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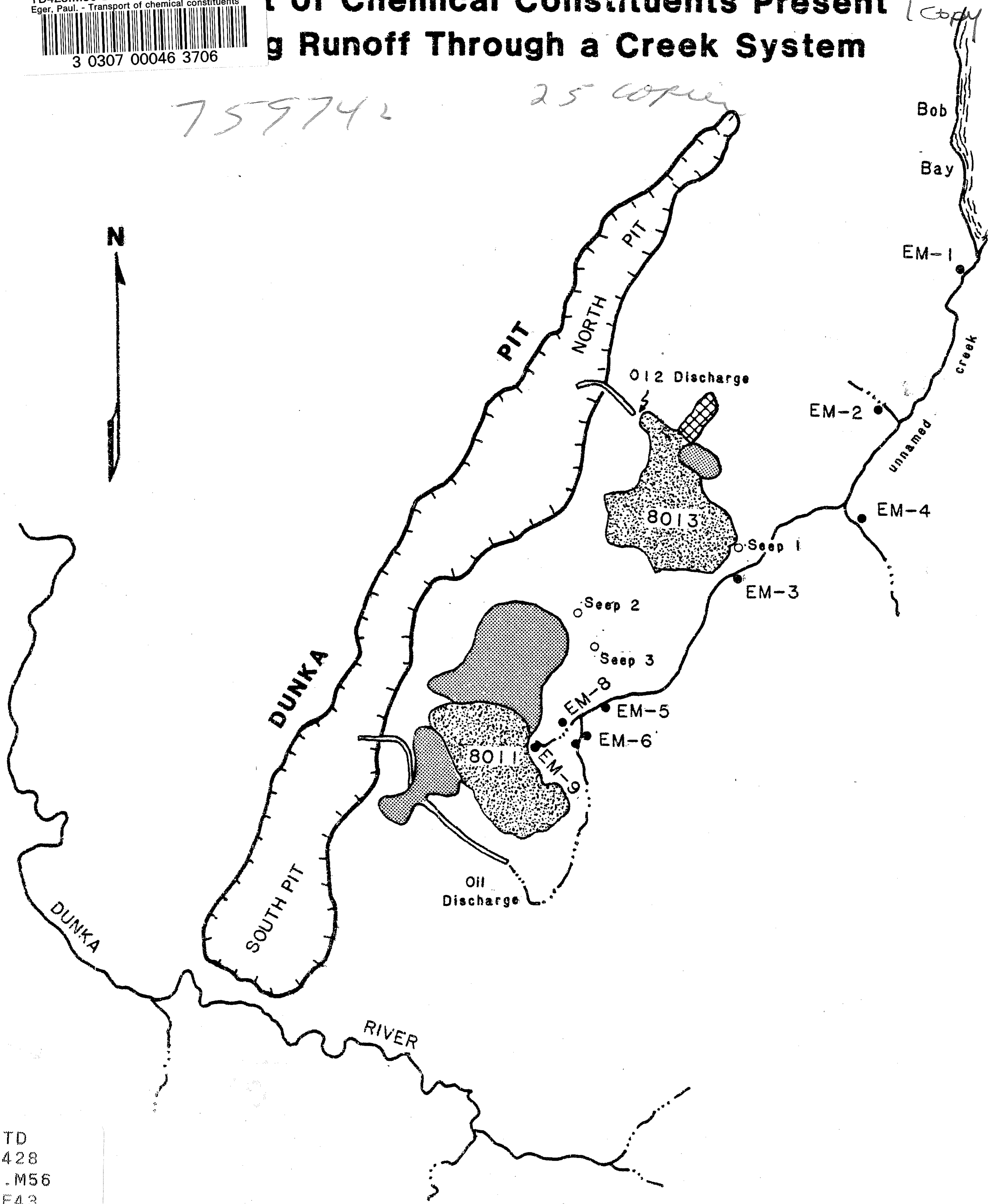

nnesota Department of Natural Resources
Division of Minerals 1980

TRANSPORT OF CHEMICAL CONSTITUENTS PRESENT IN MINING RUNOFF THROUGH A CREEK SYSTEM

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Minnesota Department of Natural Resources
Division of Minerals

1980

Acknowledgements

The data presented in this report were collected as part of the Minnesota Environmental Quality Board's Regional Copper-Nickel Study. Many people have contributed to the success of our study. Our field staff during the study, directed by Bruce Johnson, did an excellent job. Special thanks goes to Bruce for his outstanding work and dedication (and his willingness to collect critical low flow samples when the wind chill was -40°F). Our stream gaging network would not have operated successfully without the assistance of the USGS in Grand Rapids, particularly Bill Gothard and Don Erickson. Erie Mining Company's cooperation in this study has been much appreciated. Their willingness to assist us and their interest in our project have been most helpful. We would also like to thank the Minerals Division in Hibbing for its help with our stream sediment and peat sampling program. Thanks goes to Dave Meineke for his suggestions and budget balancing, Marty Vadis for his help collecting samples, and Al Kalysmat for sample analysis. A final statement of gratitude is extended to Sue Schmidt who is responsible for transforming this, and numerous other works, from cryptic script to an excellent state of legibility.

Abstract

Field studies and computer modeling (REDEQL2) were used to investigate the transport of copper, nickel, cobalt and zinc through a bog-creek system receiving water impacted by mining operations. Field studies indicated that transport of nickel was greater than copper through both the bog (10-70% vs. 0-14%) and the stream (60-100% vs. 26-51%). Aqueous and solid phase analyses indicate that metal removal resulted from adsorption onto peat, organic stream banks, and clastic sediments. Computer results are consistent with field results and further suggest that zinc would behave similar to nickel, and cobalt similar to copper.

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SEPARATE VOLUME

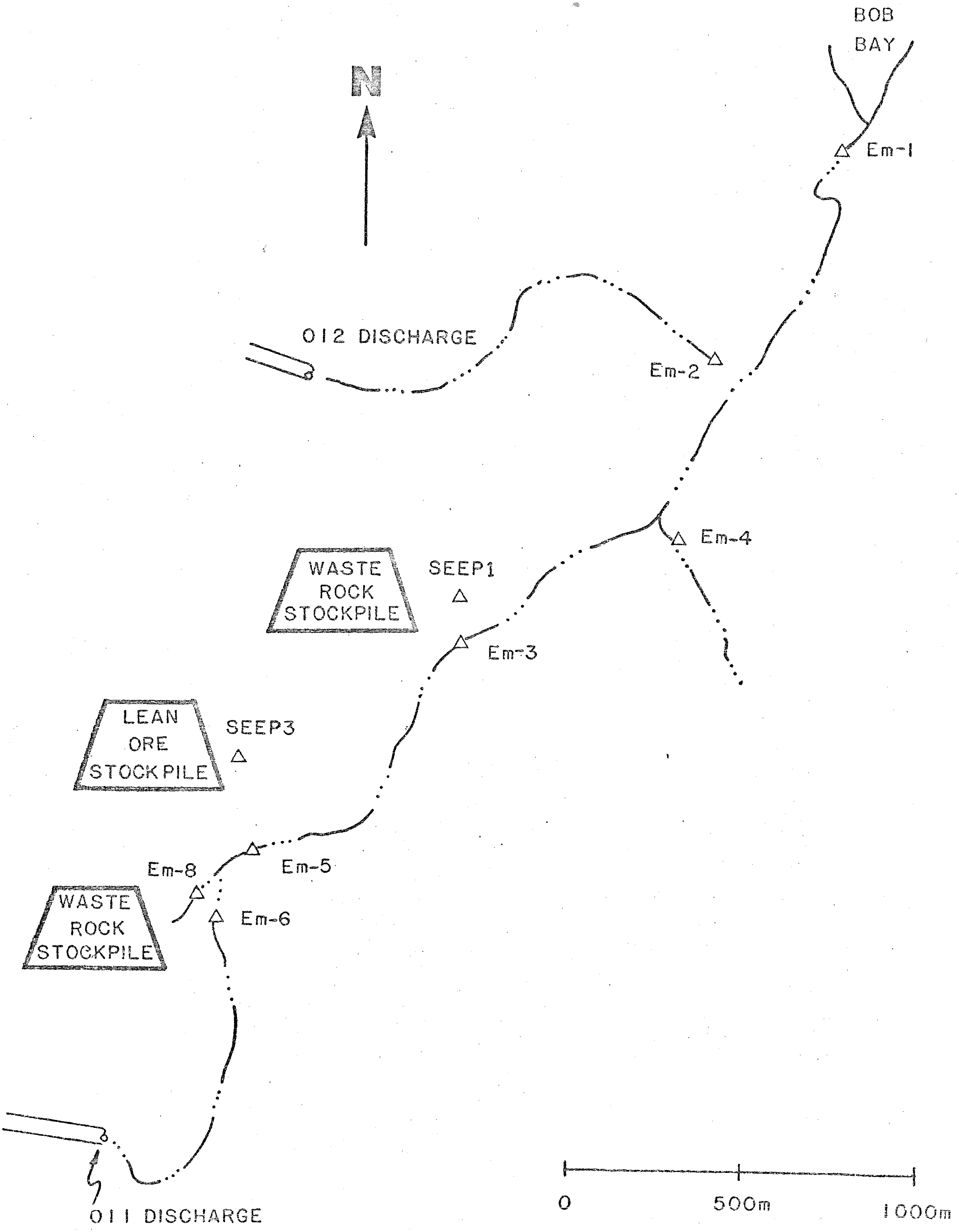
1. INTRODUCTION

The transport of copper, nickel, and sulfate along a 4.3 km creek (Unnamed Creek) was studied using water quality samples, sediment analyses, bog sampling and chemical equilibrium modeling. The study was conducted at the Erie Mining Company Dunka Site in northeastern Minnesota from July 1976 through August 1977 (Figure 1). Data collection continues in a joint program conducted by Erie Mining Company and the Minnesota Department of Natural Resources. Related information regarding regional background data, gabbro leaching, chemical transport, stockpile hydrology, and stockpile revegetation is available in other references (1-12).

Trace metals in aquatic systems may be transported as free metals, or as inorganic or organic complexes. They may be chemically removed from solution by precipitation, coprecipitation, by adsorption onto inorganic or organic solids (Figure 2), and by inorganic exchange reactions. Precipitating iron oxides may coprecipitate other trace metals by incorporating them into the solid matrix (21, 22). Inorganic adsorptive surfaces include SiO_2 (13-18), MnO_2 (19), TiO_2 (16, 17), and FeO_x (20). The sequestration of aqueous trace metals by organic surfaces such as peat has also been documented in field (28-30) and laboratory studies (31-43). Aqueous trace metals can also exchange with metals present as sulfides of greater solubility (23-27), e.g.

$$Cu^{2+}(aq) + ZnS(s) = CuS(s) + Zn^{2+} \qquad (1)$$

Figure 1. Stream sampling sites.



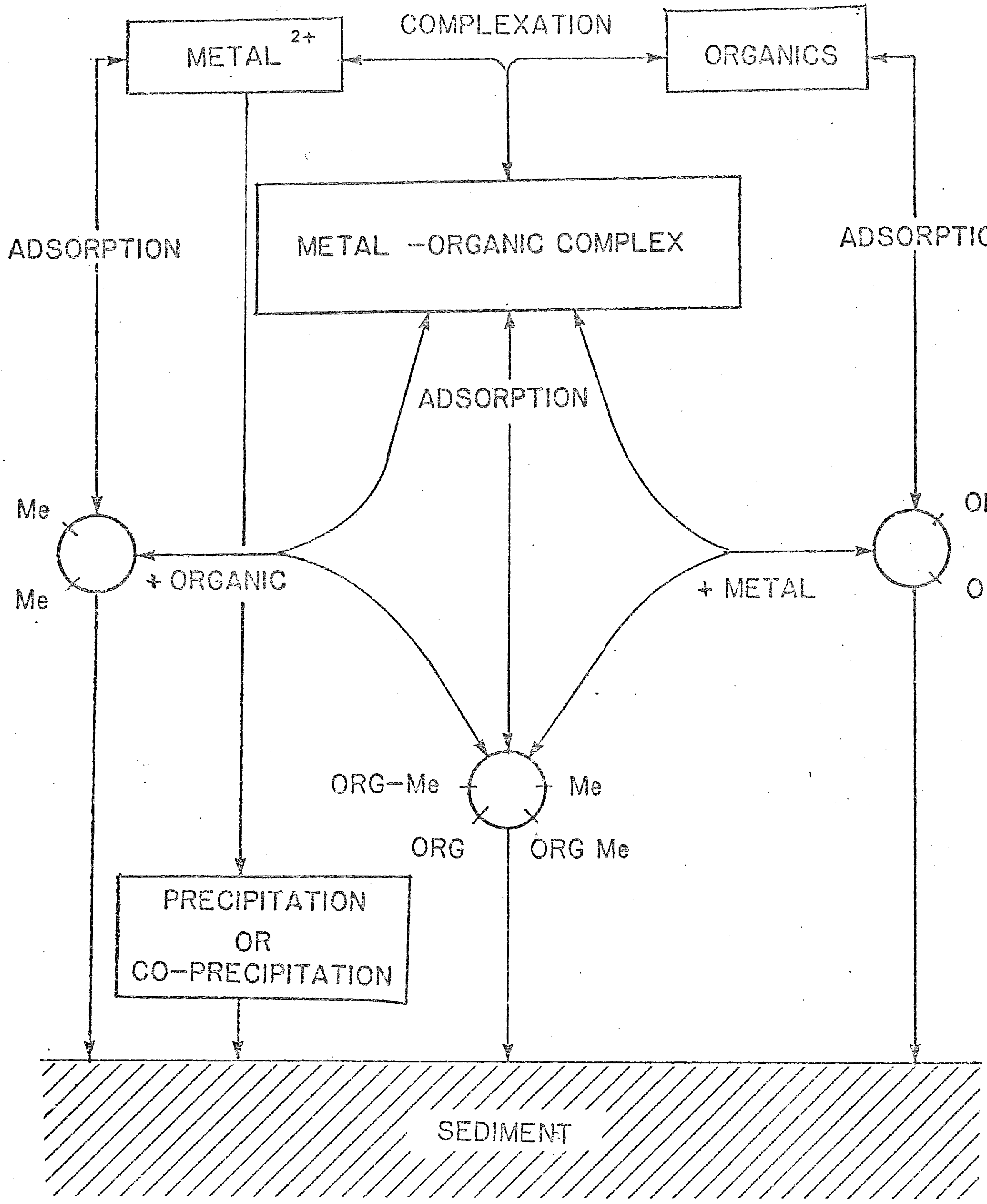


Figure 2.
Major reaction pathways for trace metal transport and deposition in sediments in natural aquatic systems. From Davis and Leckie, 1978.

The presence of soluble organics may increase or decrease trace metal adsorption (20). Trace metal-organic interaction has been extensively studied and reviewed (44-46). The extent of reaction is dependent in part on pH and hardness (47,48).

Researchers have attempted to model the chemistry of natural waters using laboratory experiments (49), and empirical and conceptual models (50, 51). Computer equilibrium models such as WATEQ2 (52), GEOCHEM (53), and REDEQL2 (54, 56) have also been employed, and the predictions of these programs compared (55).

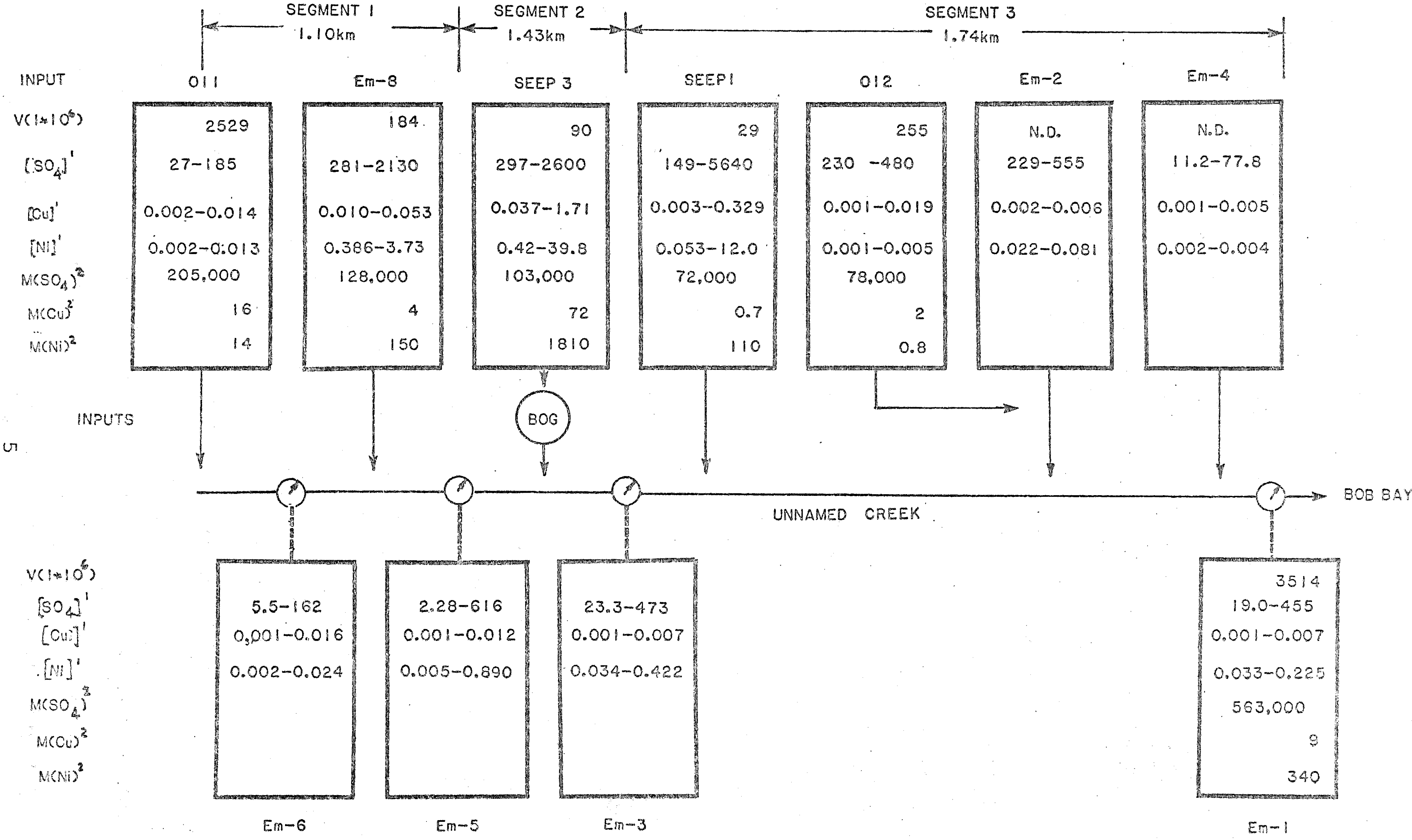
2. METHODS

2.1 Description of field study

The inputs and creek monitoring stations along Unnamed Creek and characteristic data are presented in Figure 3, with more detailed data in Table 1. The inputs included two waste rock pile seepages (EM-8, Seep 1), one lean ore pile seepage (Seep 3), two mine dewatering discharges (011, 012) and runoff from the watershed. The inputs flowed directly into the creek with the exception of the lean ore stockpile seepage (Seep 3) which first passed through a bog. The monitoring stations (EM-5, EM-3, EM-1) divided the creek into three segments prior to its discharge into Bob Bay of Birch Lake (Figures 1, 3).

Water quality was analyzed and flow measured at 11 sites along Unnamed Creek (Figure 1). Routine water quality samples were collected biweekly, although several special studies were conducted which required more intensive sampling (Appendices II, IV). Continuous flow records were obtained for E[illegible] EM3, EM8, and the 011 and 012 discharges. Staff readings were taken at least once every two weeks at the other sites.

Figure 3 .Concentrations and mass flux for Unnamed Creek inputs and stream stations (not to scale)



INPUT	011	Em-8	SEEP 3	SEEP 1	012	Em-2	Em-4
$V(l*10^6)$	2529	184	90	29	255	N.D.	N.D.
$[SO_4]^1$	27-185	281-2130	297-2600	149-5640	230 -480	229-555	11.2-77.8
$[Cu]^1$	0.002-0.014	0.010-0.053	0.037-1.71	0.003-0.329	0.001-0.019	0.002-0.006	0.001-0.005
$[Ni]^1$	0.002-0.013	0.386-3.73	0.42-39.8	0.053-12.0	0.001-0.005	0.022-0.081	0.002-0.004
$M(SO_4)^2$	205,000	128,000	103,000	72,000	78,000		
$M(Cu)^2$	16	4	72	0.7	2		
$M(Ni)^2$	14	150	1810	110	0.8		

	Em-6	Em-5	Em-3	Em-1
$V(l*10^6)$				3514
$[SO_4]^1$	5.5-162	2.28-616	23.3-473	19.0-455
$[Cu]^1$	0.001-0.016	0.001-0.012	0.001-0.007	0.001-0.007
$[Ni]^1$	0.002-0.024	0.005-0.890	0.034-0.422	0.033-0.225
$M(SO_4)^2$				563,000
$M(Cu)^2$				9
$M(Ni)^2$				340

1. mg/l,range of concentrations, total metals

2. mass flux(kg) from 7/76-8/77

Table 1. Median Values At Erie Sites, 1976-1977[1]

Site	Q	N	SO_4	N	Cu	N	Ni	N	Co	N	Zn	N	pH	N	DOC	N	DIC	N	TALK	N
011[2]			72	14	0.004	14	0.005	14												
EM-6	26.6[3]	19	106	17	0.004	19	0.005	14	0.002	1	0.003	1	7.70	19	9.4	14	17.9	13	94	18
EM-8	4.82	34	1140	24	0.019	33	1.18	33	0.015	8	0.020	10	7.26	34	20.1	22	24.7	22	142	33
EM-5	31.4	21	122	19	0.005	21	0.051	21	0.005	5	0.009	3	7.63	21	12.2	12	20.1	11	101	21
Seep 3	2.10	25	1420	17	0.617	24	19.0	24	0.910	8	0.331	12	7.16	24	19.0	14	28.2	14	109	24
EM-3	93.4	26	155	25	0.003	28	0.110	27	0.002	3	0.009	2	7.65	27	10.5	17	19.8	16	96	27
Seep 1	1.15	26	2470	20	0.018	27	1.10	27	0.130	9	0.249	13	6.95	27	28.0	16	25.2	15	98.8	27
012[2]			250	7	<0.003	7	0.002	7												
EM-4 [4]	14.2	8	77.0	3	0.002	8	0.003	4	-	0	-	0	6.46	8	20.3	7	4.3	7	14.1	8
EM-2	2.62	14	335	13	0.005	14	0.042	14	0.002	1	-	0	7.60	13	11.0	10	16.6	10	96.6	14
EM-1	110	37	159	35	0.002	37	0.087	35	0.002	5	0.010	2	7.50	38	12.7	19	18.5	19	88.0	36

[1] Q in liters/sec, concentrations in mg/l, DOC and DIC in mg/l as C, TALK in mg/ℓ as Ca CO_3

[2] Data from Erie Mining Company

[3] Calculated from data at EM-8 and EM-5

[4] Some samples were influenced by the main stream flow and may not be representative

Clastic sediment samples were taken at four sites along the creek and at one site on the EM-2 tributary (Figure 4). Organic samples were taken from the banks and bottom of the creek and its tributaries (Figure 3) and from the bog through which Seep 3 flowed (Figure 5). Methods are discussed in Appendices IX and X.

2.2 Computer Models

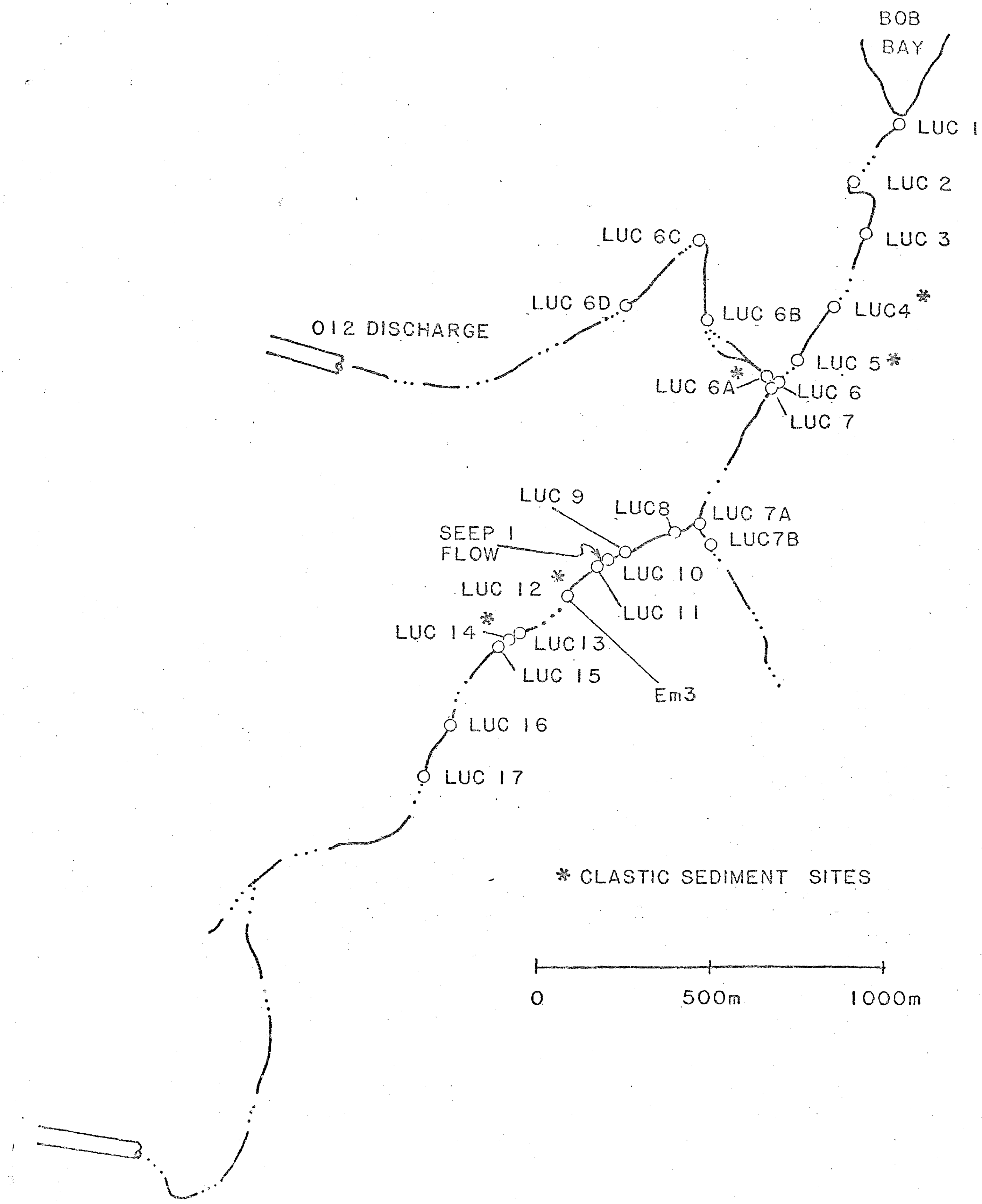
Chemical equilibrium models were generated using the REDEQL2 computer program (Morel and Morgan, 1972; modified by M.R. Hoffman of the University of Minnesota) to investigate the chemical reactions involved in the transport process. The inputs included trace metals (Cu, Ni, Co, Zn, Fe, Mn), major cations (Ca, Mg), inorganic ligands (CO_3, SO_4, Cl, OH), organic ligands (acetic, citric, tartaric, and phtalic acids, cysteine) and an adsorbing surface with the characteristics of silica.

The chemical composition of waters downstream from the chemical inputs is dependent upon:

1) input concentrations
2) the degree of dilution (or concentration, in the case of evaporation), and
3) the net input or removal due to additional sources or chemical reactions.

Trace metals can be transported as free ions (e.g. Me^{2+}) or as inorganic or organic complexes. Removal from solution can occur as a result of chemical precipitation or adsorption onto inorganic (e.g. SiO_2) or organic (e.g. peat) solid surfaces. The extent to which a given reaction occurs is dependent upon the chemistry

Figure 4. Sediment sampling sites



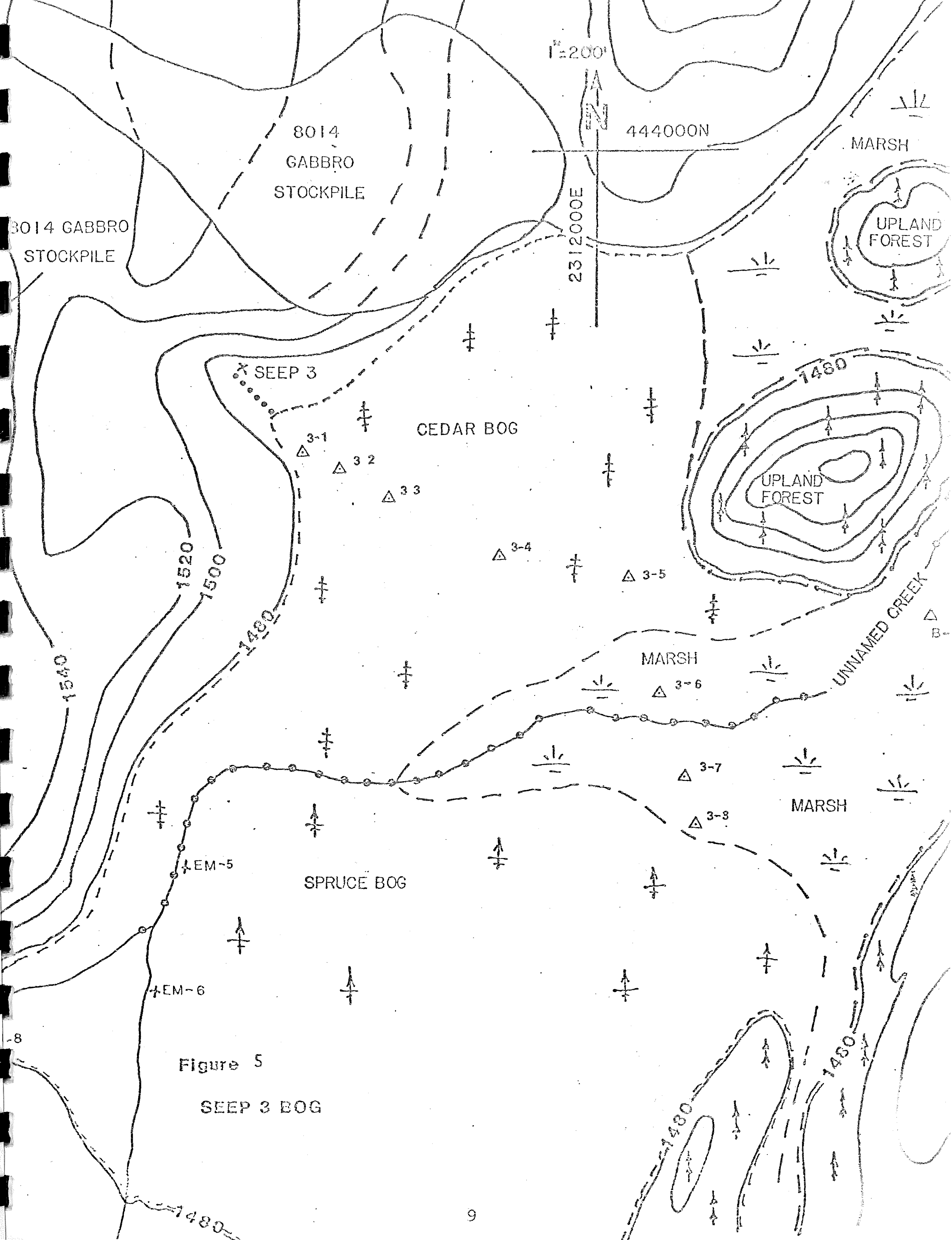


Figure 5

SEEP 3 BOG

of the individual metal, pH, alkalinity, the concentration of complexing organics and the "concentration" of adsorbing surfaces.

The first two data sets considered complexation and precipitation reactions but not adsorption. The input concentrations (Table 2) were intended to simulate conditions observed in runoff from wasterock and lean ore stockpiles (Eger and Lapakko, 1980). Trace metal concentrations in the lean ore leachate were 16 to 80 times that in the waste rock leachate.

Six additional data sets were designed to simulate conditions downstream from a leachate input. The model stockpile leachate concentrations were diluted to 1/2, 1/10, and 1/30 of their original values. These concentrations were input along with values characteristic of Unnamed Creek at EM-1 (pH 7.5, C_T = 100 mg/l as $CaCO_3$, DOC = 14.4 mg/l as C, pe 4.0) and an adsorbing surface (10 M^2/l, Table 3). It was assumed that 10% of the DOC was capable of complexation (Hoffmann, 1978). This fraction of the DOC was divided among the five model organics by allotting each compound an equal amount of carbon. More detailed information on the computer models is presented in Appendix XII.

3. RESULTS

3.1 Field Results

Mass balance calculations (Appendix II) indicated that virtually 100% of the sulfate, 16% of the nickel and 9% of the copper input was transported to the mouth of the Unnamed Creek (Figure 6). The bog downstream from the Seep 3 site removed the largest mass of

Table 2. REDEQL2 Input Data and Predicted Equilibrium Concentrations (mg/l)

	WASTE ROCK LEACHATE		LEAN ORE LEACHATE	
	INPUT	EQUIL	INPUT	EQUIL
SO_4	1680	1680	2600	2600
Cl	41.3	41.3	56.7	56.7
Cu	0.053	0.053	1.71	0.275
Ni	2.42	2.42	39.8	39.8
Co	0.029	0.029	2.40	0.097
Zn	0.040	0.040	2.40	2.40
Fe	0.208	0.096	7.19	0.005
Mn	2.85	2.85	11.2	11.2
Cr	0	0	0.123	0.123
Ca	200	200	346	346
Mg	123	123	268	268
DOC as C	2.09	2.09	1.88	1.88
Ac as C *	0.42	0.42	0.38	0.38
Cit as C *	0.42	0.42	0.38	0.38
Tart as C *	0.42	0.42	0.38	0.38
Cyst as C *	0.42	0.42	0.38	0.38
Phth as C *	0.42	0.42	0.38	0.38
SiO_2(m^2/l)$^+$	0	0	0	0
pH	7.4	7.4	7.2	7.2
CO_3(as Ca CO_3)	137	137	79.4	79.4
pE	4.0	4.0	4.0	4.0

* model organics Ac = acetic acid, Cit = citric acid, Tart = tartaric acid, Phth = phthalic acid, cyst = cysteine

\+ adsorbing surface

Table 3. Adsorption constants for REDEQL2

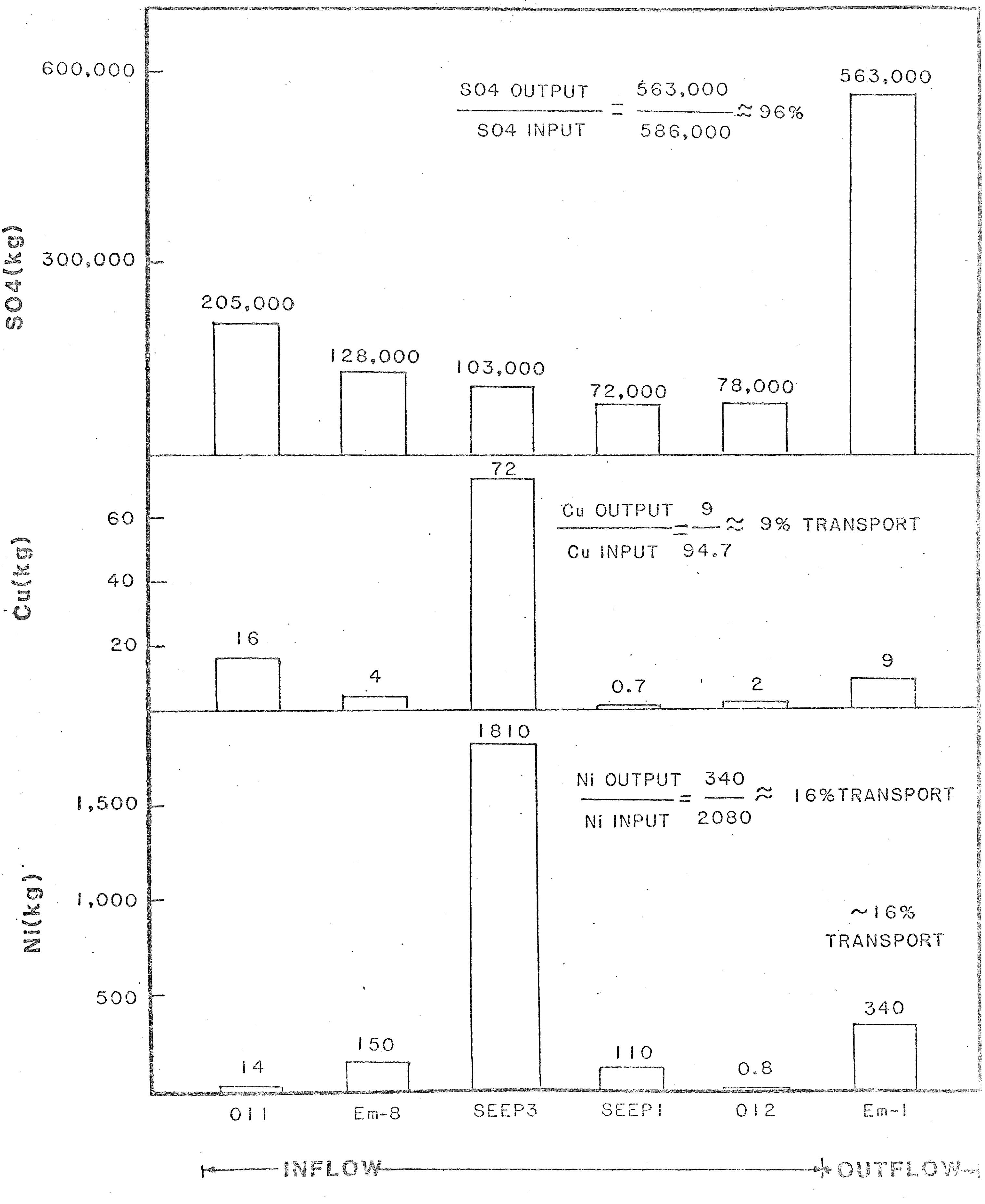
ELEMENT	$\Delta G/RT$	ELEMENT	$\Delta G/RT$
Ca	-12.0	Zn	-11.0
Mg	-12.0	Ni	-11.0
Mn	-13.5	Co	-11.0
Cu	-11.0	Cr	-11.0

Isoelectric pH, ZPC = 3.0

Dielectric constant of surface, $\varepsilon = 4.3$

Figure 6. Mass loading at Erie Mining Company sites

(Calculations for the period July 76--Aug 77)



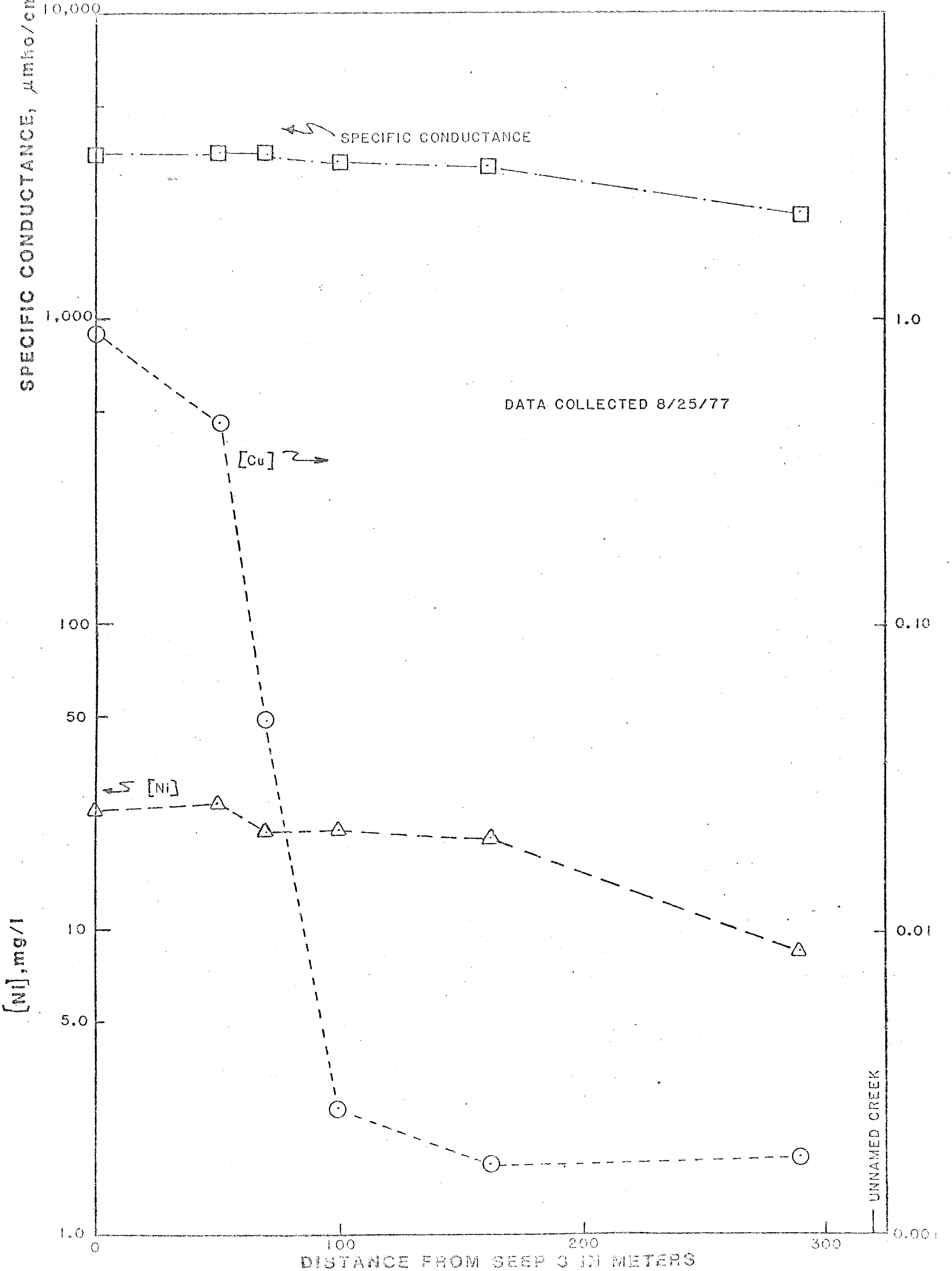
copper and nickel from solution. Additional removal occurred in the stream due to adsorption onto clastic stream sediments, and organic material on the stream banks. Plant uptake probably provided an additional removal mechanism.

3.1.1 Sulfate

Transport calculations indicate that 100% (±10%) of the sulfate input to the creek was transported out of the watershed (Figure 6 and Appendix II). Sulfate inputs from natural sources were insignificant in comparison with inputs from mine dewatering and stockpile seepage (Appendix III).

3.1.2 Nickel

The major source of nickel was the stockpile runoff at Seep 3, with other stockpile seepages (EM-8, Seep 1) as secondary sources (Figure 6). The mass transport was dependent upon the flow path with the majority of nickel removal occurring between Seep 3 and Unnamed Creek. Aqueous nickel concentrations decreased by about 65% over the 300 meter flow path between Seep 3 and the creek, the result of both dilution and removal (Figure 7). Mass balance calculations (59) indicate that 70 to 95% of the nickel discharged from Seep 3 was removed as flow traversed the bog. Analysis of water quality data collected in the bog during August 1977 indicated a 30% nickel removal.



SPECIFIC CONDUCTANCE, μmho/cm
10,000
1,000
100
50
10
5.0
1.0
[Ni],mg/l
1.0
0.10
0.01
0.001
[Cu],mg/l
SPECIFIC CONDUCTANCE
DATA COLLECTED 8/25/77
[Cu]
[Ni]
UNNAMED CREEK
0
100
200
300
DISTANCE FROM SEEP 3 IN METERS

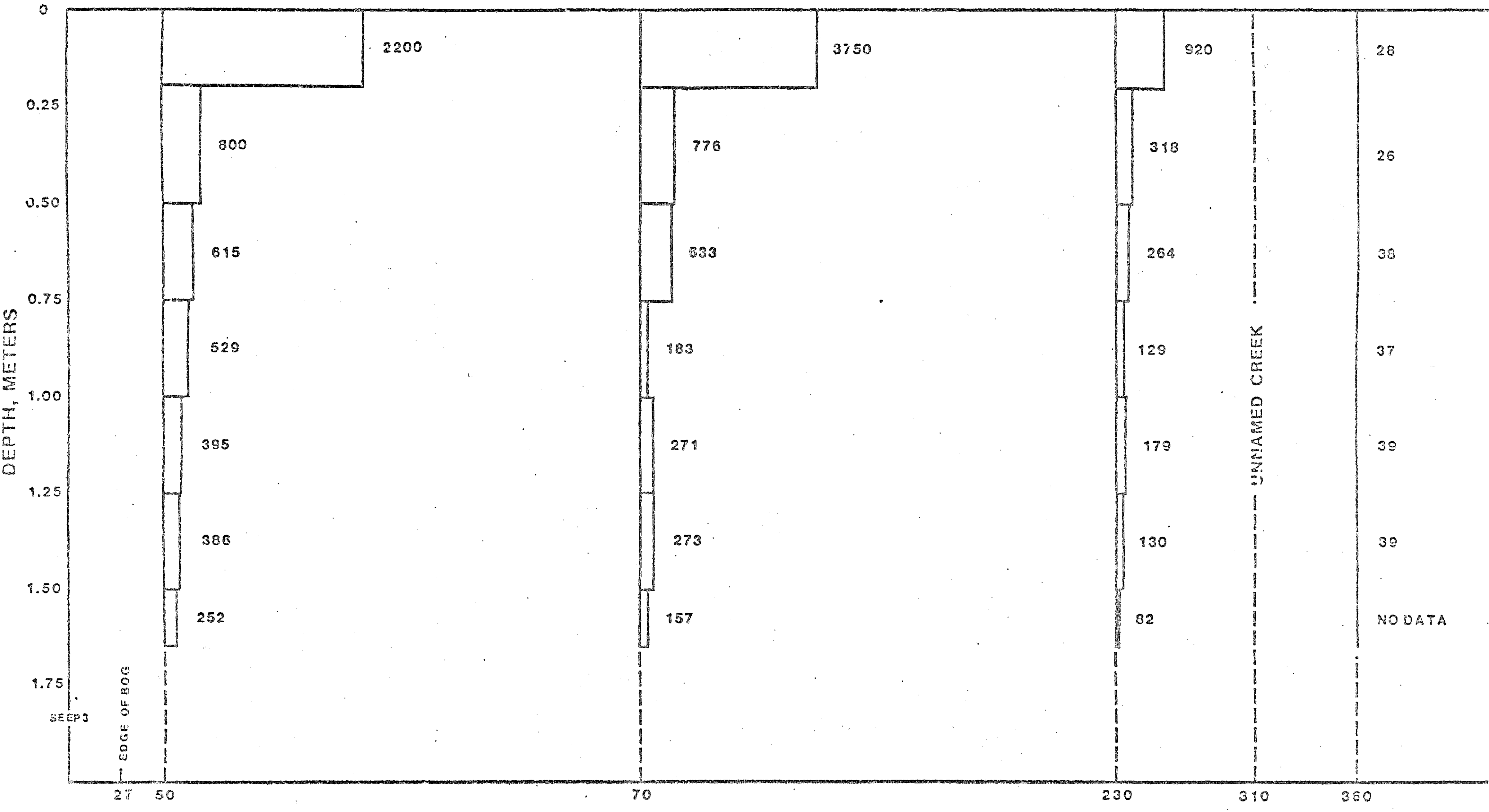
The major mechanism of removal was sequestration by peat, a conclusion supported by analyses of the organic solids in the bog. The majority of trace metal complexation occurred in the top 20 cm. of peat and generally decreased with increasing distance from Seep 3 (Figure 8). Metal analyses of white cedar and alder indicated that metals were also being accumulated in vegetation (59).

Nickel transport from the stockpile seepage at EM-8 was markedly different from that at Seep 3 since the flow did not pass through a bog. No significant removal occurred from the point of seepage to EM-5 (See Appendix IV).

Nickel transport from EM-3 to EM-1 (segment 3) ranged from 60-100% with removal occurring due to complexation and adsorption by organic creek bank material and adsorption by clastic sediments (Table 4). Uptake by aquatic plants may have caused additional removal. Nickel concentrations in the banks along Unnamed Creek (Figure 9) were an order of magnitude higher than in unimpacted streams, a result of the elevated aqueous nickel concentrations in the creek (Figure 10).

Nickel transport over segment 3 varied seasonally, with maximum transport occurring during the winter months (Figure 11). The Seep 3 bog was a major nickel input to segment 3 in the winter as indicated by a marked increase in nickel concentration between EM-3 and EM-5 (Appendix VIII). Seep flow ceased in November but nickel concentrations remained elevated throughout the winter. During the summer months intermittent mine discharge (Appendix VI) caused flooding which resulted in additional contact of stream flow and

FIGURE 8. NICKEL CONCENTRATION# (mg/kg peat) vs DEPTH AND DISTANCE FROM SEEP 3



DISTANCE FROM SEEP 3 (MEASURED ALONG LINE OF SAMPLING STATION), meters

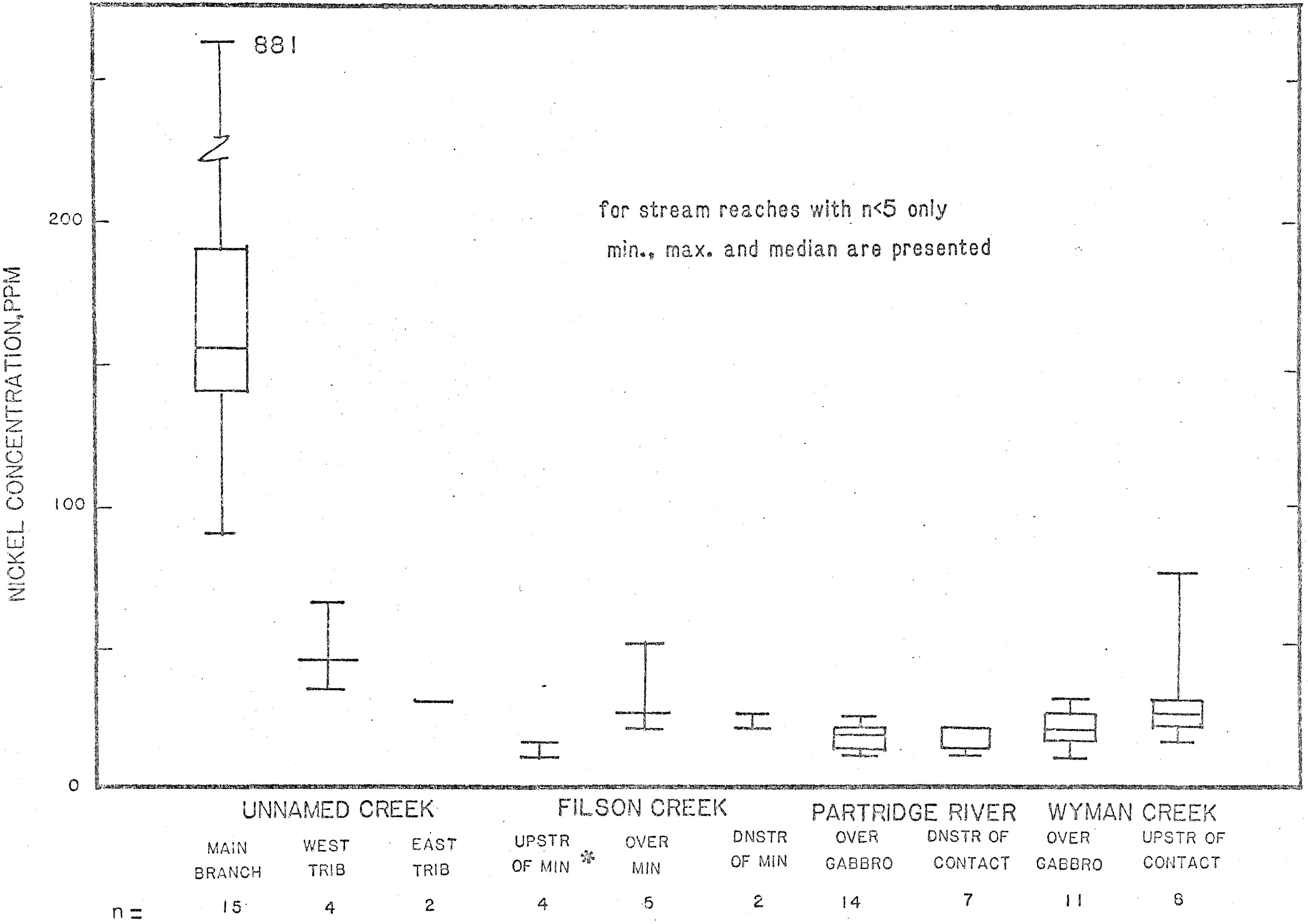
EDTA extraction

Table 4. Typical distribution coefficients from Unnamed Creek

Metal	K^1 cm^3/g Clastics	Organics
Cu	5000-8000	20,000-30,000
Ni	1000-3000	1000-5000
Co	5000-16,000	5000-10,000
Zn	1500-3000	2000-4000
Fe	35,000-50,000	50,000-100,000
Mn	7,000-12,000	4,000-8,000

$$K^1 = \frac{\text{metal concentration in sediment (mg/g)}}{\text{metal concentration in water (mg/cm}^3\text{)}}$$

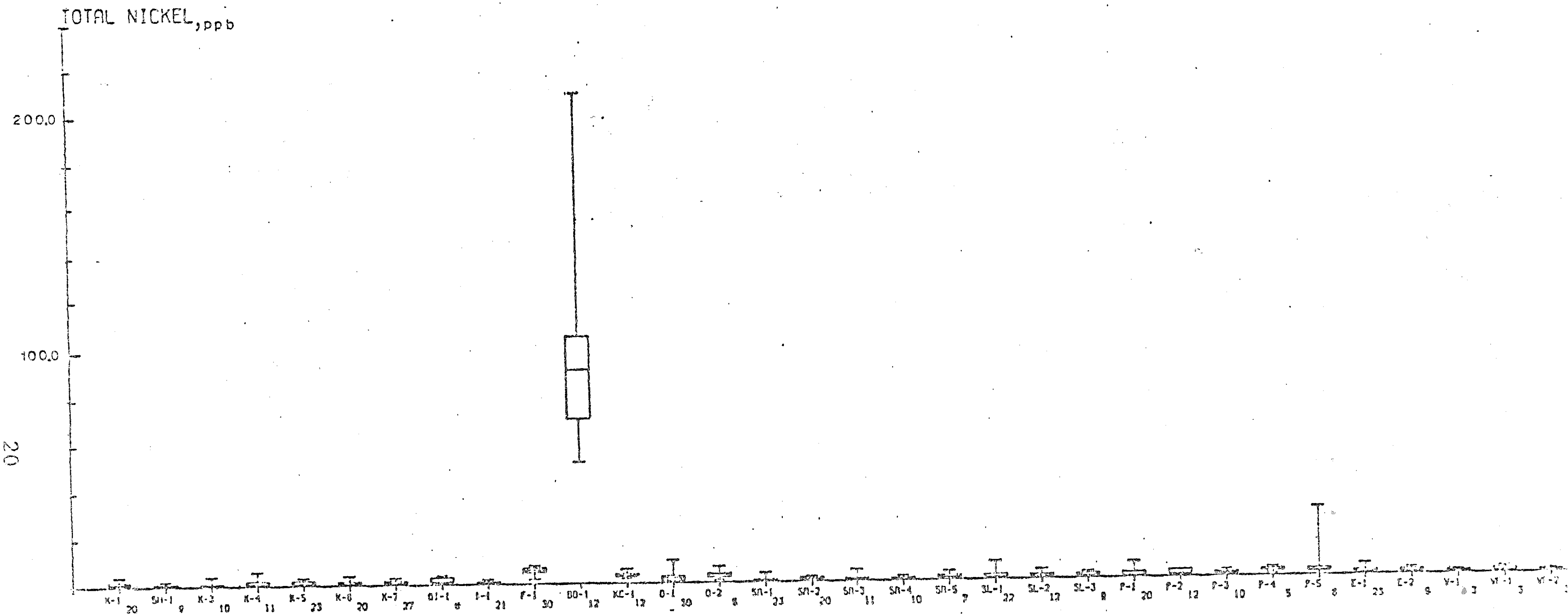
Figure 9. Nickel concentrations in organic bank samples



for stream reaches with n<5 only min., max. and median are presented

* MIN=MINERALIZED ZONE

Figure 10. Trace metal concentrations in regional streams (From the Regional Copper-Nickel Study, unpublished figure).



Numbers below x axis represent the number of samples.

K	Kawishiwi River	D	Dunka River
SH	Shagawa River	SR	Stony River
BI	Bear Island River	SL	Saint Louis River
I	Isabella River	P	Partridge River
F	Filson Creek	E	Embarass River
BB-1	Unnamed Creek at Em-1	W	Water Hen Creek
KC	Keeby Creek	WF	White Face River

Figure 10 (Contd.)

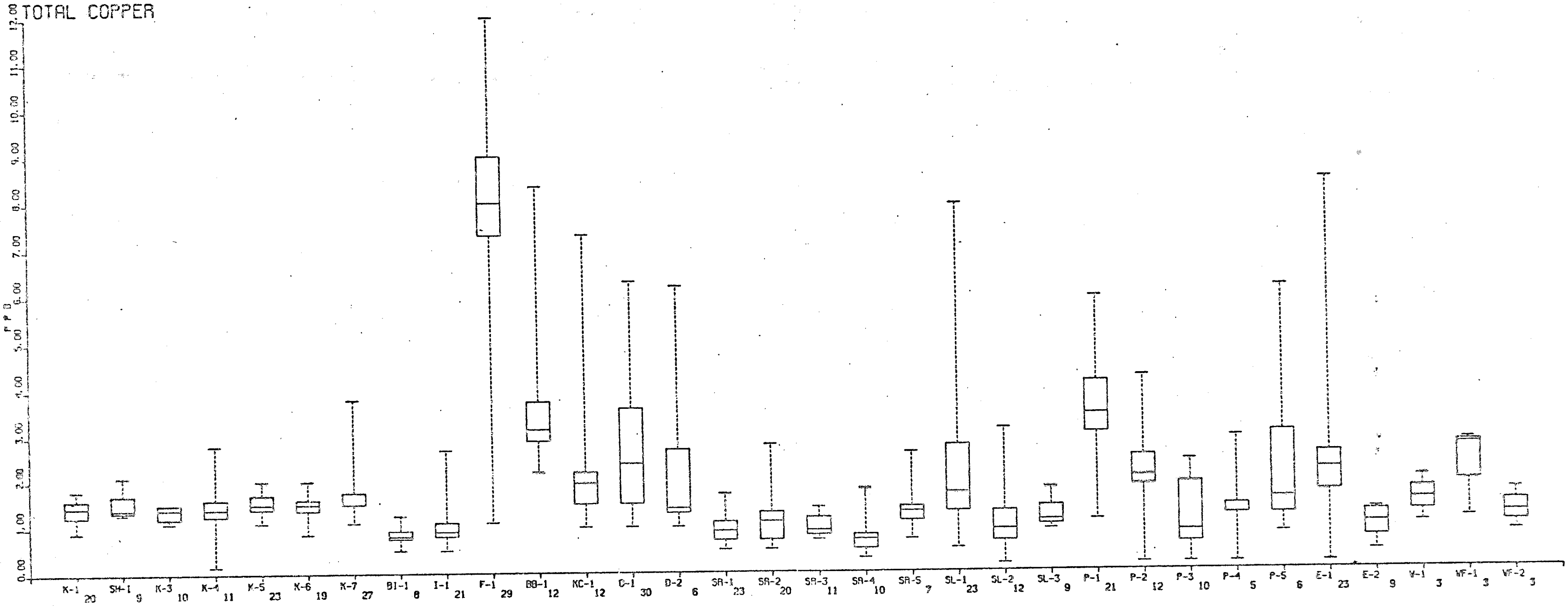
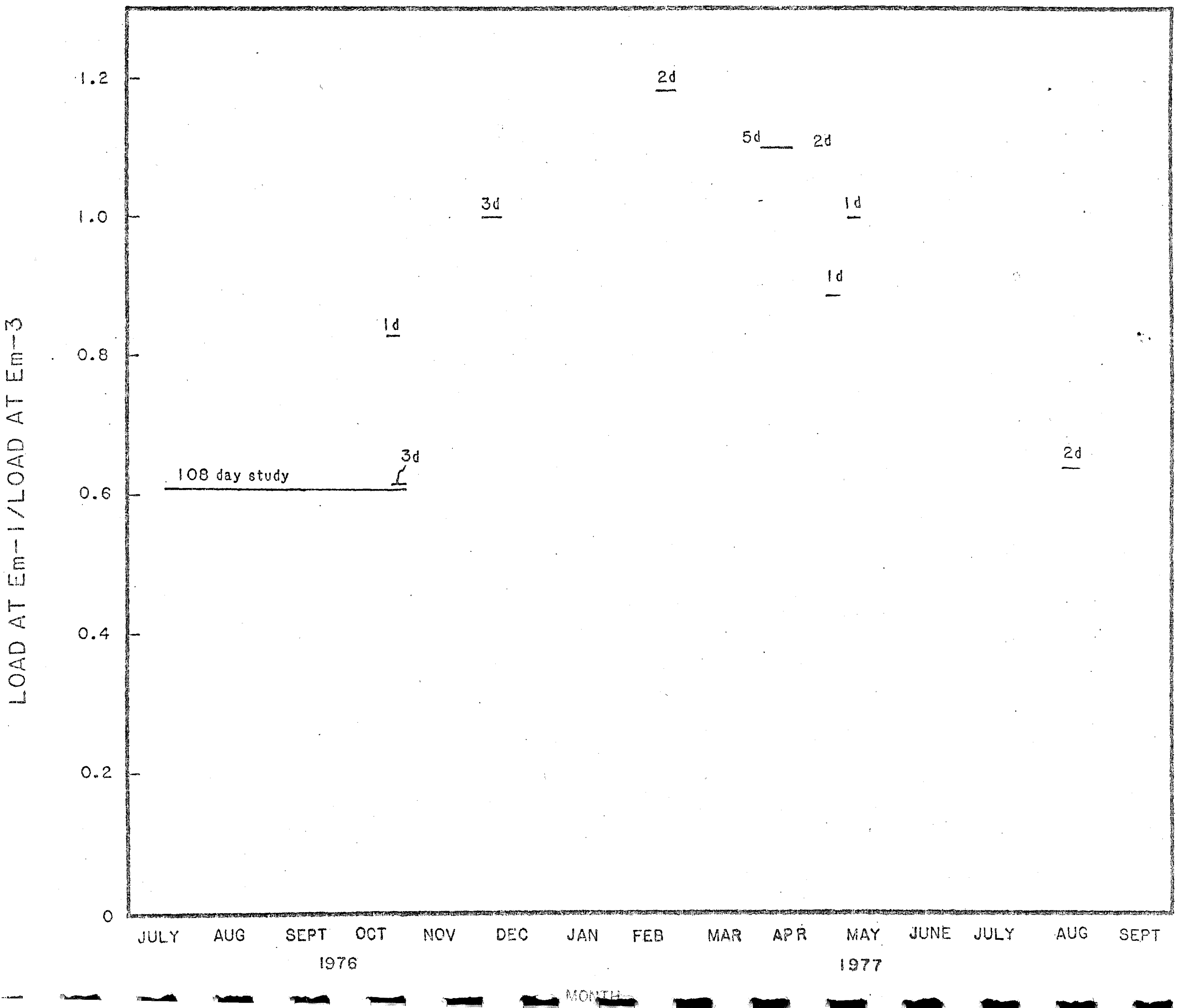


Figure 11. Nickel transport over segment 3 vs time



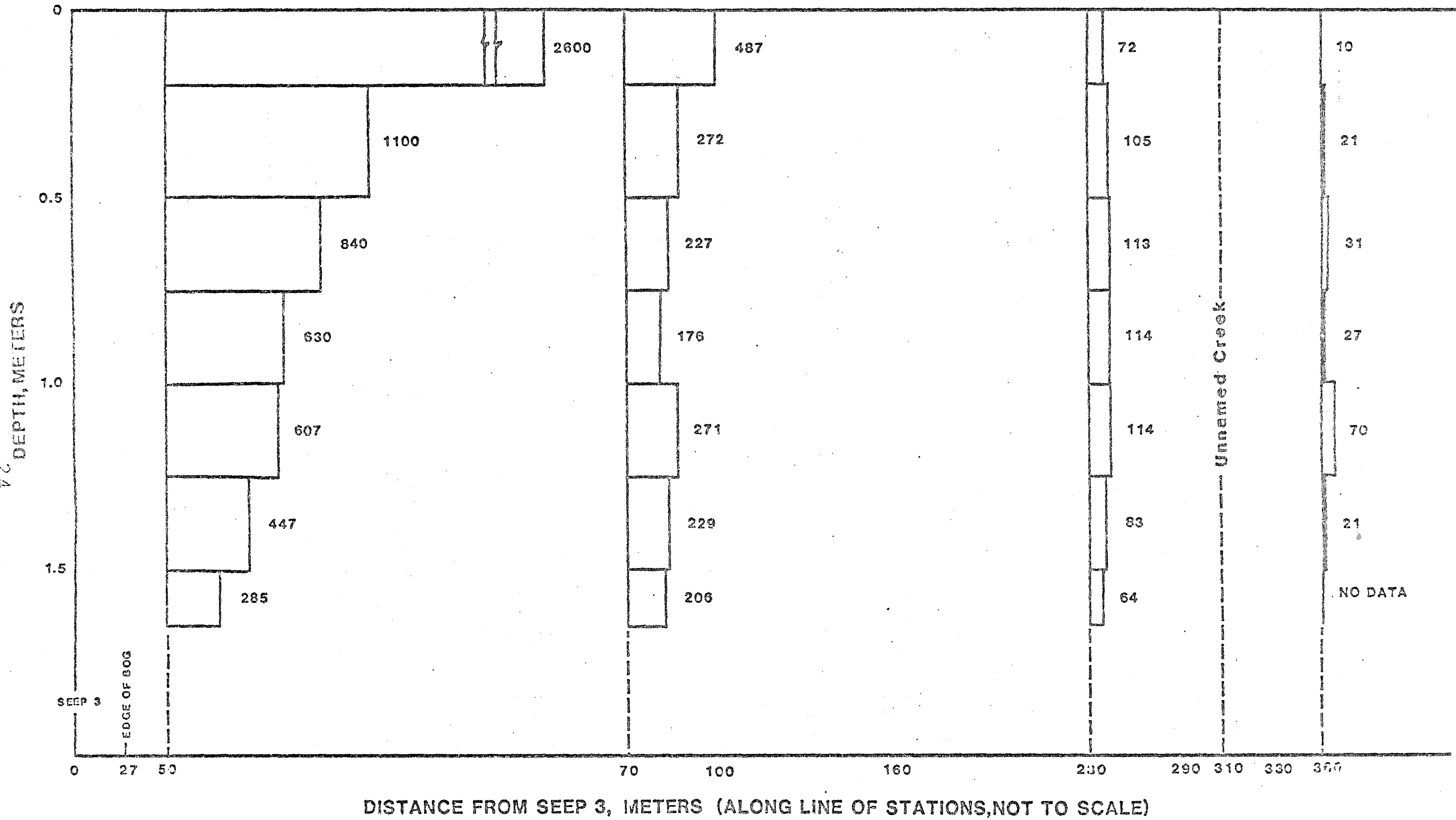
organic bank material. This contact enhanced nickel sequestration by the bank material, thereby decreasing transport. Biological uptake would also be enhanced during the summer months.

3.1.3 Copper

The accuracy of copper transport calculations was limited by the low aqueous concentrations of copper and the high flow volume from mine dewatering.

Copper transport through the Seep 3 bog was 0-14% (most likely nearer the low end) and 26-51% in the stream with overall transport approximately 10%. The major sources of copper were Seep 3 (72 kg) and the 011 mine water discharge (16 kg., Figure 6). Inputs from other mining sources were in the range of the estimated input from natural runoff (1-5 kg, Appendix II). Removal occurred due to adsorption onto peat and clastic sediments. Aqueous copper concentrations decreased two orders of magnitude as the flow from Seep 3 passed through the bog (Figure 7), indicating sequestration by peat in the bog. Analyses of the peat indicated that most sequestration occurred in the upper 20 cm and that removal decreased with increasing distance from Seep 3 (Figure 12). Copper transport estimates in the stream ranged from 26-51% with a continual loss of copper occurring despite natural inputs. Copper concentrations in Unnamed Creek were higher than those from unimpacted streams with the exception of Filson Creek (Figure 10), where concentrations were elevated due to the proximity of the stream bed to the gabbro contact. Copper concentrations in

FIGURE 12. COPPER CONCENTRATION# (mg/kg peat) vs DEPTH AND DISTANCE FROM SEEP 3



EDTA extraction

organic bank samples from Unnamed Creek, Filson Creek, and other streams increased with increasing aqueous copper concentrations (Figure 13). Copper concentrations in the bank samples from Unnamed Creek decreased slightly with the distance downstream (Figure 14), a trend also observed with the water quality samples (Table 1). Copper concentrations in clastic sediments followed a similar trend (Figure 15).

3.2 Computer results

3.2.1 Model leachates

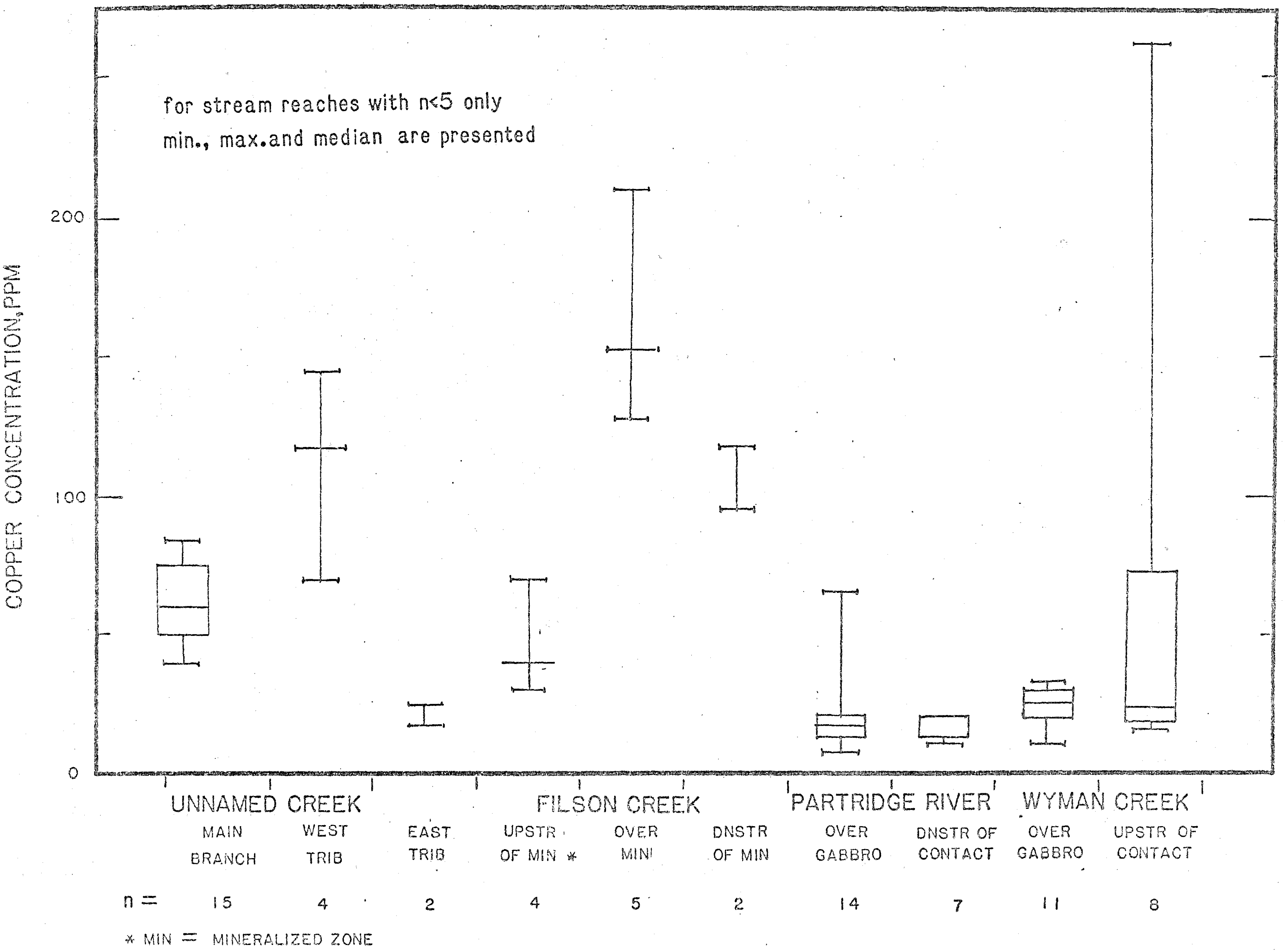
Results from the model leachate programs indicated that the trace metal concentrations were stable with respect to chemical precipitation in the leachate from wasterock but not in the lean ore leachate. In the wasterock leachate the dominant aqueous forms of copper and zinc, respectively, were complexes with citrate and cysteine (Figure 16). Nickel and cobalt existed predominantly as free metals.

Copper and cobalt were predicted to precipitate from the lean ore leachate as $Cu_2(OH)_2CO_3(s)$ and $CoCO_3(s)$. The predicted aqueous equilibrium concentrations of copper and cobalt were 0.275 and 0.097 mg/l. Zinc and copper formed organic complexes to the greatest extent (Figure 17).

3.2.2 Dilution

The predicted primary distribution of species for the various models is presented in Table 5. The degree of trace metal transport

Figure 13. Copper concentrations in organic bank samples from regional streams



for stream reaches with n<5 only
min., max. and median are presented

Figure 14. Copper concentrations in organic bank samples from Unnamed Creek

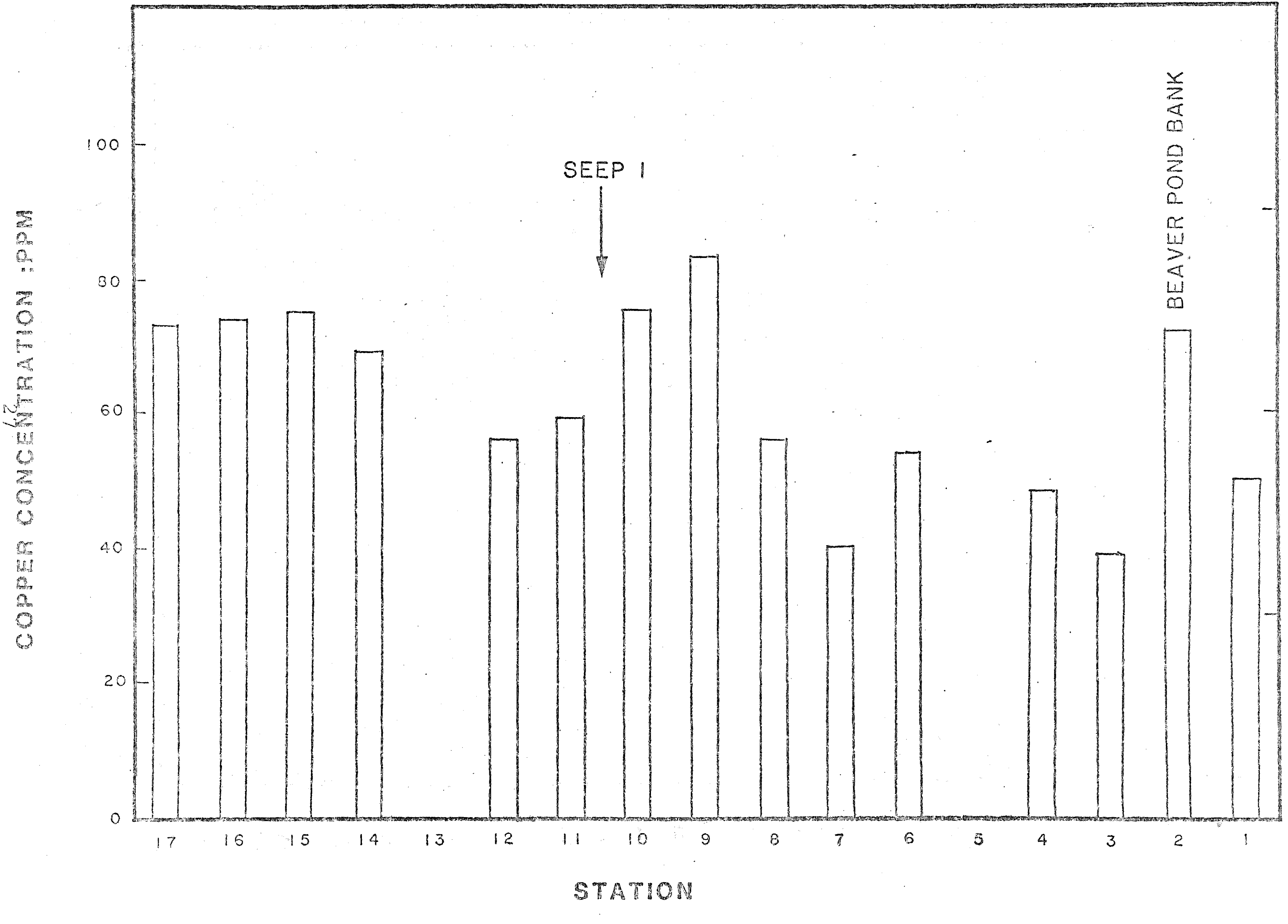
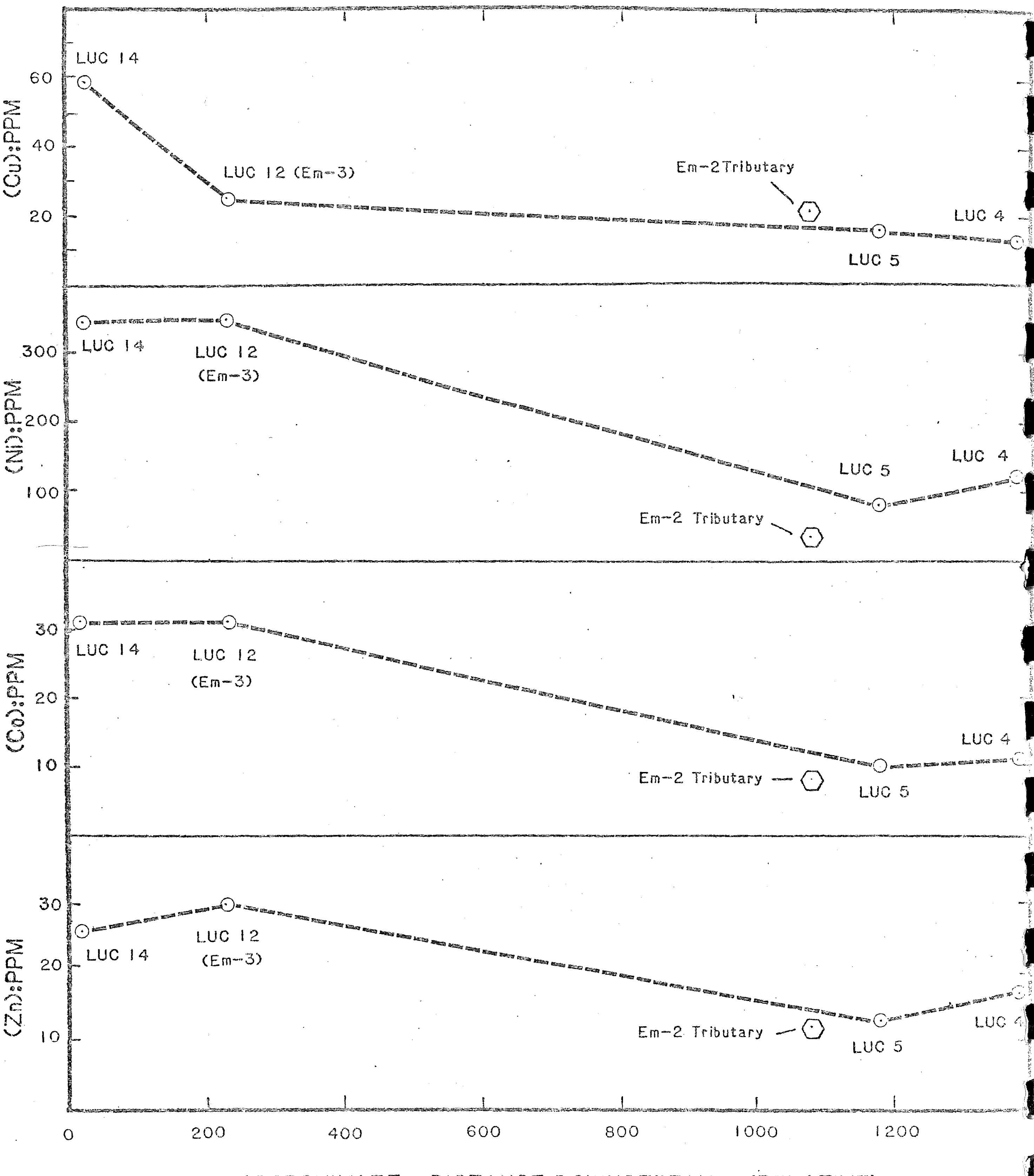


Figure 15.

Trace metal concentrations in Unnamed Creek clastic sediments



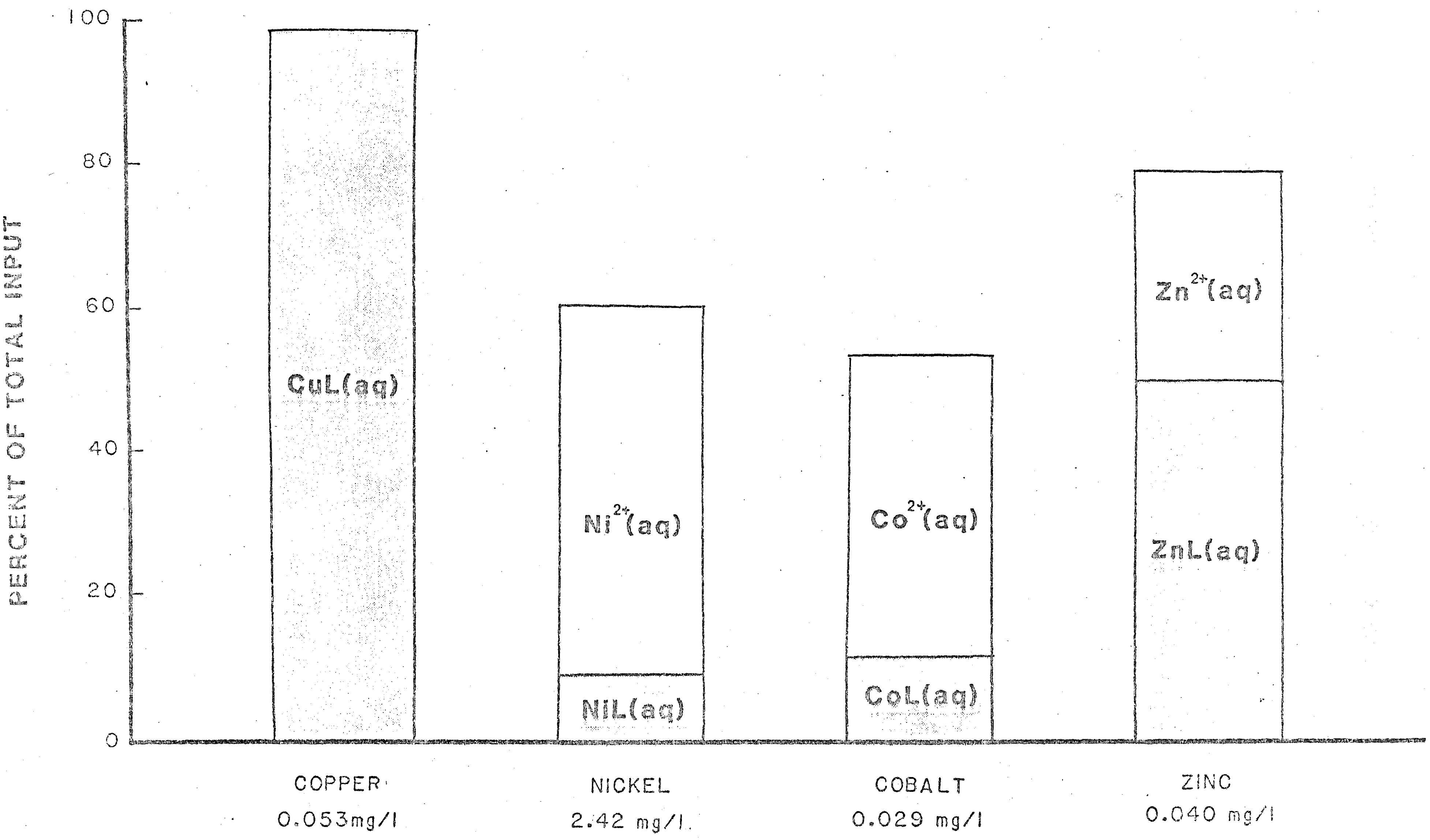


Figure 16. REDEQL2 primary distribution, Model Wasterock Leachate

L represents an organic ligand

Figure 17. REDEQL2 primary distribution, Model Lean Ore Leachate

L represents an organic ligand

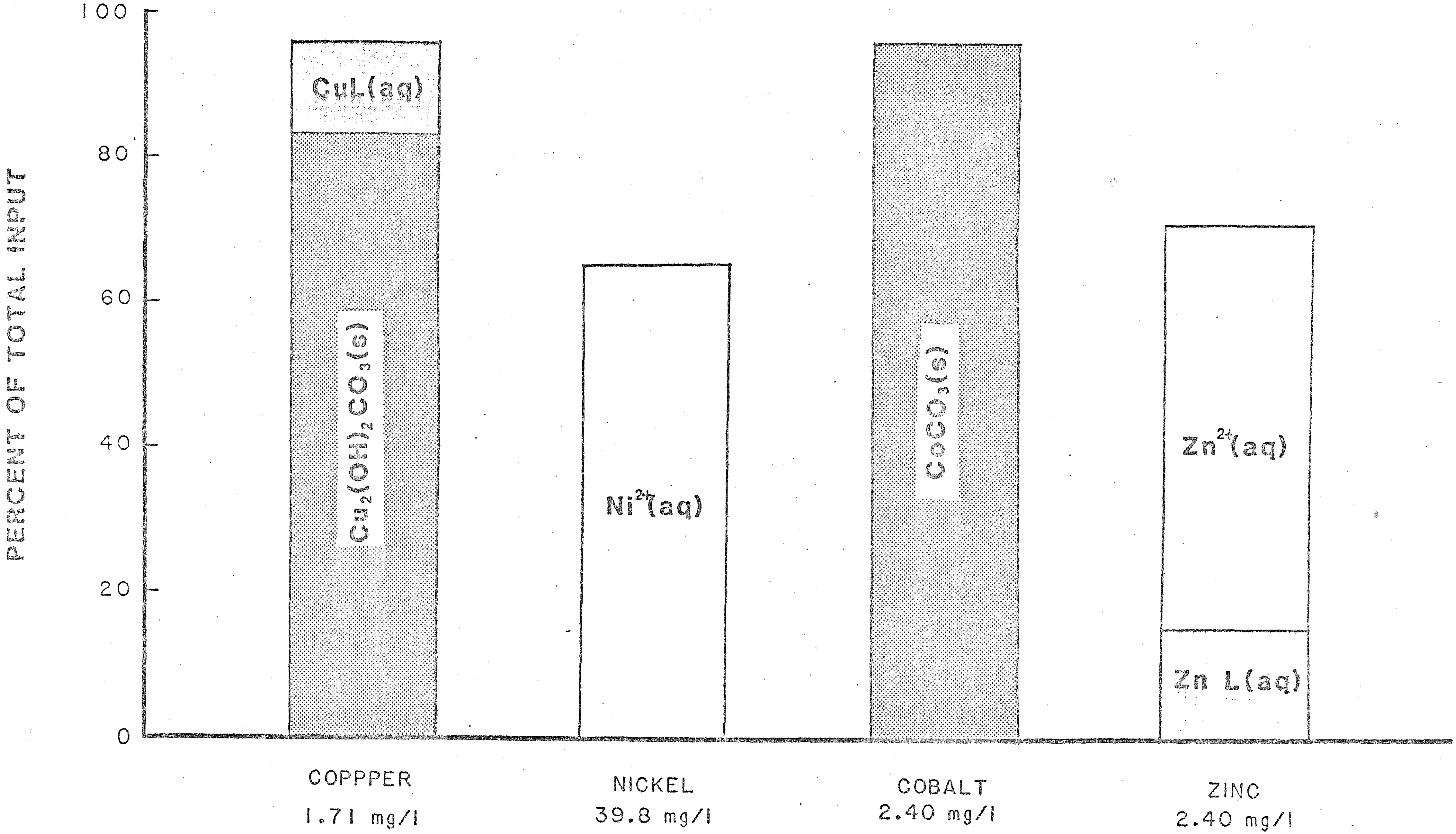


Table 5. REDEQL2 Primary Distribution for Model Wasterock and Lean Ore Leachate
pH 7.5 10m²/l SiO_2= ADSI
TALK 100 mg/l as $CaCO_3$ Complexing organics 1.44 mg/l as C

VALUES AS PERCENT OF METAL INPUT

Dilution	Wasterock 1:2	Wasterock 1:10	Wasterock 1:30	Lean Ore 1:2	Lean Ore 1:10	Lean Ore 1:30
Cu input, mg/l	0.0265	0.0053	0.0018	0.855	0.171	0.057
Cu^{2+}						
OH^-	2.0			4.6	7.8	1.7
$CO_3^=$	0.6			1.1	2.3	0.6
$SO_4^=$						
Cl^-						
Cit	94.8	98.7	99.5	14.8	82.2	95.7
Tart						
$Cu_2(OH)_2CO_3(S)$				76.8		
ADSI	2.4	0.6	0.23	2.2	7.0	1.9
Ni input, mg/l	1.21	0.243	0.081	19.90	3.98	1.33
Ni^{2+}	46.9	26.6	14.0	57.9	59.4	51.0
OH^-						
$CO_3^=$	14.1	10.9	6.5	14.0	21.7	22.3
$SO_4^=$	20.1	4.3	1.0	26.7	12.3	5.0
Cl^-						
Cit	6.9	20.9	32.9	0.5	2.3	11.3
Cyst	11.4	36.5	44.7		3.4	8.4
$Ni(OH)_2$ (S)						
ADSI	0.24	0.7	0.8		0.6	1.7
Co input, mg/l	0.0145	0.0029	0.0010	1.20	0.240	0.080
Co^{2+}	40.8	31.1	23.2	1.1	7.2	23.7
OH^-	0.6	0.5				
$CO_3^=$	9.7	10.1	8.5		2.1	8.2
$SO_4^=$	27.7	8.1	2.7	0.8	2.4	3.7
Cl^-						
Cyst	19.7	46.5	59.6		2.0	13.1
$CoCO_3$ (S)				97.7	85.8	47.5
ADSI	1.0	3.5	5.4			3.2
Zn input, mg/l	0.020	0.004	0.0013	1.20	0.240	0.080
Zn^{2+}	20.2	8.2	4.9	46.0	29.3	18.9
OH^-	0.7			1.4	1.1	0.8
$CO_3^=$	3.8	2.1	1.4	7.0	6.7	5.2
$SO_4^=$	8.7	1.3		21.2	6.1	1.9
Cl^-						
Cyst	65.3	86.3	91.2	23.1	53.8	68.5
$Zn(OH)_2$ (S)						
ADSI	1.0	1.6	1.9	0.6	2.6	4.4

for the various stream models decreased in the order Ni>Zn>Cu>Co. Formation of $CaSO_4$ (s) presented the greatest potential for sulfate precipitation, but this solubility was not exceeded in the creek system.

The REDEQL2 output indicated that little nickel removal occurred, and that significant aqueous nickel existed as a free metal and complexed with OH^-, $CO_3^=$, cysteine and citrate. The organic complexes dominated at the lower nickel concentrations, but their influence decreased with increasing nickel input. For input concentrations greater than 1 mg/l the dominant aqueous form was Ni^{2+} (Figure 18).

Adsorption was the major removal mechanism for input copper concentrations less than 0.2 mg/l, but removal was less than 7%. Precipitation of malachite, $Cu_2(OH)_2CO_3$(s) was predicted for a copper input of 0.855 mg/l, resulting in an aqueous copper concentration of 0.17 mg/l (Figure 19). The dominant form of aqueous copper was as a complex with citrate.

At low input cobalt concentrations (Co $\leq$ 0.015 mg/l) predicted removal from solution was less than 5.4% of the input and was the result of adsorption. As the input concentration increased precipitation of $CoCO_3$ (s) became the dominant removal mechanism (Figure 20). The dominant forms of aqueous cobalt are CoCyst (20-60%), Co^{2+} (20-40%), $CoSO_4$ (3-30%) and $CoCO_3$ (~10%).

Figure 18. Primary distribution of nickel as a function of input concentration

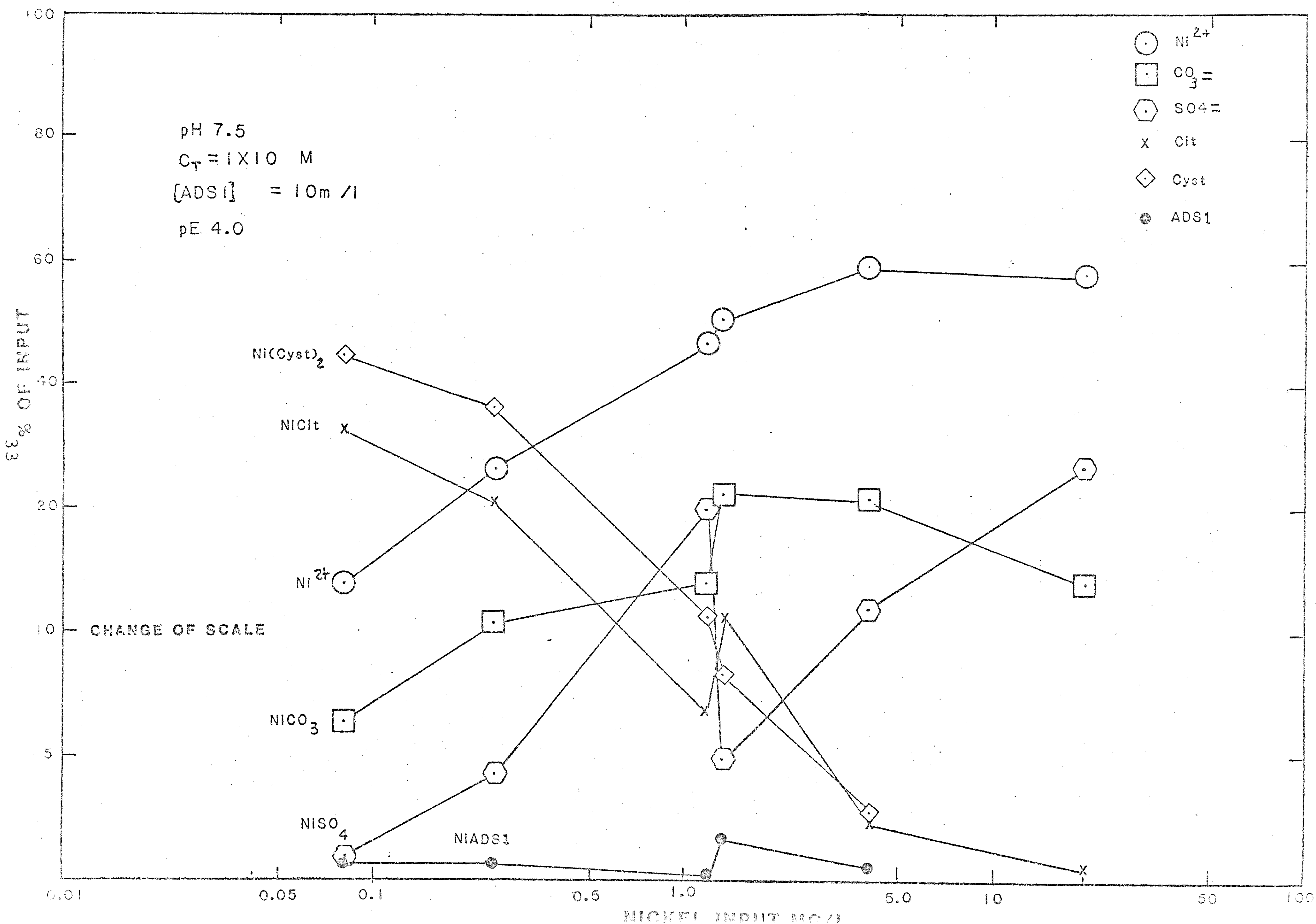


Figure 19. Primary distribution of copper as a function of input concentration

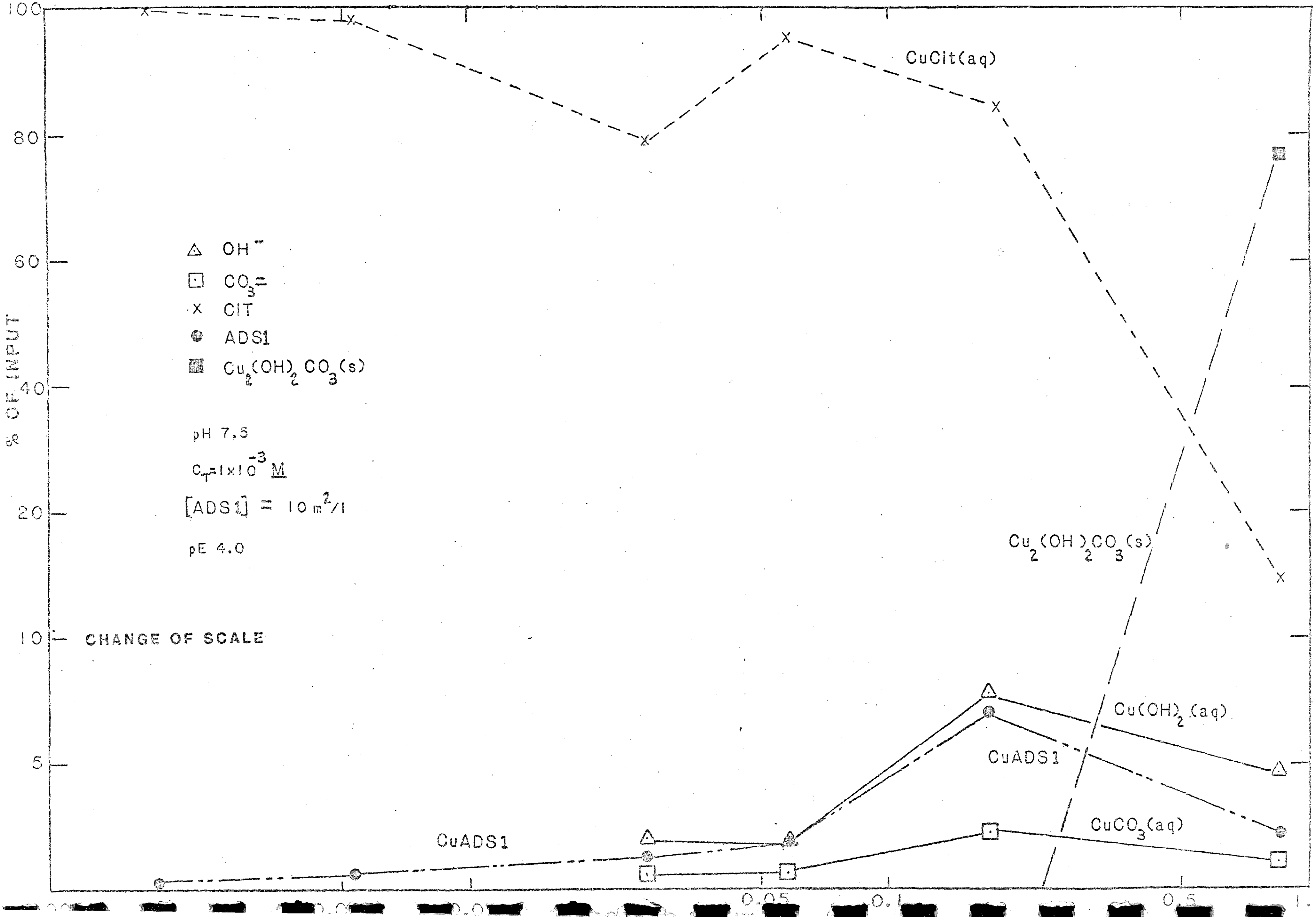
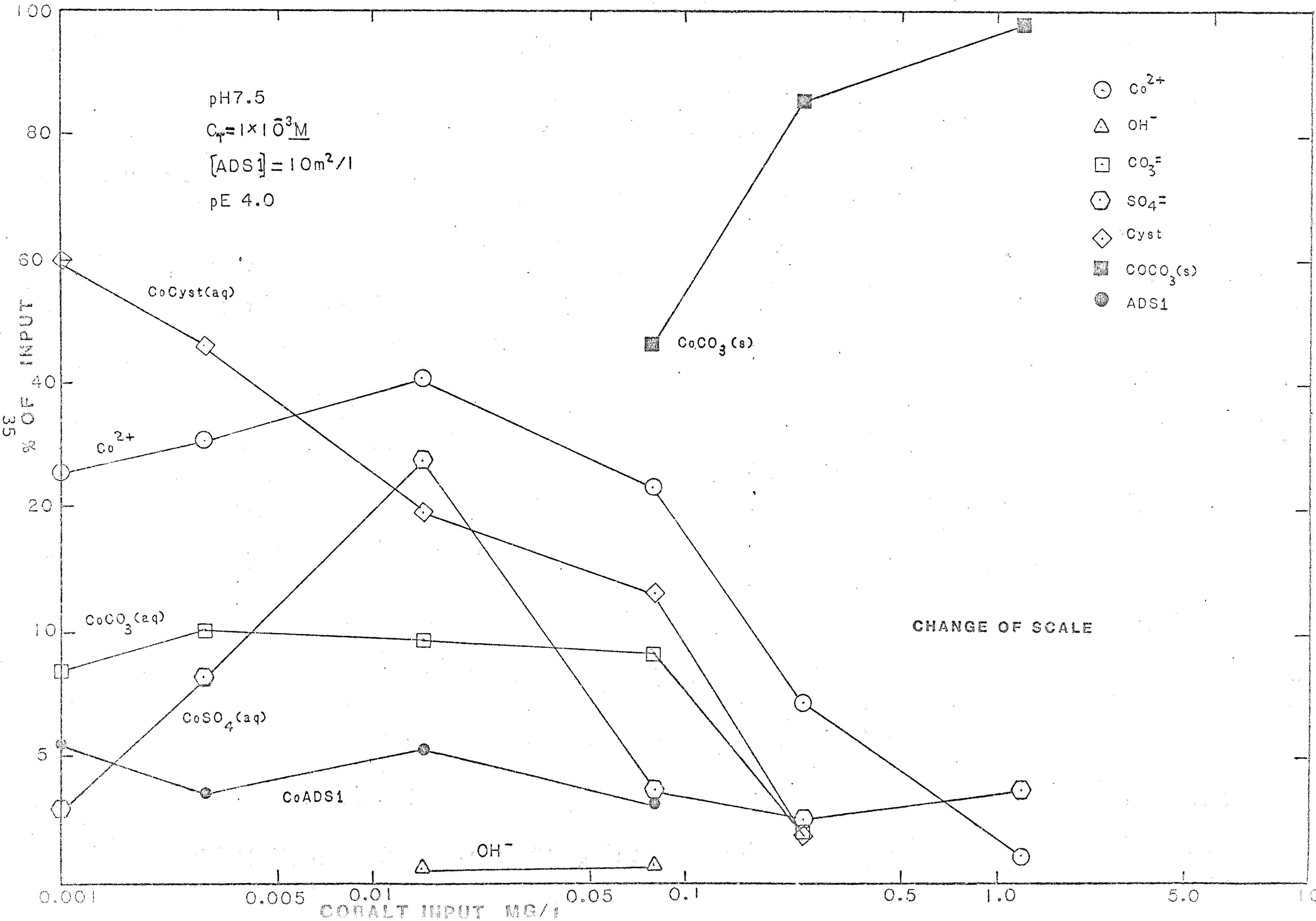


Figure 20. Primary distribution of cobalt as a function of input concentration



The only zinc removal predicted was the result of adsorption, and in all cases was less than 4.5%. The dominant aqueous forms were a zinc cysteine complex at low input concentrations and Zn^{2+} at higher inputs (Figure 21).

The concentrations in the 1:10 and 1:30 dilutions of the model waste rock leachate were similar to those observed at the mouth of the Unnamed Creek (Table 6). The results indicated that the model organics and the adsorptive surface influenced the speciation in the creek. Citrate was the most reactive of the model organics and was dominant in the complexation of copper. Cysteine was also quite reactive, playing a major role in the speciation of nickel, cobalt, and zinc (Tables 7, 8). Adsorption onto ADSI decreased in the order Ca>Mg>Mn>Ni, although the majority of the adsorptive surface was in the "free" form.

3.3 Comparison of field and computer results

The field data and computer predictions agreed fairly well on the high mobility of aqueous nickel in Unnamed Creek, but a slight discrepancy exists on transport through the bog. REDEQL2 output predicted greater than 98% transport in all cases, with removal due to adsorption. Field data indicated 100% transport from EM-8 to EM-5 and 60-100% from EM-3 to EM-1, whereas transport through the bog was less than 70%.

The discrepancies are most likely the result of adsorptive surfaces not considered in the equilibrium program (e.g. FeOOH, MnO_x, organic surfaces) and biological uptake. In a field - computer

Figure 21. Primary distribution of zinc as a function of input concentration

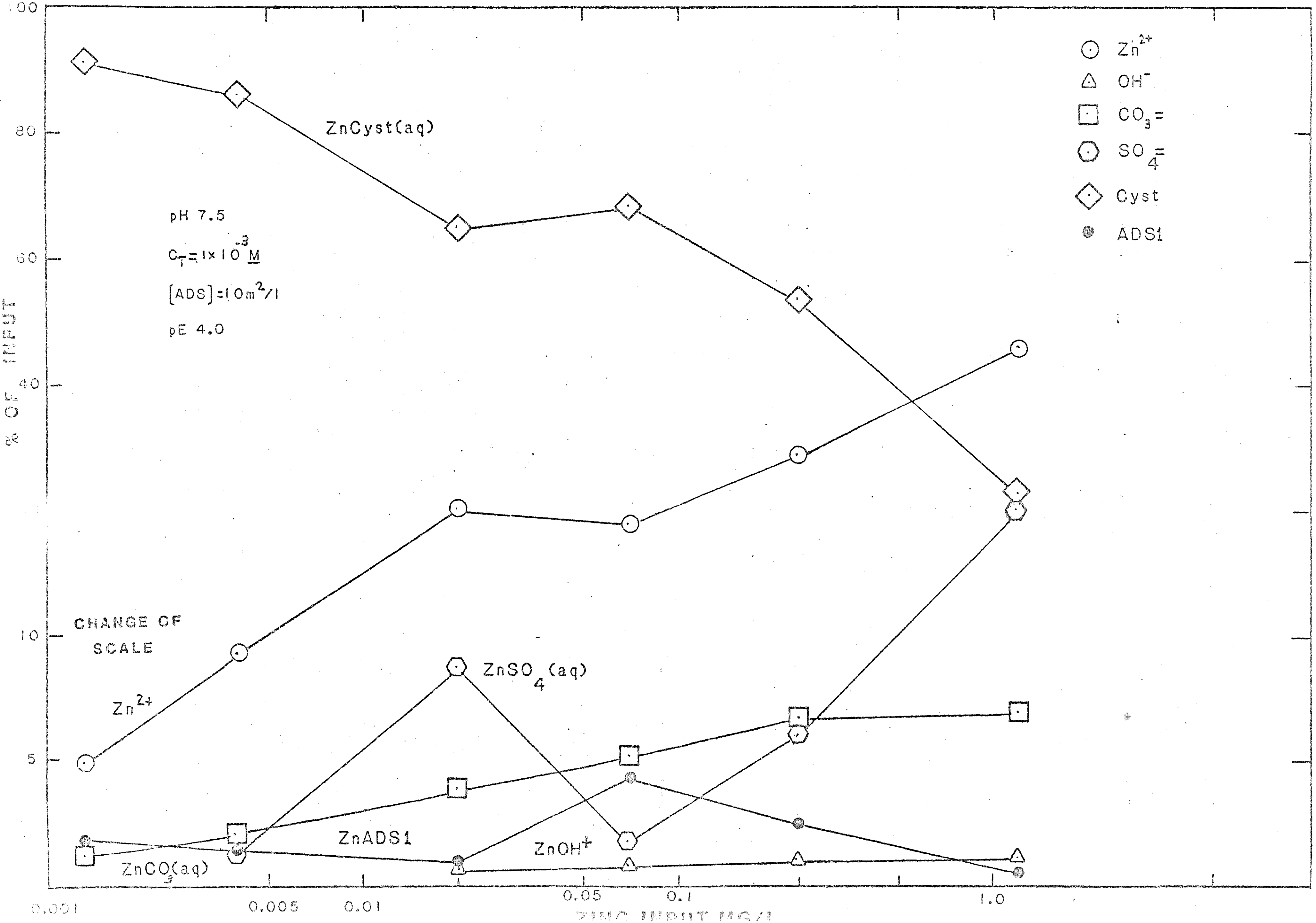


Table 6. REDEQL2 Speciation of Unnamed Creek at EM-1

Input Data and Predicted Equilibrium Concentrations, mg/1

		Unnamed Creek At EM-1			
	INPUT	EQUIL	INPUT	EQUIL	EM-1[a]
SO_4	168	168	56.1	56.1	159
Cl	4.13	4.13	1.38	1.38	25.2
Cu	0.0053	0.00526	0.0018	0.0018	0.002
Ni	0.242	0.240	0.081	0.080	0.087
Co	0.0029	0.0028	0.00096	0.00091	0.002
Zn	0.0040	0.0039	0.0013	0.00128	0.010
Fe	0.021	0.021	0.0069	0.0069	0.13
Mn	0.28	0.0196	0.095	0.00051	0.052
Ca	20.0	19.5	6.67	6.02	45.9
Mg	12.3	12.2	4.10	3.94	34.7
DOC as C	1.40	1.40	1.40	1.40	12.7
Ac as C	0.28	0.28	0.28	0.28	
Cit as C	0.28	0.28	0.28	0.28	
Tart as C	0.28	0.28	0.28	0.28	
Cyst as C	0.28	0.28	0.28	0.28	
Phth as C	0.28	0.28	0.28	0.28	
SiO_2(m^2/1)	10	10	10	10	
pH	7.5	7.5	7.5	7.5	7.5
CO_3(as Ca CO_3)	100	100	100	100	154[b]
pE	4.0	4.0	4.0	4.0	

a. median observed concentration
b. from DIC data

Table 7. REDEQL2 speciation of wasterock leachate model, 1:10 dilution
All values as pC[3]

	Free Met	CO3- (3.000)[1]	SO4 (2.757)	CL (3.934)	AC (4.921)	CIT (5.398)	TART (5.222)	CYST (5.097)	PHTH (5.523)	ADSI (3.000)	OH (6.500)
Free Lig		5.70	2.80	3.93	4.93	15.84	5.29	9.74	5.57	3.34	6.39
CA (3.302)[1]	3.39	5.23	4.17	****[2]	7.46	5.61	6.17	****	6.55	4.92	8.16
MG (3.296)	3.39	5.21	4.07	****	7.36	6.41	6.67	9.21	****	5.30	7.16
FE3 (6.430)	20.00	****	19.20	22.65	20.94	8.67	****	6.43	****	****	10.87
FE2 (9.000)	11.37	****	12.26	14.55	12.75	10.23	****	9.20	****	****	12.54
MN (5.285)	6.52	7.90	7.31	9.50	10.50	8.94	****	11.85	****	5.32	9.19
CU2+ (7.078)	10.62	9.90	11.41	12.06	13.50	7.08	11.90	****	12.28	9.27	9.39
ZN (7.213)	8.30	8.89	9.09	10.93	11.57	11.36	10.38	7.28	10.86	9.01	9.70
NI (5.385)	5.96	6.35	6.75	9.54	9.84	6.07	****	5.82	8.62	7.55	8.43
CO2+ (7.310)	7.82	8.30	8.40	10.50	11.29	24.84	10.20	7.64	14.05	8.77	9.58
HYDROGEN (7.50)	7.50	3.01	8.44	****	7.49	6.72	8.43	5.38	7.71	****	****

[1] Numbers in parentheses are input values

[2] Blank implies negligible concentration

[3] pC = - log C

Table 8. REDEQL2 speciation of wasterock leachate model, 1:30 dilution
All values as pC[3]

	Free Met	CO3- (3.000)	SO4 (3.234)	CL (4.411)	AC (4.921)	CIT (5.398)	TART (5.222)	CYST (5.097)	PHTH (5.523)	ADSI (3.000)	OH (6.500)
Free Lig		5.74	3.25	4.41	4.92	15.50	5.25	9.60	5.55	3.40	6.39
CA (3.779)[1]	3.87	5.67	5.01	****[2]	7.89	5.59	6.51	****	6.90	4.79	8.61
MG (3.773)	3.84	5.62	4.88	****	7.76	6.35	6.98	9.43	****	5.20	7.58
FE3 (6.907)	20.92	****	20.46	23.98	21.79	9.04	****	6.91	****	****	11.71
FE2 (9.477)	12.29	****	13.54	15.90	13.62	10.68	****	9.89	****	****	13.43
MN (5.762)	7.39	8.73	8.54	10.81	11.32	9.31	****	12.49	****	5.77	10.03
CU2+ (7.555)	11.57	10.79	12.71	13.42	14.39	7.56	12.71	****	13.10	10.20	10.31
ZN (7.690)	9.00	9.54	10.14	12.06	12.22	11.59	10.94	7.73	11.44	9.42	10.37
NT (5.862)	6.72	7.05	7.86	10.73	10.54	6.34	****	6.21	9.25	7.94	9.15
CO2+ (7.787)	8.42	8.86	9.36	11.53	11.84	24.94	10.66	8.01	14.50	9.06	10.15
HYDROGEN (7.50)	7.50	3.00	8.84	****	7.46	6.31	8.34	5.19	7.64	****	****

[1] Numbers in parentheses are input values

[2] Blank implies negligible concentration

[3] pC = - log C

study of heavy metal attenuation by soils (Theis and Richter, 1979) it was concluded that nickel (and zinc) were "attenuated predominantly by adsorption onto the iron oxide, manganese oxide playing a lesser role". Based on the high concentrations of iron and manganese in the creek sediments, it is likely that these surfaces were present.

The elevated nickel concentrations in organic bank samples and peat from the Seep 3 bog indicated that nickel was being sequestered by organic solids. Research by Guy et al. (1975) indicated that the interaction of Cu, Zn, and Cd with solid humic acid was similar to that with soluble humic acid. Thus, the computer predicted tendency of nickel to form organic complexes (citrate, cysteine) in solution may serve as an indicator of its tendency for sequestration by solid organics.

There was reasonable agreement between the computer predictions and field data on copper transport. The computer output indicated that copper would be removed by adsorption or precipitation, with copper-citrate being the dominant aqueous form. Field data indicated that copper transport through the Seep 3 bog was on the lower end of 0-14% and was between 26 and 51% in the stream.

The lower transport through the bog, compared to the stream, is consistent with the behavior of nickel and can be explained by a similar argument. The results from REDEQL2 indicate that copper has a greater tendency than nickel to form organic complexes in solution. This is consistent with the greater removal of aqueous copper (compared to nickel) due to sequestration by peat and organic bank materials. The predicted adsorption is also consistent with elevated copper concentrations in the clastic sediments.

4. Summary

The results of field and computer studies indicate that nickel and zinc tend to be more readily transported than copper and cobalt under stream conditions common to Unnamed Creek (pH 7.5, $C_T \sim 100$ mg/l as $CaCO_3$, DOC$\sim$14 mg/l as C, $p\varepsilon 4$). Results would be subject to change given different stream conditions. Results also indicate that trace metal transport can be significantly inhibited by contact with peat, such as in the case of the Seep 3 bog.

Copper (0-14%) and nickel (10-70%) transport through the Seep 3 bog was limited by peat sequestration and vegetative uptake. In the creek copper transport (26-51%) was also less than that of nickel (60-100%), with metal removal occurring due to sequestration by organic bank material and clastic sediments, and probably biological uptake.

Computer results are consistent with the field results. They predict that copper will be more readily removed from solution by inorganic precipitation ($Cu_2(OH)_2CO_3$), adsorption, and sequestration by peat. The tendency for organic complexation is assumed to parallel the tendency for sequestration by peat. The computer results further suggest that zinc transport would be similar to that of nickel, and cobalt transport similar to copper.

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