

TRACE METAL DISTRIBUTIONS IN ROCKS, STREAM
SEDIMENTS AND SOILS OF THE DEEP CREEK BASIN
POTTAWATOMIE COUNTY, KANSAS

by

JOHN SWITEK

B. S., Pennsylvania State University, 1974

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1977

Approved by:

Donald O. Whittemore
Major Professor

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH THE ORIGINAL
PRINTING BEING
SKEWED
DIFFERENTLY FROM
THE TOP OF THE
PAGE TO THE
BOTTOM.**

**THIS IS AS RECEIVED
FROM THE
CUSTOMER.**

CONTENTS

210

Page

Introduction

Purpose1
Location3
Previous Investigation5
Acknowledgements6

Geology

Bedrock7
Stream Sediments10
Soils.10

Methods of Investigation

General Procedure.12
Collection and Preparation of Samples.12
Rock Samples12
Stream Sediment Samples.14
Soil Samples16
Experimental Methods16
General Procedures16
Exchangeable Metals.17
Acid Soluble Metals.18
Total Metals18
Supporting Analyses.19
Analytical Sensitivity and Errors.20

Results and Discussion

Rocks.22
Stream Sediments29
Soils.37
Comparison of the Rock, Sediment and Soil Data42
Comparison of the Data with the Results of Other Studies45

Summary and Conclusions50
References54

APPENDICES

Appendix I. Soil types in the Deep Creek Basin study area.59
--	-----

TABLES

	Page
Table 1. Comparison of analyses with recommended values for minor and trace metals in U. S. G. S. standard rocks. . . .	21
2. Estimated accuracy of metal analyses.	21
3. Minor and trace metal concentrations in the rock samples	23
4. Chemical and physical properties of the rock, sediment and soil samples.	24
5. Distribution of minor and trace metals in the Deep Creek Basin samples	25
6. Correlation matrix for the extractable fraction of the rock samples.	27
7. Correlation matrix for the non-extractable fraction of the rock samples.	27
8. Metal/Mn values for the rock, sediment and soil samples	28
9. Molar order of abundance sequences for the rock, sediment and soil samples.	28a
10. Minor and trace metal concentrations in the sediment samples	31
11. Correlation matrix for the exchangeable fraction of the sediment samples.	32
12. Correlation matrix for the extractable fraction of the sediment samples.	34
13. Correlation matrix for the non-extractable fraction of the sediment samples.	36
14. Minor and trace metal concentrations in the soil samples.	38
15. Correlation matrix for the exchangeable fraction of the soil samples.	40
16. Correlation matrix for the extractable fraction of the soil samples.	41
17. Correlation matrix for the non-extractable fraction of the soil samples.	41

	Page
Table 18. Average trace metal concentrations of the rock, sediment and soil samples.	43
19. Comparison of the Deep Creek area rock data with the published data from other studies.	46
20. Comparison of the Deep Creek stream sediment data with the published data from other studies	48
21. Comparison of the Deep Creek area soil data with the published data from other studies.	49

ILLUSTRATIONS

Figure 1. The Kansas Power & Light Company's Jeffrey Energy Center, Pottawatomie County, Kansas.	2
2. Map of the study area, the northwest basin of Deep Creek	4
3. Geologic map of the study area showing the rock sample locations	8
4. Stratigraphic section for the study area	9
5. Soil map of the study area showing locations of the soil sub-samples.	11
6. Map showing the stream sediment sample locations	15

INTRODUCTION

Purpose

The Kansas Power and Light Company (KPL) is building the Jeffrey Energy Center, a large, coal-fueled energy generating facility, northwest of Saint Marys, Pottawatomie County, Kansas (Fig. 1). The processing and burning of large amounts of coal are a potential hazard to the ecosystems of the surrounding areas. The study by Ruch, et al. (1974) showed that the bituminous coal from the Gillette, Wyoming area, to be used as fuel at the energy center (KPL, 1973), contains appreciable quantities of toxic metals. Thus, the natural concentrations of these metals must be established for the surficial materials in the area to evaluate changes that may occur in those concentrations during the operational life of the center. The purposes of this investigation were:

- 1). To establish the natural concentrations of Fe, Mn, Cr, Cu, Pb, Zn, Cd, As and Se in the rocks, stream sediments and soils in an area adjacent to the energy center complex.
- 2). To determine the distribution of these metals within the rocks, stream sediments and soils.
- 3). To establish the geochemical factors controlling the movement of the metals in the basin.
- 4). To determine which of the analytical methods used would be most suitable for the future monitoring of metals in the area.

This investigation supported a study of the natural waters in the area by Dr. D. O. Whittemore, Department of Geology, Kansas State University. The results of both studies have been published by the Kansas Water Resources

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

**THIS IS AS
RECEIVED FROM
CUSTOMER.**

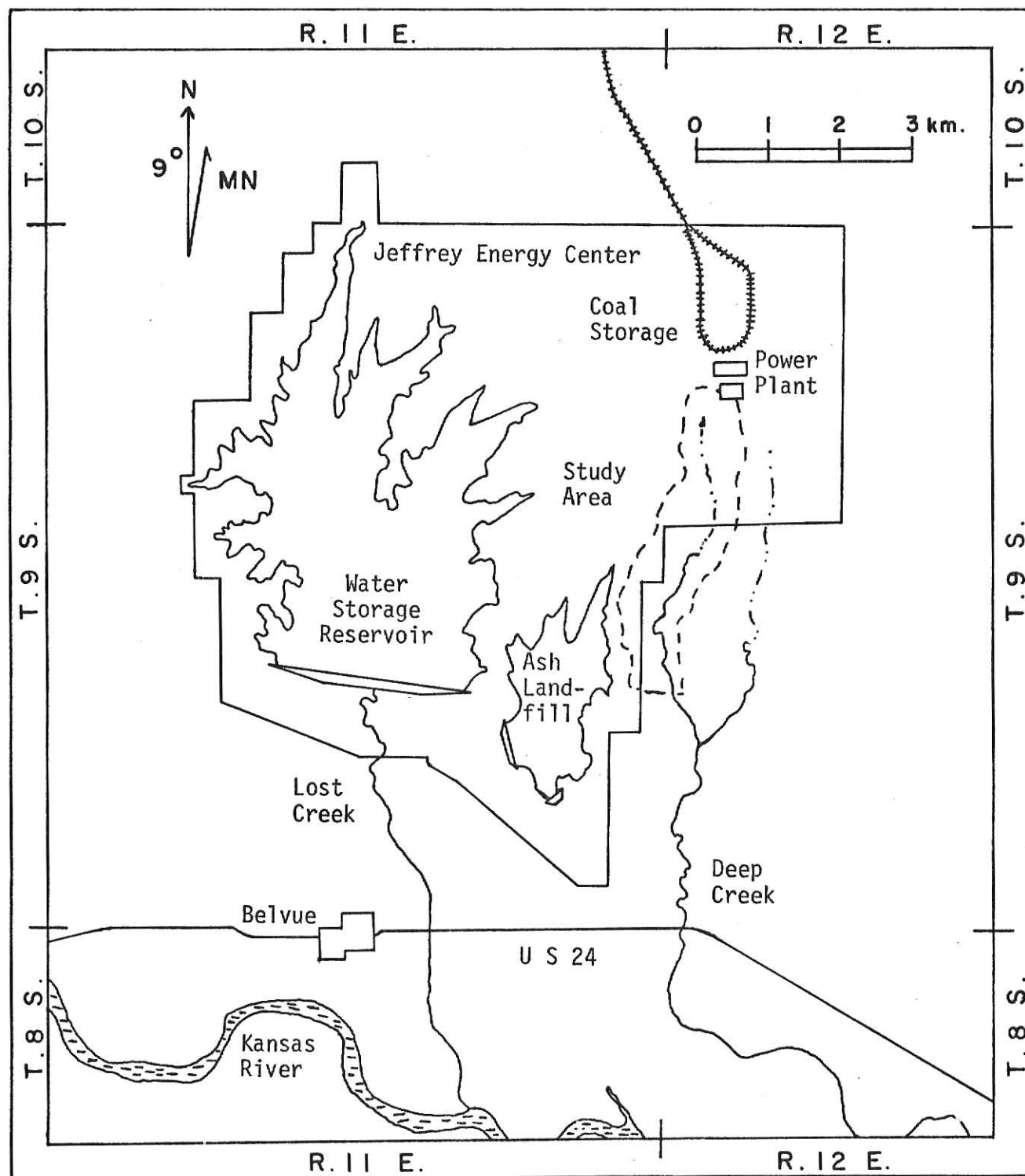


Figure 1. The Kansas Power and Light Company's Jeffrey Energy Center, Pottawatomie County, Kansas (after KPL, 1973).

Research Institute as Contribution No. 188 (Whittemore and Switek, 1977).

Location

The area is the drainage basin of the upper 4.0 kilometers of the west branch of Deep Creek, a small, perennial stream. The area is on the slope between the upland prairie and the Kansas River floodplain (Fig. F-2). Deep Creek, with headwaters arising south of the energy center complex, flows south-southeast to the Kansas River. The area extends from the southern boundary of section 19, T. 9 S., R. 12 E. north to, and including, the energy center construction area in Section 7, T. 9 S., R. 12 E. The east and west drainage divides constitute the east and west boundaries of the study area.

The area consists primarily of tallgrass prairie uplands with floodplain forest occupying the low areas adjacent to the stream (KPL, 1973). Agricultural activities in the basin seem to be limited to the grazing of livestock. The widespread occurrence of glacially deposited quartzite boulders and steep slopes would have discouraged cultivation uplands whereas the floodplain forest shows no sign of ever having been cleared. The relatively flat-lying areas, underlain by the Martin Silt-Clay soils (Fig. 5) are the most likely to have been cultivated in the past as the same soils are presently being used for wheat production in adjacent areas. Man-made structures in the area are limited to fence lines, sheds, ponds and pasture roads. KPL has recently constructed a utility and power line that follows the western drainage divide for a short distance.

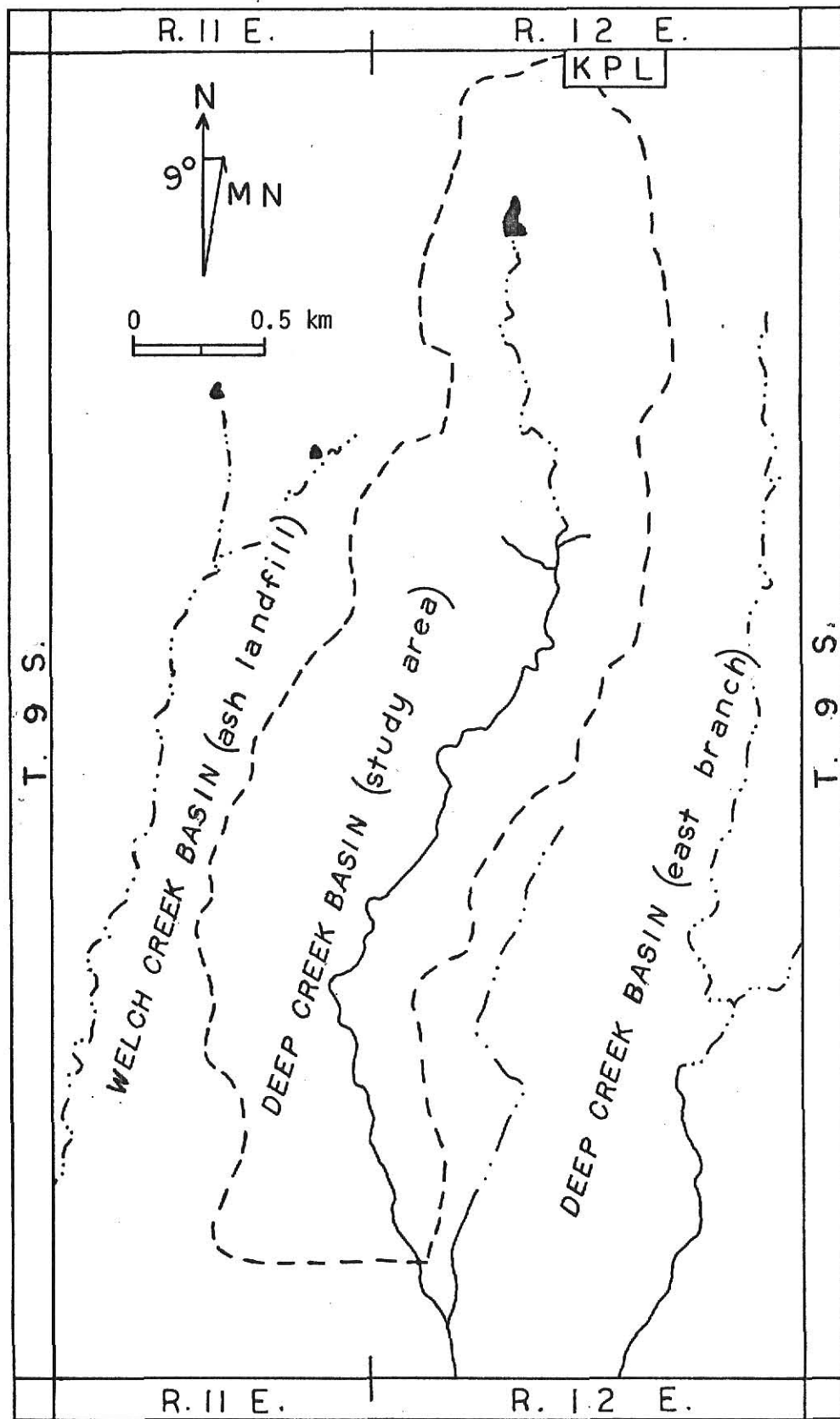


Figure 2. Map of the study area, the northwest basin of Deep Creek.

Previous Investigations

Increasing concern for environmental quality has prompted an increase in the research on the distribution and behavior of metals in the environment. The United States Environmental Protection Agency has established maximum and desirable upper limits for the concentrations of Fe, Mn, Cr, Cu, Pb, Zn, Cd, As, Se and other metals in public drinking water supplies (U. S. E. P. A., 1973) as these metals may become toxic if concentrations are higher than the recommended limits. Studies like those of Carrol (1969) and Schroeder (1965) have linked several of the above-mentioned metals to the occurrence of human disease.

Environmental studies of trace metal distributions have usually been made in areas that have long been industrialized (Beavington, 1973) or in other areas where pollution is suspected (Kaback, 1976 and Alther, 1975). Trace metal investigations of rocks have long been used in the exploration for, and the evaluation of, mineral resources (Hawkes and Webb, 1962 and Runnels and Schleicher, 1956) and in petrological studies (Sinton, 1977). Only recently has much effort been expended on establishing background data for metals in surficial materials in relatively pristine areas (Mills and Zwarich, 1975). Connor and Shacklette (1975) have provided an excellent compilation of chemical data for materials in the conterminous United States combining the results of several investigations conducted by the United States Geological Survey (U. S. G. S., 1976). Environmental impact statements, prepared to determine the potential dangers to the environment in areas surrounding proposed industrial sites, are very broad, but trace metal studies may be neglected.

Laboratory investigations, under controlled conditions, have defined the behavior of trace metals in the environment. Much work of this kind

has been done for soils (Reddy and Perkins, 1976), especially in regards to plant nutrition (Singh and Steinnes, 1976 and Shuman and Anderson, 1974), and for metals in aqueous systems (Hem, 1976 and 1972). An important development from the laboratory investigations has been the discovery of the role of hydrous iron and manganese oxides in controlling the concentration and mobility of metals in soils and aqueous systems (Suarez and Langmuir, 1976 and Jenne, 1968).

Several compilations of chemical data are available for rocks (Turekian and Wedepohl, 1961, opposite p. 186 and Rankama and Sahama, 1955). Metals data on Kansas rocks are available in Connor and Shacklette (1975) and Runnels and Schleicher (1956). Compilations of soil chemical data are available in Connor and Shacklette (1975) and Vinogradov (1959). There seems to be no general compilation of chemical data for stream sediments.

Acknowledgements

Thanks and appreciation are expressed to the Kansas Power and Light Company and to Mr. John W. Prior, Mr. Tom Prior and Mr. Carl Carlson for allowing access to the sample sites. Special thanks are extended to Drs. Sambhudas Chaudhuri and Donald O. Whittemore for their assistance in the study.

The manuscript was reviewed by Drs. Donald O. Whittemore, Sambhudas Chaudhuri, Henry V. Beck and Page C. Twiss, Department of Geology, and Dr. Roscoe Ellis Jr., Department of Agronomy, of the Kansas State University.

GEOLOGY

The geology of Pottawatomie County was worked out by Scott, et al. (1959) who also prepared the geologic map of the county. The Soil Conservation Service of the U.S. department of Agriculture, in Westmoreland, Kansas, has run a soil survey of Pottawatomie County (Kutnink, in preparation).

Bedrock

The study area is underlain by alternating shales and limestones of the Council Grove Group of the Gearyan Stage of the Lower Permian Series (Fig. 3 and 4). The units involved extend from the Americus Member of the Foraker Limestone up to, and including, the Blue Rapids Shale. The units are nearly horizontal in the study area so that one moves upsection as one moves uphill (generally, to the north). Structurally, the area lies on the southeast flank of the Nemaha Anticline.

Major topographic benches are developed on the Neva Limestone Member of the Grenola Formation and on the Cottonwood Limestone Member of the Beattie Limestone. The principal springs in the basin issue from the base of the Long Creek Limestone Member of the Foraker Limestone and from the base of the Cottonwood Limestone Member of the Beattie Limestone. All units sampled fit the descriptions given for them in the closest of the measured sections listed by Scott, et al. (1959). However, the Long Creek Limestone was found to be extensively brecciated giving the unit high porosity and permeability. The outcrop of the Long Creek in the neighboring Welch Creek Basin (Ash Storage Landfill in Fig. 1) is also brecciated. Analyses of the spring issuing from the base of the Long Creek in the Welch

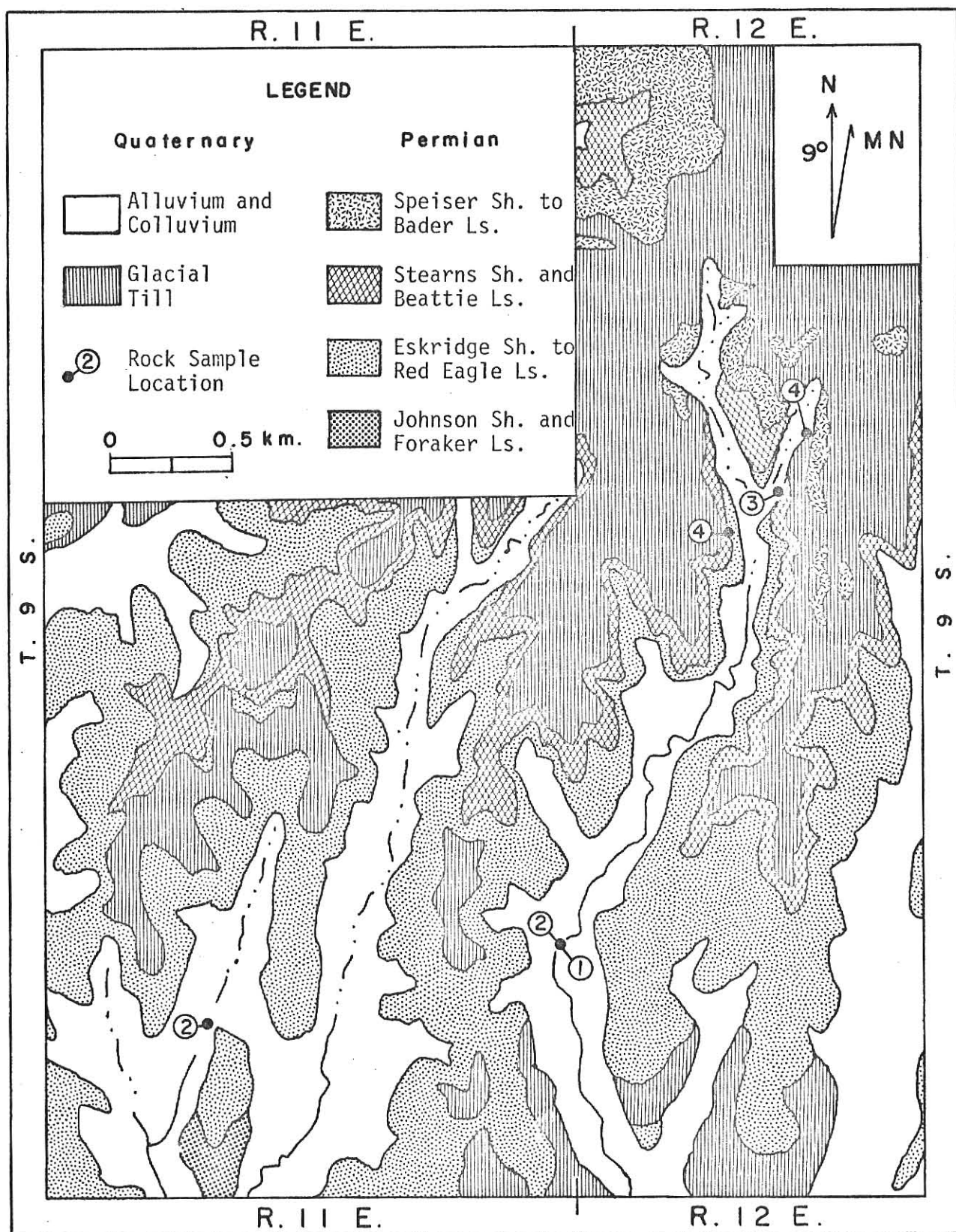


Figure 3. Geologic map of the study area showing the rock sample locations (After Scott, Foster and Crumpton, 1959).

System	Series	Stage	Group	Formation	Member	Graphic Section	General Description	Thickness (feet)	
QUATERNARY	PLEISTOCENE	WISCONSIN KANSAN		TILL			Tan gray, gray brown or red brown, silty, colluvium, alluvium and loess	0-3.5	
							Dark gray, to red brown clayey and silty till with abundant quartzite erratics	0-9.2	
PERMIAN	LOWER PERMIAN	GEARYAN	COUNCIL GROVE	BLUE RAPIDS SHALE			Variegated, olive drab, maroon and light-gray, calcareous shale.	4.5	
				CROUSE L.S.			Three gray limestones; uppermost platy, dense; middle massive, dense; lowermost cavernous, fossiliferous; separated by two tan-gray, platy shales.	4.9	
				EASLY CREEK SHALE			Light-gray, blocky shale underlain by maroon calcareous shale-siltstone	2.6	
							Gray, massive, fossiliferous ls.	0.6	
				BEATTIE SHALE	Middleburg Ls.		Gray, Maroon at bottom, calcareous at top, calcareous nodules at the base	1.5	
					Hoover Sh.				
					Eiss Ls.		Two limestones separated by shale, upper ls. gray, massive; lower ls. gray, conglomeratic, fossiliferous	1.2	
					Morrill Ls.		Gray silt-claystone with limestone partings, highly fossiliferous in parts	3.1	
					Florence Sh.		Gray, dense ls. with shale parting, fossiliferous in upper part	1.2	
					Collonwood Ls.		Dark Gray shale, highly fossiliferous with thin calcareous seams	1.2	
							Massive, gray to light tan limestone, cherty, fossiliferous	1.8	
				ESKRIDGE SHALE			Silty shale with limestone partings gray-green in upper part, variegated in lower part	9.5	
				GRENOULA LIMESTONE	Neva Ls.		Gray, massive limestone with shale partings; upper ls. platy, middle ls. shows honeycomb weathering, lower ls. hard, dense	5.5	
					Salem Point Sh.		Tan, silty shale, weathers gray	2.1	
					Burr Ls.		Gray, massive, dense limestone	0.9	
					Legion Sh.		Tan-gray, silty, calcareous shale	1.2	
					Sallyards Ls.		Tan-gray, dense, hard limestone	0.3	
				ROCA SHALE			Variegated-olive drab, blocky shale with gray, shaley limestone parting	6.7	
				RED EAGLE L.S.	Howe Ls.		Tan, massive limestone in upper part, gray, calcareous siltstone and shaley limestone in lower part	1.5	
					Bennett Sh.		Tan, blocky siltstone, weathers tan	0.6	
					Glenrock Ls.		Tan-gray, massive, dense, fossiliferous, petroliferous limestone	0.6	
				JOHNSON SHALE			Olive drab, blocky shale; two gray platy to nodular limestone, upper dense, lower silty, limonitic	5.2	
				FORAKER LIMESTONE	Long Creek Ls.		Tan, shaley limestone with calcit-crystalline pockets; brecciated, cavernous	1.8	
							Intercalated tan, gray, olive drab or black shales and limestones, upper shales calcareous		
					Hughes Creek S.			10.7	
					Americus Ls.		Gray, massive, dense limestone divided by tan-gray silty shale	0.9	

Figure 4. Stratigraphic section for the study area (from Zeller, 1968; descriptions from Scott, Foster and Crumpton, 1959).

Creek Basin (Whittemore and Switek, 1977) show moderately high concentrations of Ca and SO_4 indicating evaporites in the section, probably gypsum. Thus, one interpretation is that the brecciation is a collapse feature associated with the dissolution of gypsum and/or carbonate.

Stream Sediments

The stream sediments are distributed in an alternating pattern of gravel riffles and quiet water pools. Limestone fragments, with some quartzite, comprise the bulk of the gravel, whereas disaggregated shales and soils make up most of the finer sediment. The general distribution of riffles and pools is determined by stream velocity, meander length and the resistance of bedrock outcrops in the stream channel (Leopold, et al., 1964, P. 203-215). The position of most stream deposits is subject to change in a matter of hours during periods of high stream flow. A small pond has been built to receive the spring water issuing from the base of the Cottonwood Limestone. The pond has accumulated over a half meter of sediment since it was built. Pond sediments differ from the stream sediments by a lack of particles larger than granule size.

Soils

The Soil Conservation Service lists and describes six soil types in the study area (Fig. 5 and Appendix 1). Five of these (Dwight-Irwin Complex, Martin Silty Clay (1 - 4 percent slope and 4 - 8 percent slope), Kipson-Sogn Complex, and Oska-Sogn Complex) are shallow, well drained uplands soils derived from the weathering of shales and limestones and a thin cover of glacial till. The sixth soil (Wabash Silty Clay) underlies

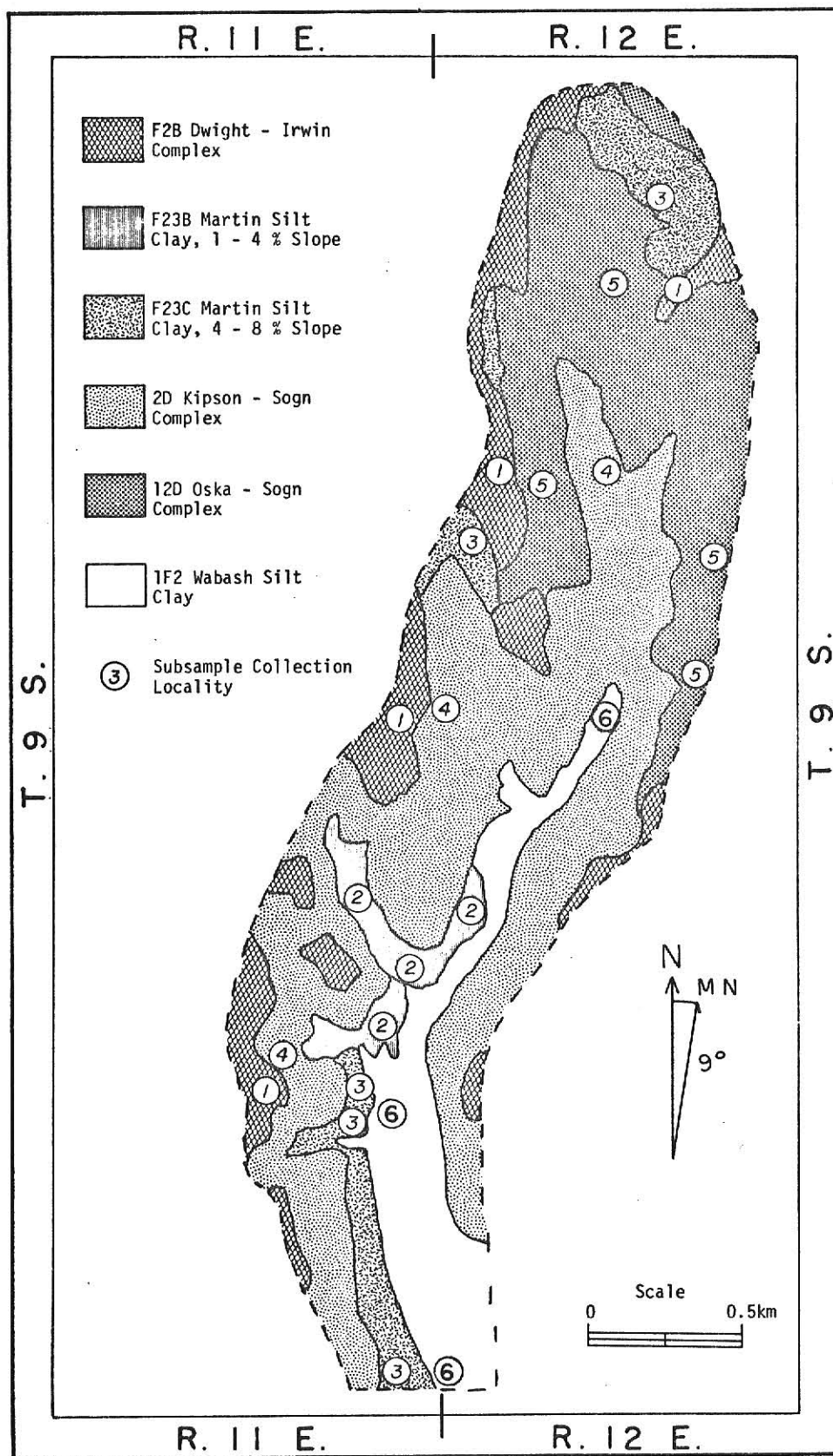


Figure 5. Soil map of the study area showing the locations of soil subsamples (after Kutnink, in preparation).

the floodplain forest and is relatively deep and poorly drained. Soils occurring on the hilltops and steeper slopes are thin and contain abundant rock fragments. Soils lying at the base of slopes and in relatively flat-lying areas are thicker but still immature with poorly developed soil horizons. Vegetation on the upland soils consists mainly of grasses whereas the floodplain forest contains numerous trees and moderately heavy underbrush.

METHODS OF INVESTIGATION

General Procedure

Reagent grade chemicals and redistilled acids were used in the preparation of all solutions used for analytical purposes. All water used in the preparation of solutions and for rinsing was distilled and deionized. All glass, plastic and other non-metallic-were used in the collection and storage of samples and in the preparation of extractant, standard and sample solutions were precleaned by soaking in 3 percent or 10 percent nitric acid and rinsing with water. Standards were prepared in extractant solutions to minimize the matrix differences between standards and samples.

Collection and Preparation of Samples

Rock Samples.--The Cottonwood Limestone Member of the Beattie Limestone and the Long Creek Limestone Member of the Foraker Limestone were sampled. Both units are the host units for major springs in the basin and are well exposed with whole sections available for sampling. Shale units

sampled included, in ascending order, the Huges Creek Shale, Johnson Shale, Eskridge Shale and Stearns Shale. As a secondary concern of the study was to observe the distribution of metals in rocks having an influence on the water quality in the basin, the shales were sampled only in the intervals immediately overlying, or underlying, the spring-bearing Long Creek and Cottonwood Limestones were possible. The samples of the overlying and underlying shale for each aquifer limestone were combined in the field and the composite treated as a single sample.

All rock units were sampled in the Deep Creek Basin, except for the Johnson Shale while could not be located there and, so, was sampled in the Welch Creek Basin (see Fig. 3). The Florena Shale Member, immediately overlying the Cottonwood Limestone Member, also, could not be found in the study area. In place of the Florena Shale, the Stearns Shale, the next shale unit in the section to be exposed in the study area, was sampled.

Limestone samples were sampled by prying, or hammering, a vertical section of blocks from the outcrop, after its surface had been cleared of vegetation and debris. The blocks were arranged in the order of their removal from the outcrop and broken down to produce pieces with their longest dimension less than 10 cm. from which the samples were selected. Care was taken to sample the entire section uniformly and to select pieces that showed little or no weathered surfaces. The samples were stored in polyethylene jars until they could be prepared for analysis.

Shale outcrops were first cleared of debris and weathered shale to expose fresh-looking shale. Samples were collected from within an interval of 30 cm. immediately adjacent to the associated aquifer limestone. The samples were stored in polyethylene jars until they could be processed for analysis.

Limestone samples were crushed to less than 2 mm in diameter using an iron mortar and pestle. Prior to crushing, an excess piece of sample was ground to a fine powder in order to coat the surfaces of the mortar and pestle to minimize the chance of iron contamination. Shale samples were crushed to less than 2 mm with a ceramic mortar and pestle. After crushing, the samples were mixed and quartered on an acid-cleaned plastic sheet and then stored in glass jars sealed with Parafilm.

Streams Sediment Samples.--Four sediment samples were taken from Deep Creek. Sample SD-1 was collected near the southern boundary of the study area whereas sample S-5 was collected close to the headwaters of Deep Creek (Fig. 6). Samples SD-2 and SD-3 were taken immediately upstream and downstream, respectively, of the spring issuing from the base of the Long Creek Limestone. Sample SD-4 was collected from the pond receiving the flow of the spring issuing from the Cottonwood Limestone.

Stream sediments were taken by pushing a section of polyvinyl chloride pipe into the sediment to a depth of 10 cm, sealing the top of the pipe, then withdrawing the sampler, with core, from the sediment. Five to seven cores were collected across the pond, or stream section at each location shown in Figure 6. Reddy and Perkins (1976) indicated that significant changes in the amounts of exchangeable metals can occur if the samples are allowed to dry out. Therefore, the pore water collected with the sediment was retained to preserve the chemical condition of the clay and colloid surfaces and to facilitate wet sieving of the sample. The samples were stored in polyethylene jars.

Each sample was wet sieved, with its own pore water, to remove particles larger than 2 mm. After allowing the suspended fines to settle

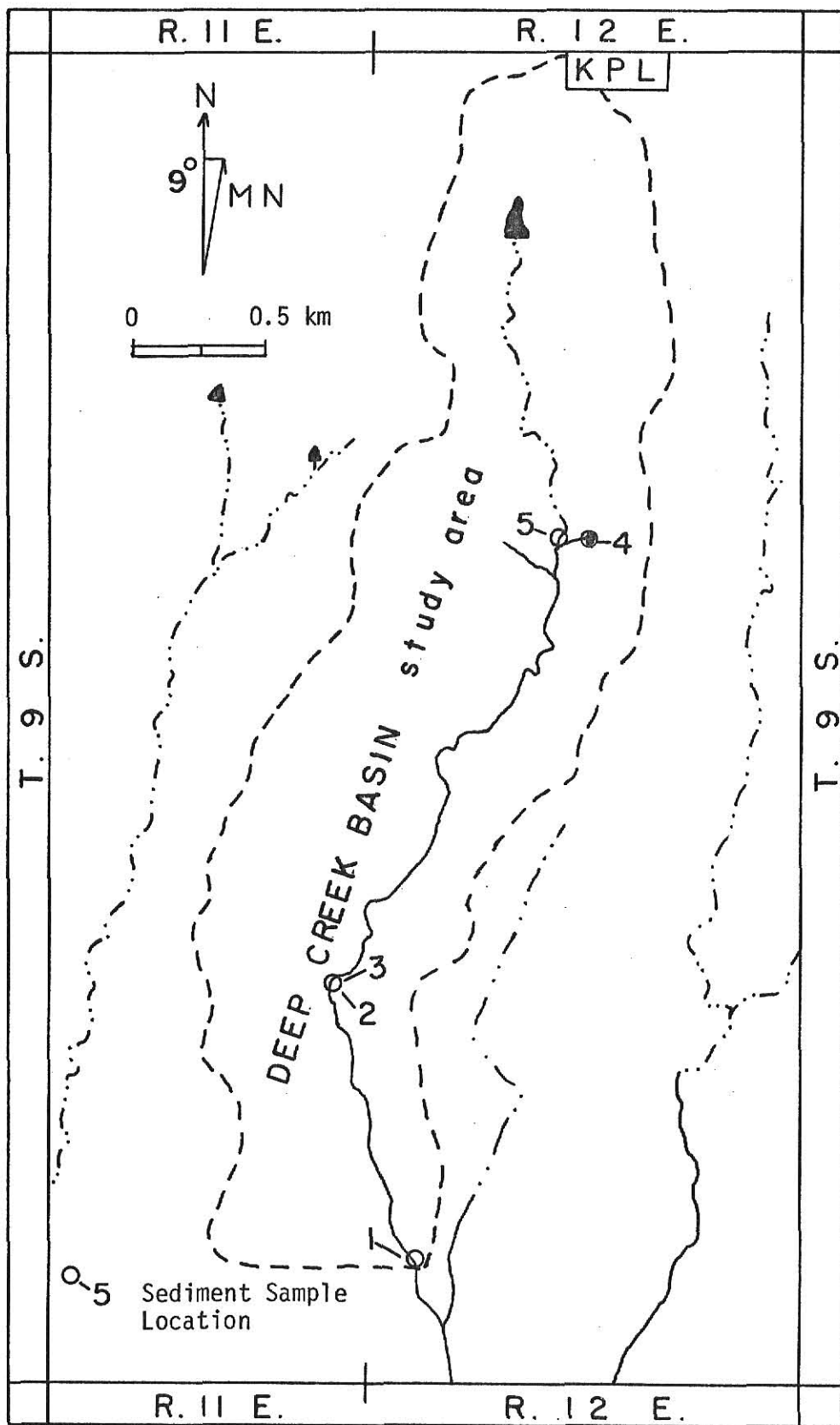


Figure 6. Map showing the stream sediment sample locations.

for about 24 hours, the clear, standing water was pipetted off. The sample was mixed and quartered on a clean plastic sheet and stored moist in polyethylene jars. The samples were stored under refrigeration to inhibit biologic activity.

Soil Samples.--Several soil types in the study area occur over areas underlain by more than one parent bedrock unit. Thus, each type was subsampled at several locations and the subsamples combined. Subsamples were collected using a hand auger with a core diameter of 4.5 cm. Core was taken to a maximum of 50 cm, or to bedrock in the thinner soils. Several test cores were made in thin soils to establish the true thickness. The thickest core was taken as the subsample for that locality. One subsample was collected from each of the localities shown in Figure 5. The samples were stored in polyethylene jars until they could be processed.

Soil samples were dried in a laboratory oven at approximately 80°C to facilitate the disaggregation of the clods. Rock and plant fragments larger than 1 cm long were picked out. The clods were broken down into particles less than 2 mm long using a ceramic mortar and pestle. Each sample was mixed and quartered on a precleaned plastic sheet and stored in glass jars sealed with Parafilm.

Experimental Methods

General Procedures.--Metal concentrations were determined using a Perkin-Elmer Model 305B atomic absorption spectrophotometer. Most analyses were made using an air-acetylene flame and 10.2 cm burner head mounted parallel to the source beam. Where greater sensitivity was needed, an HGA 2100 graphite furnace was attached and the samples analyzed by the method of standard additions. A deuterium background correct-

or was employed to eliminate interference from gasses evolved during sample atomization for all metals but Cr. The absorption wavelength of Cr occurs outside the optimum range of wavelengths of the corrector and the deuterium beam could not be made intense enough to match the signal of the Cr lamp while retaining the needed sensitivity. Thus, Cr values reported in this paper may be slightly slightly higher than the actual values (Table 1).

Exchangeable Metals.--Trace metals were extracted from 10 gm dry soil with 20 ml 0.005 M diethylene triaminepentaacetic acid (DTPA) - 0.01 M CaCl_2 in triethanolamine (TEA) buffer adjusted to pH 7.3 (Lindsey and Norvell, 1969). The mixture was shaken for two hours on a reciprocal shaker. The slurry was suction filtered through a 0.45 micron membrane filter and the slurry rinsed with 20 ml water which was then filtered and added to the supernatant. The filtrate was brought to a total volume of 100 ml with water. All analyses were completed within seven days of extraction.

The extractant was intended to extract those metals present in water soluble form and those metals loosely absorbed to mineral and colloid surfaces. The term exchangeable metals was chosen as being most appropriate for this mode of metal occurrence, although it is recognized that most of the metals exist as chelates in the extractant solution.

For the sediment samples, the amount of moist sample needed to provide 10 gm dry sample was computed after the moisture content had been determined by drying a separate portion of the sample and measuring the weight loss. The computed amount of sample was then extracted with DTPA as described above except that the sample slurry was filtered through a double thickness of Whatman No. 44 filter paper instead of through a

membrane filter. This was due to the fact that the sediments were the first samples analyzed and the vacume filtration had not been developed yet. The suction filtration method was found to be superior to the filter paper method and was used in all subsequent extractions.

The rock samples were not extracted with DTPA because the large specific surface area, artificially produced by crushing, would not have been representative of the rocks in the environment.

Acid Soluble Metals.--Metals occurring primarily in carbonates and relatively soluble hydrous oxides of iron and manganese were extracted by leaching 2 gm of dry sample for 20 hours with 40 ml 1.0 N HNO_3 . Soil and sediment slurries were then suction filtered, the residue rinsed with 20 ml water which was filtered and added to the filtrate. The sample solution was brought to a total volume of 100 ml with water. The rock samples, after being leached for 20 hours, were centrifuged at 2000 rpm for 15 minutes in an IEC International Centrifuge Size 2, Model K with a radius of 24.3 cm equipped with 100 ml centrifuge tubes. The supernatant was collected and filtered. The residue was rinsed with 20 ml water, resuspended, centrifuged and the supernatant collected and filtered. The sample solutions were brought to a total volume of 100 ml with water.

Total Metals.--The total metals extraction used was a modification of the method of Rantala and Loring (1975). One gram of dry sample was digested for a minimum of 18 hours with 9 ml concentrated HF and 2 ml aqua regia in a sealed teflon bomb at 110°C . After the bombs had been cooled to room temperature, they were opened and the contents transferred to a beaker containing a solution of 4.0 gm H_3BO_3 dissolved in water. After mixing, the samples were suction filtered through a 0.45 micron filter and rinsed with water. The total volume of the sample solution

was brought to 100 ml. All analyses of the samples was completed within five days of extraction.

It was felt that the carbonate content of the rock samples might neutralize the extractant before complete digestion of the sample had occurred and that the generation of CO_2 , due to the dissolution of carbonate in the sealed bombs at an elevated temperature, might be hazardous. Therefore, instead of digesting 1 gm of fresh sample, as was done for the sediments and soils, the residue remaining after the rocks had been leached with HNO_3 was digested. The results of the HNO_3 and HF extractions were added together to give the total metal concentrations for the rocks.

Supporting Analyses.--The pH, cation exchange capacity and organic matter content were determined for the total stream sediment and soil samples following the procedures of Hesse (1971, sections 3:4:1, 7:3:1 and 11:3:3, respectively). The carbonate content was determined from the weight lost on ignition for the sediments and soils using the method described by Fischer (1956, p. 111-112). The weight lost as a result of the HNO_3 extraction was used to determine the carbonate content of the rock samples. The carbonate contents of the sediments and soils were corrected for the organic matter content by subtracting the weight per cent organic matter from the per cent lost on ignition.

Three particle size separations were made for each sediment sample. Sand-sized particles were separated by wet sieving to remove the particles smaller than 0.062 mm in diameter. Silt-sized particles were separated by repeatedly suspending and centrifuging the remaining sample to settle out particles larger than 3.9 microns. The suspended slurry was decanted and fresh, distilled water added to the sample in order that the process

could be repeated. The procedure was repeated until the supernatant was clear after centrifugation. Clay-sized particle content was calculated from the difference in weight of the total sample and the combined weight of the sand and silt fractions. Particle size class limits were taken from Griffiths (1967, p. 76-77). The relative amounts of particles in the three size ranges represented estimates of the differences in the specific surface areas of the sediment samples.

Analytical Sensitivity and Errors.--Analytical sensitivity was, often, not sufficient to detect As and Se even though high intensity electrodeless discharge lamps and the graphite furnace attachment were used. Further, the use of HNO_3 as an extractant was shown by Kunselman and Huff (1976) to reduce the sensitivity of the graphite furnace method for Se, but to increase the sensitivity for As. The graphite furnace could not be used for the total metals analyses due to the corrosive nature of the HF extractant. Analysis for total Cd concentration produced small, but negative instrument responses which were shown not be related Cd content of the sample. The phenomenon must have been caused by the emission of light, near the Cd wavelength, by another element or complex.

Results of the analyses of the U.S. Geological Survey standard rocks (G-2, AGV-1, and BCR-1), made during the course of this investigation, are compared to published values for these standards in Table 1. Estimated analytical accuracy of the metal analyses done in this study are given in Table 2. The errors will be smaller than the listed average values for those samples in which the metal in question was present in relatively large concentrations and larger than the listed values for those samples in which the metal was present in concentrations near the analytical detection limit.

Table 1. Comparison of analyses with recommended values^a for minor and trace metals in U. S. G. S. standard rocks. Values are in parts per million, except for Fe which is in weight percents.

Standard Rock	Fe%	Mn	Cr	Cu	Pb	Zn	Date Analyzed
Andesite AGV-1	4.91	716	24	54	47	92	12-29-76
Andesite AGV-1 Recommended	5.08	523	25	55	39	89	10-12-76
Basalt BCR-1	9.07	1237	37	16	22	130	10-12-76
Basalt BCR-1 Recommended	9.37	1406	18	18	18	120	
Granite G-2	2.48	220	38	10	47	85	6-30-76
Granite G-2 Recommended	1.85	260	7	12	31	85	

^aRecommended values from Flanagan (1971).

Table 2. Estimated accuracy of metal analyses. Values are in weight percent.

Extractant	Fe	Mn	Cr	Cu	Pb	Zn	Cd	As	Se
DTPA ^a	2	2	20	5	15	5	20	40	50
HNO ₃	2	2	20	8	10	3	20	30	50
HF & Aqua	2	2	20	5	15	3			

^aErrors for Cu, Pb, and Zn analyses in HNO₃ extraction of rocks are ± 30 , ± 30 , and $\pm 15\%$, respectively.

RESULTS AND DISCUSSION

Rocks

The results of the metal analyses of the rocks are in Table 3 and the results of the supporting analyses of all samples are in Table 4. Rock carbonate contents (Table 4) show the Johnson and Huges Creek Shales and the Stearns and Eskridge Shales to be calcareous whereas the Long Creek Limestone Member is argillaceous. The Long Creek Limestone and the Johnson and Hughes Creek Shales are close to the 50 percent carbonate content dividing line between shales and limestones given by Krumbein and Sloss (1963, p. 153). The Cottonwood Limestone Member, in contrast, has a relatively low insolubles content.

The coefficients of variation for all chemical data of the total and acid-soluble fraction of the rocks, as well as for those in the sediments and soils were less than 100 percent and most were less than 60 percent. Thus, metals data could be averaged for the rock samples to allow comparisons among the different fractions and with the average values for the different fractions of the sediments and soils (Tables 5 and 18).

The extractable fraction/total metal concentration (extractable/total) data (Table 5) show that large proportions of the total Mn, Cr and Pb concentrations are extractable. The similarity in the extractable/total values for these three metals may indicate that they are present in the same source phases. Clay minerals and crystalline iron oxides would be relatively insoluble in the dilute HNO_3 extractant and would not be prime contributors to the metal concentrations in this fraction. The extractable Cr and Pb concentrations show significant

Table 3. Minor and trace metal concentrations in the rock samples. Values are in micromoles per gram.

Sample	Fe	Mn	Cr	Cu	Pb	Zn	Cd	As	Se
Extractable Fraction									
Long Creek Ls. Mbr.	25.3	3.45	1.37	0.149	0.101	0.199	0.0027	0.0067	ND ^a
Johnson Sh., Hughes Creek Sh.	23.3	5.68	0.67	0.038	0.063	0.130	0.0009	0.0174	ND
Cottonwood Ls. Mbr.	13.2	4.64	1.75	0.025	0.116	0.032	0.0009	0.0067	ND
Stearns Sh., Eskridge Sh.	22.8	6.21	0.94	0.038	0.092	0.084	0.0018	0.0067	ND
Total Metals									
Long Creek Ls. Mbr.	229	4.81	1.98	0.456	0.125	0.566	ND	ND	ND
Johnson Sh., Hughes Creek Sh.	475	9.68	1.85	0.252	0.116	0.857	ND	ND	ND
Cottonwood Ls. Mbr.	75	4.84	1.96	0.535	0.164	0.168	ND	ND	ND
Stearns Sh., Eskridge Sh.	424	8.08	2.04	0.362	0.111	0.597	ND	ND	ND
Non-Extractable Fraction									
Long Creek Ls. Mbr.	204	0.86	0.61	0.307	0.024	0.367	0.006	0.4	0.19
Johnson Sh., Hughes Creek Sh.	451	4.00	1.18	0.214	0.053	0.727	0.008	0.4	0.19
Cottonwood Ls. Mbr.	62	0.20	0.21	0.510	0.048	0.136	0.008	0.4	0.19
Stearns Sh., Eskridge Sh.	402	1.87	1.10	0.324	0.019	0.513	0.007	0.4	0.19

^aNot Detectable: Extractable Fraction - Se 0.2; Total Metals - Cd 0.009,

As 0.401, Se 0.2 micromoles per gram.

Table 4. Chemical and physical properties of the rock, sediment and soil samples. Values are in weight per cent except for pH and CEC.

Sample	pH	CEC ^a	Organic Matter	CO ₃	Sand	Silt	Clay
Rocks							
Long Cree, Ls. Mbr.				65.8			
Johnson Sh., Hughes Creek Sh.				33.7			
Cottonwood Ls. Mbr.				86.9			
Stearns Sh., Eskridge Sh.				48.6			
Soils							
Dwight-Irwin cmpx.	6.43	37.8	3.26	14.7			
Martin SiCl, 1-4 percent	6.56	34.6	2.28	12.1			
Martin SiCl, 4-8 percent	5.62	41.4	2.86	11.9			
Kipson-Sogn cmpx.	6.47	41.8	3.46	12.6			
Oska-Sogn cmpx.	5.50	45.5	3.46	12.8			
Wabash SiCl	7.31	33.7	1.58	14.6			
Sediments							
DC-SD-1	7.27	49.2	0.77	29.8	50.5	24.2	25.3
DC-SD-2	7.27	36.5	0.71	31.8	39.5	28.7	31.8
DC-SD-3	7.16	30.3	0.27	41.5	18.5	34.8	46.7
DC-SD-4	6.83	21.9	2.09	40.6	33.6	25.6	40.8
DC-SD-5	6.99	37.6	1.04	19.3	24.6	37.3	38.1

^aCation exchange capacity in meq-100 grams dry sample.

Table 5. Distribution of trace metals in the Deep Creek Basin samples.
 Values are averages in per cent.^a

	Fe	Mn	Cr	Cu	Pb	Zn
Rocks						
Extractable/Total	7.0	74.5	60.2	15.7	72.1	20.4
Non-Extractable Total	93.0	25.5	9.8	84.3	28.9	79.6
Sediments						
Exchangeable/Total	0.1	9.0	0.01	5.6	5.0	0.7
Extractable/Total	10.9	41.6	30.1	25.0	33.2	14.2
Non-Extractable/Total	89.0	49.4	69.9	69.4	61.8	85.1
Soils						
Exchangeable/Total	0.2	25.6	0.1	8.9	10.1	1.7
Extractable/Total	6.1	55.1	3.8	11.7	25.9	10.6
Non-Extractable/Total	93.7	19.3	96.1	79.4	64.0	87.7

^a Total Metal values not available for Cd, As and Se.

correlations with the carbonate contents (Table 6). Manganese oxide staining was noticed in the Long Creek Limestone and the shales. These oxides would be leached by the HNO_3 extractant and could be the prime source for the extractable Mn and other metals.

The non-extractable fraction/total metal concentration (non-extractable/total) data (Table 5) show that large proportions of the total Fe, Cu and Zn occur in minerals that are not soluble in dilute HNO_3 . The non-extractable Fe, Cu, Zn and, to a lesser extent, Mn concentrations show significant negative correlations with the carbonate contents (Table 7) emphasizing control by the insoluble minerals. The non-extractable Fe, Cr and Zn concentrations show significant correlations with each other suggesting the occurrence of these metals in the same minerals. However, Cu does not show any indication of being associated with Fe, Zn or Cr in the non-extractable fraction. The association of the non-extractable Zn and Mn concentrations and the weak negative correlation of the Mn concentration with the carbonate content suggests that Mn is associated with Fe, Cr and Zn in the non-extractable fraction.

The metal/Mn data (Table 8) show that Cr/Mn and Pb/Mn are similar for the extractable and non-extractable fractions suggesting the possible control of these metals by Mn-rich phases (Suarez and Langmuir, 1976). Fe/Mn, Cu/Mn and Zn/Mn all show an order of magnitude increase from the extractable to the non-extractable fraction. The similarity of these increases may indicate the association of these metals which would support the conclusions reached above. The molar order sequences (Table 9) show the extractable fraction to be relatively enriched in Pb.

Table 8.-Metal/Mn values for the rock, sediment and soil samples, Values are averages.

	Fe/Mn	Cr/Mn	Cu/Mn	Pb/Mn	Zn/Mn	Cd/Mn	As/Mn
Rocks							
Extractable	4.13	0.23	0.012	0.018	0.022	0.0004	0.0018
Non-Extractable	162	0.45	0.196	0.021	0.252		
Sediments							
Exchangeable	0.72	-	0.0091	0.0056	0.0030	0.0003	0.0036
Extractable	6.25	0.05	0.0088	0.0080	0.013	0.0047	0.0049
Non-Extractable	42.5	0.10	0.020	0.013	0.067		
Soils							
Exchangeable	0.44	0.0008	0.015	0.0060	0.0082	0.0006	
Extractable	5.95	0.011	0.0094	0.0071	0.024	0.0006	
Non-Extractable	264	0.78	0.184	0.050	0.565		

Table 9. Molar order of abundance sequences for the rock, sediment and soil samples. Sequences are based on average values.

	Rocks
Extractable Fraction	Fe > Mn > Cr > Zn > Pb > Cu > As > Cd
Non-Extractable Fraction	Fe > Mn > Cr > Zn > Cu > Pb
Total Metals	Fe > Mn > Cr > Zn > Cu = Pb
	Sediments
Exchangeable Fraction	Mn > Fe > Cu > Pb = As > Zn = Se > Cd > Cr
Extractable Fraction	Fe > Mn > Cr > Zn > Cu > Pb > As > Cd
Non-Extractable Fraction	Fe > Mn > Cr > Zn > Cu > Pb
Total Metals	Fe > Mn > Cr > Zn > Cu > Pb
	Soils
Exchangeable Fraction	Mn > Fe > Cu > An > Pb > Cr > Cd > Se
Extractable Fraction	Fe > Mn > Zn > Cr > Cu > Pb > As > Cd
Non-Extractable Fraction	Fe > Mn > Cr > Zn > Cu > Pb
Total Metals	Fe > Mn > Cr > Zn > Cu > Pb

This is mainly the result of the large proportion of Pb in the extractable fraction. Otherwise, the sequence for the extractable fraction is nearly identical to the sequence for the total metal concentrations.

Thus, the metals appear to be divided among three mineral groups in the rocks. The carbonates apparently contain most of the Cr and Pb concentrations whereas Mn is associated with manganese oxides. Crystalline iron oxides and clays probably are the main sources for Fe, Cu and Zn.

Stream Sediments

Sediment samples SD-1, SD-2 and SD-3 are representative of typical stream sections. Their measured pH's fall within the range of pH's measured for spring waters of the Deep Creek Basin (pH 7.0 - 7.3, Whittemore and Switek, 1977). The sediment pH's are lower than those measured for the Deep Creek stream waters (pH 8.1 - 8.4) as the decomposition of organics in the sediments maintains a higher partial pressure of CO_2 in the sediment pore water than is found in the stream water. Samples SD-4 and SD-5 were collected from a small pond and a marshy area, respectively. Both sites contained abundant vegetation as shown by the high organic matter content of these samples. The relatively low pH's of SD-4 and SD-5 are attributed to relatively high rates of organic decomposition at these sites. Sediment pH's are kept relatively high (greater than pH 6.5) by the buffering action of the carbonates present in the form of limestone fragments. The relatively high carbonate contents of SD-3 and SD-4 may be due to the precipitation of calcite from spring waters emerging just upstream of the sampling sites.

Cation exchange capacity in the sediments was moderately high

indicating expandable layer clays. The lower exchange capacities obtained for samples SD-3 and SD-4 (Table 4) were not expected in light of the higher clay-sized particle contents of these samples. The high carbonate content of these samples together with the location of both localities downstream from springs suggests that calcite has been precipitated. Possibly, a larger proportion of non-clay minerals is in the clay-sized fraction at these sites, especially considering the high upper size limit (3.9 microns) used in this study. The sediment size distributions are apparently related to the nature of the deposit sampled. Sample SD-1 was collected from a gravel bar riffle as shown by the high percentage of sand-sized particles in this sample. Sample SD-3 was from another riffle, this one formed by a bedrock out-cropping, which consisted of fine material (less than cobble size) deposited between limestone blocks. The riffle from which SD-5 was collected was formed by the pinching of the stream channel between grass-matted banks. SD-2 and SD-4 were stream pool and pond samples, respectively. The grain size distributions for these quiet water deposits appear to be similar.

The metal data for the Deep Creek sediments are presented in Table 10. Table 5 shows that significant percentages of the Mn, Cu and Pb concentrations occur in the exchangeable fraction. The correlation of the exchangeable Fe concentration and the organic matter content (Table 11) indicates the chelation of Fe, and probably other metals, by organics. A negative relationship between As and Zn is the only other significant correlation for the exchangeable metal data. A correlation at the 90 percent level suggests that the exchangeable Mn and Pb are associated with the same phases.

Table 10. Minor and trace metal concentrations in the sediment samples. Values are in micromoles per gram.

Sample	Fe	Mn	Cr	Cu	Pb	Zn	Cd	As	Se
Exchangeable Fraction									
SD-1	0.328	0.171	ND ^a	0.007	0.006	0.0064	0.00050	0.0028	0.017
SD-2	0.453	2.04	ND	0.023	0.011	0.0064	0.00071	0.0075	ND
SD-3	0.154	0.131	ND	0.007	0.007	0.0037	0.00050	0.0286	0.005
SD-4	2.27	1.62	ND	0.031	0.014	0.0058	0.00028	0.0048	ND
SD-5	0.389	5.92	ND	0.023	0.016	0.0061	0.00077	0.0096	ND
Acid Soluble Metals									
SD-1	66.8	11.6	0.552	0.080	0.088	0.150	0.0074	0.029	ND
SD-2	66.8	14.0	0.552	0.085	0.083	0.127	0.0078	0.048	ND
SD-3	44.4	8.4	0.237	0.083	0.057	0.170	0.0022	0.084	ND
SD-4	39.4	4.9	0.621	0.137	0.072	0.083	ND	0.025	ND
SD-5	71.3	16.7	0.381	0.104	0.117	0.106	0.0038	0.092	ND
Total Metals									
SD-1	466	26.0	1.37	0.242	0.249	0.826	ND	ND	ND
SD-2	483	26.4	1.44	0.255	0.265	0.832	ND	ND	ND
SD-3	555	18.0	1.77	0.390	0.216	1.100	ND	ND	ND
SD-4	501	8.0	1.76	0.436	0.161	0.733	ND	ND	ND
SD-5	591	31.5	1.47	0.261	0.227	0.794	ND	ND	ND
Extractable Fraction									
SD-1	66.5	11.5	0.552	0.073	0.082	0.144	0.0068	0.026	0.008
SD-2	66.3	11.9	0.552	0.062	0.072	0.121	0.0071	0.041	0.025
SD-3	44.3	8.2	0.237	0.076	0.050	0.166	0.0017	0.056	0.020
SD-4	37.1	3.3	0.621	0.106	0.058	0.077	0.0006	0.020	0.025
SD-5	70.9	10.7	0.381	0.081	0.101	0.100	0.0031	0.082	0.025
Non-Extractable Fraction									
SD-1	399	14.4	0.82	0.162	0.161	0.676	0.01	0.8	0.036
SD-2	417	12.4	0.88	0.170	0.182	0.705	0.01	0.8	0.038
SD-3	511	9.6	1.53	0.307	0.159	0.930	0.02	0.7	0.038
SD-4	462	3.1	1.14	0.299	0.089	0.650	0.02	0.8	0.038
SD-5	520	14.8	1.09	0.157	0.110	0.688	0.01	0.7	0.038

^a Not Detectable: Exchangeable Fraction - Cr 0.00009, Se 0.002; Acid Soluble - Cd 0.009, Se 0.025; Total Metals - Cd 0.02, As 0.8, Se 0.4 Micromoles per gram.

Examination of the data on exchangeable metals in Table 10 shows that the even numbered (pond-pool) samples have distinctly higher concentrations of Fe, Cr, Cu and Pb than do the odd numbered (riffle) samples. The reverse situation exists for As and Se, which occur as oxyanions, rather than as cations in the stream and sediment waters. The absence of any correlations to explain this indicates a complex interrelationship of several physical and chemical properties of the sediment and pore water characteristic of the site of deposition that controls the availability of exchangeable metals.

The extractable/total data (Table 5) show that large proportions of the total Mn, Cr, Cu and Pb are extractable in dilute HNO_3 . The extractable Fe and Pb concentrations show negative correlations with the carbonate contents, at the 95 percent and 99 percent levels, respectively, and positive correlations with each other at the 90 percent level (Table 12). This indicates the occurrence of both metals in soluble non-carbonate minerals. Hydrous oxides of iron and manganese are likely candidates as sources of Fe and Pb (Jenne, 1968). The rather large proportion of the total Mn concentration in the extractable fraction (Table 5) and the higher solubilities of the manganese compounds, relative to the corresponding hydrous iron oxides, indicates that hydrous manganese oxides contribute a large proportion of the metals in the extractable fraction. The extractable Cu concentration, however, shows negative correlations with the Mn concentration, pH and organic matter and does not appear to be related to the hydrous manganese oxides. The extractable Zn concentration, also, shows a negative correlation with the organic matter content. The extractable As concentration correlates with the silt-sized particle content whereas the Cd concentration cor-

Table 12. Correlation matrix for the extractable fraction of the sediment samples. Correlation coefficients of .80, .88 and .96 are significant at the 90, 95 and 99 percent levels, respectively.

	pH	Org ^a	Co ₃ ^b	Sand	Silt	Clay	Fe	Mn	Cr	Cu	Pb	Zn	Cd
Fe			-.89										
Mn	.82								.91				
Cr					.84								
Cu	.93	-.86						-.92					
Pb			-.99				.86						
Zn		-.91											
Cd				.86		-.95							
As					.96								

^aWeight percent organic matter

^bAs weight percent CaCO₃

relates with the sand-sized particle content. The association of As and Cd with the coarser sediment particles indicate that their host phases occur as coatings on the particle surfaces (Hawkes and Webb, 1962 and Hem, 1972).

The non-extractable/total data (Table 5) show that the largest proportions of all metals analyzed, except Mn, occur in the non-extractable fraction. The non-extractable Fe and Cr concentrations correlate with the clay and silt size fractions indicating clay minerals or oxide coatings on fine particles as the sources. The non-extractable Cu concentration shows an inverse correlation (Table 13) with Mn concentrations indicating that the Cu occurs in clay minerals or crystalline iron oxides.

The metal/Mn data (Table 8) for Cu, Pb and As are similar in the exchangeable and extractable fractions suggesting a manganese-bearing phase as the source. Table 5 shows that appreciable proportions of the Mn, Cu and Pb occur in the exchangeable and extractable fractions. The molar abundance sequences (Table 9) show the Mn, Cu and Pb concentrations to be enriched in the exchangeable fraction when compared to the relative abundances of the total metals in the sediments. These aberrations are consistent with the hypothesis that these metals occur with hydrous manganese oxides. However, the negative correlation of the extractable Mn and Cu concentrations argue against the occurrence of Cu in the hydrous oxides.

Possibly, the extractable Cu is associated with the carbonates in a relationship similar to that found by Ashry (1973) in the Nile River Sediments where the Cu occurred in or on clay-sized (less than 2 microns) calcite particles. The molar order of abundance sequences for the extractable and non-extractable metal fractions are nearly identical to the

Table 13. Correlation matrix for the non-extractable fraction of the sediment samples. Correlation coefficients of .80, -.8 and .96 are significant at the 90, 95 and 99 percent levels, respectively.

	pH	Org ^a	CO ₃ ^b	Sand	Silt	Clay	Fe	Mn	Cr	Cu	Pb
Fe				-.95	.87	.84					
Mn											
Cr				-.89		.94					
Cu			.88					.85			
Pb	.97	-.83									
Zn											.82

^aWeight percent organic matter

^bAs weight percent CaCO₃

sequence for the total metal concentrations.

Soils

The cation exchange capacities of the soils in the Deep Creek Basin are moderately high (Table 4) indicating expandable layer clay minerals. Evidence for active soil erosion in the study area occurs in the form of gullies that have grown deeper and longer during the course of the investigation and in the form of shale outcrops in the upper (northern) part of the basin. The soils that show signs of active erosion (Martin silty clay and Oska-Sogn complex) have lower pH's than do the other soils.

The Wabash silty clay shows signs of active erosion along the stream bank but this soil has the highest pH measured in this study. However, because of the differences in the type and amount of vegetation and in the soil moisture content between the Wabash silty clay and the other soils, probably, the controls on pH in the Wabash silty clay are different than those in the other soils and a direct comparison may not be justified. The soils developed on steep slopes and hilltops (Dwight-Irwin complex, Kipson-Sogn complex and Oska-Sogn complex) have higher organic matter contents than do those soils found at the base of slopes and on the floodplain (Martin silty clay, 1-4 percent and 4-8 percent and Wabash silty clay). There appears to be no correlation between the organic matter content and the pH of the soils. The range of soil carbonate contents is relatively small revealing the mechanical homogeneity of the Deep Creek soils.

The concentration of metals for the soil samples are given in Table 14. The exchangeable/total data (Table 5) show that appreciable amounts of the total Mn, Cu, Pb and Cd concentrations occur in the exchangeable fraction. The large proportion (26 percent) of the total

Table 14. Minor and trace metal concentrations in the soil samples. Values are in micromoles per gram.

Exchangeable Metals									
Sample ^a	Fe	Mn	Cr	Cu	Pb	Zn	Cd	As	Se
F2B	1.44	1.60	0.0011	0.039	0.015	0.028	0.0012	ND ^b	ND
F23B	0.72	2.88	0.0014	0.041	0.023	0.017	0.0017	ND	0.0015
F23C	1.32	3.91	0.0025	0.046	0.015	0.026	0.0017	ND	0.0008
2D	0.90	2.22	0.0019	0.038	0.013	0.023	0.0016	ND	ND
12D	1.74	3.39	0.0035	0.049	0.018	0.023	0.0015	ND	ND
1F2	0.92	2.18	0.0019	0.038	0.013	0.020	0.0018	ND	0.0019
Acid Soluble Metals									
F2B	34.4	5.92	0.048	0.101	0.059	0.179	0.0034	0.016	ND
F23B	37.1	10.19	0.069	0.107	0.064	0.194	0.0066	0.033	ND
F23C	35.5	7.92	0.085	0.079	0.051	0.179	0.0058	0.043	ND
2D	28.7	7.52	0.054	0.096	0.054	0.127	0.0051	0.041	ND
12D	35.7	6.64	0.069	0.096	0.041	0.133	0.0045	0.043	ND
1F2	41.1	12.52	0.050	0.098	0.075	0.174	0.0060	0.024	ND
Total Metals									
F2B	573	8.28	1.29	0.286	0.154	1.15	ND	ND	ND
F23B	598	10.94	1.40	0.362	0.159	1.28	ND	ND	ND
F23C	587	9.34	1.75	0.464	0.142	1.15	ND	ND	ND
2D	556	9.88	1.98	0.379	0.155	1.39	ND	ND	ND
12D	487	8.57	1.89	0.408	0.151	1.42	ND	ND	ND
1F2	577	15.71	1.40	0.880	0.185	1.38	ND	ND	ND
Extractable Fraction									
F2B	32.9	4.32	0.047	0.062	0.044	0.151	0.0022	0.016	0.2
F23B	36.4	7.31	0.68	0.066	0.041	0.177	0.0049	0.033	0.2
F23C	34.1	4.01	0.082	0.033	0.036	0.153	0.0041	0.043	0.2
2D	27.9	5.30	0.052	0.058	0.041	0.104	0.0035	0.041	0.2
12D	34.0	3.25	0.066	0.047	0.023	0.110	0.0030	0.043	0.2
1F2	40.2	10.34	0.048	0.060	0.062	0.127	0.0042	0.024	0.2
Non-Extractable Fraction									
F2B	539	2.36	1.24	0.185	0.095	0.97	0.005	0.8	0.4
F23B	561	0.75	1.33	0.255	0.095	1.09	0.002	0.8	0.4
F23C	552	1.42	1.67	0.385	0.091	0.97	0.003	0.8	0.4
2D	528	2.36	1.93	0.283	0.101	1.26	0.004	0.8	0.4
12D	451	1.93	1.82	0.312	0.110	1.29	0.004	0.8	0.4
1F2	536	3.19	1.35	0.782	0.110	1.23	0.003	0.8	0.4

^a F2B - Dwight-Irwin Complex; F23B - Martin silt clay, 1-4 percent slope; F23C - Martin silt clay, 4-8 percent slope; 2D - Kipson-Kogn complex; 12D - Oska-Sogn complex; 1F2 - Wabash silt clay.

^b Not Detectable: Exchangeable Fraction, As 0.01, Se 0.001; Acid Soluble Metals, Se 0.19; Total Metals, Cd 0.0089, As 0.801, Se 0.38 micromoles per gram.

Mn concentration in the exchangeable fraction indicates a soluble, manganese-rich phase. The concentration of exchangeable Cu correlates with the Mn and Cr concentrations and shows negative correlations with pH (Table 15). If manganese oxides are proposed as sources of these metals, the above correlations appear to be contradictory. For example, lower pH's would mean a more positive oxide surface and less absorbed Cu, but more absorbed Cr which tends to occur in anionic form in high Eh environments (Hawkes and Webb, 1962). The above relationships, more likely, represent changes in the chelating abilities, or oxide mineralogy, in the different soils. The exchangeable Se concentration shows negative correlation with cation exchange capacity and the organic matter content. This is consistent with the anionic nature of Se in the soil and the low selectivity of organic matter for Se (Hawkes and Webb, 1962).

Major proportions of the total concentrations of all metals analyzed, but particularly Mn, Pb and Cd, are extractable in dilute HNO_3 (Tables 5 and 14). The extractable Mn and Fe concentrations do not correlate with each other but both show negative correlations with the organic matter content (Table 16). The extractable Pb concentration correlates with the pH and the Mn concentration whereas the extractable Cr concentration correlates with the carbonate content.

Table 5 shows that the bulk of all metals analyzed, except Mn, occurs in acid-insoluble minerals. The lack of many significant correlations for the non-extractable metal data (Table 17) indicate a complex mineral assemblage or differences in mineral assemblages or chemical conditions in the different soil types. The correlation between the Pb and Zn concentrations is not unexpected as both metals

Table 15. Correlation matrix for the exchangeable fraction of the soil samples. Correlation coefficients of .73, .81 and .92 are significant at the 90, 95 and 99 percent levels, respectively.

	pH	CEC ^a	Org ^b	CO ₃ ^c	Fe	Mn	Cr	Cu	Pb	Zn	Cd
CEC	-.85										
Org		.84									
CO ₃											
Fe											
Mn				-.78							
Cr			.75								
Cu	-.89				.82		.81				
Pb											
Zn											
Cd											
Se		-.81	-.98							-.73	

^aCation exchange capacity

^bWeight percent organic matter

^cAs weight percent CaCO₃

Table 16. Correlation matrix for the extractable fraction of the soil samples. Correlation coefficients of .73, .81 and .92 are significant at the 90, 95 and 99 percent levels, respectively.

	pH	Org ^a	CO ₃ ^b	Fe	Mn	Cr	Cu	Pb	Zn
Fe		-.87							
Mn	.90	-.91							
Cr			-.83						
Cu	.75					-.73			
Pb	.93	-.76			.87				
Zn									
Cd									

^aWeight percent organic matter

^bAs weight percent CaCO₃

Table 17. Correlation matrix for the non-extractable fraction of the soil samples. Correlation coefficients of .73, .81 and .92 are significant at the 90, 95 and 99 percent levels, respectively.

	pH	Org ^a	CO ₃ ^b	Fe	Mn	Cr	Cu	Pb
Fe								
Mn			.80					
Cr								
Cu		-.77						
Pb								
Zn								.88

^aWeight percent organic matter

^bAs weight percent CaCO₃

have similar chemical affinities.

As pointed out earlier, the largest proportions of the total Mn in the exchangeable and extractable fractions indicates soluble, manganese-rich phases. The metal/Mn values for Cu, Pb and Cd in the exchangeable fraction are similar to the corresponding metal/Mn values in the extractable fraction suggesting the occurrence of those metals in the manganese-rich phases (Suarez and Langmuir, 1976). It is probable that hydrous oxides of manganese are the sources of these metals (Jenne, 1968). Carbonates and organic matter are other possible extractable metal sources but the low concentrations of both these constituents in the Deep Creek soils do not seem to support either of them.

The molar abundance sequence (Table 9) for the exchangeable fraction of the soils show that the metals that have been associated with hydrous manganese oxides (Mn, Cu and Pb) to be enriched relative to Fe, Cr and Zn when compared to the molar abundances for the total metal concentrations. The molar sequence for the extractable fraction is, except for the position of Cr, identical to the total metal sequence. The position of Cr in both the exchangeable and the extractable fraction sequences is attributable to the insolubility of soil Cr compounds (Hawkes and Webb, 1962). The molar order sequence for the non-extractable fraction is identical to the total metals sequence.

Comparison of the Rock, Sediment and Soil Data

The soils and sediments are enriched in the total concentrations of Fe, Mn and Zn, and of Pb for the sediments, relative to the rocks (Table 18). This enrichment can be attributed to the removal of much of the metal-diluting carbonate during rock weathering. The rocks are

Table 18. Average trace metal concentrations of the rock, sediment and soil samples. Values are in micromoles per gram.

Material	Fe	Mn	Cr	Cu	Pb	Zn	Cd	As	Se
Exchangeable Fraction									
Soils	1.17	2.68	0.002	0.041	0.016	0.022	0.0016	ND ^a	0.0008
Sediments	0.72	1.97	ND	0.018	0.011	0.006	0.0005	0.06	0.006
Acid Soluble Metals									
Rocks	21.1	5.11	1.18	0.063	0.093	0.112	0.0018	0.0093	ND
Sediments	57.7	11.1	0.47	0.100	0.083	0.127	0.0042	0.056	ND
Soils	35.4	8.45	0.063	0.086	0.057	0.161	0.0052	0.033	ND
Total Metals									
Rocks	300	6.86	1.96	0.401	0.129	0.548	ND	ND	ND
Sediments	521	21.9	1.56	0.317	0.224	0.857	ND	ND	ND
Soils	566	10.5	1.62	0.463	0.158	1.29	ND	ND	ND
Extractable Fraction									
Rocks	21.1	5.11	1.18	0.063	0.093	0.112	0.0018	0.0093	-
Sediments	57.0	9.12	0.47	0.080	0.073	0.122	0.0043	0.045	-
Soils	34.3	5.76	0.061	0.054	0.041	0.137	0.0037	0.033	-
Non-Extractable Fraction									
Rocks	280	1.73	0.775	0.339	0.036	0.436	--	--	--
Sediments	462	10.9	1.09	0.219	0.140	0.730	--	--	--
Soils	528	2.00	1.56	0.367	0.100	1.13	--	--	--

^aNot Detectable: Exchangeable, Soils - As 0.01; Acid Soluble Metals, Rocks and Soils - Se 0.2, Sediments - Se 0.03; Total Metals, Rocks - Cd 0.009, As 0.4, Se 0.2, Sediments - Cd 0.02, As 0.8, Se 0.4, Soils - Cd 0.009, As 0.8, Se 0.4 micromoles per gram.

richer in Cr than both the sediments and soils, and richer in Cu than the sediments. The depletion of Cr during rock weathering is possibly due to the formation of the highly mobile chromate ion. Similarly, oxidizing conditions in the thin, upland soils would also lead to the formation of chromate ion (Hawkes and Webb, 1962).

Both the sediments and the soils contained higher amounts of extractable metals than the rocks (Table 18), with the exception of Cr and Pb. Large proportions of the total concentrations of Cr and Pb are extractable from the rocks due to the occurrence of these metals in carbonates.

The soils are enriched in total concentrations of Fe, Cu and Zn, but are depleted in Mn and Pb, relative to the sediments. The higher metal concentrations in the soils may be due to larger amounts of glacial till but is more likely due to the lack of the constant presence of water that occurs in the sediments. The enrichment of Mn and Pb in the stream sediments is probably due to the low mobility of these metals in the neutral to slightly alkaline pH's found in the Deep Creek stream sediments.

The exchangeable fraction of the soils is richer in all the analyzed metals, except As and Se, than the exchangeable fraction of the sediments. The higher DTPA availability of metals in the soils is probably due to the greater concentration of chelating organic matter in the soils. The reduced availability of soil As and Se is probably related to the tendency of those metals to become fixed in hydrous iron oxides and to form insoluble compounds, respectively, in soils (Hawkes and Webb, 1962).

The extractable fraction of the soils contains lower concentrations of all metals, except Zn, than the extractable fraction of the sediments.

Reddy and Perkins (1976) showed that metals become fixed to clay Minerals if soils are subjected to alternating wet and dry conditions. Thus, the relatively low extractable metal concentrations of the soils may be due to such metal fixation.

The molar order sequences (Table 9) show the influence of the bed-rock parent material on the metal distribution in the sediments and soils. The sequences for the total, extractable and non-extractable metal fractions of the sediments, and the sequences for the total and non-extractable fractions of the soils are nearly identical to the total metals sequence for the rocks. The sequence for the extractable fraction of the soils differs from the total metals sequence for the rocks only in the positions of Cr and Zn. The sequences for the exchangeable fractions of both the sediments and the soils are very different from the total metals sequences. In both cases Mn, Cu and Pb are enriched relative to Fe, Cr and Zn.

Apparently, then, the distributions of metals in the sediments and soils are inherited from the parent bedrock, though glacial deposits probably can have a large effect locally. The availability of the metals to organic chelating agents, and, thus, to plants and animals, seems to depend on the local physical and chemical conditions affecting the surfaces of minerals and colloids.

Comparison of the Data With the Results of Other Studies

Table 19 compares the average data for the Deep Creek area limestones and shales with the data published by Connor and Shacklette (1975), Rankama and Sahama (1955) and Turekian and Wedepohl (1961). The units for the data for the Deep Creek samples have been converted to parts per

Table 19. Comparison of the Deep Creek area rock data with the published data from other studies. Values are in parts per million, except for Fe which are in weight percent.

Reference										
Rankama and Sahama, 1955	Shale	4.73	620	540	192	20	510	0.3		
	Limestone	0.40	385	2	20.2	7.5	50	-		
Turekian and Wedepohl, 1961	Shale	4.72	850	90	45	1.5	95	0.3		
	Limestone	0.38	1100	11	4	0.01	20	0.04		
Connor and Shacklette, 1975	Miss. Shale	1.80	140	130	13	11	55	1		
	Penn. Shale	3.80	170	95	--	17	82	1		
	Miss. Limestone	0.15	160	9.4	0.85	10	19	1		
	Penn. Limestone	2.10	830	16	3.5	4.2	24	1		
Deep Creek Rocks	Shale	2.50	480	101	20	24	48	0.2		
	Limestone	0.85	265	103	30	30	24	0.2		

million, or weight percent in Tables 19, 20 and 21 to allow comparison with the data from the literature. The Deep Creek area limestones show relatively high concentrations of Cr, Cu and Pb when compared to the published data. The metal concentrations in the Deep Creek shales are consistent with the published values. The high metal concentrations of the Deep Creek limestones may be due to a slightly higher than normal metal content in the source area for the Deep Creek limestones.

Table 20 compares the metal concentrations of the Deep Creek sediments with data published by Collinson and Shimp (1972), Frye and Shimp (1973) and Helz (1976). It must be noted that the sediments of Lake Peoria (Collinson and Shimp, 1972) and the top layer of sediments from Lake Michigan (Frye and Shimp, 1973) have been affected by pollution and their metal concentrations are a little high. When compared to the published data, the Deep Creek samples contain relatively high Mn concentrations whereas the Cr concentrations in the Deep Creek samples compare favorably with the Cr data for the polluted sediments. The high Mn and Cr concentrations in the Deep Creek sediments can be related to the bedrock of the area. The parent materials of the sediments in the other studies were glacial debris from the Canadian Shield, for the lake sediments, and rocks of the Piedmont Province of the Atlantic Coast, for the bay sediments, both areas rich in granite rocks. Limestones and shales are usually higher in Mn and Cr than granitic rocks (Krauskopf, 1972).

The concentrations of metals in the Deep Creek soils are compared to data for other soils published by Connor and Shacklette (1975), Connor, et al. (1976) and Hawkes and Webb (1962) in Table 21. The Deep Creek area soils have been divided into the floodplain forest soil (Wabash

Table 20. Comparison of the Deep Creek stream sediment data with the published data from other studies. Values are in parts per million, except for Fe which are in weight percent.

Reference									
Helz, 1976	Chesapeake Bay	3.90	690	25	20	27	128	0.9	
Frye and Shimp, 1973	Top Layer Lake Michigan	2.82	557	77	37	88	446	----	
	Lake Saline, Altonian Age	3.35	465	24	25	18	700	----	
	Lake Saline, Farmdalian Age	2.55	465	33	16	24	89	----	
Collinson and Shimp, 1972	Peoria Like, Illinois River	3.36	651	151	62	145	446	----	
Deep Creek Sediments	Deep Creek Basin, Kansas	2.91	1208	81	20	46	56	0.9	

Table 21. Comparison of the Deep Creek area soil data with the published data from other studies.
Values are in parts per million, except for Fe which are in weight percent.

Reference	Sample Type	Fe	Mn	Cr	Cu	Pb	Zn	Cd
Hawkes and Webb, 1962	Soils, General	2.70	850	200	20	10	50	0.5
Connor, et. al, 1976	River Basin, Wyoming and Montana	1.90	250	45	14	17	59	--
Connor and Shacklette, 1975	Glaciated Prairie Missouri	2.95	505	65	21	22	68	1
	Floodplain Forest Missouri	1.85	530	39	14	19	50	1
Deep Creek Soils	Glaciated Prairie	3.15	517	86	24	32	83	0.6
	Floodplain Forest	3.22	863	73	56	38	90	0.7

^aData from Vinogradov, 1959.

silt clay and the prairie soils to correspond to the classification of Connor and Shacklette (1975). The Deep Creek soils have metal concentrations that are consistent with the published data of Vinogradov (1959), with the exception of Pb, Zn and Cd. The Deep Creek prairie soils similar amounts of all metals as the Missouri prairie soils.

The Deep Creek area floodplain soil has higher concentrations of all analyzed metals, except Mn and Cr, than the soils from Vinogradov (1959), but consistently higher concentrations of those metals than the soils reported on by Connor, et al. (1976) and Connor and Shacklette (1975). All the Deep Creek soils are higher in the metal concentrations than the soils of the Powder River Basin (Connor, et al., 1976). The Powder River Basin soils are derived from glacial debris and probably have a much higher quartz content (quartz is usually low in trace metals) than the Deep Creek area soils. The relatively low metal concentrations of the Missouri soils is probably the result of the higher annual rainfall there, which would promote a more complete leaching of metals from those soils.

SUMMARY AND CONCLUSIONS

Soluble carbonates and relatively insoluble clays and oxides are the principle sources of metals in the rocks of the Deep Creek area. Large proportions of the total Mn, Cr and Pb concentrations are acid soluble but only Cr and Pb correlate with the carbonate content. The Mn probably occurs as an oxide phase. The largest proportions of the Fe, Cu and Zn concentrations occur in the insoluble oxides and clay minerals.

The formation of sediments and soils, concomitant with rock weathering,

concentrates all metals but Cr and Cu. The primary mechanism of concentration is believed to be the dissolution of carbonate. The residual carbonate acts to keep pH's relatively high, thereby restricting the mobility of most metals. The decrease in Cr and Cu concentrations resulting from rock weathering is the result of the mobility of those metals under the prevailing chemical conditions.

Hydrous oxides of manganese and iron, formed during sediment and soil development, are probably a major control on the distribution and availability of metals in the Deep Creek area. Such oxides are capable coprecipitating, occluding and absorbing appreciable amounts of metals. The relative solubility of the hydrous oxides, to a large part controlled by the crystallinity (Whittemore and Langmuir, 1974), is a major control on the release of the metals back to the environment.

The distribution of the dilute acid extractable and total metals is inherited from the parent bedrock. The distribution of those metals available for chelation by organics (available for plant uptake) is the result of the effect of local physical and chemical conditions on the mineral and colloid surfaces and of the concentration of organic matter. The bulk of all metals, but Mn, in the sediments and soils occur in acid-insoluble clay minerals and oxides.

The Deep Creek area limestones appear to have relatively high concentrations of Cr, Cu and Pb when compared to data for other limestones from the literature. The high concentrations may be related to a high regional background for those metals in the study area. Except for relatively high Mn and Cr concentrations, the Deep Creek sediments have metal concentrations that are comparable to the data from other studies. The relatively high Mn and Cr concentrations in the Deep Creek

area is due to the type of parent material present.

The Deep Creek area prairie soils have metal concentrations that are comparable to those in limestone-derived soils in Missouri. The floodplain soil in the study area appears to have high concentrations of metals when compared to soils in Missouri and to the other soils in the Deep Creek Basin. The differences in soil metal concentrations between the Deep Creek area and the other areas can be related to differences in parent material and climate.

The Cr concentrations reported in this study tend to be high partly because of the difficulty with the deuterium background corrector (Table 1). Most metals dissolved during rock weathering probably remain in the Deep Creek Basin, not far from their source. The buffering action of carbonate keeps the pH relatively high, limiting the mobility of most metals which become fixed to clays, oxides or organic matter. The low concentrations of dissolved metals in the natural waters of the Deep Creek Basin (Switek and Whittemore, 1977 and Whittemore and Switek, 1977) supports this hypothesis.

The comparisons of the Deep Creek sediment and soil data with the data from other studies and the evidence provided by the molar order of abundance sequences indicate that there is no appreciable amount of pollution presently occurring in the Deep Creek Basin. Thus, the baseline values obtained in this investigation are those that would be expected to occur naturally in the Deep Creek area.

Environmental monitoring of the study area should involve analysis of the exchangeable and extractable fractions of the sediments and/or the soils. Any influx of metals would precipitate or become absorbed on clay mineral or oxide surfaces, as long as chemical conditions remain the

same. Changes in the metal/Mn and the molar order sequences would be most diagnostic and any change in metal distribution caused by pollution. Total metals analysis would not produce data diagnostic of short term changes in metal concentrations.

Analyses of the extractable fraction of the sediments and soils would be most useful for geochemical prospecting for Cr, Cu, Pb, Zn and Cd in areas similar to Pottawatomie County. The concentrations of metals in this fraction would represent accumulations during the long-term weathering of an ore body, if present, and would not be much affected by anthropogenic metal sources. The continuous leaching of metals from a mineral deposit would result in the formation of poorly crystalline hydrous iron and manganese oxides, leachable in dilute HNO_3 . These hydrous oxides increase in crystallinity as they age and their metals may not be available to chelating extractants, like DTPA. Changes in metal/Mn and in the molar order of abundance sequences, as well as high metal concentrations, would be most diagnostic of metal anomalies.

REFERENCES

- Ashry, M. M., 1973, Occurrence of Li, B, Cu and Zn in Some Egyptian Nile sediments: *Geochim. et Cosmochim. Acta*, v. 37, p. 2449 - 2458.
- Alther, G. R., 1975, Geochemical analysis of streamsediment as a tool for environmental monitoring: a pigyard case study: *Geol. Soc. America Bull.*, v. 86, p. 174-176.
- Beavington, F., 1973, Contamination of soil with zinc, copper, lead and cadmium in the Wollongong City area: *Australian Jour. Soil Research*, v. 11, p. 27-31.
- Carroll, R. E., 1969, The relationship of cadmium in the air to cardiovascular death rates: *Jour. American Medical Assoc.*, v. 189, p. 267-269.
- Collinson, C. and Shimp, N. F., 1972, Trace metals in bottom sediments from upper Peoria Lake, middle Illinois River - a pilot project: *Illinois Geol. Survey, Environmental Geol. Notes No. 56*, Urbana, Illinois, 21 p.
- Connor, J. J., Kieth, J. R. and Anderson, B. M., 1976, Trace metal variations in soils and sagebrush in the Powder River Basin, Wyoming and Montana: *Jour. Research U.S. Geol. Survey*, v. 4, p. 49-59.
- Connor, J. J. and Shacklette, H. T., 1975, Background geochemistry of some rocks, soils, plants and vegetables in the conterminous United States: *Statistical studies in field geochemistry: U.S. Geol. Survey Prof. Paper 475 - F*, Washington, D. C., 168 p.
- Fischer, R. B., 1956, *Quantitative chemical analysis: W. B. Saunders Co., Philadelphia, Pennsylvania*, p. 111-112.
- Flanagan, F. J., 1973, 1972 values for international geochemical reference samples: *Geochim. et Cosmochim. Acta*, v. 37, p. 1189-1200.
- Frye, J. C. and Shimp, N. F., 1973, Major, minor and trace elements in sediments in Late Pleistocene Lake Saline compared with those in Lake Michigan sediments: *Illinois Geol. Survey, Environmental Geol. Notes No. 60*, Urbana, Illinois, 14 p.
- Griffiths, J. C., 1967, *Scientific methods in analysis of sediments: McGraw - Hill, New York, New York*, p. 76-77.
- Hawkes, H. E. and Webb, J. S., 1962, *Geochemistry in mineral exploration: Harper and Rowe, New York, New York*, 415 p.
- Helz, G. R., 1976, Trace metal inventory of the northern Chesapeake Bay with emphasis on the influence of man: *Geochim. et Cosmochim. Acta*, v. 40, p. 573-580.

- Hem, J. D., 1972, Chemistry and occurrence of Cd and Zn in surface waters: *Water Resources Research*, v. 8, p. 661-679.
- Hem, J. D., 1976, Geochemical controls on lead concentrations in stream water and sediments: *Geochim. et Cosmochim. Acta*, v. 40, p. 599-609.
- Hesse, P. R., 1971, A textbook in soil chemical analysis: Chemical Publishing Co., New York, New York, 520 p.
- Jenne, E. A., 1968, Controls on Fe, Mn, Co, Ni, Cu and An concentrations in soils and waters: the significant role of hydrous Mn and Fe oxides, *in* Trace inorganics in water - a symposium: American Chem. Soc. *Advances in Chemistry Series No. 73*, p. 337-387.
- Kaback, D. S., 1976, Transport of molybdenum in mountainous streams, Colorado: *Geochim. et Cosmochim. Acta*, v. 40, p. 581-582.
- Kansas Power and Light Company, 1973, A new electric energy center for the Kansas Power and Light Company: The Kansas Power and Light Co., Topeka, Kansas, 101 p.
- Krauskopf, K. B., 1972, Geochemistry of micronutrients, *in* Micronutrients in agriculture - a symposium: Soil Sci. Soc. America, Inc., Madison, Wisconsin, p. 7-40.
- Krumbein, W. C, and Sloss, L. L., 1963, Stratigraphy and sedimentation: W. H. Freeman and Company, San Francisco, California, p. 153.
- Kunselman, G. C. and Hugg, E. A., 1976, The determination of arsenic, antimony, selenium and tellurium in environmental water samples by flameless atomic absorption: *Atomic Absorption Newsletter*, v. 15, p. 29-32.
- Kutnink, P. R., in preparation, Soil survey of Pottawatomie County, Kansas, U. S. Dept. of Agriculture, Soil Conservation Service, Westmoreland, Kansas.
- Leopold, L. B., Wolman, G. M. and Miller, J. P., 1964, Fluvial processes in geomorphology: W. H. Freeman and Co., San Francisco, California, p. 203-215.
- Lindsey, W. L. and Norvell, W. A., 1969, Development of the DTPA micronutrient soil test: *Agronomy Abstracts*, v. 69, p. 84.
- Mills, J. G. and Zwarich, M. A., 1975, Heavy metal content of agricultural soils in Manitoba: *Canadian Jour. Soil Sci.*, v. 55, p. 295-300.
- Rankama, K. and Sahama, T. G., 1955, Geochemistry: Chicago University Press, Chicago, Illinois, p. 226.

- Rantala, R. T. T. and Loring, D. H., 1975, Multi-element analysis of silicate rocks and marine sediments by atomic absorption spectrophotometry: *Atomic Absorption Newsletter*, v. 14, p. 117-120.
- Reddy, M. R. and Perkins, H. F., 1976, Fixation of manganese by clay minerals: *Soil Sci.*, v. 121, p. 21-24.
- Ruch, R. R., Gluskoter, H. G. and Shimp, N. F., 1974, Occurrence and distribution of potentially volatile trace elements in coal, a final report: *Illinois Geol. Survey, Environmental Geol. Note No. 72*, Urbana, Illinois, 96 p.
- Runnels, R. T. and Schleicher, J. A., 1956, Chemical composition of eastern Kansas limestones: *Kansas Geol. Survey Bull.* 119, pt. 8, p. 81-103.
- Scott, G. R., Foster, F. W. and Crumpton, C. F., 1959, Geology and construction material resources of Pottawatomie County, Kansas: *U.S. Geol. Survey Bull.* 1060 - C, p. 97-178.
- Schroeder, H. A., 1965, The biological trace elements of peripatetics through the periodic table: *Jour. Chronic Diseases*, v. 18, p. 217-228.
- Shuman, L. M. and Anderson, O. E., 1974, Evaluation of six extractants for their ability to predict manganese concentrations in wheat and soybeans: *Soil Sci Soc. America Proc.*, v. 38, p. 788-790.
- Singh, B. R. and Steinnes, E., 1976, Uptake of trace metals in barley in zinc-polluted soils 2: Pb, Cd, Hg, Se, As, Cr and V in barley: *Soil Sci.* v. 121, p. 38-43.
- Sinton, J. M., 1977, Equilibration history of the basal alpine-type peridotite, Red Mountain, New Zealand: *Jour. Petrology*, v. 18, p. 216-246.
- Suarez, D. L. and Langmuir, D., 1976, Heavy metal relationships in a Pennsylvania soil: *Geochim. et Cosmochim. Acta*, v. 40, p. 588-598.
- Switek, J. and Whittemore, D. O., 1977, Heavy metal distributions in soils, sediments and natural waters in a small watershed in north-eastern Kansas: *Geol. Soc. America Abstracts with Programs*, v. 9, p. 658-659.
- Turekian, K. K. and Wedepohl, K. H., 1961, Distribution of the elements in some major units of the earth's crust: *Geol. Soc. America Bull.*, v. 72, p. 175-192.
- United States Environmental Protection Agency, 1973, 1972 water quality criteria: *U.S. Environmental Protection Agency Pub. R2-73-033*, Washington, D. C., 599 p.

- United States Environmental Protection Agency, 1976, Draft environmental impact statement for proposed steam electric power plant, George Neal Steam Electric Station, Neal Unit No. 4, Port Neal Industrial District, Salix County, Iowa: U. S. Environmental Protection Agency Pub. 907/9-76-002, 611 p.
- Vinogradov, A. P., 1959, The geochemistry of rare and idspersed chemical elements in soils, 2nd ed., (from Russian): New York Consultant Bureau, 209 P. (Original published by Akad. Nauk S. S. S. R., Moscow, 1957, 238 p.), in Hawkes and Webb, 1962, Geochemistry in mineral exploration: Harper and Rowe, New York, New York, p. 359-377.
- Whittemore, D. O. and Langmuir, D., 1974, Ferric oxyhydorxide microparticles in water: Environmental Health Perspective, v. 9., p. 173-176.
- Whittemore, D. O. and Switek, J., 1977, Geochemical controls on trace element concentrations in natural waters of a proposed coal ash landfill site: Kansas Water Resources Research Inst. Contribution No. 188, Manhattan, Kansas, 76 p.
- Zeller, D. E., 1968, The stratigraphic succession in Kansas: Kansas Geol. Survey Bull. 189, Lawrence, Kansas, 81 p.

APPENDIX I

Appendix 1. Description of Soil Types in the Deep Creek Basin Study Area.

Descriptions from the United States Department of Agriculture,
Soil Conservation Service, Westmoreland, Kansas.

Soil Type: Dwight-Irwin Complex

Map Designation: F28 (1 - 4 percent slopes)

Dwight Series - Nearly level to gentle slopes, deep, moderately well drained, formed in old clayey alluvium and loess on uplands. Surface is dark gray silt loam, 5 inches, subsoil, 30 inches, dark grayish brown clay (upper 17 inches) and brown silty clay (lower 13 inches). Underlying material is pale brown light silty clay, 54 inches, overlying cherty limestone.

Slope 0 - 3%.

Irwin Series - Deep, moderately well drained to well drained, slope 0 - 8% slowly permeable, developed on uplands. A horizon dark grayish brown silty clay loam. B horizon dark gray brown to brown silty clay or clay.

Soil Type: Martin Silt Clay

Map Designation: F23B (1 - 4 percent slopes)
F23C (4 - 8 percent slopes)

Martin Series - deep, dark colored, moderately well drained soil on uplands. Surface, very dark brown or black silty clay loam, 14 inches. Subsoil 34 inches, very dark grayish brown silty clay mottled with yellowish brown (upper 23 inches), lower 11 inches is grayish brown silty clay mottled with yellowish brown and brown. Bedrock at 48 inches. Formed from weathered, interbedded silty and clayey shales. Slope 2 - 10%.

Soil Type: Kipson-Sogn Complex

Map Designation: 2D

Kipson Series - shallow, excessively drained upland soils. Surface, dark grayish brown silt loam, 7 inches. Subsurface, grayish brown shaley silt loam, 8 inches. Total thickness 7 - 20 inches. Developed on silty shale and limestone. Slope 1 - 25%.

Sogn Series - very shallow to shallow, excessively drained upland soils. Surface, very dark gray silty clay loam, 9 inches. Derived from weathered limestone. Slope 0 - 8%.

Soil Type: Oska-Sogn Complex

Map Designation: 12D

Oska Series - moderately deep, well drained soils on upland. Surface, dark grown silty clay loam, 7 inches. Subsoil, dark reddish brown silty clay loam, 4 inches, reddish brown clay, 23 inches. Derived from interbedded limestone and calcareous shale. Slopes 1 - 8%.

Sogn Series - as above.

Soil Type: Wabash Silt Clay

Map Designation: 1F2

Wabash Series - deep, very poorly drained, very slowly permeable soils. Surface, very dark brown silty clay. Subsurface, very dark gray to dark gray or black silty clay. Found in low areas of large floodplains. Slopes less than 1 percent.

TRACE METAL DISTRIBUTIONS IN ROCKS, STREAM
SEDIMENTS AND SOILS OF THE DEEP CREEK BASIN,
POTTAWATOMIE COUNTY, KANSAS

by

JOHN SWITEK

B. S., Pennsylvania State University, 1974

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1977

Metal distributions were studied in surficial materials from a small, upland drainage basin in Pottawatomie County, Kansas near the construction site of the large, coal-fueled power plant of the Kansas Power and Light Company. The purpose of the investigation was to establish baseline metal concentrations and to determine the geochemical controls on metal mobility in the area. The soils and sediments were derived from limestone and shale bedrock and a thin cover of glacial till. The concentrations of Fe, Mn, Cr, Cu, Pb, Zn, Cd, As and Se were determined by atomic absorption spectrophotometry in the exchangeable (DTPA), extractable (dilute HNO_3) and total metal fractions of rock, stream sediment and soil samples. Correlation analyses were made for the metal concentrations and pH, cation exchange capacity, organic matter content, carbonate and particle size classes.

The total metal concentrations for all samples ranged from 0.42 - 3.34 weight percent for Fe, 226 - 1730 ppm for Mn, 11 - 106 ppm for Cr, Cu, Pb, and Zn, and 2ppm for Cd. Molar order of abundance sequences for the total metal concentrations were the same for the rocks, sediments and soils (Fe Mn Cr Zn Cu Pb). The molar sequences for the extractable fraction of the rocks (Fe Mn Cr Zn_Pb Cu As Cd), sediments (Fe Mn Cr Zn Cu_Pb_As Cd) and soils (Fe Mn Zn Cr-Cu Pb As Cd) are, basically, similar to the total metals sequence. The molar sequences for the exchangeable fraction of the sediments (Mn Fe Cu Pb=As Zn=Se Cd Cr) and soils (Mn Fe Cu Zn Pb Cr_Cd Se) are distinctly different from the total metals sequence.

In the rocks, Mn, Cr, and Pb Occurred primarily in carbonates and acid soluble oxides whereas Fe, Cu, and Zn occurred mainly in acid insoluble clays and oxides. In the sediments and soils, all metals, except Mn, occurred primarily in the acid insoluble phases whereas Mn apparently occurred primarily as an acid-soluble oxide.

Both the sediments and soils had higher total Fe, Mn, Pb, and Zn, but lower Cr contents than the rocks. Also, the sediments and soils had higher extractable concentrations of all metals, except Cr, Cu, and Pb, than the rocks. The extractable fraction of the sediments contained higher amounts of all metals, except Zn and Cd, than did the same fraction of the soils. In the exchangeable fraction, the soils contained higher concentrations of all metals, but Se, than the sediments.

Generally, the metals were concentrated during bedrock weathering through the dissolution of carbonate, but the distribution of metals in the sediments and soils remained, largely, the same as in the parent material. The distribution of metals in the exchangeable fractions reflected the relative stability of mineral or colloid surfaces under the existing chemical conditions. The differences in metal distribution between the same fractions of the sediments and soils were related to differences in the physical environments of the deposits.