

**Determination of Heavy
Metals on the Rock River
through the Analysis of
Sediments**

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**Department of Nuclear Engineering and
Institute for Environmental Studies**

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THROUGH THE ANALYSIS OF SEDIMENTS

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TABLE OF CONTENTS

	<u>Page</u>
Acknowledgments.....	iii
List of Tables.....	vi
List of Figures.....	vii
Abstract.....	ix
Executive Summary.....	xi
Chapter 1. Introduction.....	1
Chapter 2. Description of Study Area.....	3
A. Location and Topography.....	3
B. Geology.....	3
Chapter 3. History.....	5
Chapter 4. Sites.....	7
A. Site Selection.....	7
B. Individual Site Description.....	7
1. South Fork, Kent Creek.....	7
2. North Fork, Kent Creek.....	9
3. Rock River.....	10
Chapter 5. Samples.....	13
A. Sample Collection and Storage.....	13
B. Sample Preparation for Neutron Activation Analysis.....	13
Chapter 6. Analysis.....	15
A. Neutron Activation Analysis (NAA) Theory.....	15
1. Method.....	15
2. Calculation of Trace Metal Concentrations.....	15
B. Quality Control.....	15
C. General Remarks.....	16
D. Specific Site Remarks.....	21
E. Particle Size.....	21
F. Enrichment Factors.....	30
G. Toxicity Tests.....	32
Chapter 7. Conclusion.....	35
Chapter 8. Recommendations.....	37
References.....	39

LIST OF TABLES

TITLE	<u>Page</u>
1. Physical Location of Sampling Sites.....	11
2. Comparison of Neutron Activation Analysis Results with Certified Values to Ensure Quality Control.....	17
3. Particle Size Testing Results from Site F.....	27
4. Particle Size Testing Results from Site E.....	29
5. Indications of Elevated Concentrations as Calculated from Enrichment Factors.....	31
6. Indications of Increased Concentrations as Calculated from Enrichment Factors to Indicate Transport Downstream.....	31
7. Toxicity Test Results.....	34

LIST OF FIGURES

TITLE	<u>Page</u>
1. Location of sampling area and sample sites.....	8
2. Mn concentration, upstream, South Fork Kent Creek (Site A).....	18
3. Mn concentration, downstream, South Fork Kent Creek (Site C)....	19
4. Sm concentration, midstream, North Fork Kent Creek (Site E).....	20
5. Mn concentration, downstream, North Fork Kent Creek (Site F)....	22
6. V concentration, downstream, Rock River (Site H).....	23
7. Co concentration, downstream, Rock River (Site H).....	24
8. Cu concentration, downstream, North Fork Kent Creek (Site F). Samples from depths 0-17 cm had Cu concentrations below the detection limit of 30 ppm.....	25

ABSTRACT

Neutron activation analysis has been used to analyze sediment cores from the Rock River and two branches of Kent Creek, one of its tributaries, to determine the concentrations of thirteen heavy metals (Ti, Cu, V, Mn, As, Sb, Se, Cr, Ni, Sc, Fe, Zn, and Co) and two rare earths (Sm and La). The downstream sites of both the Rock River and the two branches of Kent Creek have elevated concentrations of several heavy metals including arsenic, antimony, and zinc. In addition, hundreds of parts per million of copper have been found in samples from the downstream site of the North Fork of Kent Creek. Toxicity tests of the sediments also indicate that the downstream sites are detrimental to lifeforms. Analyses of the data from the two branches of Kent Creek clearly indicate that heavy metal concentrations increase as the distance from the center of industrial activity (Rockford) decreases.

EXECUTIVE SUMMARY

The Rock River and its tributaries in Winnebago County have been the recipients of large amounts of various wastes during the last century of industrialization. Some industries responsible for these unwanted wastes include furniture manufacturing, agriculture, tool making, textile trades, leather workings, printing and metal plating and casting. Several previous studies have looked into groundwater contamination and biological investigations. A detailed historical review of waste disposal practices had also been compiled.

The study reported here was initiated 1) to collect and analyze sediment cores from eight sites of the Rock River and its tributaries in order to establish historical levels of heavy metal pollution, 2) to establish an analytical protocol using neutron activation to best determine the levels of selected heavy metal concentrations, 3) to determine the toxicological impact of heavy metals on aquatic life, and 4) to establish background levels of metals upstream from sources of known pollutant discharges.

Results of the study include:

- A non-destructive, cost-effective analytical protocol to determine heavy metals (excluding cadmium, lead and mercury) has been established using neutron activation analysis.
- High concentrations of anthropogenic metals including antimony, arsenic, copper, selenium, and zinc were found in the sediments.
- Concentrations of these metals appeared in the Rock River and the North and South Forks of Kent Creek.
- Enrichment factor calculations showed that metal loadings increased significantly the closer the sites were to the city of Rockford.
- Toxicity tests showed that downstream sites seemed to be the most toxic due to increased concentrations of metals such as copper, arsenic and zinc.
- Upstream sites away from the potential heavy metal contamination were stimulatory to the nematode test. That is, survival was greater than 100%.
- In general, toxic potential of the stream sediments increased as the stream progressed toward and in the immediate area of the city of Rockford.

Although this study was only funded for one year, the investigators feel that further research should be carried out in the following areas:

- The development of a more detailed sampling protocol with the help and expertise of sedimentologists from the HWRIC and Illinois State Water Survey.
- The determination of cadmium, lead, and mercury levels which are not possible by neutron activation analysis.
- The evaluation of the role of atmospheric deposition on trace element concentrations.
- The study of sequential extraction of the heavy metals to have a clearer indication of speciation.

CHAPTER 1. INTRODUCTION

Many industrial wastes contain potentially toxic concentrations of heavy metals. These metals may be considered stabilized and not of any potential harm if they cannot be easily mobilized. If, on the other hand, the metals can become mobilized either through sediment transport or by solubilization, then they may pose a severe environmental threat to both human and aquatic life.

The State of Illinois has some of the most industrialized areas in the country. In particular, Winnebago County, which includes Rockford and the Rock River Valley, has been the recipient of large amounts of various wastes over the last hundred years. Some industries that have produced and disposed of waste in this area include furniture manufacturing, agriculture, tool making, textile trades, leather workings, printing, and metal plating and casting. In addition, land disposal was unregulated until the mid 1970s. Early waste disposal practices not only threatened aquatic life but have also resulted in widespread groundwater contamination (Wehrmann *et al.*, 1988).

In the late 1970s, a comprehensive assessment of the water quality of the Rock River basin derived from biological investigations was performed for the United States Environmental Protection Agency (USEPA) (Brigham, 1978). A detailed historical review of waste disposal practices in Winnebago County was compiled by Colten and Breen for the Illinois Hazardous Waste Research and Information Center (HWRIC) in 1986. The authors of this report recommended the analysis of sediments, biological life and water from sand and gravel aquifers of the Rock River Valley be made to assess the extent of heavy metal contamination in the Rock River basin. This recommendation was made to remedy the lack of information that existed regarding the concentrations of potentially toxic substances that had been discharged into the Rock River system. Of particular importance would be a study to determine the historical levels of metal pollutants in river sediments that results from metal plating, machine tool manufacturing, and casting industries.

A comprehensive scientific investigation of eight sites was initiated to study several important environmental aspects of the Rock River basin. These investigations required: 1) the collection and analysis of sediment cores to establish historical levels of heavy metal pollutants; 2) the establishment of an analytical protocol to best determine as many of the elements as practical; 3) analysis of the sediment samples for their toxicity to aquatic life; and 4) the establishment of background levels of certain trace metals upstream from specific sources of known pollutant discharge.

To achieve the project objectives, sediment core samples were taken at eight sites. These cores were processed and analyzed using neutron activation analysis to determine the concentration of thirteen heavy metals (arsenic, antimony, cobalt, copper, chromium, iron, manganese, nickel, selenium, scandium, titanium, vanadium and zinc) and two rare

earths (lanthanum and samarium). The validity of using neutron activation analysis for these metal determinations is supported by previous investigations of river sediments (Uken et al., 1977; Moxham et al., 1977; Nakahara et al., 1978; Shuman et al., 1977; Labrecque et al., 1986; and Madaro and Moauro, 1985).

CHAPTER 2. DESCRIPTION OF STUDY AREA

A. Location and Topography

The Rock River basin in Illinois is bounded on the north by the Wisconsin state line; on the east and south by the Fox River, Big Bureau Creek, and the Spoon River, also on the south by the Edwards River system, and on the west by the Mississippi River basin (north). The portion of the watershed which lies in Illinois comprises approximately 1,361,365 ha., and includes portions of the following fifteen counties: Boone, Bureau, Carroll, DeKalb, Henry, Jo Davies, Kane, Lee, McHenry, Mercer, Ogle, Rock Island, Stephenson, Whiteside, and Winnebago. Drainage of the watershed is into the Mississippi River at Rock Island.

The present physiography of the watershed reflects the Pleistocene history of the area. The Rock River has its origin in the Horicon Marsh, Dodge County, Wisconsin, and flows southwest cutting through low, rolling hills of the Rock River Hill Country of the Till Plain Section of the Central Lowland Province. Most of the knobs and ridges present in this physiographic region are the result of direct glacial deposition.

In Illinois, the glacial physiography of the river basin is complex. The entire watershed is covered by Illinoian deposits and the eastern and southern portions are overlain by more recent Wisconsinan deposits. As with most of Illinois, the Rock River basin lies within the Central Lowland Province. With the exception of the extreme eastern tributaries to the Kishwaukee River, which drain the Wheaton Moraine Country of the Great Lakes Section, the entire watershed is confined to the Till Plain Section of the Central Lowland Province (Brigham, 1978).

To the north, the river drains the Rock River Hill Country, which is characterized by low, rolling hills and ridges. To the east, the Wheaton Moraine Country is characterized by a complex morainal topography. To the southeast the Bloomington Ridged Plain consists largely of moraines separated by extremely flat lake deposits. In Bureau County to the south, the Rock River basin drains the Green River Lowland, a poorly drained plain with prominent sand ridges and a former channel of the Mississippi River. At its present junction with the Mississippi River, the Rock River flows through the Galesburg Plain, a region characterized by low, poorly drained plains with prominent ridges and dunes (Brigham, 1978).

B. Geology

The original bedrock underlying the Rock River basin was capped with Silurian strata. Glacial movement and more recent erosion has broken this cap into scattered remnants of the former flat Dodgeville peneplain. The Racine (upper) and Marcus (lower) Formations of the Niagaram Series and the Sweeney (uppermost), Blanding, Tete des Morts, and Mosalem (lowermost) Formations of the Alexandrian Series are

represented in these sediment cores. Silurian rocks are predominantly carbonates and almost entirely dolomite (William et al., 1975).

Underlying the Silurian strata is a thick layer of the Maquoketa Shale Group. This shale is soft and disintegrates easily. In areas where it is not capped with resistant Silurian rock, it has eroded into a rolling plain. Maquoketa Shale is the uppermost rock in most of the basin. It is covered by sufficient loess and till deposits and slumps from the Silurian strata so that outcrops occur only on steep slopes. Brainard Shale (upper) and the Clermont (upper) and Elgin (lower) Shale members of the Scales Shale (lower) are represented. These shales are calcareous and rich in fossils (Willman et al., 1975).

Underlying the Maquoketa Shale is Galena dolomite. It is the principle basal rock in the deeper valleys. Five formations are recognized in the study area including Dubuque (uppermost), Wise Lake, Dunleith, Guttenberg, and Spechts Ferry. These dolomites are coarse grained and porous frequently containing thin-bedded, weathering shale and chert.

The preglacial Rock River flowed south into Illinois about 2 km east of and parallel to its present course. At the southern edge of Winnebago County, however, it continued southward to the LaSalle County line. There it turned southwest and joined the Mississippi River northwest of Princeton in Bureau County. The Wisconsin glacier (Shelbyville advance) blocked the Mississippi River near its junction with the Illinois River, pushing the river west and forming Lake Cordova which occupied the Princeton Valley. The Mississippi River finally cut through the Cordova Gorge and took its present course along the western border of Illinois. The Rock River also was pushed west flowing through a former channel of the Mississippi River and joining the Mississippi River at Rock Island.

CHAPTER 3. HISTORY

The city of Rockford was founded in 1834 and incorporated in 1839. The location of the town was dictated by the nearness of an inexpensive source of water power for sawmills (Federal Writers, 1946). The presence of water and waterpower was a key element in the industrial expansion of the city. The 1870's saw the growth of grain milling, foundries, and machine shops which replaced the sawmills as the major industrial contributors to the city. From 1870 to 1880 the number of industries doubled. Between 1900 and 1920, the industrial base of the city continued to increase, particularly in the production of machinery. Electroplating began in this region in the 1920s (Colten and Breen, 1986).

Colten and Breen (1986) described the pre-1931 waste disposal practices in the following manner: "...most Rockford industries built private sewers to the Rock River or the nearest stream and allowed natural processes to carry away their effluents." In 1931, a sewage treatment facility began operation but since there was no regulation forcing local industries to process their wastes, many industries continued the practice of direct disposal of untreated wastes. The total amount of sewage decreased during the Depression but the increased industrialization during the Second World War offset this decline. Industries that were not connected to the city's sewage system existed as late as 1960. The industrial level remained fairly constant during the period between 1965 and 1980 but the amount of waste discharged decreased due to improved methods for pretreating waste before disposal into the river. Some industries evaded this treatment of the waste by using land disposal until this practice was regulated in 1976 (Colten and Breen, 1986).

The preceding summary of the industrial waste disposal practices in Winnebago County clearly indicates that there is a potential for residual heavy metal contamination in the Rock River. The prevalence of the tool and electroplating industries that routinely produce waste that contain heavy metals created the major pollution threats.

CHAPTER 4. SITES

A. Site Selection

In order to adequately characterize the heavy metal concentration in the drainage system of Winnebago County, a large number of sample sites would be needed on both the Rock River and its tributary streams. However, in this initial study, economic and time limitations restricted the number of sampling sites to eight. These eight sites were selected to achieve a set of data that characterized the area as well as possible.

The concept implemented in site selection was simple: Choose sites along the stream such that the movement of the heavy metal contaminants could be monitored as they progressed downstream. Of the two major tributaries of the Rock River in Winnebago County (Keith Creek and Kent Creek), the decision was made to sample Kent Creek, both north and south forks, because it is easier to access the sampling sites there than Keith Creek. There is also historical evidence indicating heavy metal waste disposal on the western side of the Rock River (i.e., the area around Kent Creek) (Colten and Breen, 1986). Two sites on the Rock River itself were also selected for sampling. A detailed map showing the sites is seen in Figure 1.

B. Individual Site Description

1. South Fork, Kent Creek

Three sites were selected to characterize the South Fork of Kent Creek. According to historical evidence, the 'headwaters' of the stream should be relatively free of heavy metal contamination. By 'headwaters' it is meant the region of the stream where the stream is no longer intermittent but a stream all year long. Site A was chosen to serve as a reference site for the downstream sites. This area of the creek is bordered by rural farmland and the sample site can be described as a small stream with ample vegetation. The stream bed was free of a rock/gravel substrate and there was a negligibly small sand layer at the top of the cores. Four cores were taken in close proximity to each other. The core sites were chosen to minimize any influence from the nearby road bridge.

The second site chosen for the South Fork of Kent Creek (Site B) was selected at the half way point between where the stream originates and where the stream merges with the North Fork of Kent Creek. A short distance above this site is a petrochemical storage plant. Data from the analysis of cores taken from this site would reflect that facilities influence on contamination of the creek. Physically, Site B is very similar to Site A in that they are both located in rural areas with large amounts of vegetation along the stream. The two major differences between the two sites is that at Site B, the upper sand layer becomes more pronounced and a gravel/rock substrate begins to appear in the creek bed. This substrate increases the difficulty of sampling since it

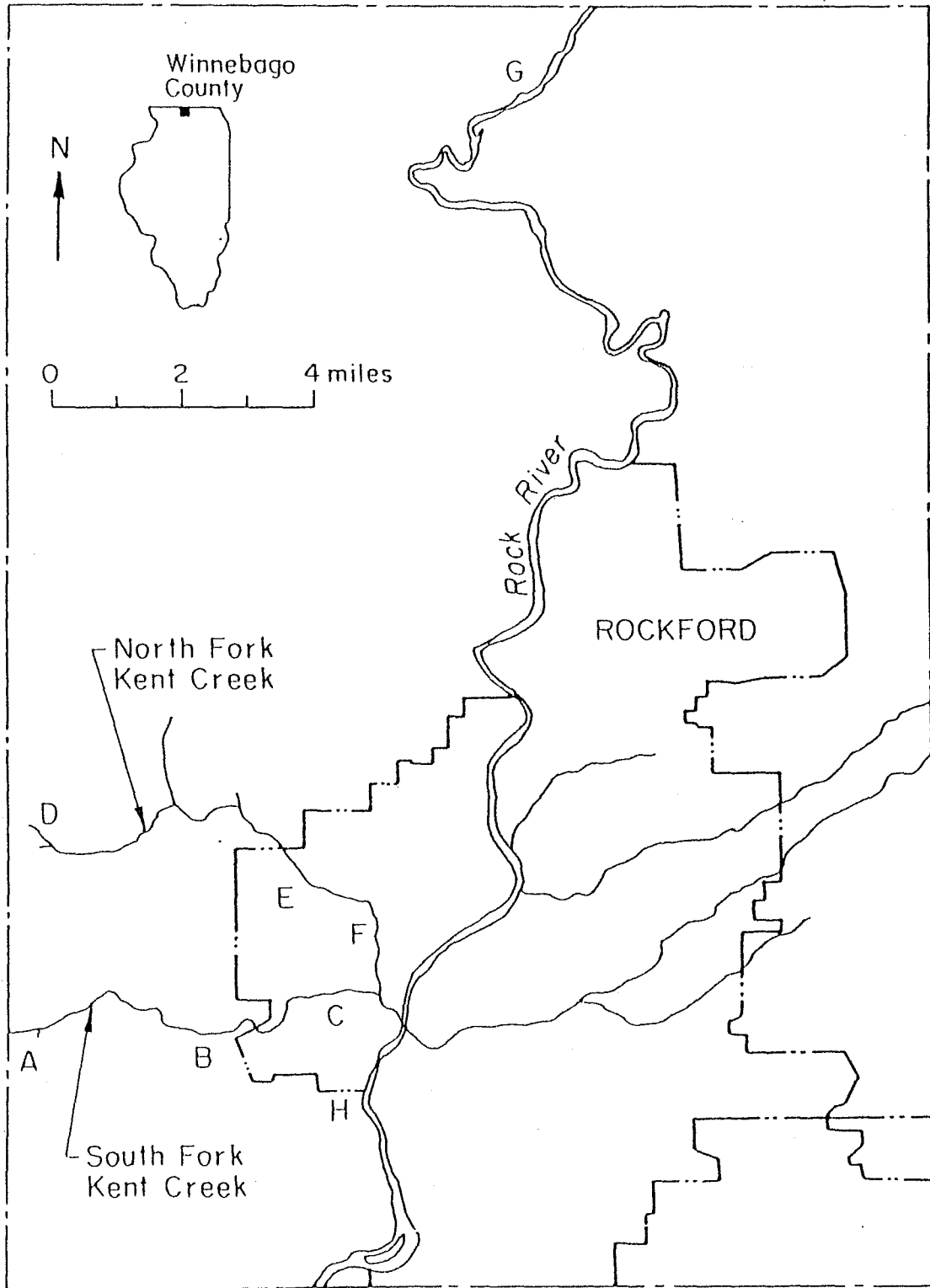


Figure 1. Location of sampling area and sample sites.

becomes harder to find spots in the creek bed where samples can be taken. However, at this point in the creek, four adequate cores were taken in relative close proximity to each other.

Whereas Sites A and B were located in rural areas, Site C was located in the middle of the city of Rockford. This site was very near the confluence of the North and the South Forks of Kent Creek, and thus this site could provide some indication of the trace metal contamination that resulted from upstream disposal into the South Fork of Kent Creek. Near this site are several metal finishing plants and other potential sources of heavy metal contamination. In addition, there is ample historical evidence that this area has been the site of industries that could contribute heavy metal contamination (see Colten and Breen, 1986).

The area immediately adjacent to the creek has undergone some recent changes. All of the trees and the vegetation that lined the creek had been removed several weeks before the samples were taken. Additionally, a sluice gate to a small retention pond about ninety meters upstream of this site was recently opened. Sediment that had settled in this retention pond was washed over the sampling site and further downstream once this gate was opened. As a result, the water of the stream was extremely murky. Samples were very easy to take at this site, primarily due to this eroded soil.

2. North Fork, Kent Creek

Sampling sites were also chosen on the North Fork of Kent Creek to map the heavy metal contamination in that area. The upstream location, Site D, was situated in a rural area, very similar to the location of the upstream site on the South Fork of Kent Creek. This site was located away from potential sites of contamination and serves as a reference for the downstream sites. There was not a gravel/rock substrate in this area making sampling with four cores much easier than the downstream sites. Also, at this site there did not exist a significant sand layer on the top of the sediment.

Sampling the midstream portion of the North Fork of Kent Creek posed several problems. A few sampling sites in the midstream area had to be discarded because of the extreme difficulty in obtaining samples. The bed of the North Fork of Kent Creek in this area is very rocky and it was very difficult to drive the corer into the sediment. In order to obtain samples, the sampling site was moved downstream towards Rockford. This movement of the sampling site introduced other problems. The location where samples were finally obtained was adjacent to an industrial park and near a public park. The stream had been modified to make the area more 'beautiful.' The banks of the stream were changed to be more sloped and the bed of the stream seemed to have been widened. Nevertheless, four cores were taken in this area (Site E) because of historical evidence pointing towards potential heavy metal contamination of both the creek and nearby wells.

Finally, the downstream site (Site F) was taken near the confluence of the two forks of Kent Creek. This site area was near a railroad switching yard and downstream from an industrial area. Sampling was difficult due to the presence of a rock/gravel substrate relatively near the surface of the stream bed. This particular area of the stream appears to be used as an open garbage dump. Among the items found in the stream bed were an automobile radiator, two tires, and a box spring.

3. Rock River

Although the main conduit of the Winnebago County drainage system is the Rock River, only two sampling sites were chosen to monitor the heavy metal contamination in the Rock River itself. Sampling on the Rock River is both difficult and hazardous because of the rapid current and the dense surface rock layer. Attempts at sampling the center of the Rock River met with failure when the corer would not penetrate the surface of the river bed. Therefore, it was decided to sample wherever it was physically possible. At both sites on the Rock River, the samples were taken along the river's edge. An attempt was made to sample on one of the midstream islands but this proved to be impossible because of the rocky base.

As with the two forks of Kent Creek, one sample site was chosen upstream (Site G) to act as a reference for the downstream site. Finding a sample site upstream of the small dam located in the center of Rockford proved to be very difficult. However, a site was finally located well away from any contamination from Rockford or any of the other nearby towns. The upstream samples were taken along the shore near a private boat launch. All four cores were taken within five meters of the shore because this area was the only accessible point.

Downstream of the dam, the final site (Site H) was taken along the shore just down current of a bend in the river. It was hoped that at this point in the river, sediments would have had a chance to deposit and the historical record could be investigated. The site was very similar to the upstream site in that the majority of the samples taken were sand with little silt present. The site was located downstream of the Kent Creek confluence with the Rock River so the influence of contamination documented in Kent Creek could be monitored on the Rock River. Site H is located behind a large industrial area in Rockford and any contamination from this locale would be detected. An exact description of the site locations is presented in Table 1.

TABLE 1. PHYSICAL LOCATION OF SAMPLING SITES

Locations of the sites as taken from U. S. Geological Survey topographic quadrangle maps (7.5' series, 1971 ed., 1976 PR).

SITE:

- A. IL, Winnebago County, South Branch Kent Creek, 15 m downstream Falconer Road Bridge, 2.6 km E Winnebago. 4th Principle Meridian: T.26N, R.11E, NW/4, SW/4, SE/4, Sec. 10. U.T.M.: ³¹⁷560m E, ⁴⁶⁸¹140m N. Winnebago, IL.
- B. IL, Winnebago County, South Fork Kent Creek, 20 m upstream Centerville Road bridge, just southeast of Rockford. 3rd Principle Meridian: T.44N, R.1E, NE/4, NE/4, SE/4, Sec. 30. U.T.M.: Zone 16, ³²²200m E, ⁴⁶⁸⁰500m N. Winnebago, IL.
- C. IL, Winnebago County, South Fork Kent Creek, along north side of old industrial complex, 40 m upstream Independence Street bridge, in southwest Rockford. 3rd Principle Meridian: T.44N, R.1E, SW/4, SE/4, NE/4, SE/4, Sec. 21. U.T.M.: Zone 16, ³²⁵320m E, ⁴⁶⁸¹780m N. Rockford North, IL.
- D. IL, Winnebago County, (south fork of the) North Fork Kent Creek, 20 m upstream Wempletown Road bridge, 5.2 km NE Winnebago. 4th Principle Meridian: T.27N, R.11E, SE/4, SE/4, NE/4, NE/4, Sec. 34. U.T.M.: Zone 16, ³¹⁸330m E, ⁴⁶⁸⁵420m N. Winnebago, IL.
- E. IL, Winnebago County, North Fork Kent Creek, 50 m downstream Central Avenue bridge along bike path, in west Rockford. 3rd Principle Meridian: T.44N, R.1E, SW/4, NW/4, SW/4, NW/4, Sec. 15. U.T.M.: Zone 16, ³²⁵620m E, ⁴⁶⁸⁴000m N. Rockford North, IL.
- F. IL, Winnebago County, North Fork Kent Creek, 20 m upstream to 20 m downstream Cedar Street bridge, in southwest Rockford. 3rd Principle Meridian: T.44N, R.1E, SE/4, SW/4, NW/4, SE/4, Sec. 22. U.T.M.: Zone 16, ³²⁶460m E, ⁴⁵⁸¹760m N. Rockford North, IL.
- G. IL, Winnebago County, Rock River, 1.5 km upstream Latham/Ralston Road bridge, just north of Latham Park (town). 3rd Principle Meridian: T.45N, R.2E, SE/4, NE/4, NW/4, NW/4, Sec. 18. U.T.M.: Zone 16, ³³⁰870m E, ⁴⁶⁹⁴020m N. South Beloit, IL-WI.
- H. IL, Winnebago County, west edge of Rock River, in Rockford, 750 m downstream dam (300 m downstream confluence with Kent Creek). 3rd Principle Meridian: T.44N, R.1E, N/2, NW/4, NW/4, SW/4, sEC. 26. U.T.M.: Zone 16, ³²⁷200m E, ⁴⁶⁸⁰500m N. Rockford North, IL.

CHAPTER 5. SAMPLES

A. Sample Collection and Storage

At each site, four sediment cores were taken for analysis. The cores were obtained by using a hollow, bronze cylinder approximately two inches in diameter and thirty inches in length. To prevent possible metal contamination and to facilitate sample storage, the corer was lined with a CAB (cellulose/acetate/buterate) liner that was replaced after each core was taken. This liner was inserted into the cylinder of the corer prior to the sampling and then removed after the core was taken. The cores were taken by manually inserting the corer into a site and using a sledge hammer to drive the corer into the river or creek bed until it became impossible to move the corer downward. The average length of the core was 30 cm. After forcing the corer into the sediment, the corer was then removed by hand. To help prevent the loss of any of the sediment, an 'eggshell' was inserted into the liner before sampling. This 'eggshell' is a plastic device that will allow the sediment to be pushed into the liner but impedes the flow of sediment out of the liner into the tube of the corer. After the core was taken, the liner containing the samples was removed and end caps were attached to the liner to isolate and contain the sediment sample. These cores were then frozen with dry ice and stored in coolers.

B. Sample Preparation for Neutron Activation Analysis

After freezing, the cores were then transported to the laboratory where they were kept in a freezer until processed. Since the purpose of this project was to determine heavy metal concentrations as a function of time, it was decided to slice the cores into one centimeter discs and then to prepare each disc as a separate sample. A wooden jig, very similar to a miter box, was constructed to hold the cores while they were being cut. The cores were then partially thawed so that they would retain their shape but would still have some pliability. The end caps were removed from the liners and the sediments were extruded. Once 1 centimeter of the sediment was extruded, nylon fishline, held taut, was used to slice the cores. The 1 centimeter disc was then placed on a clean watchglass and dried in an oven at 110°C overnight.

Once the sample had been dried, it was visually inspected for color, composition, and any unusual artifacts. Artifacts and rocks were removed by hand and the remaining sample was sifted in a 660 micrometer mesh brass sieve. There was some concern that the sieve would introduce some contamination-most notably copper-but the data does not indicate any contamination caused by this device. The sieved portion of the sample was then placed in vials containing a methacrylate ball. These vials were placed in a ball mill for ten minutes to homogenize the sample. After homogenization, a half gram sample was placed in another vial. This vial was labeled with the origin of the core and the depth of the sample in that core. The samples in these vials were then analyzed by neutron activation analysis to determine the metal content.

CHAPTER 6. ANALYSIS

A. Neutron Activation Analysis (NAA) Theory

1. Method

Neutron activation analysis entails the interpretation of a gamma-ray spectrum from an irradiated sample. There are several distinct advantages to utilizing neutron activation analysis. First, the process is non-destructive and hence dissolution of the material is not necessary. Nondestructive neutron activation analysis will give results for many of the heavy metals of interest; approximately thirty to forty elements are measurable with the notable exceptions being mercury, lead, and cadmium. Without chemical separation, mercury and cadmium have detection limits that are too high for most environmental work while lead has only one reaction that would be useable for neutron activation analysis and this half-life is much too short for analytical purposes. Finally for a multielemental study NAA is very cost competitive (there are many commercial and academic laboratories doing these analyses). The methods and techniques of NAA are described by Tolgyessy and Klehr (1987).

2. Calculation of Trace Metal Concentrations

A mathematically simple method to calculate the concentration of an element is available using the comparator method. Essential to neutron activation analysis is a reliable and consistent neutron source. All activation was performed using the 1.5 MW TRIGA reactor at the University of Illinois. Each sample was irradiated twice. The first irradiation consisted of a ten second irradiation at 500 MW (1.5×10^{12} n/cm² sec) using the pneumatic rabbit system. This rabbit system places the sample in the reactor for a set period of time and then pneumatically removes the sample to a holding area. Irradiation time and delay time are recorded electronically. The second irradiation consists of five hours at 500 kW in the lazy susan. The lazy susan is a tray that revolves around the reactor at one revolution per minute, capable of holding eighty samples. In order to acquire the spectra, an ORTEC multichannel analyzer circuit board was installed in an IBM AT personal computer. This analyzer allowed the accumulation, analysis, and storage of the gamma-ray spectra.

B. Quality Control

Calibration of the system was done using prepared atomic absorption solutions. To assure that the results from the activation analysis were accurate, neutron activation analysis was performed on a certified reference material for a sediment prepared by the National Research Council of Canada. This reference material has certified values for trace metal concentrations. These concentrations were experimentally determined by various analytical methods including atomic absorption, inductively coupled plasma, neutron activation analysis, etc. A comparison of the results from the activation analysis of a certified

reference material and the established values for these materials allows a measure of the precision of the experimental analysis. As can be seen from Table 2, the results are in excellent agreement. These certified reference materials were continually analyzed during the course of the project as blind samples.

C. General Remarks

Since the cores were cut into slices and each slice analyzed individually, the metal concentrations for each site can be plotted as a function of depth. These graphs can provide an estimation as to the deposition of the heavy metals as a function of time. Because of the rapid current in the Rock River, the deposition rate of sediment cannot be very great, perhaps a millimeter each year. This approximation is based on the general rule of 1 centimeter of sediment deposition per year in static lakes. Similarly, Kent Creek has a fairly swift current so the approximation of 1 millimeter of deposition per year in either fork of the creek should be reasonable. Applying this approximation to the graphs of concentration reveals a salient point. Almost every graph of concentration as a function of depth has a common concentration peak towards the upper portion of the depth profile. By concentration peak, it is meant that the concentration is fairly constant from the bottom towards the surface until a certain depth is reached where the concentration suddenly increases. The location of this rise in concentration varies in proportion to the distance downstream. The upstream graphs will generally have the concentration peak begin somewhere near 6 or 7 centimeters deep while the downstream sites show the increase in concentration much lower, approximately 9 to 11 centimeters deep. However, in most cases, the magnitude of the increase in concentration does not appear to be dependent upon the site location. The downstream sites have similar magnitude increases in concentration as the upstream sites (for comparative purposes, see Figures 2 and 3: graphs of Mn as a function of depth for the upstream site of the South Fork of Kent Creek (Site A) and the downstream site of the South Fork of Kent Creek (Site C)). Coupling the supposition of a deposition rate of 1 millimeter of sediment per year and the 9 centimeter thickness of the concentration peak at the downstream site indicates that the sudden increase in the heavy metal concentration could be due to anthropogenic causes. The 9 centimeter thickness would correspond to approximately one century of time which is roughly the length of time that industries have been present in Winnebago County.

It should be noted that only the heavy metals exhibit the sudden increase in concentration. The two rare earths investigated do not have the peak on the concentration as a function of depth graphs (See Figure 4). Of course, among the many graphs plotted, there are some graphs of samarium and lanthanum that exhibit increases in concentration but these patterns are fairly rare. Also, the increases in concentration for the rare earths are not as drastic as the heavy metals and the location of the increases are not consistent as the increases in the heavy metal concentrations.

TABLE 2. COMPARISON OF NEUTRON ACTIVATION ANALYSIS RESULTS
WITH CERTIFIED VALUES TO ENSURE QUALITY CONTROL

Element	BCSS - 1	
	NAA values (ppm)	Certified values (ppm)
Sb	0.69 ± 0.12	0.59 ± 0.01
As	11.5 ± 1.2	11.4 ± 2.1
Cr	130 ± 6	123 ± 14
Co	13 ± 1	11.4 ± 2.1
Mn	229 ± 21	229 ± 15
Ni	56.8 ± 4.7	55.3 ± 3.8
Ti	3785 ± 117	3800 ± 150
V	95.7 ± 7.8	93.4 ± 4.9
Zn	115 ± 8	119 ± 12

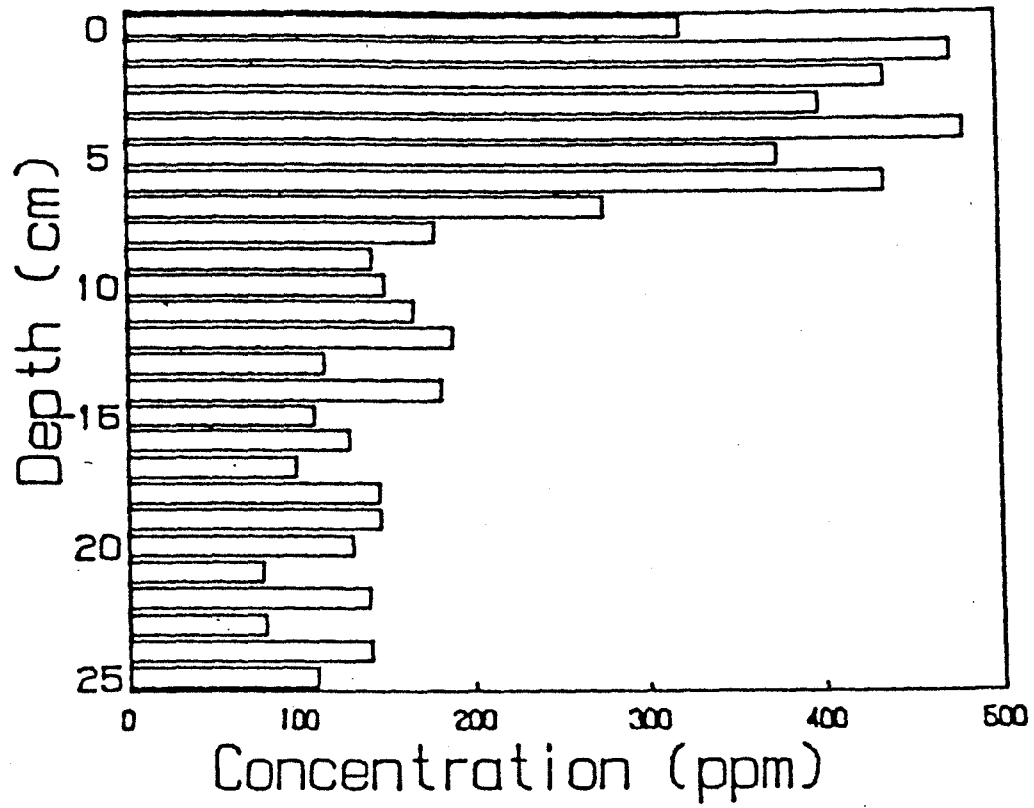


Figure 2. Mn concentration, upstream, South Fork Kent Creek (Site A).

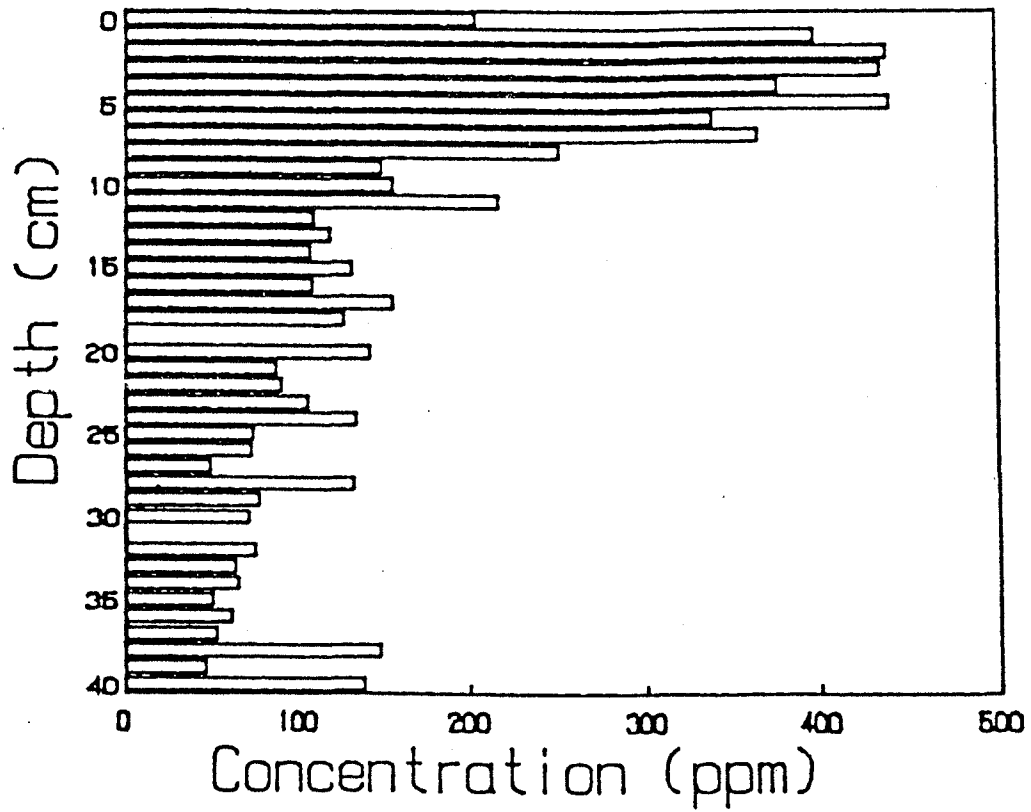


Figure 3. Mn concentration, downstream, South Fork Kent Creek (Site C).

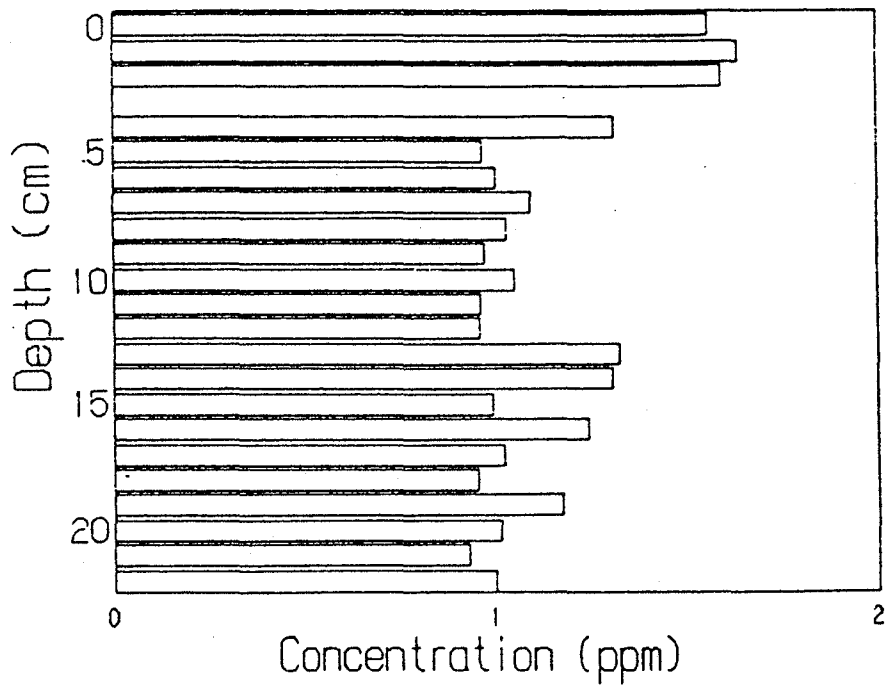


Figure 4. Sm concentration, midstream, North Fork Kent Creek (Site E).

D. Specific Site Remarks

The major anomaly that appears in the data for the sites on both forks of Kent Creek is from the downstream site on the North Fork of Kent Creek (Site F). Whereas most of the other concentration as a function of depth graphs had the increased concentrations towards the surface, the majority of the graphs plotted for this site had the concentration peaks at the lowest depths (Figure 5). At first it was believed that the analyzed core had become inverted during sample preparation but replicate analysis of the other cores taken at the same site indicate that the increased concentrations are at the lower depths (see, for example, the data presented for the particle size analysis; the copper concentrations only appear at the lowest depths). An explanation for this inversion is not apparent at this time. The site where these cores were taken has not been disturbed in the recent past.

The two sites on the Rock River exhibited different concentration as a function of depth characteristics than the sites on the two forks of Kent Creek. The upstream site (Site G) had the increased concentrations at the lowest depths, similar to the pattern found in the downstream site on the North Fork of Kent Creek. However, the downstream site on the Rock River (Site H) does not have any consistent heavy metal concentration deposition pattern as was exhibited at the other sites. Some of the metals tend to have increased concentrations at the lower depths (see Figure 6) while other heavy metals have a plateau of elevated concentration approximately between eight to eighteen centimeters (see Figure 7). The explanation for this behavior is unknown.

Another aspect about the downstream site of the North Fork of Kent Creek is the presence of copper in significant concentrations. Most of the samples analyzed contained concentrations of copper well below the minimum detection limit. As can be seen in Figure 8, this site has copper concentrations on the order of hundreds of parts per million. As mentioned earlier in reference to the data from this site, the copper also appears in lower depths with the concentration diminishing rapidly as the surface is approached. Duplicate tests on other cores from this site confirm the presence of copper at the same depths with approximately the same concentrations.

All the elemental concentrations in raw data form are available from HWRIC.

E. Particle Size

The Rock River has a very rapid current. Because of this current, the question arises as to the possibility of the heavy metal contamination washing downstream. Smaller particles would be more susceptible to movement by the current so an analysis was made to determine the heavy metal contamination relative to the size of the particle. Samples were sieved at 100 μm and neutron activation analysis was performed on both the fine and the coarse portions. The purpose of

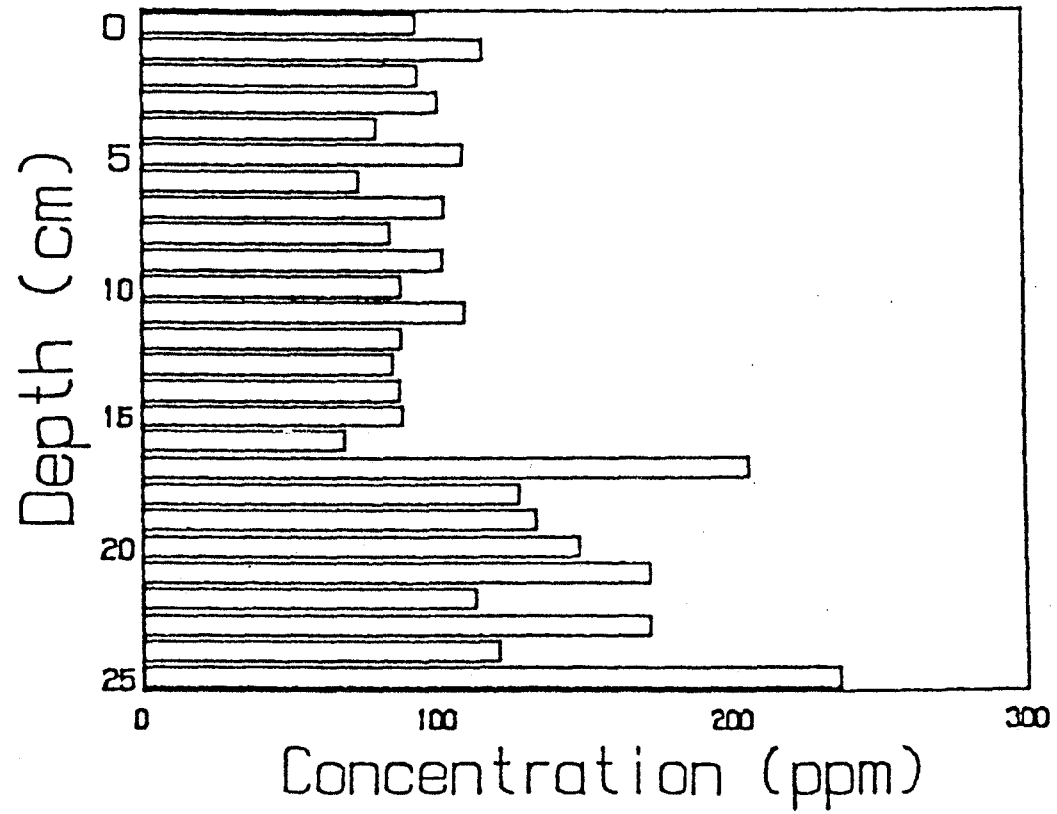


Figure 5. Mn concentration, downstream, North Fork Kent Creek (Site F).

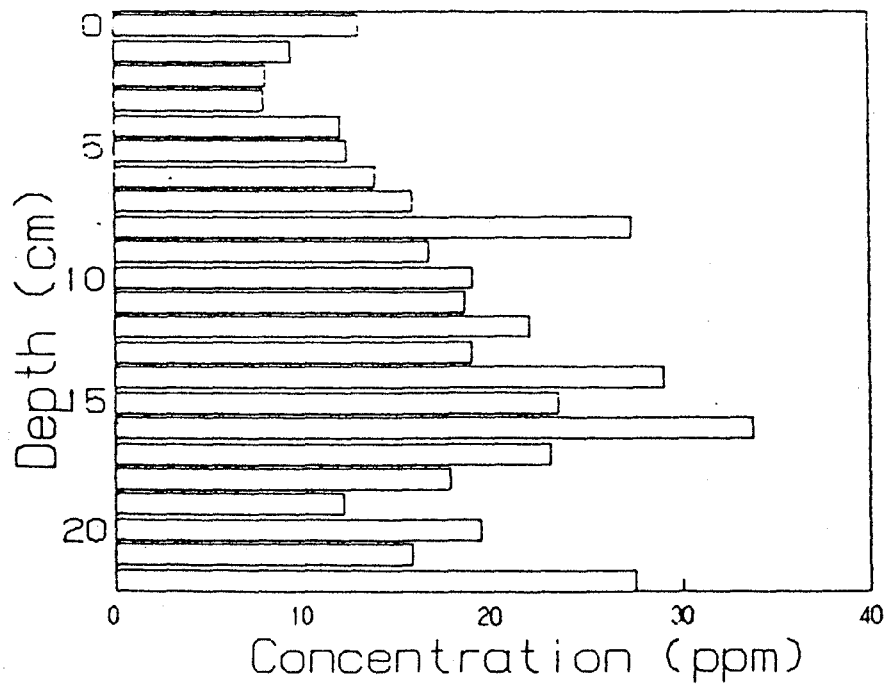


Figure 6. V concentration, downstream, Rock River (Site H).

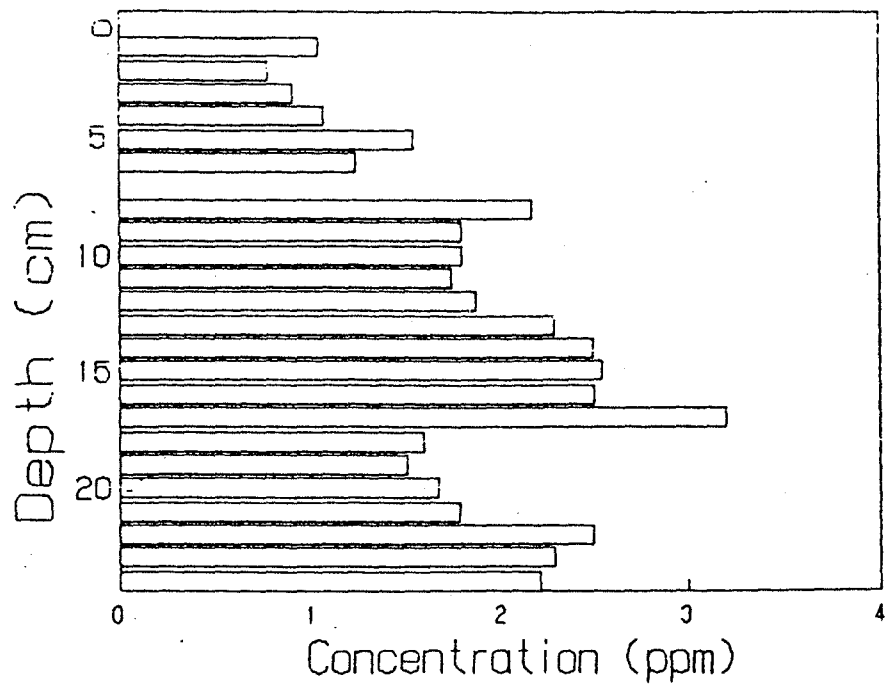


Figure 7. Co concentration, downstream, Rock River (Site H).

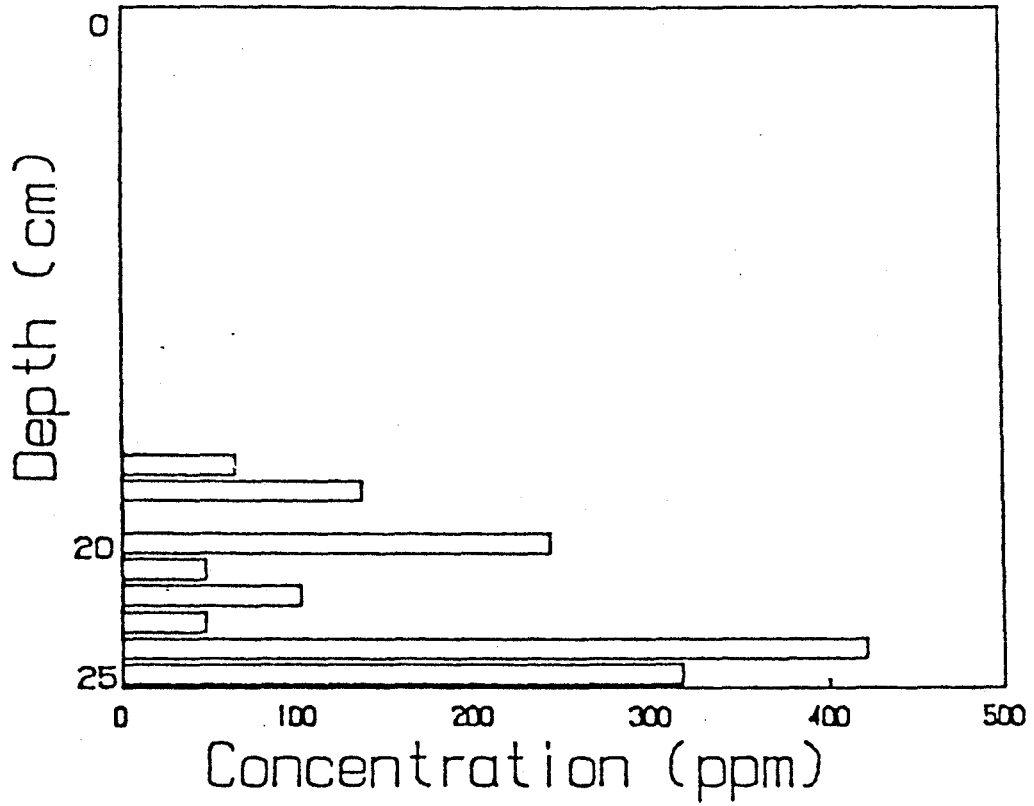


Figure 8. Cu concentration, downstream, North Fork Kent Creek (Site F). Samples from depths 0-17 cm had Cu concentrations below the detection limit of 30 ppm.

this testing was to determine if the heavy metal contamination preferentially concentrated on the smaller particles. If this preferential concentration on the smaller particles could be shown, then it may be concluded that the majority of the heavy metal contamination would have washed downstream.

Five slices at various depths and various locations on the North Fork of Kent Creek were sieved for the particle size analysis. Neutron activation analysis was performed on these ten samples (five coarse, five fine) and the results are presented in Tables 3 and 4. A comparison of the concentration of an element in the fine portion with the concentration of the same element in the coarse portion of the same slice reveals that the fine portion consistently has a much higher concentration than the coarse portion. Several of the elemental concentrations in the fine portion are an order of magnitude larger than the concentration in the coarse portion. From these data, it is concluded that the heavy metal contamination is preferentially associated with the smaller particles. Over the course of time, these smaller particles would have a larger probability of being washed downstream. Based on our initial premises and the just mentioned probability, we believe that the majority of the heavy metal contamination was washed downstream.

TABLE 3. PARTICLE SIZE TESTING RESULTS FROM SITE F

Element	Fine Concentration (ppm)	± (ppm)	Coarse Concentration (ppm)	± (ppm)
Depth 22-23 cm				
Ti	65	9	22	4
Cu	550	60	340	40
V	0.370	0.031	0.089	0.009
Mn	166	16	49	5
Sm	4.5	0.6	1.49	0.19
Se	<1		<1	
Cr	128	10	39.9	3.4
Hf	59	7	3.8	0.5
As	13.3	0.8	7.0	0.5
Sb	32.5	3.0	7.6	0.7
Ni	97	20	<1	
Sc	6.85	0.33	2.37	0.12
Fe	60700	1700	25300	700
Zn	365	17	129	6
Co	11.5	0.8	6.4	0.4
Ta	<1		<1	
La	23.7	3	10.2	1.4
Depth 17-18 cm				
Ti	34	6	21	4
Cu	<1		340	40
V	0.159	0.014	0.101	0.011
Mn	116	11	33.6	3.4
Sm	5.2	0.6	3.17	0.40
Se	<1		<1	
Cr	20.5	2.9	54	5
Hf	13.1	1.6	6.0	0.7
As	5.95	0.35	7.5	0.4
Sb	4.6	0.4	4.4	0.4
Ni	51	17	<1	
Sc	5.70	0.28	5.33	0.21
Fe	25500	800	23600	700
Zn	128	12	200	10
Co	5.9	0.5	6.1	0.9
Ta	<1		<1	
La	21.5	2.9	19.9	2.7

TABLE 3 (continued)

Element	Fine Concentration (ppm)	± (ppm)	Coarse Concentration (ppm)	± (ppm)
Depth 0-1 cm				
Ti	119	25	<1	
Cu	<30		<1	
V	0.40	0.05	0.062	0.009
Mn	410	40	45	5
Sm	4.7	0.6	1.49	0.19
Se	<1		<1	
Cr	165	16	13.6	1.5
Hf	16.8	2.2	1.49	0.19
As	7.7	0.6	2.37	0.23
Sb	1.72	0.19	0.333	0.038
Ni	<1		<1	
Sc	6.85	0.36	1.88	0.09
Fe	46800	1900	18700	500
Zn	570	40	60	4
Co	32.2	2.3	4.85	0.33
Ta	<1		<1	
La	27.3	3.7	10.6	1.4

TABLE 4. PARTICLE SIZE TESTING RESULTS FROM SITE E

Element	Fine Concentration (ppm)	± (ppm)	Coarse Concentration (ppm)	± (ppm)
Depth 22-23 cm				
Ti	68	9	13.3	3.5
Cu	<30		<1	
V	0.4	0.031	0.062	0.009
Mn	198	19	22.8	2.4
Sm	24.5	3.1	1.24	0.15
Se	<1		<1	
Cr	<1		9.9	1.1
Hf	10.4	1.3	1.27	0.16
As	17.5	1.0	3.08	0.34
Sb	0.74	0.07	0.265	0.032
Ni	43	13	<1	
Sc	9.8	0.5	1.45	0.07
Fe	44500	1200	6860	210
Zn	105	8	26.6	2.4
Co	11.0	0.7	3.51	0.24
Ta	<1		<1	
La	33	4.0	8.9	1.2
Depth 14-15 cm				
Ti	163	19	32	5
Cu	<30		<1	
V	0.72	0.05	0.171	0.015
Mn	211	20	47	5
Sm	<1		1.46	0.18
Se	<1		<1	
Cr	48.3	3.7	42.2	3.4
Hf	29.8	3.6	2.60	0.33
As	10.6	0.7	2.89	0.20
Sb	0.85	0.08	0.293	0.033
Ni	33	5	<1	
Sc	9.8	0.5	1.95	0.10
Fe	63700	1700	13500	400
Zn	132.8	3.8	36	5
Co	11.9	0.8	3.68	0.26
Ta	0.26	0.05	<1	
La	47	6.0	11.1	1.5

F. Enrichment Factors

The anthropogenic influence on the metals found in the sediments was determined through calculation of enrichment factors. An enrichment factor is a comparison of the concentration of a particular element with the concentration of that element in a reference material such as geological material. The enrichment factors are normalized using a single element that is common to all samples. This normalizing element is usually aluminum or scandium.

$$EF = \frac{[x/Sc]_{\text{sample}}}{[x/Sc]_{\text{standard}}}$$

Scandium was chosen for this study and was used with the standard rock values from the data compiled by Rahn (1976). Scandium was chosen since it is considered to a pollutant and is easily determined by NAA. Standard rock values were used because a normalizing material for uncontaminated sediment does not exist.

Although the calculation of enrichment factors allows a quick estimation of the effects of anthropogenic activity, the results should not be construed as definitive. Only general conclusions can be inferred from enrichment calculations. Therefore, the enrichment factors were divided into three categories: 1) those data indicating no significant contribution to the concentration of heavy metal (an enrichment factor of two or less); 2) those data indicating a possible increase in the concentration caused by the presence of humans (enrichment factors between two and ten); and 3) clear indications of substantially increased values caused by human influence (enrichment factors greater than ten). The data for the enrichment factors for the downstream sites are presented in Table 5. Each element listed has had the enrichment factors calculated for each slice of that particular core. The most predominant value among all of the slices calculated dictated into which category that element would be entered. This approach was used to eliminate the effect of one or two samples that had unusually high or unusually low enrichment factors in a site.

In all three downstream sites antimony, arsenic and zinc have enrichment factors high enough to indicate contamination. In addition, each site has many other elements whose enrichment factors imply heavy metal contamination.

One objective of this investigation was to study the transport of heavy metal contamination downstream. One method of achieving this goal is to examine the enrichment factors for all of the sites on a particular river or creek. These results are shown in Table 6 for the North Fork of Kent Creek. As can be seen, there are relatively low enrichment factors at the upstream site (Site D). The number of elements indicated by the enrichment factors as possibly contributing to the heavy metal contamination increases at each succeeding site

TABLE 5. INDICATIONS OF ELEVATED CONCENTRATIONS
AS CALCULATED FROM ENRICHMENT FACTORS

Downstream site of	No additional increase (EF<2)	Possible increase (2<EF<10)	Definite increase (EF>10)
South Fork Kent Creek	Ti, Cu, V, Mn Cr, Ni, Fe	Sm, As, La, Zn, Co	Sb, Se
North Fork Kent Creek	Ti, V, Cr, Se	Mn, Sm, La, Fe, Co, Ni	Cu, As, Sb, Zn
Rock River	Cu, Ni, Cr	Ti, V, Mn, Sm, La, Fe, Co	As, Sb, Se, Zn

TABLE 6. INDICATIONS OF INCREASED CONCENTRATIONS AS CALCULATED
FROM ENRICHMENT FACTORS TO INDICATE TRANSPORT DOWNSTREAM

Site	No additional loading (EF<2)	Possible Loading (2<EF<10)	Definite Loading (EF>10)
D	Ti, Cu, V, Mn, La, Cr, Fe, Co Se, Ni	Sm, As, Zn	Sb
E	Ti, Cu, V, Cr, Se, Ni	Mn, Sm, La, Fe Zn, Co	As, Sb
F	Ti, V, Cr, Se	Mn, Sm, La, Fe Co, Ni	Cu, As, Sb, Zn

downstream. The downstream site (Site F) enrichment factors indicate that the majority of the heavy metals examined are present in concentrations far greater than can be expected to occur naturally.

G. Toxicity Tests

While chemical analyses of the sediment provides an inventory of the contaminants present in the samples, the potential for biological availability or chemical mobility of these contaminants cannot be determined using only these bulk material measurements (Engler, 1980). Bulk sediment material may, however, be the major exposure medium for organisms such as aquatic plants and benthic organisms that recycle sedimentary material at the sediment-water interface. Sediment constituent mobility is a function of many factors. Even though the sediment may be grossly contaminated, the conditions which favor interaction between water and sediment may preclude significant movement of the contaminants into the water column (Brannon et al., 1980).

To simulate the short-term release of contaminants to the water column after disturbance of the sediment, an elutriate test, a water leachate prepared from one part sediment to four parts water, was used. This technique has been used since 1973 and has been evaluated under a wide range of conditions in marine, estuarine, and freshwater systems (Engler, 1980). None of the extract procedures developed to measure the degree of chemical mobility of sediment constituents have been shown to be universally successful in defining chemical availability and exchangeability. The elutriate test will likely strip volatile compounds from the sediment and is limited to leaching under aerobic conditions (unless an inert compound, such as nitrogen (N₂), is used as the mixing gas). Some contaminants may be more readily released under anaerobic conditions; however, the anoxic regime is prohibitive for bioassay use. The elutriate test was shown by Brannon et al. (1980) to be the most useful extract procedure in assessing water quality problems.

The liquid phase filtrate of the elutriate test may be used in bioassays as one way to evaluate the biological impact of the released sediment constituents and to project the earliest measure of toxicity of the sediment (Engler, 1980). Elutriates from Rock River sediments were used to assess biological response to contamination with three bioassay methods: luminescent inhibition of the marine bacterium *Photobacterium phosphoreum* (MicrotoxTM), photosynthetic inhibition of the freshwater green alga *Selenastrum capricornutum*, and mortality of the free-living nematode worm *Panagrellus redivivus*.

The MicrotoxTM bacterial assay was developed on the principle that the luminescent properties of healthy cultures of *Photobacterium phosphoreum* will be inhibited upon exposure to toxic substances. The luminescence of cultures exposed to a series of dilutions of a sample is measured with the MicrotoxTM analyzer, a specially-designed fluorometer.

The protocol for the *Selenastrum capricornutum* assay is based on the principal that algae under normal conditions will use carbon from the surrounding medium to grow and photosynthesize. Under conditions of stress, including toxic aggression, photosynthesis will be inhibited and carbon consumption will decrease. In the laboratory, progressive inhibition of photosynthesis by increasing doses of test mixture is the measure of toxic response. This is easily measured using a ^{14}C -labeled HCO_3^- as a tracer in the carbon source pool.

The assay using the microscopic, free-living nematode *Panagrellus redivivus* is based on the survival of the worm exposed to test samples. The assay exposes 10 replicate groups of 10 juveniles to a concentration of test material. After 96 hours, the survivorship is measured relative to control tests. This measurement is a reflection of the lethal nature of the sediment elutriate.

At each site, surface grab samples were taken. Three different toxicity tests were performed to help identify the sites that would potentially be lethal or inhibitory to the indigenous biota. The results of these tests are presented in Table 7. Each entry in Table 7 represents the percentage of the elutriate that would elicit a 50% response (mortality or inhibition) from the organisms tested. A low percentage indicates a station that has a greater amount of toxic potential.

The three downstream sites (Sites C, F, and H) seem to be the most toxic. This may be due, at Site F and H, to an increased loading of toxic metals such as copper, arsenic, and zinc. The upstream sites, away from the (potential) heavy metal contamination, were stimulatory to the nematode (percent survival was greater than 100). In other words, the sediment elutriate increased the survival of the test nematodes over that of the control animals. These sites were also less inhibitory to the algae and bacteria. In general, it can be seen that the toxic potential of the stream sediments increases as one progresses downstream, which does correlate to the metal concentrations in the upper layers of sediment.

TABLE 7. TOXICITY TEST RESULTS

Location (site designation in parenthesis)	Nematode Survival	Algal Photosynthesis	Microtox™ Luminescence
upstream, south fork, Kent Creek (A)	76%	67%	180%
midstream, south fork, Kent Creek (B)	10%	57%	145%
downstream, south fork, Kent Creek (C)	45%	24%	428%
upstream, north fork, Kent Creek (D)	93%	305%	98%
midstream, north fork, Kent Creek (E)	104%	77%	76%
downstream, north fork, Kent Creek (F)	6%	62%	47%
upstream, Rock River (G)	110%	78%	269%
downstream, Rock River (H)	8%	67%	149%

CHAPTER 7. CONCLUSION

In this investigation we have completed the collection of sediment cores to establish a historical record of the heavy metal contamination in the Rock River and Kent Creek. This record can be graphically depicted in histograms of concentration as a function of depth. Such histograms indicate a rise in the heavy metal contamination coinciding with the presence of industrialization of the region. Heavy metal contamination levels were obtained using neutron activation analysis as the analytical method. In the selection of sampling sites along the waterways, the upstream sites along each river were chosen to obtain general background measurements of contaminants. The other sites sampled provided an estimate of the downstream migration of these contaminants from their probable source.

Particle size analysis has shown that the heavy metal contamination is concentrated in the smaller particles of sediment. Combining the particle size information with the swift current of the Rock River leads to the supposition that the majority of heavy metal contaminants have been washed downstream. The contamination that has remained midstream is generally in trace quantities. Although these trace quantities are difficult to detect, the anthropogenic disturbance of the environment can readily be seen in the general shape of the concentration versus depth graphs. Additionally, the enrichment factors clearly indicate that the downstream sites in the tributaries studied have elevated concentrations of several heavy metals, most notably elevated levels of copper in the downstream site of the North Fork of Kent Creek, and arsenic, antimony, and zinc in all three downstream sites. Enrichment factor calculations have also shown that the heavy metal concentration has moved downstream.

Because of the limited number of sample sites on the Rock River, conclusions concerning propagation of heavy metals downstream are speculative at best. The difference between the two sites on the Rock River of the heavy metal concentration as a function of depth data indicates that more detailed research must be done before any valid conclusions can be drawn.

CHAPTER 8. RECOMMENDATIONS

As is evident from the histograms, the increased concentrations of heavy metals generally appear near the surface of the sediment. Therefore, taking cores of depths greater than ten centimeters does not increase the information base considerably. Any elevated concentrations at those lower depths would not pose as great a potential health or environmental threat as elevated concentrations on or near the surface. The deeper the elevated concentration, the less likely the sediment would be mobilized. Surficial sediment has the greatest potential to be mobilized barring such events as dredging or construction. Therefore, surficial grab samples (several centimeters) should be sufficient to characterize the heavy metal concentration that could pose a health risk. By using grab samples, a larger number of sites could be analyzed thereby better characterizing the area.

With the limited number of sites for this investigation (particularly on the Rock River itself), correlation of heavy metal contamination with potential sources of the contamination is impossible. However, if a relatively large number of grab samples were used, it might be possible to correlate elevated heavy metal contamination with specific sources. This is not to say that the correlation would be an easy task. Many parameters that are not characterized by this investigation would need to be assessed to accurately prepare any correlation. Foremost among these parameters would be an accurate deposition rate for the two creeks and the Rock River.

This investigation could be used to direct future research in this region. By analyzing the data from this research, further characterization of the area could pin point sites where contamination has been indicated by this study and therefore devote increased attention to that area. This study has established a general framework upon which future work could elaborate.

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