	16.8	13.1	28
Mn	PPM	588	627	6.14
La	PPM	27.0	28.0	3.67
Sm	PPM	4.89	5.15	5.01
U	PPM	2.61	2.67	2.28
Ce	PPM	62.4	59.2	5.36
Cs	PPM	6.88	5.55	24.0
Sc	PPM	8.29	8.47	2.15
Fe	Wt. %	2.55	2.58	1.24
Th	PPM	7.84	8.04	2.54
Cr	Wt. %	55.3	58.4	5.30
Eu	PPM	0.918	0.975	5.85
Co	PPM	9.56	9.22	3.67
Sb	PPM	1.75	1.69	3.49
Sn	PPM	10.6	-	-
Ba	PPM	255	260	2.02
Zn	PPM	145	-	-
Zr	PPM	167	-	-
Rb	PPM	59.6	58.0	2.68
Ta	PPB	755	762	0.93
Al	Wt. %	5.36	4.74	13.2
V	PPM	81.4	80.0	1.75

<sup>a</sup> (Experimental Conc. - Literature Conc.) x100/  
Literature Conc.

- Value not listed

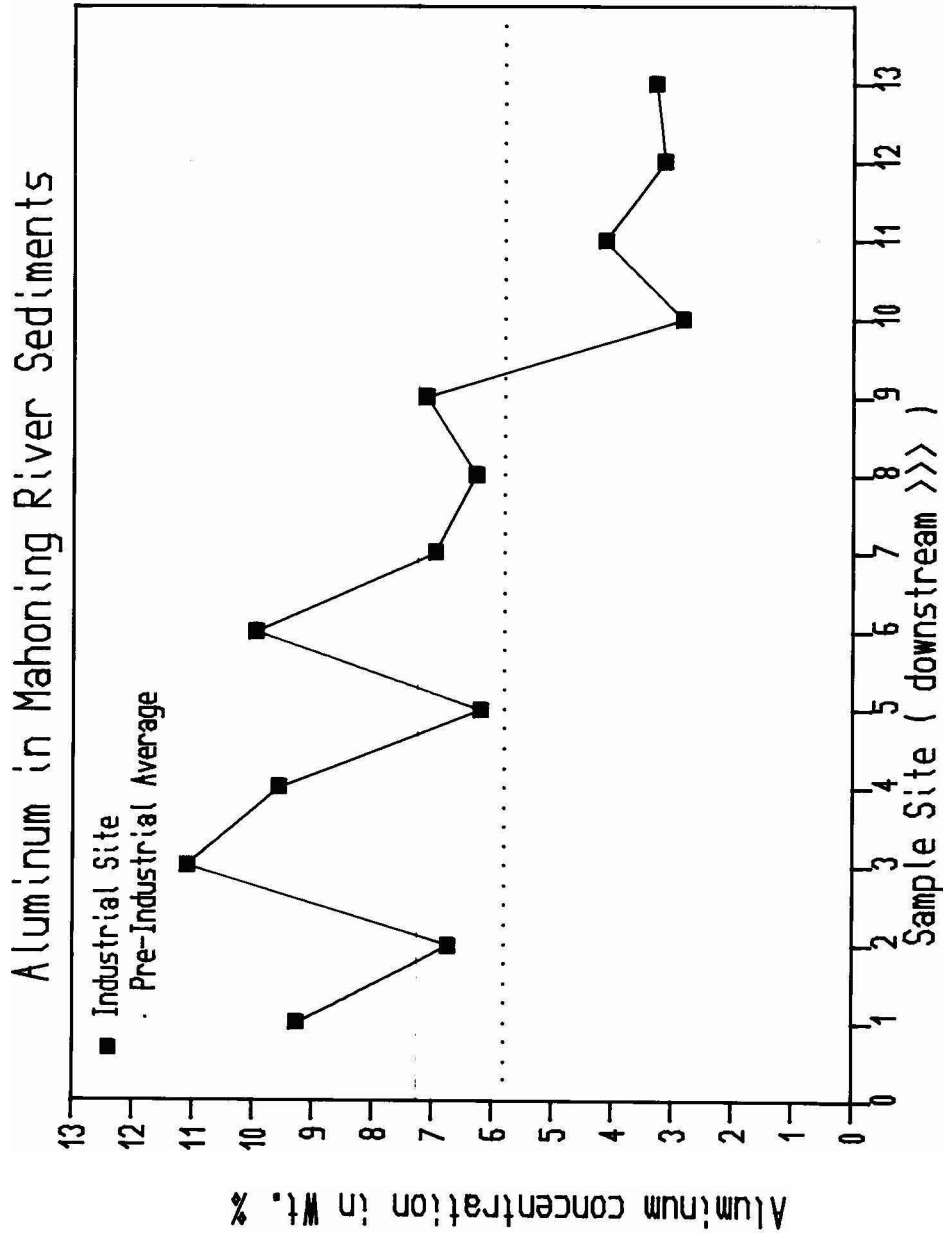


Figure 3. Solid Line Indicates Average + 2SD

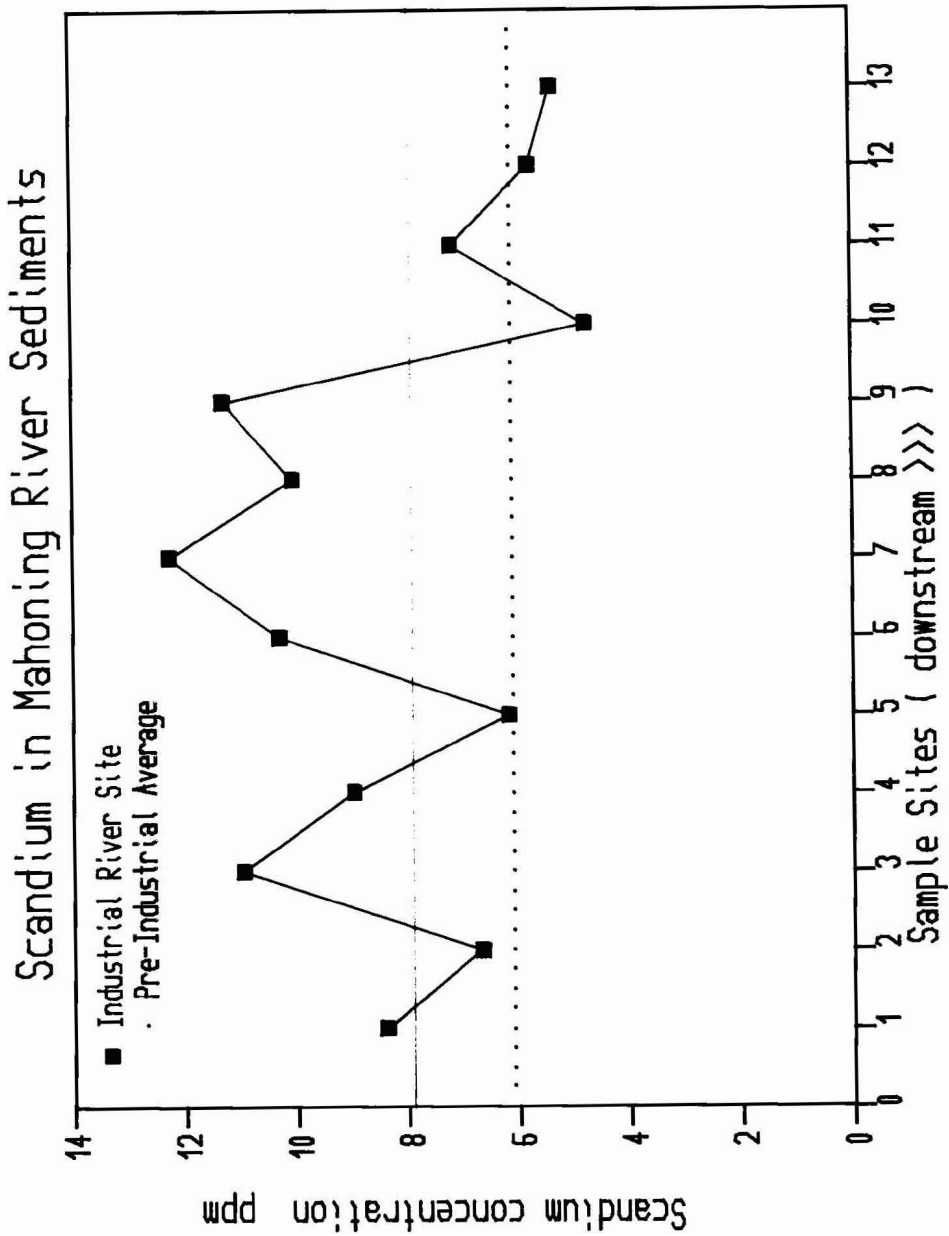


Figure 4. Solid Line Indicates Average + 2SD



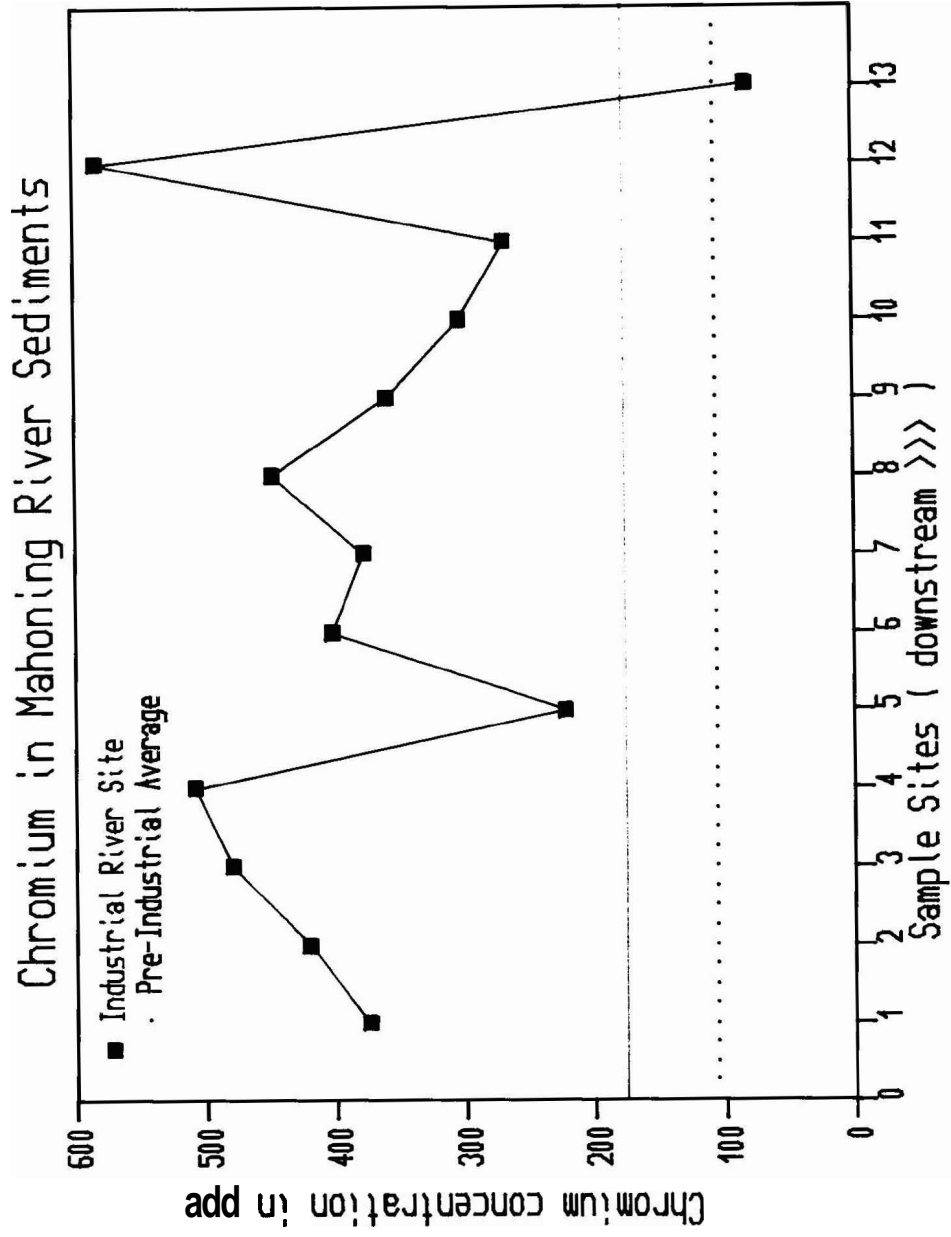


Figure 5. Solid Line Indicates Average + 2SD

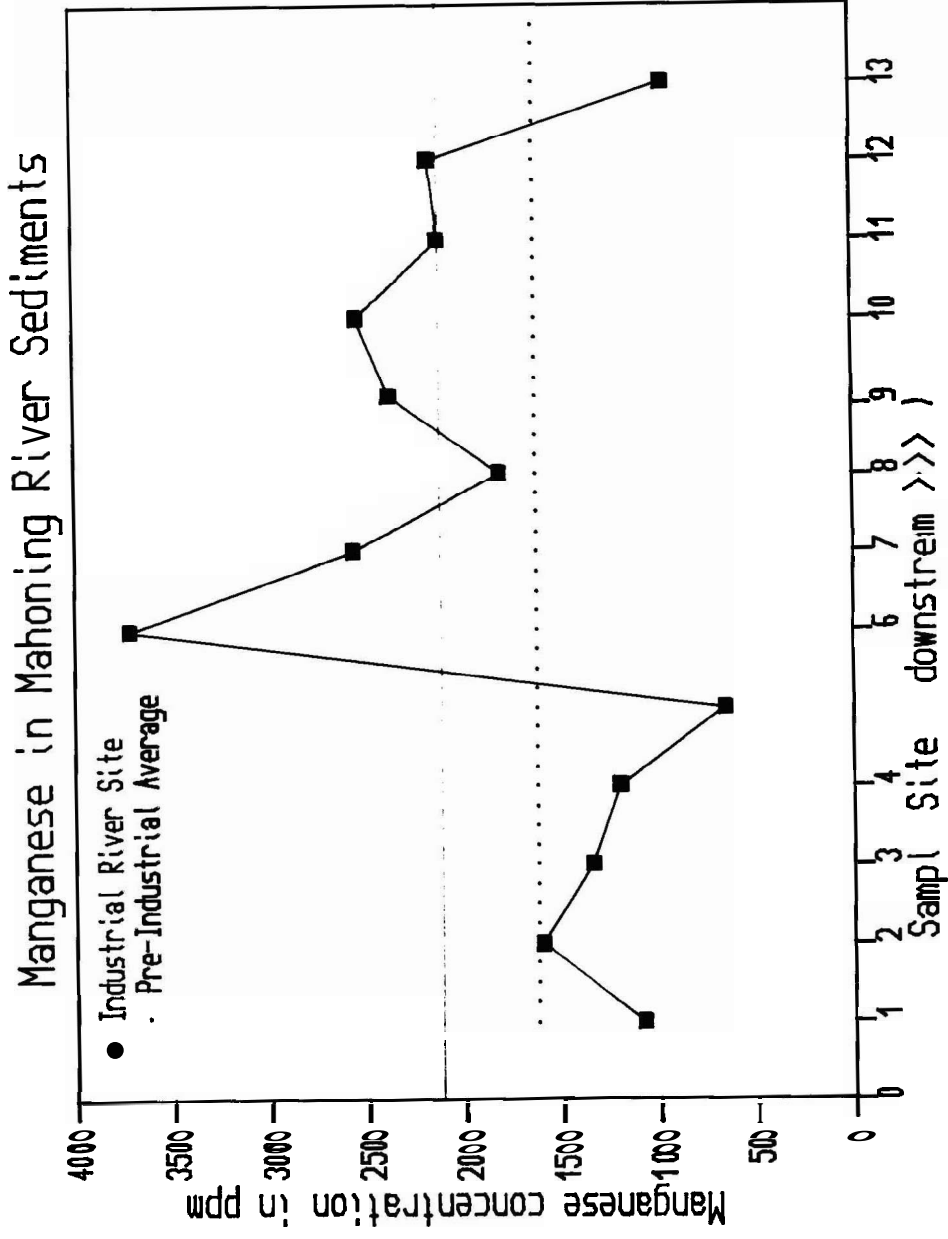


Figure 6. Solid Line nd.cates Average + 2SD  
 . Pre-Industrial Average

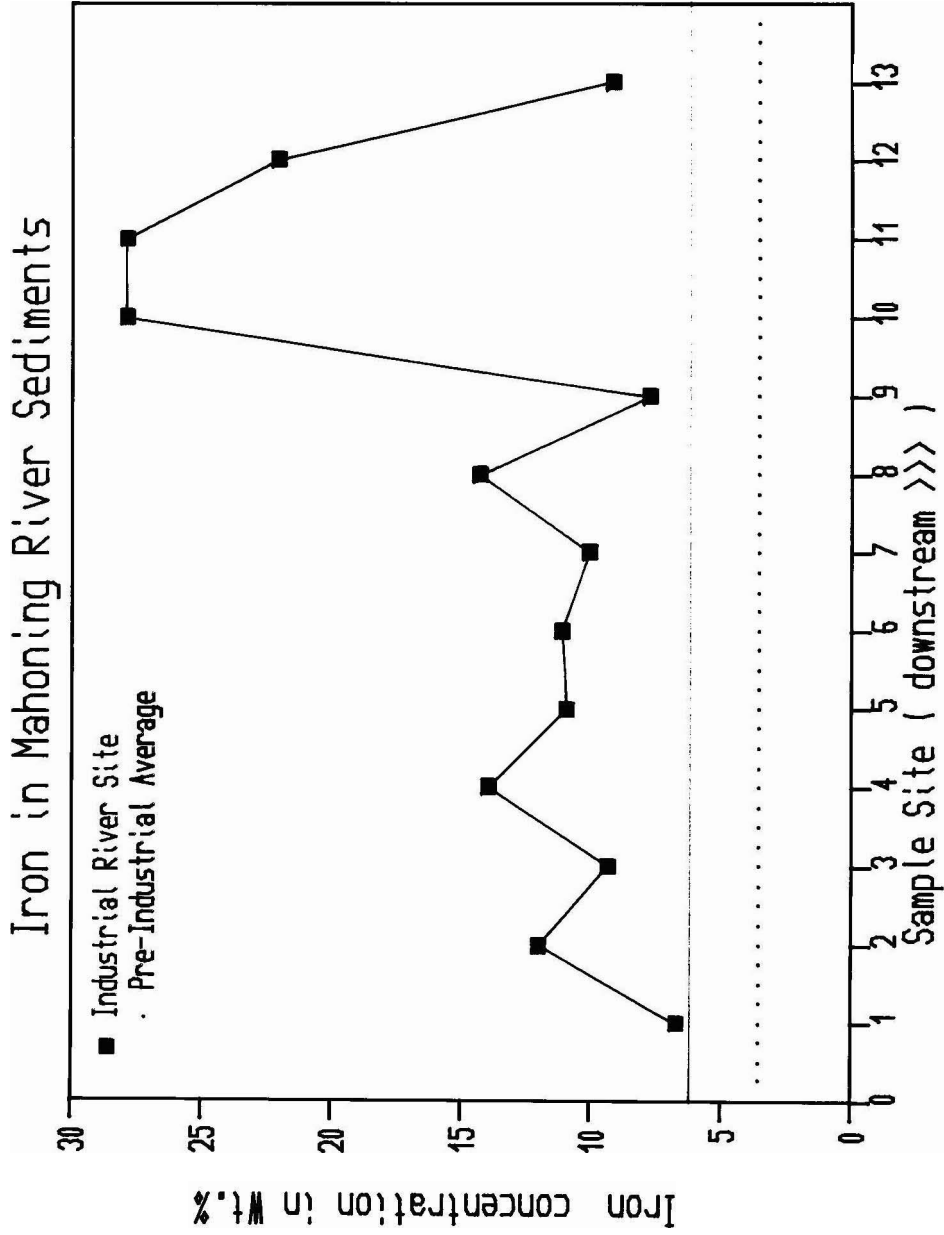


Figure 7. Solid Line Indicates Average + 2SD

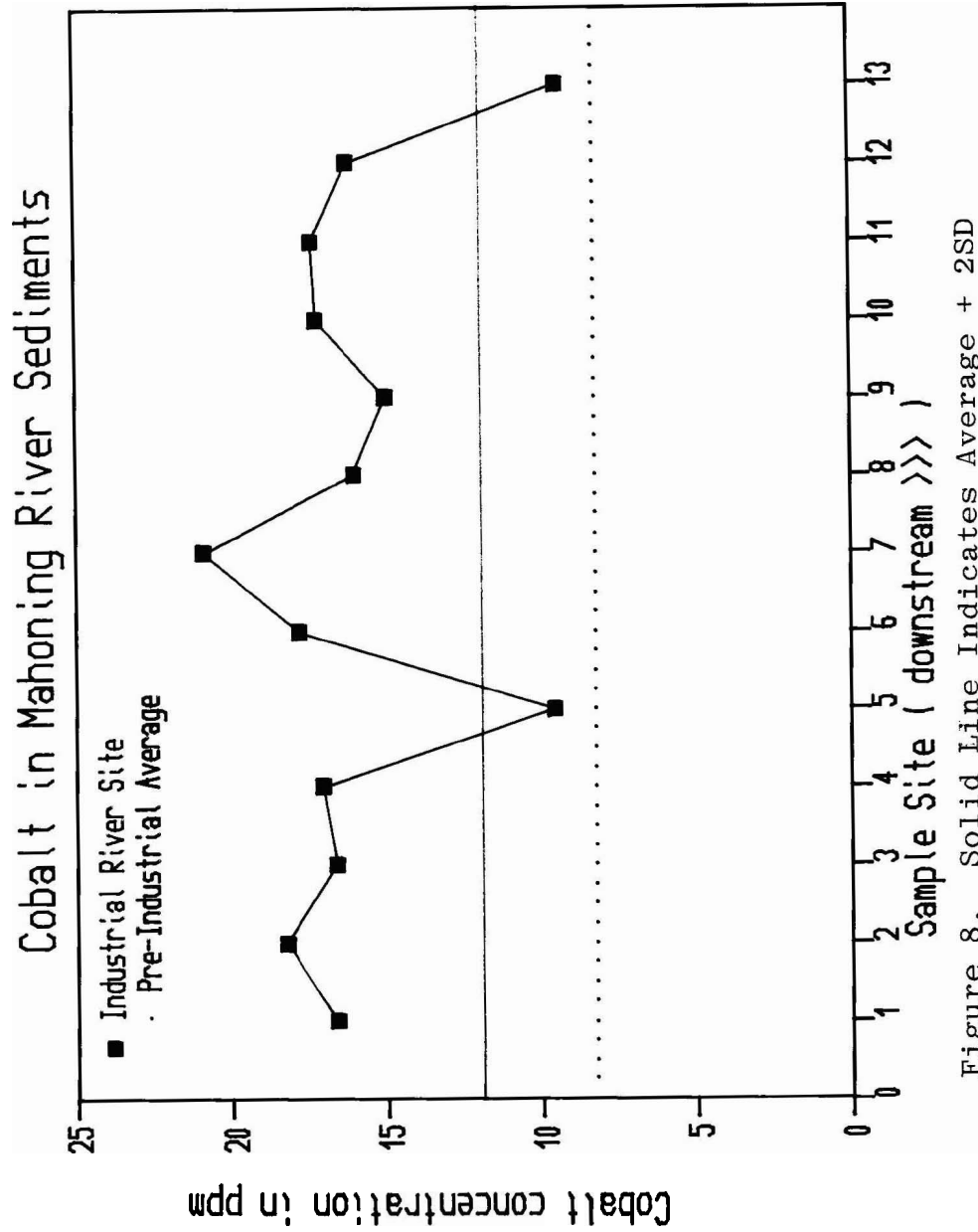


Figure 8. Solid Line Indicates Average + 2SD

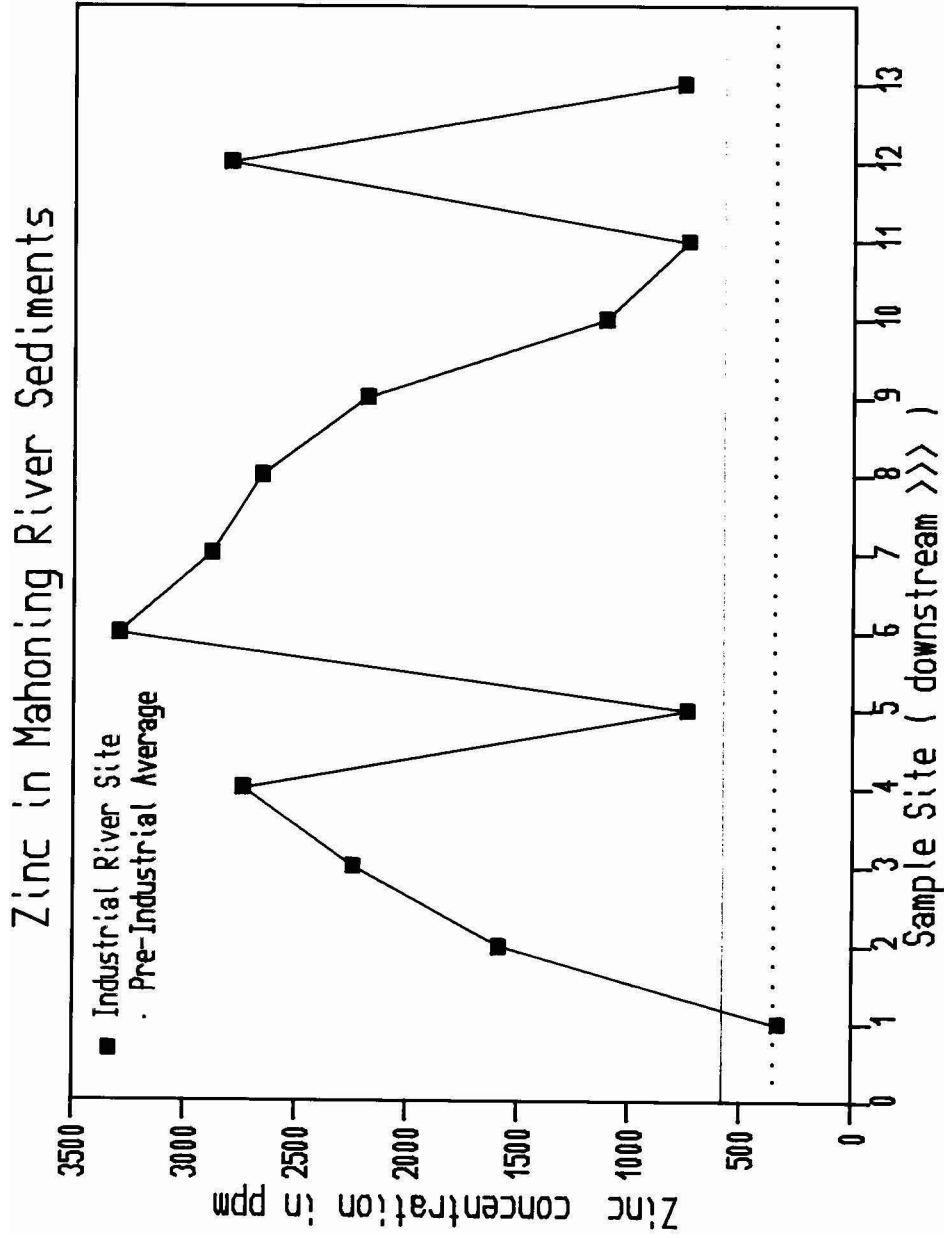


Figure 9. Solid Line Indicates Average + 2SD

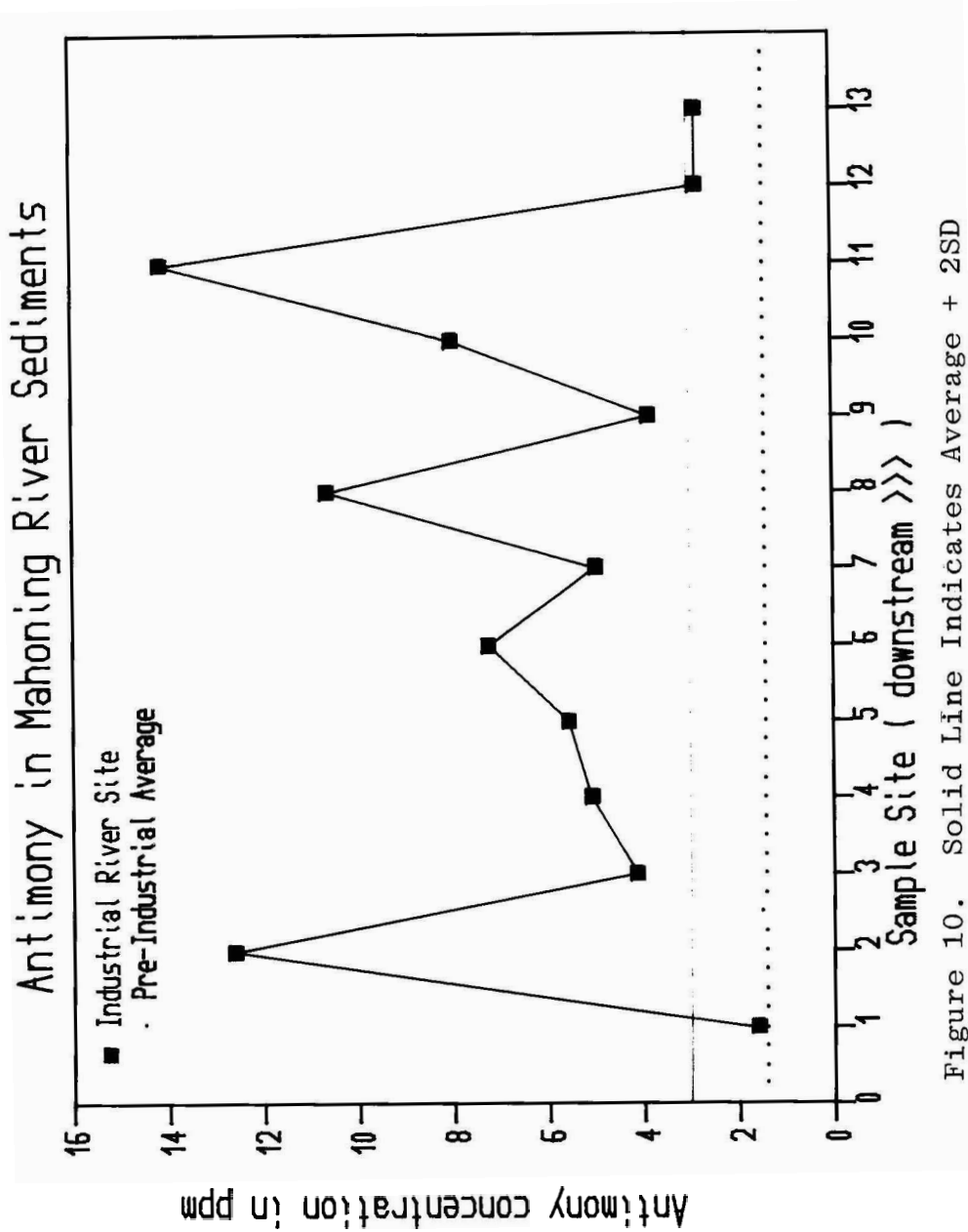


Figure 10. Solid Line Indicates Average + 2SD

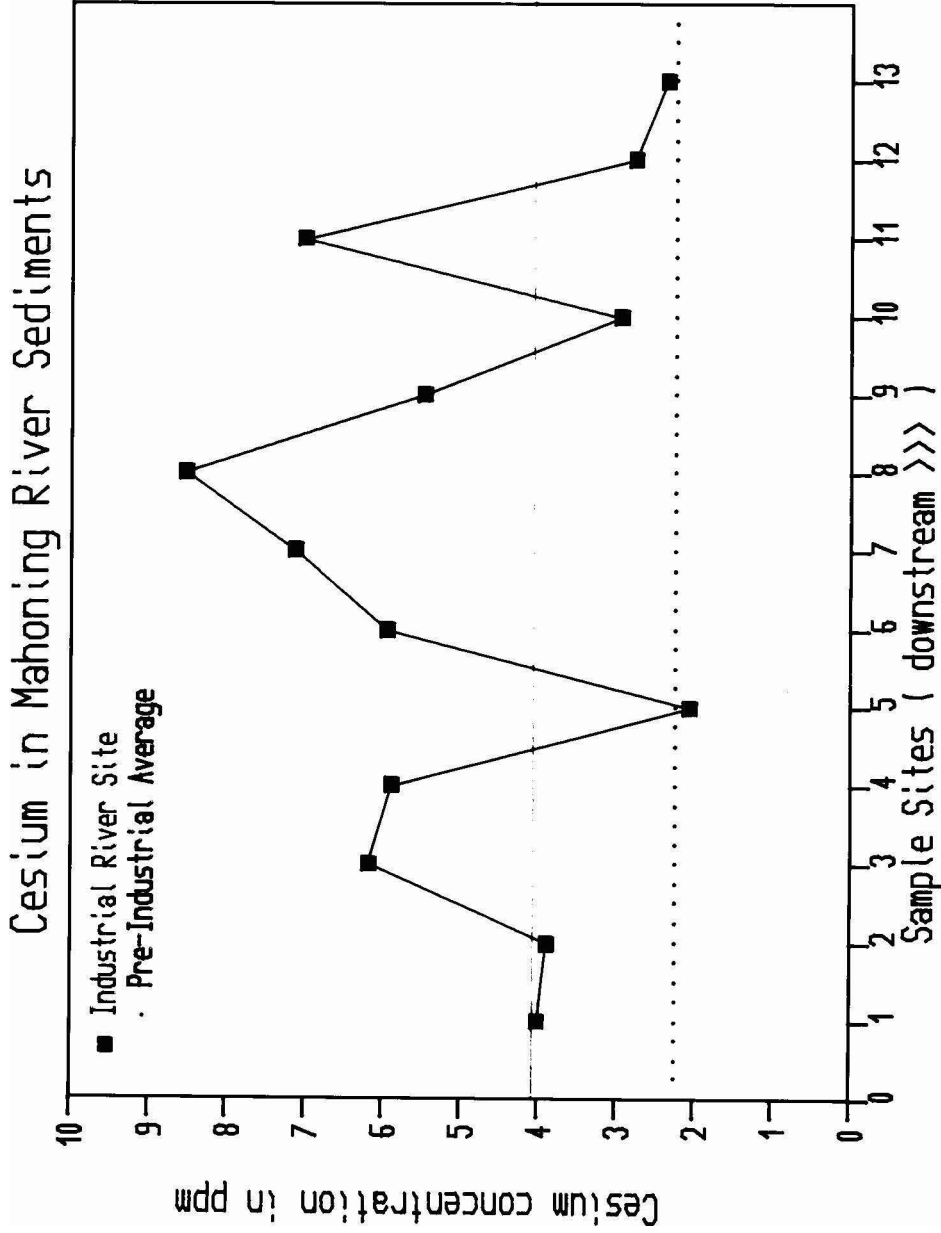
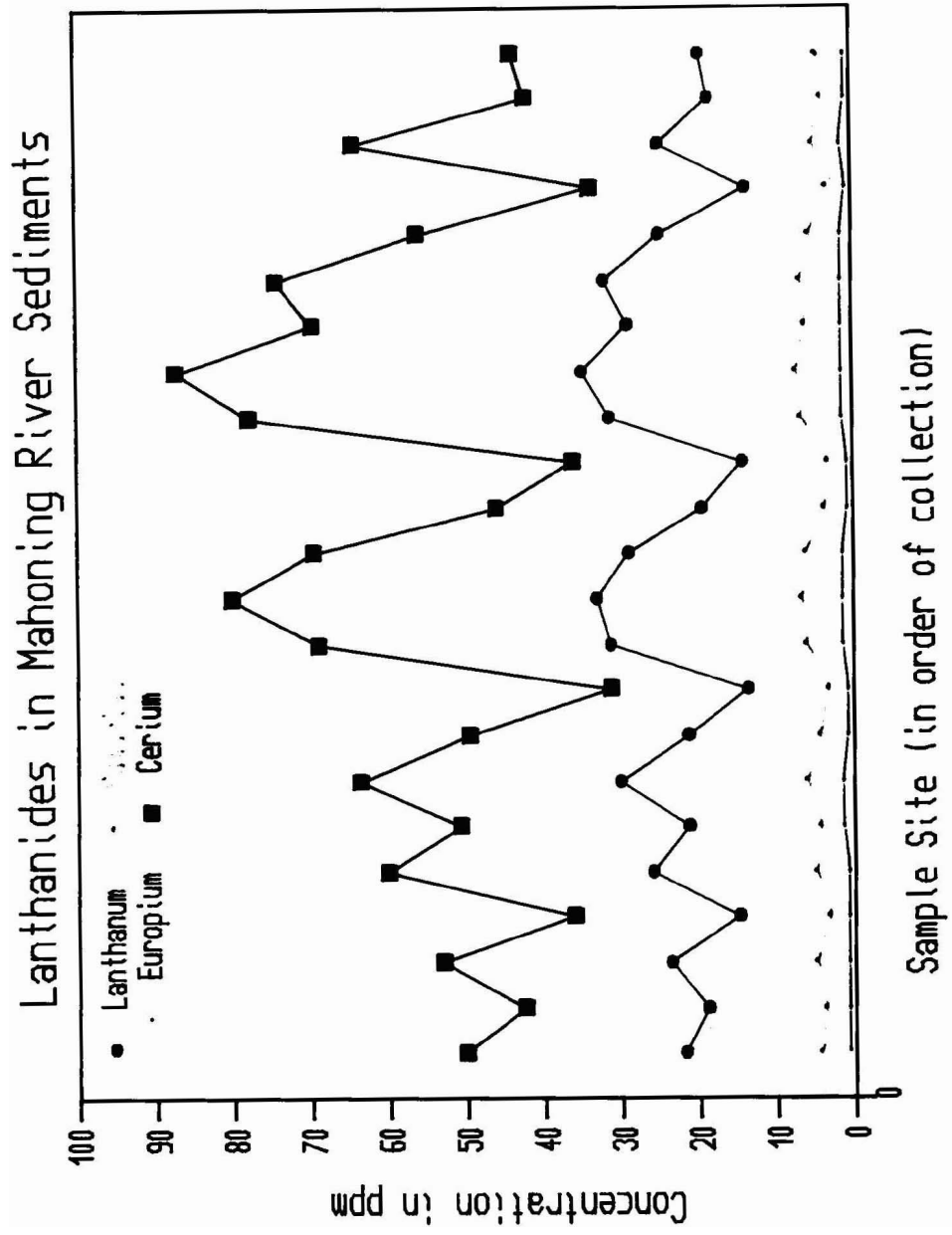


Figure 11. Solid Line Indicates Average + 2SD



Sample Site (in order of collection)

Figure 12



## WATER ANALYSIS

### ICP Analysis

Using the multiquant program provided a rapid analysis of the water samples, with the use of a small amount of each sample. It does however, add an extra source of error with the calibration ratios. Torch conditions could change between running the header standard and the actual water analysis, since each analysis took approximately 8 minutes. Thus the ICP concentration values listed in Tables 32 and 33 are accurate to only + or - 15%.

The definition for pollutants used in the sediment analysis is also used in the water analysis. By this method, iron and zinc show up as water pollutants. A plot of Fe and Zn concentrations vs. sample site is shown in figure 13. The other elements do not show up as pollutants, but show some interesting trends. Pre-industrial sites G and J show high levels of Na, Ca, Mg, Sr, Ba, and Si, with phosphorus also detected at site G. Both of these locations are streams, apparently running through rock formations high in these elements. Also, a plot of Ca, Mg, Sr, and Ba, concentrations vs. all sample sites (fig. 14) shows that the elemental levels correlate as do the lanthanides in the sediments. Ba did not show this correlation.

TABLE 32

## WATER CONCENTRATIONS~BY ICP ANALYSIS

SITE	CONCENTRATION IN PPM (mg/l)					
	Fe	Zn	Mn	Si	P	Al
<b>Pre-Industrial</b>						
A	0.45	0.012	-	2.3	-	-
B	0.47	0.019	1.1	2.4	-	-
C	0.73	0.022	0.26	3.1	-	-
D	0.78	0.023	0.48	2.8	-	-
E	0.90	0.021	0.56	3.6	-	-
F	0.89	0.010	0.49	3.6	-	-
G	0.56	0.059	0.40	9.2	18.	-
H	1.1	0.026	0.68	2.8	-	0.51
I	0.97	0.060	0.60	5.8	-	-
J	0.081	0.052	0.06	1.4	-	-
<b>AVERAGE</b>	0.69	0.030	0.51	3.7	-	-
<b>Industrial</b>						
1	0.72	0.021	0.34	3.4	-	-
2	0.66	0.064	0.27	4.0	-	-
3	0.67	0.039	-	3.4	-	-
4	0.97	0.36	0.39	3.9	2.5	-
5	2.3	2.2	0.52	4.8	-	-
6	2.0	1.5	0.54	5.2	-	-
7	0.73	0.097	0.29	2.4	-	-
8	0.73	0.090	0.30	2.4	-	-
9	1.3	0.095	0.32	3.1	3.0	-
10	0.96	0.16	0.27	3.0	-	-
11	0.90	0.11	0.26	3.2	3.0	0.42
12	1.1	0.12	0.27	3.4	2.5	-
13	1.0	0.093	0.23	3.1	2.5	-

<sup>a</sup>All Values +/- 15%.  
 -Not Detected.

TABLE 33  
WATER CONCENTRATIONS<sup>a</sup> BY ICP ANALYSIS

<u>SITE</u>	CONCENTRATIONS IN PPM (mg/l)				
	<u>Na</u>	<u>Ca</u>	<u>Mg</u>	<u>Sr</u>	<u>Ba</u>
<b>Pre-Industrial</b>					
A	24	40	32	0.15	0.030
B	23	39	31	0.15	0.027
C	25	32	25	0.11	0.021
D	23	38	30	0.14	0.025
E	25	38	29	0.14	0.030
F	25	39	28	0.14	0.025
G	96	67	44	0.36	0.015
H	21	25	14	0.086	0.029
I	38	46	27	0.15	0.034
J	42	76	68	0.45	0.081
<b>AVERAGE</b>	<b>34</b>	<b>44</b>	<b>33</b>	<b>0.19</b>	<b>0.032</b>
<b>Industrial</b>					
1	27	40	28	0.15	0.028
2	35	44	28	0.16	0.030
3	31	37	23	0.14	0.025
4	32	37	26	0.14	0.026
5	35	38	24	0.16	0.029
6	34	40	25	0.15	0.032
7	28	34	21	0.13	0.030
8	27	34	22	0.13	0.031
9	35	38	23	0.14	0.030
10	33	39	25	0.15	0.028
11	34	41	26	0.16	0.028
12	35	41	26	0.16	0.030
13	30	43	25	0.16	0.029

<sup>a</sup>All values +/- 15%.

# Fe and Zn in Industrial Mahoning River Waters

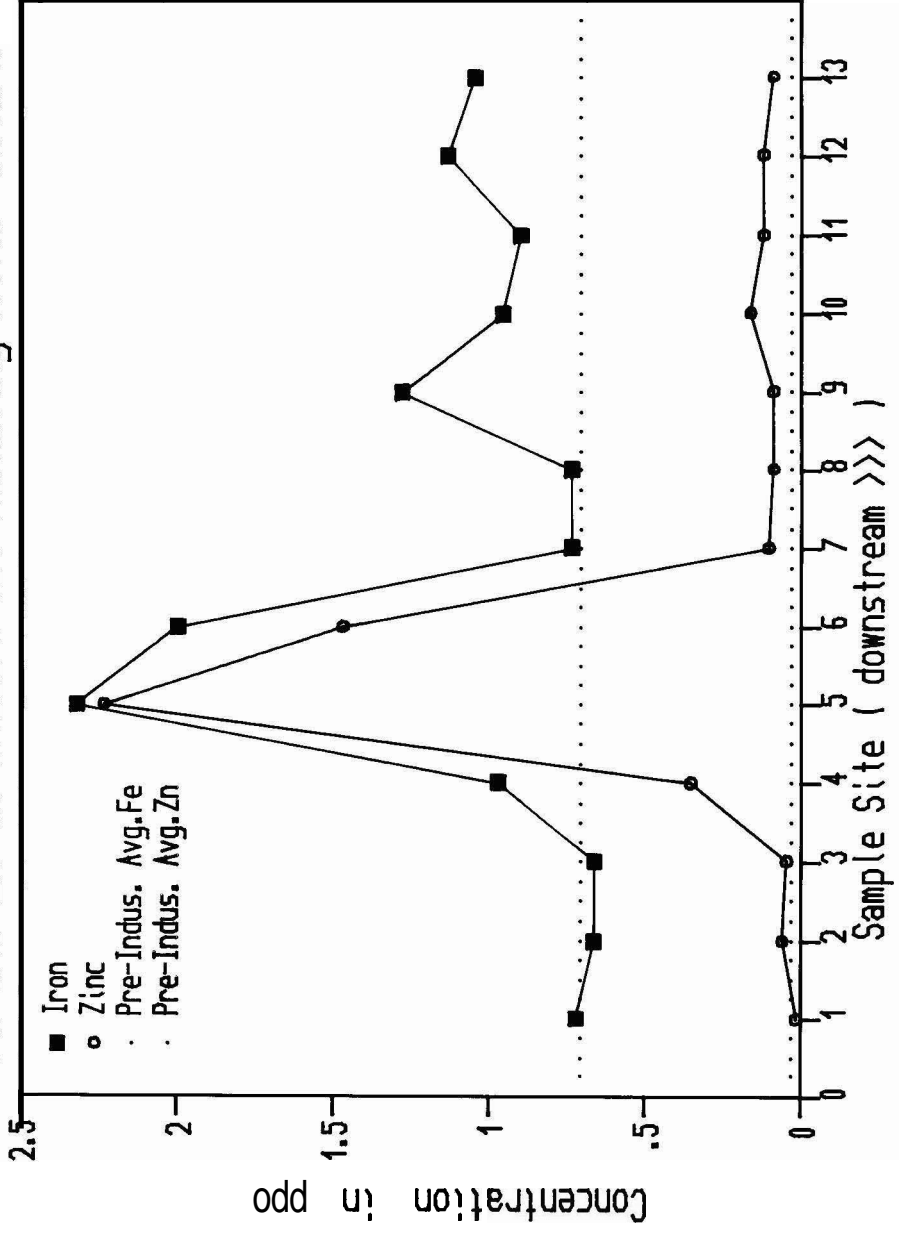
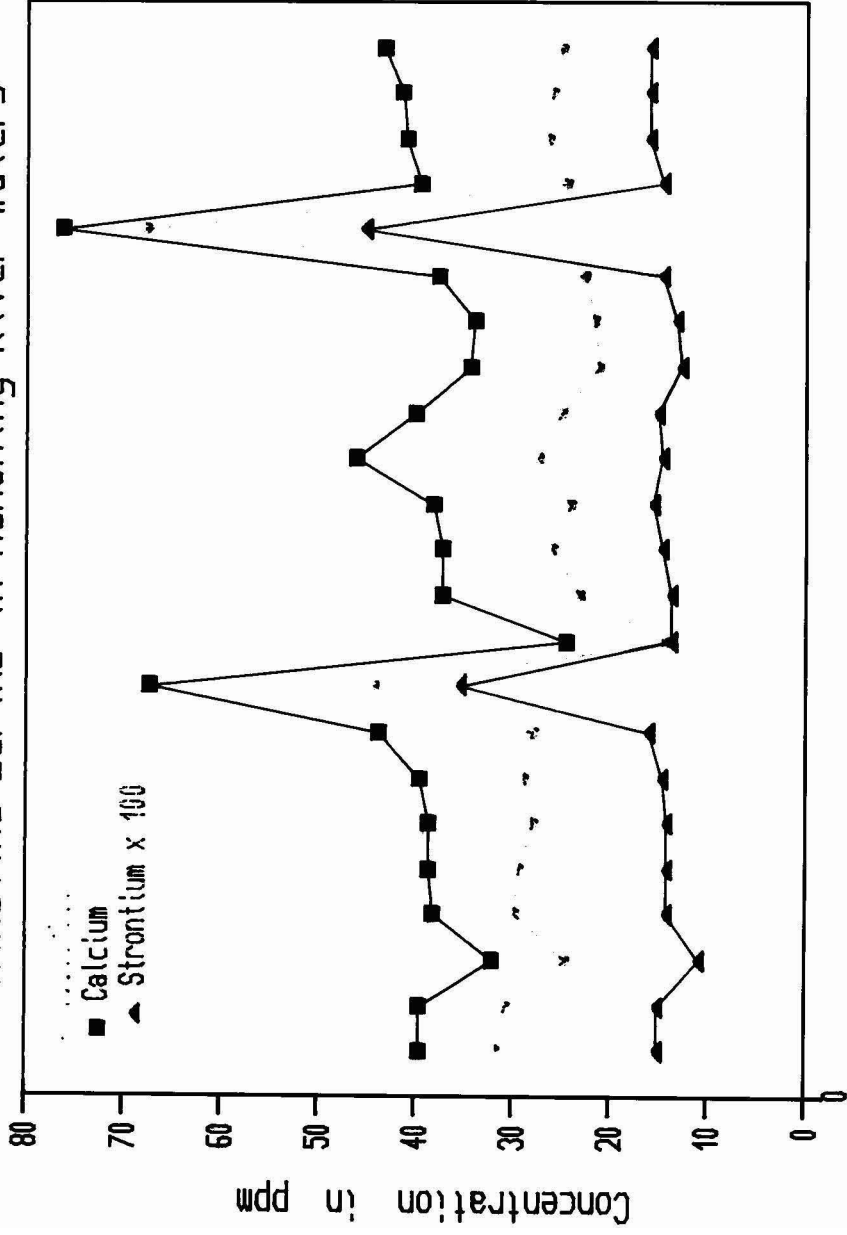


Figure 13.

# Alkaline Earths in Mahoning River Waters



Sample Site (in order of collection)

Figure 14.

## Atomic Absorption Analysis

Analysis by AA was made for both iron and copper. Results of this study are shown in Table 34. Comparing the Fe concentrations from ICP and AA analyses shows that the ICP values are systematically higher. The values do not agree with each other within experimental error. A possible explanation is that the **air/acetylene** flame used in AA analysis may not be hot enough to atomize all the iron present in the water if it is bound to a stable complexing agent such as phosphate. If some of the iron is present in molecular form in the AA flame, the measurements will be systematically low. Another explanation may be an interfering peak near the iron ICP emission line, which would cause systematically high results. However, no such interference was detected.

Copper was too low to be detected in all but one pre-industrial site.

Only potassium was determined by AE. An attempt to do sodium also by this method was unsuccessful, because a concentration vs. absorbance plot was not linear over the entire concentration range. The potassium concentration vs. absorbance plot showed some curvature, but was reliable enough to extract measurements from. The concentration data, listed in Table 35, show levels slightly above the 2 SD limit at industrial sites 2 and 12. These differences are, however, too small to show

TABLE 34  
 Fe AND Cu CONCENTRATIONS IN  
 WATER SAMPLES BY FLAME AA

<u>SITE</u>	<u>Fe (PPM)</u>	<u>Cu (PPM)</u>
<b>Pre-Industrial</b>		
A	0.324 ± .013	-
B	0.334 ± .017	-
C	0.509 ± .016	-
D	0.532 ± .020	-
E	0.611 ± .018	-
F	0.613 ± .016	-
G	0.371 ± .024	-
H	0.761 ± .015	-
I	0.686 ± .011	-
J	0.052 ± .020	.021 ± .010
<b>AVERAGE</b>	0.479 ± .192	
<b>Industrial</b>		
1	0.505 ± .015	-
2	0.467 ± .016	-
3	1.563 ± .024	-
4	0.648 ± .017	-
5	1.563 ± .024	-
6	1.388 ± .016	-
7	0.522 ± .016	-
8	0.547 ± .019	-
9	0.840 ± .016	-
10	0.638 ± .013	-
11	0.610 ± .017	-
12	0.757 ± .017	-
13	0.706 ± .018	-

-Not detected, variance values are standard deviations.

Table 35

## K CONCENTRATIONS IN WATER SAMPLES BY FLAME AE

<u>SITE</u>	<u>K (PPM)</u>		
<b>Pre-Industrial</b>			
A	5.61	±	.11
B	5.81	±	.12
C	4.13	±	.08
D	5.49	±	.11
E	5.32	±	.11
F	5.99	±	.12
G	14.77	±	.18
H	4.37	±	.09
I	6.89	±	.06
J	7.35	±	.04
<b>AVERAGE</b>	<b>6.57</b>	<b>±</b>	<b>.37</b>
<b>Industrial</b>			
1	6.17	±	.02
2	8.88	±	.25
3	6.63	±	.08
4	6.82	±	.00
5	7.32	±	.08
6	7.15	±	.02
7	6.12	±	.03
8	6.14	±	.02
9	6.98	±	.09
10	6.73	±	.20
11	6.67	±	.24
12	7.73	±	.09
13	7.22	±	.03

Variance values are standard deviations.



a significant variance between industrial and pre-industrial sites.

### Neutron Activation Analysis

Two river samples (10 and 11) were analyzed using NAA. The gamma peaks measured and resulting concentration values are given in Table 36. These samples were analyzed mainly to reference the NAA values with those from ICP. Of the 21 elements tested for, 13 were detected in both samples.

Four elements (Na, Mn, Ca, Ba) detected by ICP were also detected by NAA. The comparison of these values however, is rather poor. For sample 10, the Na and Mn concentrations agree within experimental error, but the Ca and Ba concentrations in this sample are an order of magnitude off (low for Ca and high for Ba) when compared to ICP values. In sample 11, Na shows up 2 times lower, Ca 10 times lower, Mn 100 times lower, and Ba 10 times higher than the corresponding ICP values.

In general, the NAA values for the water samples are unreliable as quantitative data. To begin with, the concentrations of elements in the water samples is very low. Thus, neutron bombardment will produce only weak activity for the elements present and make them difficult or impossible to detect. The small activity produced also makes for large statistical errors in gamma peaks that can be resolved, since background radiation levels

TABLE 36

GAMMA ENERGIES AND CONCENTRATION VALUES FOR WATER ANALYSIS BY NAA

<u>ISOTOPE</u>	<u>ENERGY (KeV)</u>	<u>SAMPLE CONCENTRATION</u>				<u>UNIT</u>
		<u>10</u>		<u>11</u>		
Na-24	1,368.00	30.4	± .5	16.3	± .3	PPM
Mn-56	846.75	0.20	± .01	.003	±	PPM
	1,810.66	0.23	± 3.1	.003	±	PPM
U-238	228.14	13.5	± 3.1	7.1	± 3.7	PPB
	277.56	9.1	± .08	3.0	± 3.8	PPB
Sc-46	889.26	0.19	± .08	0.27	± .07	PPB
	1,120.52	0.49	± .02	0.51	± .07	PPB
Au-198	411.79	0.15	± 2.9	0.54	± .04	PPB
	675.87	5.3	± 14.	6.9	± 3.6	PPB
	1,087.66	32.	± 17.	33.	± 17.	PPB
Br-82	554.33	351.	± 18.	271.	± 21.	PPB
	776.50	323.	± 17.	317.	± 22.	PPB
	619.09	351.	± 51.	291.	± 35.	PPB
	827.81	368.	± 52.	431.	± 69.	PPB
	1,043.97	409.	± 47.	382.	± 69.	PPB
	1,317.44	338.	± 64.	301.	± 59.	PPB
	1,474.85	321.	± 1.1	354.	± 85.	PPB
Co-60	1,173.21	6.6	± 1.3	7.7	± 1.1	PPB
	1,332.49	9.8	± .8	8.4	± 1.1	PPB
Cs-134	604.73	2.3	± 11.	2.3	± .7	PPB
	795.84	1.5	± 5.	1.5	± .8	PPB
	801.94	23.	± 10.	36.	± 10.	PPB
	569.35	10.	± 5.	6.	± 4.	PPB
	563.27	74.	± 10.	103.	± 11.	PPB
Rb-86	1,076.77	49.	± 19.	34.	± 18.	PPB
Cr-51	320.08	87.	± 8.	113.	± 9.	PPB
Ca-47	159.38	2.85	± .29	3.06	± .33	PPM
Ba-133	81.00	0.13	± .22	.024	± .10	PPM
	276.40	0.33	± .34	.058	± .36	PPM

are comparable to disintegration counts from the isotopes measured. Finally, since bigger vials were used, the geometry for detection is worse, lowering the amount of radiation measured from the sample. With these factors taken into account, the only useful data that can be extracted from the NAA concentrations is for bromine. Seven gamma peaks were used to measure this element, with only a 24% error for the worst value. The concentration values of Br in sample 10 all agree with each other within experimental error, and 5 of 7 in sample 11 are in agreement. All the other elemental concentrations are not reliable and are not used, but constitute a qualitative determination of their presence.

## CHAPTER V

### DISCUSSION

Residual pollution from the mostly defunct basic steel industry was found in the river bed. Of the nine elements classified as pollutants, six (Cr, Mn, Fe, Co, Zn, Sb) are common raw materials used in steel making. The high levels of aluminum may be from metal fabrication works along the river bank. Elevated levels of Sc and Cs probably arise from the various ores used in steelmaking. Since the ores were brought in from outside the area, they may have had higher levels of Sc and Cs and these elements could have accumulated in the river sediments after being introduced into the river. Another possibility to explain the high scandium levels is that the usual state of this element is  $\text{Sc}^{3+}$ , which is chemically similar to  $\text{Al}^{3+}$ . It's possible the high Sc levels are from the aluminum in the sediments, and a comparison of the graphs of both elements (Figures 3 and 4) shows they have similar trends. Of the other elements showing above average concentrations in the industrial sites, but not classified as pollutants (Th, Rb, V, As, La, Sm, Ce), vanadium can be directly linked to the steel industry since it is used in specialty steels and found in lubrication oils commonly discharged into the river. High levels of the other elements may also arise from the foreign ores used in steelmaking.

The water samples showed no indication of residual pollution or of elements from the sediment into the river water up to our detection limits. It does, however, show that iron and zinc are still being introduced into the river. This constitutes an active pollution of the water by industries now using the river. Because Fe and Zn were the active pollutants, it is easy to tie them to some sort of steel processor, such as a plating operation. This type of work is common in the **Mahoning** Valley.

Accumulation of the pollution elements in the river sediment is probably favored by the moderate pH (approximately 6 for the whole river) resulting in the low solubility of the hydroxides and oxides of these elements (excluding Cs), and the fact that the **Mahoning** River is rather shallow and slow flowing. Since no leaching of the river bed pollutants was observed from the water analysis, it must be assumed that the elements are flushed out of the river in particulate form. Flushing the elements out of the river as particulate matter will be very slow, thus the impact of these elements on the aquatic environment will be felt for a long time.

Comparison of these findings with previous analyses is limited. Iron and zinc were detected only in water samples by Muntean, Kline and Evans. Aluminum was found in sediments and waters by Muntean, but the

results are in the part per million range and do not compare with the weight percent values found in this study. All other elements found as pollutants in the river sediments were undetected by the earlier workers.

The question also arises of the concentration of elements in the **Mahoning** River System compared to other water systems. A study by Bart and Von Gunten lists mean concentration values for trace elements in relatively non-polluted river waters.<sup>15</sup> By this study, **Mahoning** River waters contain a higher level of Na, K, Ca, Sr, and Mn. Compared to this study, iron and zinc levels are very much greater in **Mahoning** River waters at sites classified as polluted, with Fe and Zn concentrations more than two and ten times higher, respectively. Other sites show Fe and Zn levels close to the mean value.

For the sediment concentrations, data from a lake sediment analysis by Nadkarni and Morrison was used for comparison.<sup>16</sup> Listed in this study are concentration ranges they determined for trace elements in lake sediments, in a relatively pollution free lake. By comparison, the elements Al, Fe, Co, and Cr, in **Mahoning** sediments are above the ranges listed by the above authors, being nine and seven times higher in the case of Fe and Cr, respectively. Of the other

elements detected in **Mahoning** River sediments and listed as ranges in the above study, all lie inside the range reported.

A suggestion for future work is the study of the distribution of different forms of the elements in the river water. Similar to the work by Bart and Von **Gunten**, a determination of particulate versus dissolved species of each element can be made.<sup>15</sup> This would be particularly interesting for iron, which is the major pollutant in the river system. Also possible is the investigation of pollution in Mosquito Creek (Site H), which showed elevated levels of many elements.

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