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WATER QUALITY CHARACTERIZATION OF THE COPPER-NICKEL WATER QUALITY RESEARCH AREA

December, 1979

WATER QUALITY CHARACTERIZATION OF THE COPPER-NICKEL WATER QUALITY RESEARCH AREA

Regional Copper-Nickel Study
Minnesota Environmental Quality Board

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INTRODUCTION TO THE REGIONAL COPPER-NICKEL STUDY

The Regional Copper-Nickel Environmental Impact Study is a comprehensive examination of the potential cumulative environmental, social, and economic impacts of copper-nickel mineral development in northeastern Minnesota. This study is being conducted for the Minnesota Legislature and state Executive Branch agencies, under the direction of the Minnesota Environmental Quality Board (MEQB) and with the funding, review, and concurrence of the Legislative Commission on Minnesota Resources.

A region along the surface contact of the Duluth Complex in St. Louis and Lake counties in northeastern Minnesota contains a major domestic resource of copper-nickel sulfide mineralization. This region has been explored by several mineral resource development companies for more than twenty years, and recently two firms, AMAX and International Nickel Company, have considered commercial operations. These exploration and mine planning activities indicate the potential establishment of a new mining and processing industry in Minnesota. In addition, these activities indicate the need for a comprehensive environmental, social, and economic analysis by the state in order to consider the cumulative regional implications of this new industry and to provide adequate information for future state policy review and development. In January, 1976, the MEQB organized and initiated the Regional Copper-Nickel Study.

The major objectives of the Regional Copper-Nickel Study are: 1) to characterize the region in its pre-copper-nickel development state; 2) to identify and describe the probable technologies which may be used to exploit the mineral resource and to convert it into salable commodities; 3) to identify and assess the impacts of primary copper-nickel development and secondary regional growth; 4) to conceptualize alternative degrees of regional copper-nickel development; and 5) to assess the cumulative environmental, social, and economic impacts of such hypothetical developments. The Regional Study is a scientific information gathering and analysis effort and will not present subjective social judgements on whether, where, when, or how copper-nickel development should or should not proceed. In addition, the Study will not make or propose state policy pertaining to copper-nickel development.

The Minnesota Environmental Quality Board is a state agency responsible for the implementation of the Minnesota Environmental Policy Act and promotes cooperation between state agencies on environmental matters. The Regional Copper-Nickel Study is an ad hoc effort of the MEQB and future regulatory and site specific environmental impact studies will most likely be the responsibility of the Minnesota Department of Natural Resources and the Minnesota Pollution Control Agency.

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4.3.1 Introduction

Northeastern Minnesota has abundant water resources of generally high quality. This resource has intrinsic esthetic value and is extensively used for recreational purposes. This resource is also used by municipalities and industry for a variety of purposes including appropriation and as a receiver of waste water.

Historically, the extraction and refinement of base metal ore deposits has had a damaging impact on the environment. The mining of copper-nickel sulfide ore from the Duluth Complex will likely cause changes in the quality of the surface and ground water in this region.

There are eight different phases of the mineral operation which can affect water quality: mineral exploration, mine development, mineral extraction, ore and concentrate transport, milling and processing, concentrate storage, solid waste disposal, and smelting and metal refining. Besides the direct effects of mineral development on water quality there are the secondary effects from increased urban development and recreation which would accompany copper-nickel development.

The types of pollutants and the circumstances under which they enter the aquatic system is different for each mining phase and for different types of secondary development. The mode by which these pollutants enter the aquatic system is by point-discharge, area runoff, and by atmospheric deposition.

In order to assess the potential impact of copper-nickel mining on water quality, obviously the quality of the region's water be understood. Thus, a comprehensive regional monitoring program was conducted for three main purposes:

1) To begin the long-term process of gathering environmental data for the establishment of a pre-development environmental base line against which change resulting from development can be assessed.

2) To characterize the surface and ground water quality in the Study Area.

3) To assess the susceptibility of the surface waters to potential impacts from copper-nickel mining and associated development.

Hydrologically the area monitored is a headwater region, that is, surface flow originates in this area. This region encompasses portions of two major drainage basins, the Rainy River basin and the St. Louis River basin, which are separated by the Laurentian Divide. The former drains eventually to Hudson Bay, and the latter to Lake Superior and thence to the Atlantic Ocean via the Great Lakes.

Nine watersheds north of the Laurentian Divide and five south of the Divide were monitored (Table 1). The total drainage area studied north of the Divide is 3,489 km^2 (1,347 mi^2); and the total area south is 1,249 km^2 (482 mi^2). The boundaries of the watersheds and the location of the Divide are shown in Figure 1.

Table 1, Figure 1

In addition, the U.S. Geological Survey monitored groundwater using wells predominantly located in areas most likely to be affected by copper-nickel development but also in other areas in order to present a general picture of ground water quality of the whole region.

The Kawishiwi system which drains into the Rainy River is the major river north of the Divide. Nine minor systems feed the Kawishiwi system (Table 1). This

Table 1. Regional Copper-Nickel Study watersheds (refer to Figure 2 for locations).

NORTH OF LAURENTIAN DIVIDE (Rainy River Drainage)

WATERSHED NAME	SUBWATERSHED NAME	SUBWATERSHED AREA (km^2)	FEEDER SUBWATERSHEDS	TOTAL DRAINAGE THROUGH SUB-WATERSHED, km^2	(mi^2)
Isabella River	Little Isabella	132	none	132	(50.95)
	I-1	751	Little Isabella	883[a]	(340.84)
Filson Creek	F-1	27	none	27[a]	(10.42)
Keeley Creek	KC-1	29	none	29[a]	(11.19)
Stony River	SR-5	125	none	125	(48.25)
	SR-4	161	none	161	(62.15)
	SR-3	180	sr5+sr4	466	(179.88)
	SR-2	101	sr5+sr4+sr3	567	(218.86)
	SR-1	65	sr5+sr4+sr3+sr2	632[a]	(243.95)
Unnamed Creek	BB-1	11	none	11[a]	(4.25)
Dunka River	D-2	44	none	44	(16.98)
	D-1	84	d2	128[a]	(49.41)
Bear Island R.	BI-1	177	none	177[a]	(68.32)
Shagawa River	SH-1	256	none	256[a]	(98.82)
Kawishiwi River	K-6	655	none	655	(252.83)
	K-7	236[b]	Little Isabella+il+½k6	1447[b]	(568.96)
	K-5	262[b]	Little Isabella+il+fl+kcl+sr5+sr4+sr3+sr2+srl+bbl+d2+dl+½k6+k7	2536[b]	(978.90)
	K-4	66[b]	Little Isabella+il+fl+kcl+sr5+sr4+sr3+sr2+srl+bbl+d2+dl+bil+½k6+k7+k5	2779[b]	(1072.69)
	K-3	64	Little Isabella+il+fl+kcl+sr5+sr4+sr3+sr2+srl+bbl+d2+dl+bil+k6+k7+k5+k4	3170	(1223.62)
	K-1	63	Little Isabella+il+fl+kcl+sr5+sr4+sr3+sr2+srl+bbl+d2+dl+bil+shl+k6+k7+k5+k4+k3	3489	(1346.75)

Table [illegible] continued.

SOUTH OF LAURENTIAN DIVIDE (Lake Superior Drainage)

WATERSHED NAME	SUBWATERSHED NAME	SUBWATERSHED AREA (km^2)	FEEDER SUBWATERSHEDS	TOTAL DRAINAGE THROUGH SUB-WATERSHED, km^2	(mi^2)
Embarrass River	E-2	46	none	46	(17.76)
	E-1	183	e2	229[a]	(88.39)
Partridge River	P-5	32	none	32	(12.35)
	P-4	48	none	48	(18.53)
	P-3	47	none	47	(18.14)
	P-2	137[c]	p5+p4+p3	264[c]	(101.90)
	P-1	71	p5+p4+p3+p2	335[c]	(129.31)
St. Louis River	Second Creek	69	none	69	(26.63)
	SL-3	157	none	157	(60.60)
	SL-2	86	sl3	243	(93.80)
	SL-1	107	p5+p4+p3+p2+p1+Second Creek+sl3+sl2	754[c]	(291.04)
Whiteface River	WF-1	24	none	24	(9.26)
	WF-2	124	none	124	(47.86)
Water Hen Creek	W-1	118	none	118	(45.55)

SOURCE: U.S. Geological Survey, St. Paul, Minn.

[a] Drainage area of entire watershed.
[b] Drainage areas estimated because of North/South Kawishiwi River split.
[c] Includes 13 km^2 in subwatershed p2 defined by USGS as noncontributing.

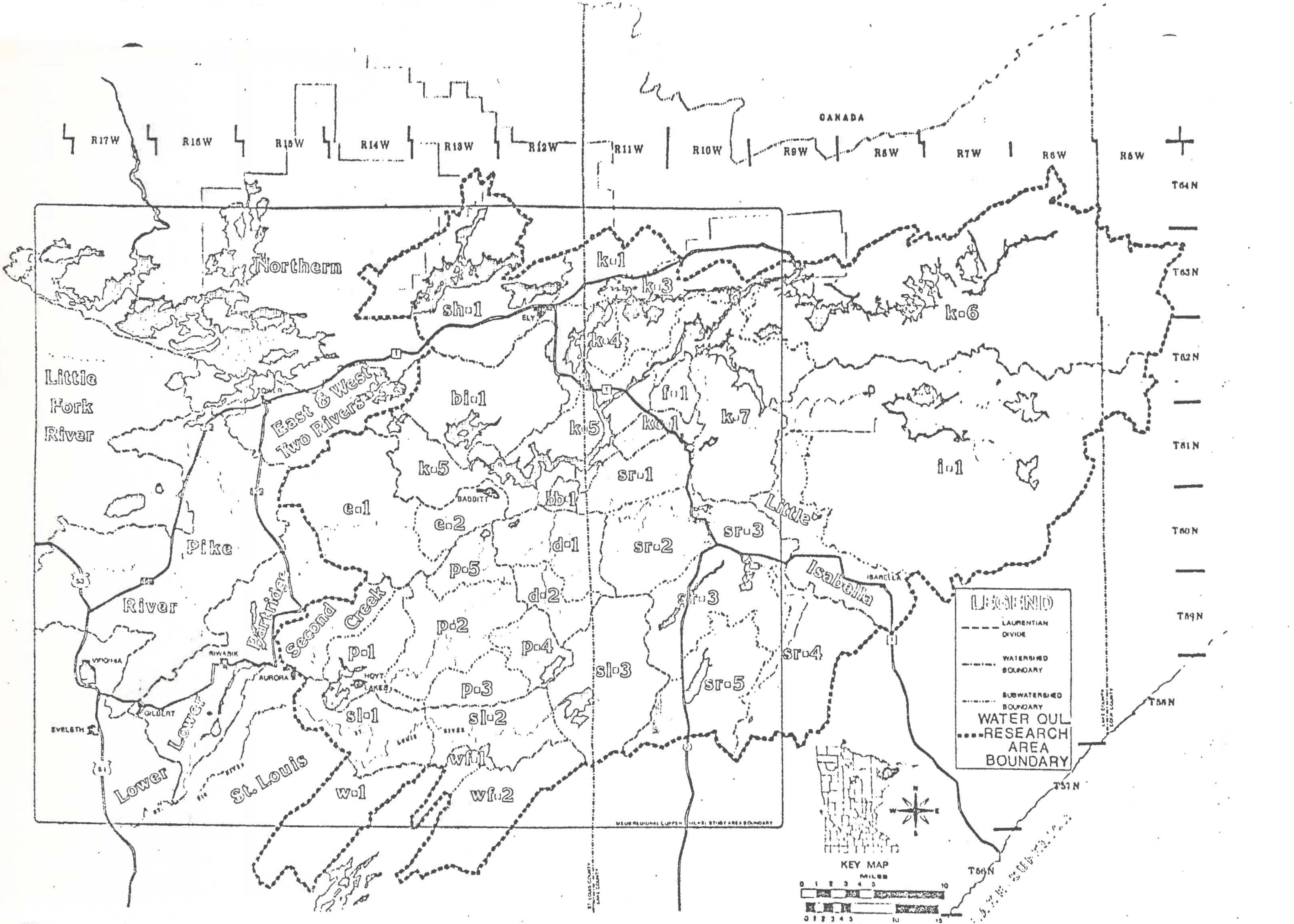

FIGURE 1 THE WATER QUALITY RESEARCH AREA

area is predominantly forested, with pine accounting for about 30 percent of the growth. Ninety-one percent of the surface waters of the study area is located north of the divide. Mining activities (taconite) occupy a small portion of this drainage area (0.3%). The soil thickness north of the divide is very shallow (0-3 meters) and bedrock outcropping is common. The soils are nutrient poor, high in trace metals and acidic (see Volume 3-Chapter 2).

All waters in the Study Area south of the divide flow through the St. Louis system and thence to Lake Superior. Although the St. Louis River drains the entire area, only the Partridge river joins the St. Louis within the confines of the area monitored. This area is also heavily forested but aspen-birch predominate. Spruce, fir and pine, in that order, are the next important species. The soils deepen in this area (3-30 meters) but the ground water system is generally meager, although there are two excellent but small aquifers located in this region. One-third of the area is classified as bog; and drumlins, eskers, and other glacial features dominate the landscape.

4.3.1.1 Monitoring Approach--The surface water quality of the Study Area was sampled from March, 1976 through September 1977. Thirty-two stream sites on thirteen different river systems were established, and 35 lake stations on 26 lakes were established (Figure 2). Because the area is blessed with numerous streams and lakes [181 lakes over 20 hectares (50 acres) in size], critria were established for lake and stream site selection based on location, size, shoreline characteristics, depth, and other factors.

Figure 2

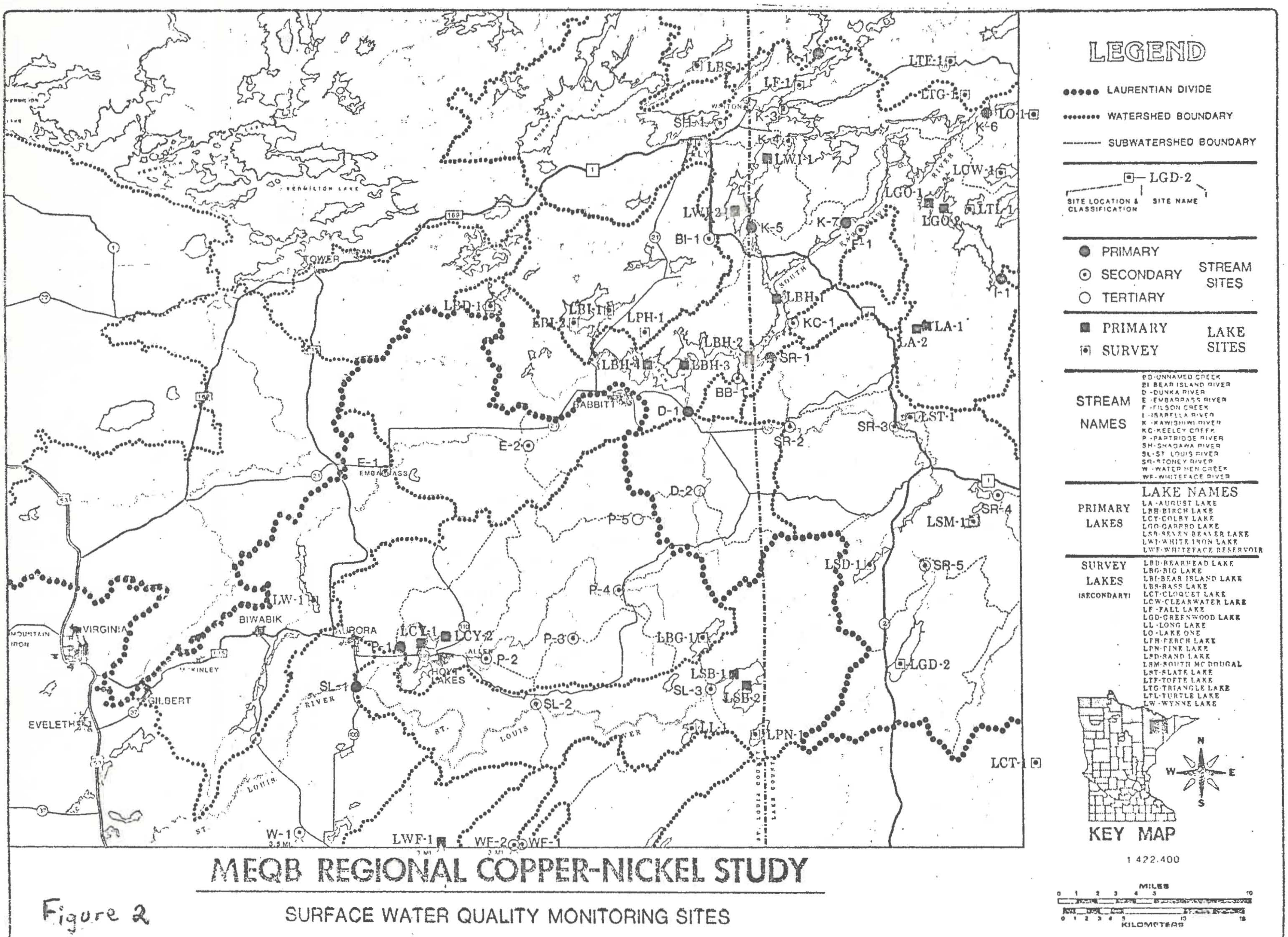

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Figure 2

SURFACE WATER QUALITY MONITORING SITES

Stream sampling was conducted on a monthly (primary), bi-monthly (secondary), or quarterly (tertiary) basis, depending on the importance of the site and the parameter in question. More samples were collected at sites representing the mouths of important watersheds than sites upstream. Stream sites were established north and south of the Laurentian Divide (Figure 2); in both small and large watersheds (Table 1); and in areas upstream and downstream from known human disturbance which may be affecting water quality. The primary intent was to establish sites that would provide a representative cross-sampling of terrestrial, topographic, and anthropogenic features which presumably affect water quality.

During the second year of the program, some sampling sites were dropped and the sample collection schedule was switched to event-sampling. Event-sampling provided additional information about the effect of rainstorm events and spring-melt on water quality (first-year periodic sampling schedules provided some event-oriented water quality information).

Prior to this surface water program, the U.S. Forest Service under a cooperative agreement with INCO (in 1975) conducted a water monitoring program in the general area of Filson Creek. This program was part of a requirement pertaining to the permit request by INCO to the U.S. Forest Service. When the Regional Copper-Nickel Study monitoring program commenced, it was integrated with the Forest Service program. Thus, some of the results reported here are from the U.S. Forest Service Program (U.S. Forest Service 1976). A complete description of the Forest Service program and the results is on record at the Forest Supervisor's Office, Superior National Forest and is integrated with Copper-Nickel Study data files at the Land Management Information Center (LMIC), Minnesota State Planning Agency.

Less emphasis was placed on the lake sampling program, because the large number and diversity of lakes precluded a more complete sampling program. The selection of lakes was predicated on the same criteria as for streams. Large and small lakes; headwater and downstream lakes; deep and shallow lakes; lakes in various soil types basins; and lakes north and south of the divide were selected. Seven lakes were sampled six times per year (Primary); and nineteen lakes were sampled only twice (survey lakes) (see Table 2).

Table 2

Continuous stream flow data were collected at eleven major stream sites and stream flow data were collected at the other sites by staff and the U.S. Geological Survey. Not only did this provide information about water quantity but it also permitted evaluation of the relationship between concentration of constituents and flow.

Ground water samples were collected for chemical analysis quarterly during 1976-1977 for 12 observation wells finished in glaciofluvial sand and gravel, 11 wells finished in the Rainy Lobe till, and 2 wells finished in peaty material. An additional single sampling (during a drought period in October, 1976, when ground water levels were extremely low) of the U.S. Forest Service campground wells was added. This sampling included 3 wells finished in sand and gravel, 5 wells finished in Rainy Lobe till, and 3 wells in the Duluth Complex. Three other wells in the Duluth Complex were sampled during 1976. Locations of sampled wells are given in Figure 3.

Figure 3

Table 2. Morphometry of lakes sampled by the Regional Copper-Nickel Study.

LAKE	HEADWATER LAKE	SURFACE AREA A_o (km^2)	DRAINAGE AREA A_d (km^2)	MEAN DEPTH $\bar{z}$ (m)	MAXIMUM DEPTH Z max(m)	VOLUME VX10^6(m)	MEAN ANNUAL DISCHARGE QX10^6 (m^{3}yr^{-1})		AREAL WATER LOAD q_a=Q/A_o		FLUSHING RATE e (yr^{-1})		STRATIFICATION
Kawishiwi River Watershed													
							b	c	b	c	b	c	
Birch	No	25.62	2536	4.15	7.62	106.18	596.36	490	23.28	19.1	5.62	4.61	Does not stratify
Gabbro	No	3.63	1034	3.66	15.24	13.27	254.22	193	70.03	53.1	19.16	14.54	Does not stratify
White Iron	No	13.85	2779	6.00	14.33	83.13	650.55	539	46.97	38.9	7.83	6.48	Weakly dimictic
August	Yes	.90	9.6	2.46	5.79	2.20	2.98	1.48	3.31	1.65	1.35	.67	Does not stratify
Clearwater	Yes	2.61	9.2	7.44	14.00	19.39	2.86	1.42	1.10	.54	.15	.07	Does not stratify
Lake One	No	3.55	638	3.14	17.37	33.30	160.66	117	45.26	32.9	4.82	3.51	Strongly dimictic
Turtle	Yes	1.36	6.4	1.13	3.05	1.55	1.95	.97	1.43	.72	1.22	.63	Does not stratify
Fall	No	8.93	3489	3.99	9.75	35.70	807.59	683	90.44	76.5	22.62	19.13	Weakly dimictic
Bear Island River Watershed													
Bear Island	Yes	8.64	85	8.74	21.95	75.46	23.66	14.3	2.74	1.66	.31	.19	Strongly dimictic
Perch	Yes	.44	3.2	2.30	9.14	1.01	1.05	.47	2.39	1.08	1.04	.47	Weakly dimictic
Stony River Watershed													
Greenwood	Yes	5.06	105.7	1.27	2.13	6.43	29.10	18.0	5.75	3.56	4.53	2.80	Does not stratify
Sand	Yes	2.05	41	1.45	11.58	2.98	11.82	6.72	5.77	3.28	3.97	2.56	Does not stratify
So. McDougal	Yes	1.12	37.4	.51	1.52	.57	10.84	6.11	9.68	5.45	19.02	10.72	Does not stratify
Slate	No	.96	466	1.51	3.05	1.45	119.19	84.12	124.16	87.8	82.20	58.07	Does not stratify
Partridge River Watershed													
Colby	No	2.24	332	3.13	10.36	7.00	86.31	59.2	38.53	26.4	12.33	8.46	Weakly dimictic
Big	No	3.21	9.2	?	4.57	4.92	2.87	1.42	.89	.44	.58	.29	Weakly dimictic

Table 2 continued.

LAKE	HEADWATER LAKE	SURFACE AREA A_o (km^2)	DRAINAGE AREA A_d (km^2)	MEAN DEPTH $\bar{z}$ (m)	MAXIMUM DEPTH z max(m)	VOLUME VX10^6(m)	MEAN ANNUAL DISCHARGE QX10^6 (m^{3}yr^{-1})		AREAL WATER LOAD q_a=Q/A_o		FLUSHING RATE e (yr^{-1})		STRATIFICATION
St. Louis River Watershed													
Seven Beaver	Yes	5.63	157	1.46	1.68	8.24	42.38	27.1	7.53	4.82	5.14	3.29	Does not stratify
Pine	Yes	1.77	14.8	2.34	4.27	4.14	4.50	2.33	2.54	1.32	1.09	.56	Does not stratify
Long	Yes	1.79	21.6	.50	1.83	.90	6.43	3.45	3.59	1.93	7.14	3.83	Does not stratify
Other Watersheds													
Whiteface Res.	Yes	17.22	337	3.15	9.14	54.19	87.59	60.1	5.09	3.49	1.62	1.11	Weakly dimictic
Tofte	Yes	.47	1.7	10.73	22.25	5.09	.56	.25	1.19	.52	.11	.05	Monomictic[d]
Triangle	Yes	1.32	5.5	3.99	12.19	5.29	1.75	.83	1.33	.63	.33	.16	Strongly dimictic
Bass	No	.68	13	5.51	10.67	3.77	3.97	2.03	5.84	2.99	1.04	.54	Strongly dimictic
Bearhead	Yes	2.74	13.1	4.49	13.72	12.31	4.01	2.05	1.46	.75	.33	.17	Weakly dimictic
Wynne	No	1.15	374.9	11.1	15.85	12.80	96.93	67.1	84.29	58.4	7.57	5.24	Strongly dimictic
Cloquet	Yes	.74	5.8	.85	2.13	.63	1.86	.88	2.51	1.19	2.95	1.40	Does not stratify

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[a] See Appendix B5 for definitions.
[b] Ten-year average.
[c] March 1, 1976, through February 28, 1977, average.
[d] Overturns in late fall.

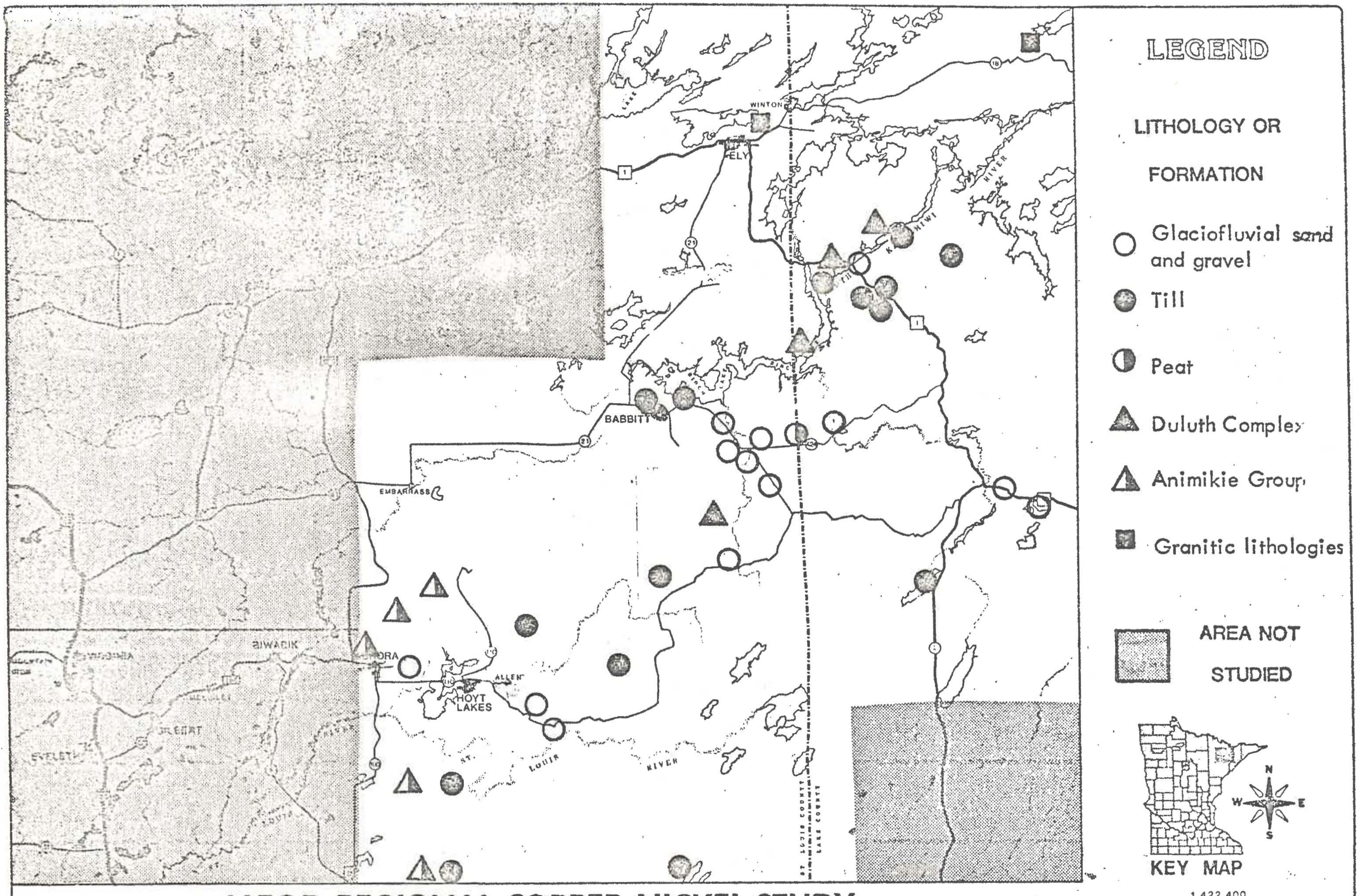

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FIGURE 3

WELLS SAMPLED FOR CHEMICAL ANALYSIS

4.3.1.2 Sampling Methodology and Laboratory Analysis--Surface water samples were collected according to acceptable methods of EPA, USGS, and the Minnesota Department of Health. Analysis of samples was performed by the USGS (Denver), the Minnesota Department of Health, and University of Minnesota labs. In situ measurements (i.e. field measurements) included water temperature, dissolved oxygen, specific conductance, secchi disk, and pH. Initially, both total and filtered (0.45 micron filters) samples were collected and analyzed. Filtering was dropped when it was learned that certain trace metal contamination was occurring and that there was little difference analytically between the two sample types. Thus, all values reported, except for iron, are as "total".

All samples collected during the study were analyzed by USGS laboratories in Denver, Colorado, and Salt Lake City, Utah. Sampling procedures and analytical methodology followed USGS standards, as outlined by Brown, Skougstad, and Fishman (1970), with modifications to current technological precision and accuracy for trace metals.

A suite of chemical parameters were analyzed (Table 3) because regional water quality for many parameters was desired. Thus, the water quality data developed under this study can be used toward the establishment of a base line and to assess future changes, either with or without copper-nickel development. More monitoring information, especially of a site specific nature, is required before a statistically valid base line can be established which addresses short- and long-term natural and existing anthropogenic variations.

Table 3

Table 9. Water quality parameter list.

General

Residue: filterable and nonfilterable
Turbidity
Color
TOC
DOC
Specific Conductance

DO
Temperature
Secchi Disk
pH
Alkalinity

Metals, Nutrients, Cations, Anions

Copper
Nickel
Zinc
Cadmium
Lead
Iron
Cobalt
Aluminum
Mercury

Arsenic
Selenium
Titanium
Phosphorus: Total & Ortho
Nitrogen: Total, NO_2, NO_3, Kjd, NH_4
Calcium
Magnesium

Manganese
Potassium
Sodium
Chloride
Sulfate
Fluoride
Bicarbonate

Others

Oil & Grease
MBAS
Phenols
BOD

Fecal Coliforms
Gross Alpha, Beta
Chlorophyll a
Barium

4.3.2 Quality of Surface Waters of the Regional Copper-Nickel Study Area

The various parameters monitored have been organized into five general groupings for ease of presentation. They are: (1) general parameters; calcium, chloride, color, magnesium, potassium, silica, sodium, specific conductance, hardness, turbidity, and total organic carbon; (2) parameters reflecting acidity and acid buffering; alkalinity, bicarbonate, pH, Calcite Saturation Index (CSI), and sulfate; (3) nutrient parameters; total nitrogen, total phosphorus, and Trophic State Index (TSI); (4) mineral fibers; and (5) metals; aluminum, arsenic, cadmium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc.

Each grouping is discussed on a parameter-by-parameter basis along with a presentation of the overall levels observed for the region. The Study values are compared to Mississippi River values (St. Paul), and to values observed in streams in the Coeur d'Alene district (Idaho), an area impacted by mining, in order to provide a perspective. Where appropriate, various water quality criteria for each parameter are also presented, (e.g. EPA and Minnesota Pollution Control Agency). Copper-Nickel Study impact assessment guidelines based on results of aquatic toxicology literature reviews and experiments are also presented (see Volume 4-Chapter 1). Following the parameter discussions, a general discussion for the grouping is presented to provide a regional perspective.

Box plots (Figure 4), which display range, midpoint, and variability of data, are used to make comparison between parameters and various sampling sites (Appendix 1). The line in the middle of the box represents the median (50th percentile) value, and the upper and lower ends of the box represent the upper quartile (75th percentile) and the lower quartile (25th percentile), respectively. The endpoints of the lines extending above and below the box represent the highest and the lowest values observed, respectively. (Data outliers believed to be erroneous have been removed from the data base use for the statistical summaries presented in this report but have been retained in primary data files.)

Figure 4

Analysis of variance and univariate analysis of variance methods were used to examine the spatial variability of chemical parameters for the stream sites. These tests were used to determine whether any significant differences in the concentration levels exist between the monitoring sites, and if there are any distinguishable patterns. The results of these tests indicate that six sites show the highest levels, based on median values, of most chemical parameters: Bob Bay (BB-1), St. Louis-1 (SL-1), and Partridge-1 (P-1); Partridge-2 (P-2), Embarrass-1 (E-1) and Dunka-1 (D-1). All of the remaining sites are quite comparable to each other (Group C). The six sites previously listed can be divided into two additional groups (A and B) on the basis of water quality, but the group ranking varies parameter by parameter (Figures 5 and 6).

Figures 5 and 6

Monitoring results for the three stream grouping (A, B, and C) are summarized in Appendix 2. The parameters which show little difference between the site groups are: copper, zinc, aluminum, cadmium, mercury, cobalt, non-filterable residue, dissolved oxygen, titanium, methylene blue active silica (MBAS), selenium, silver, oil and grease (O&G), biochemical oxygen demand (BOD), turbidity, total

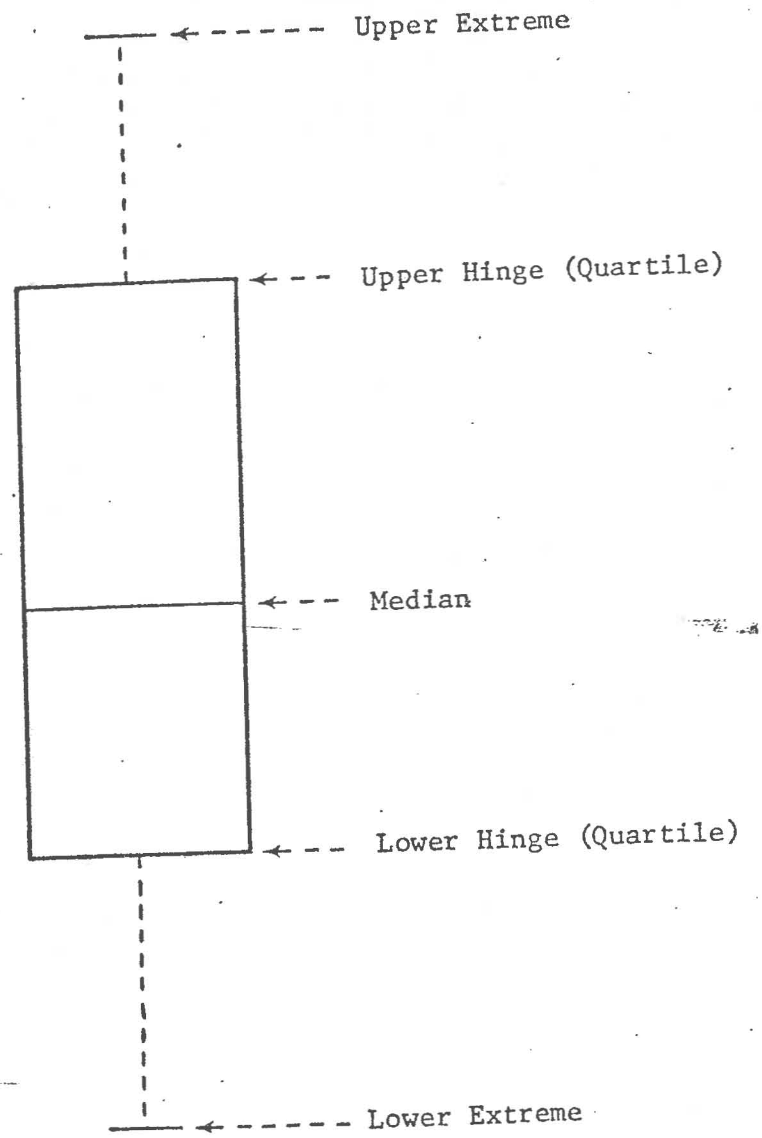
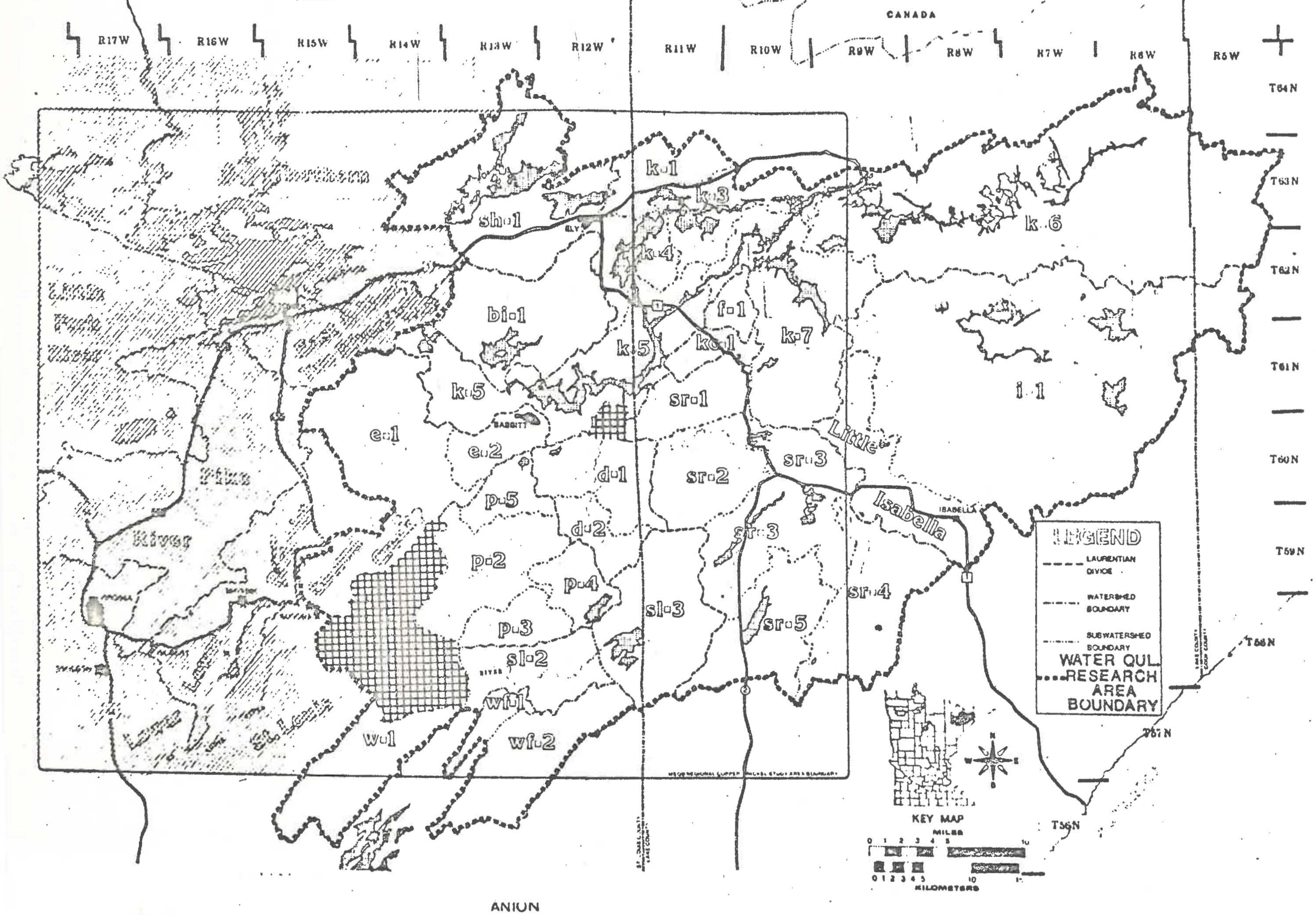


Figure 4 Example, box plot.

FIGURE 5

▦ GROUP A STATIONS AND CORRESPONDING WATER SHEDS

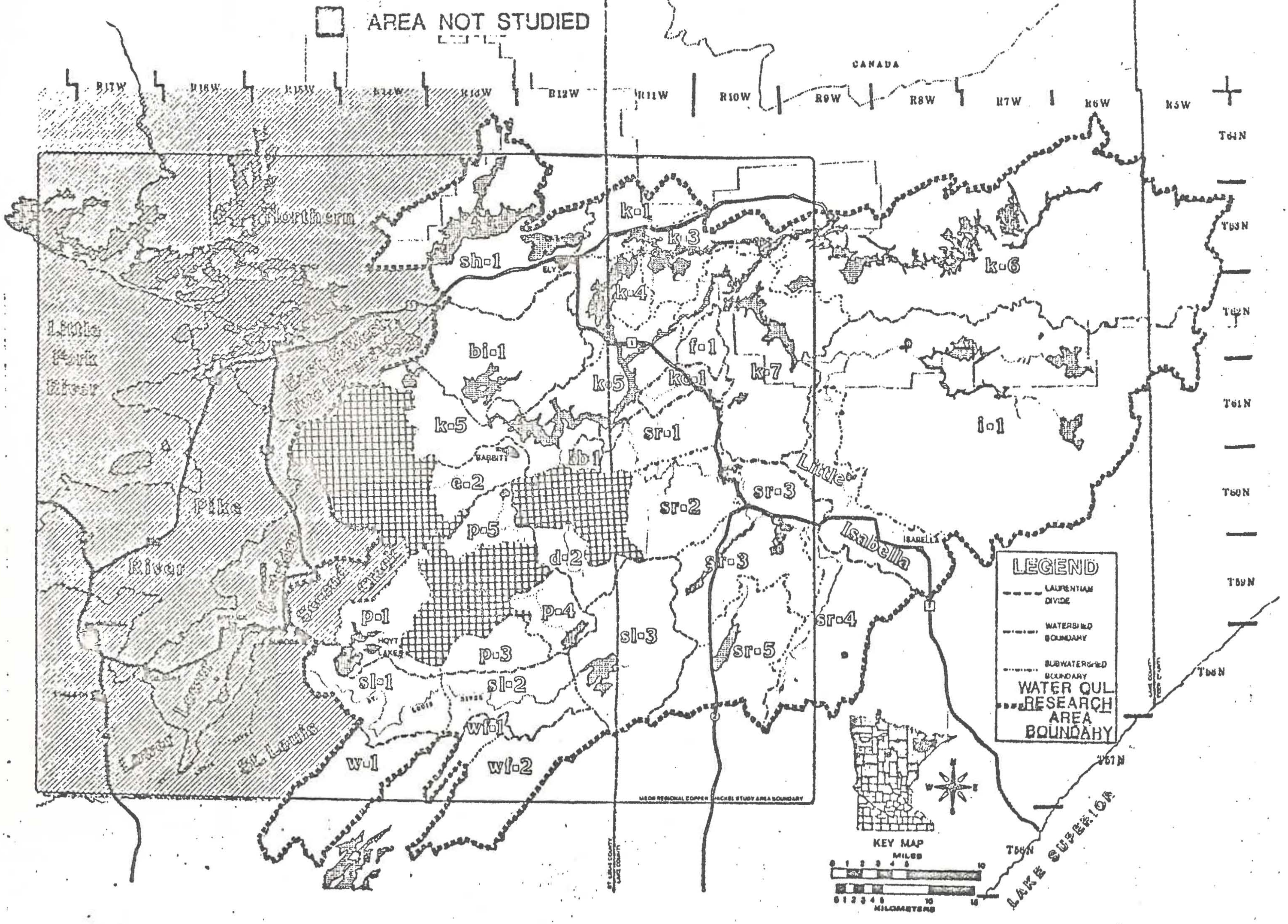
☐ AREA NOT STUDIED



ANION

FIGURE 6

▦ GROUP B STATIONS AND CORRESPONDING WATER SHEDS



organic carbon (TOC), the various radioactive measurements, nitrate and nitrite (NO_3 & NO_2), ammonia (NH_3), and total Kjeldahl (KJD) Nitrogen. The following parameters generally appear to be higher in group A than group B with both groups higher than group C: nickel, calcium, magnesium, hardness, filterable residue, pH, specific conductance, alkalinity, bicarbonate, sulfate (SO_4), dissolved inorganic carbon (DIC), silica, manganese, fluoride, chromium, potassium, fecal coliform, ortho phosphorus, and total phosphorus. In contrast, other parameters (lead, iron (both total and dissolved), complexing capacity, color, chloride, arsenic, chemical oxygen demand (COD), barium, and total nitrogen) resulted in the relationship of group B streams higher than both groups A and C. Four parameters were higher in group C than in groups A or B: dissolved organic carbon (DOC), hydrogen ion (H^+), sodium, and cyanide.

While generalized statements of classifications based on the water quality of streams can be made, enough variability exits to justify caution when applying these generalizations to impact assessment. For example, group C stations are considered to be representative of relatively undisturbed watersheds for this area of northeastern Minnesota and can be considered indicative of background levels. Group A and B stations are located in watersheds where significant human disturbance of the land has occurred. However, caution is required when linking the increased (or decreased) water quality parameter value observed to specific human activities in the watershed. Geological and topographical natural conditions within the watershed; such as natural weathering of outcrops of sulfide materials cannot be overlooked.

The lake data base was not large enough to permit a similar evaluation (see Appendix 3 for lake summaries).

4.3.2.1 General Parameters--Calcium is a major constituent of many common igneous-rock minerals (such as feldspars, pyroxenes, and amphiboles) and is widely distributed in soils. Waters draining such regions contain varying concentrations of calcium, generally in the ionic form (Ca^{+2}). Because of the relative insolubility of igneous rocks compared to sedimentary materials such as limestone, calcium concentrations are generally low in waters draining igneous basins such as the Study Area (Refer to Volume 3-Chapter 1 for a detailed discussion on the geology and mineralogy of the area). Calcium concentrations of surface waters in the Study Area are generally lower than waters of the Mississippi River where it enters the municipal waterworks in the Twin Cities (Table 4). The lower calcium values for Study Area waters are probably due to the characteristics of the rocks and soils of the Study Area, the principal source for calcium. Rocks and glacial materials of most of the Study Area are less calcareous than elsewhere in the state. On the other hand, calcium concentrations of waters in the Study Area are comparable to those of the Coeur d'Alene River, Idaho, which drains an area of Precambrian igneous rocks.

Table 4

Acidification of surface water by acidic precipitation or by acid-mine drainage is an important environmental issue. (See section 4.3.5 of this chapter). Frequency distributions (not shown) were used to examine the susceptibility of surface waters to acidification. For stream waters north of the Laurentian Divide; 84 percent of the calcium levels measured were at or below 10 mg/l, and 93 percent of the values were at 15 mg/l, or lower. South of the Divide only 29 percent of the values were 10 mgl/l, or less, and 84 percent of the values were

Table 4. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Calcium (Ca) in mg/l (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1.8-80.0	7.4	333
Lakes	1.9-46.0	7.2	129

Standards and Protection Guidelines

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/l

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
38.8-51.3	6.8

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.
[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.
[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.
[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.
[e]
[f]

31.5 mg/l or less. Clearly surface waters in the southern portion of the Study Area contain, on the average, more calcium (although both areas have low levels), which no doubt reflects the presence of calcareous glacial material which is largely absent north of the Divide. The significance of these results as they pertain to the susceptability of surface waters to acidic precipitation is discussed in more detail in section 4.3.5 of this chapter.

For lakes north of the Divide, 84 percent of the samples were 10 mg/l or less (the same as measured in streams). For lakes south of the Divide, 59 percent of the values were 10 mg/l or less and 84 percent of the values were 22 mg/l or less. This comparison shows that lakes south of the Divide tend to remove the calcium from stream waters, and lakes north of the Divide tend to reflect stream calcium values.

Other than spring events, concentrations of calcium in streams of the Study Area were generally independent of flow except in the St. Louis and Partridge River systems. The concentration of major cations and anions in these streams were significantly higher than any other stream studied, except for Unnamed Creek (BB-1). During runoff and storm events, the chemical mass contribution from the atmosphere was small compared to that already in the watershed from natural (bedrock and soils) and anthropogenic (mining, road salt, etc.) sources, so the net observed effect was dilution by the event water. In other watersheds where cation and anion concentrations were not so large, the influence of atmospheric inputs was greater and may be a dominant process affecting observed water quality.

Tofte Lake had greater calcium levels than Colby and Wynne, which in turn were greater than all others. Although the presence of higher calcium concentrations in Colby and Wynne can be explained by their location in watersheds affected by mining, the same cannot be said for Tofte. The chemistry of Tofte Lake is probably closely related to either groundwater seepage, surrounding soils, or its sediments, but specific data explaining the higher (31 mg/l median, 46 mg/l maximum) calcium levels found in this lake are not available.

Chloride, the most widely distributed halogen in natural waters, is found in the Study Area in apatite and amphibole minerals. Upon weathering, chloride ions (Cl^-) are released into solution. High concentrations are usually associated with either high-chloride groundwater seepages, road salt applications, or industrial wastewaters. Chloride is not very reactive chemically, and is therefore very mobile. It does not significantly adsorb onto mineral surfaces, is not involved in key biochemical processes, forms no significant complexes with other ions, forms no salts of low solubility, and enters into few oxidation-reduction reactions.

Chloride ion in high concentrations represents a part of the total dissolved solids in water. It can be detected by taste and can lead to consumer rejection of the water supply. On the basis of taste, the wide range of taste perception of humans, and the absence of information on objectionable concentrations, the U.S. EPA recommends a limit for public water supplies of 250 mg/l chloride (EPA 1976).

Chloride concentrations were relatively constant over time throughout the region, with the greatest variability at the seven stations which exhibited higher concentrations (BB-1, D-1, SL-1, P-1, P-2, P-5, and E-1)(Appendix 1). Elevated levels at these stations may be the result of road salt (sodium chloride), dust suppressants (calcium chloride) or sewage effluent from cities or taconite mining operations. Table 5 shows the amount of road salt used in this area for the winter period 1975-1976.

Table 5

The median chloride concentration in lakes was about 1.6 mg/l (Table 6), the same as for group C streams (remember that group C streams are considered background). Streams in disturbed areas (group A & B) had median values 5 to 10 times higher than background (see Appendix 2).

Table 6

The color of natural waters is caused by the presence of organic material (e.g. humus, peat materials, algae, weeds), organic acids, and inorganic compounds (e.g. iron, manganese).

The intensity of color in a water sample is determined by comparing it to a standard platinum-cobalt solution. Because color is a composite property that may result from a variety of constituents, a direct relationship between color and concentration of any given organic or inorganic constituent is not expected.

Increasing color in lakes and streams appeared to be primarily related to the total organic carbon and dissolved iron (Mustalish et al. 1978). In addition, greater color was associated with two terrestrial characteristics--increasing soil depth (the drumlin areas) and the presence of bogs in a watershed. These conditions are found, for the most part, in the southern portion of the Study Area between South McDougal Lake and Whiteface Reservoir. By contrast, areas in

Table 5. Application of road salt in northeastern Minnesota during winter season 1975-1976.

COMMUNITY	AMOUNT	TYPE	RESPONSIBLE AGENCY Mun	Cnty	State	
Aurora	Approx 26 tons	Fortified ice control salt	X	X		No State Highway
Babbitt	Approx 10 tons Approx 10 tons	Crushed rock salt Chloride pellets	X	X		No State Highway
Biwabik	Approx 40 tons	Crushed rock salt	X	X	X	
Ely	Approx 28 tons	Crushed rock salt	X	X	X	
Eveleth	Approx 30 tons	Crushed rock salt	X	X	X	
Gilbert	Approx 40 tons	Crushed rock salt	X	X	X	
Hoyt Lakes	Approx 5 tons	Crushed rock salt	X	X		No State Highway
Tower	Approx 3 tons	Sand & crushed rock salt	X	X	X	
Virginia	Approx 100 tons	Crushed rock salt	X	X	X	
St.Louis County	Approx 3,884 tons Approx 10 tons	Sod. Chol. Cal. Chol				
Minn. Dept. of Transportation District 1B	Approx 9,253 tons	Rock salt			X	Includes parts of St. Louis, Koochiching, and Itasca counties

Table 6. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Chloride (Cl) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.1-88.0	2.0	462
Lakes	0.1-9.3	1.6	94

Standards and Protection Guidelines

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
250-domestic consumption	250-domestic consumption	250-domestic consumption	NA
50-250-industrial consumption			

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
8.6-16.5	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

which frequent bedrock outcroppings occurred and where soil depth was minimal had less colored water, and water of less variable color. The Kawishiwi River system, which drains the northern portion of the area, is low in color and is a good example of such conditions.

Water color in the Study Area was higher than that reported for the lower Mississippi by the Geological Survey, but only St. Louis River water was higher than that reported by the Minneapolis Water Works (Table 7).

Table 7

Magnesium is typically found in several igneous rock types including: olivine, pyroxenes, and amphiboles. It is also a constituent of such altered rocks as chlorite, serpentine, ilmenite, and talc, and is widely distributed in soils.

In natural waters, its most common soluble form is as magnesium ion (Mg^{+2}). Because magnesium is less abundant than calcium in most rocks, magnesium concentrations in water are usually less than calcium and this was observed in the region's surface waters. Although differential retention of magnesium (in comparison with calcium) has been reported for some very dilute waters of northeastern Wisconsin (Hutchinson, 1957) there is no evidence of such a process in the Study Area.

Seasonal variations of magnesium concentrations were slight. Like calcium, magnesium concentrations were found to be relatively constant over a wide range of stream discharges.

Magnesium was found to correlate (P 0.05) with calcium, suspended solids, total dissolved solids, and conductance. Like calcium, magnesium values were higher in

Table 7. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Color values in platinum-cobalt units (PCU) (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	4-500	90	463
Lakes	1-400	80	141

Standards and Protection Guidelines in PCU

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
15-domestic consumption	75-domestic consumption	75-domestic consumption	NA
30-fisheries and recreation			

Comparative Data in PCU

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
19-120	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

disturbed watersheds and those with deep soils, such as Bob Bay (disturbed) and the St. Louis and Partridge watersheds.

Magnesium values were highest in watersheds impacted by mining, including Bob Bay (BB-1), St. Louis (SL-2), and Partridge (P-1) watersheds. As with calcium, magnesium concentrations in lakes are comparable to background stations (Table 8 and Appendix 2).

Table 8

With the exception of Bob Bay and the St. Louis River, concentrations of magnesium in Study Area waters were lower than in Mississippi River at the Twin Cities municipal water intakes and generally comparable to Twin Cities tap water. The higher magnesium concentrations of the lower Mississippi reflect the passage of this river through areas of Minnesota overlain by glacial tills higher in calcium and magnesium than the surficial materials of the Study Area. As is the case with calcium, magnesium content of the Coeur d'Alene River is comparable to that of waters in the northeastern part of the Study Area.

The occurrence of potassium in the environment is closely related to sodium, except that potassium feldspars are more resistant to weathering than similar sodium compounds. As such, potassium is usually found at lower concentrations than sodium in water from igneous basins. In surface waters, potassium is usually present in ionic form (K^+). Potassium concentrations in streams were relatively constant over time.

Spatial variations in potassium values appear to be related to the degree of disturbance of the watershed. The highest median values were observed in St.

Table 8. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Magnesium (Mg) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1.0-40.0	3.8	333
Lakes	0.6-12.2	3.1	129

Standards and Protection Guidelines

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
11.9-19.0	3.02

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Louis (SL-1), Partridge (P-2), Dunka (D-1) rivers, and Bob Bay (BB-1), areas all impacted by taconite mining. The Embarrass watershed also showed elevated levels, possibly due in part to urbanization and/or silviculture. Lake water potassium concentrations were comparable to background levels found at Group C stations (Table 9 and Appendix 2).

Table 9

Potassium values in the most heavily impacted streams were comparable to Mississippi River values of the Twin Cities municipal water intakes. Potassium values in the St. Louis River (SL-1), slightly exceeded those in Twin Cities drinking water, as might be expected based on the composition of bedrock in the Study Area as compared with the potassium sources elsewhere in the state. Potassium values in the Coeur d'Alene River, Idaho, are comparable to those of the Study Area.

Silica in the form of silicon in the tetrahedral structure SiO_4^{-4}, is the basic unit of most igneous rocks, and was identified in nearly all minerals analyzed from the Study Area. Silica is common in natural waters in the form of SiO_2, as a result of weathering processes. Silica is an important (in some cases limiting) nutrient for diatoms and is also used by chrysophytes and freshwater sponges. In the surface waters of lakes it undergoes a seasonal cycle of depletion following diatom blooms and redistribution at turnover. Bottom waters of thermally stratified lakes exhibit increased concentrations of silica during anaerobic periods, possibly because of reduction of ferric silicate from the sediments.

Table 9. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Potassium (K) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.2-8.4	0.6	310
Lakes	0.2-2.2	0.6	84

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
2.0-2.7	0.98

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

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Within the Study Area spatial variations were closely related to the presence or absence of upstream disturbance. Stations downstream of mining (BB-1, SL-1, P-1, and P-5) exhibited higher concentrations of silica than those upstream (Appendix 1). The highest concentrations of silica in lakes were found in Gabbro and Wynne, with the lowest concentrations in Tofte and Clearwater. Temporal variations of silica were not analyzed.

The range of silica concentrations in the Study Area is broader than those in the Mississippi River at St. Paul. The median concentration of silica in Group C (undisturbed) streams is greater than in lakes within the Study Area (Table 10 and Appendix 2).

Table 10

Sodium in the Study Area occurs in unaltered minerals, particularly feldspars (e.g. plagioclase) and amphiboles, as well as altered minerals, such as smectite. Plagioclase, the main source of sodium in the Study Area, readily yields its sodium, and some silica, into solution when in contact with water, where sodium is found in ionic form (Na^+). Although it is not considered one of the ten elements essential to plant growth, sodium is actively concentrated by aquatic plants, suggesting some metabolic need for the element.

Watersheds exhibiting anthropogenic disturbances had the highest median concentrations of sodium in solution, i.e. background stream sites have lower sodium levels (Appendix 2). It is not unusual to expect sodium trends to parallel chloride trends. No clear spatial distinctions were observed in the lakes monitored.

Table 10. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Silica (Si) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1-34	7	465
Lakes	1-19	4.8	135

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
5.7-11	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Sodium concentrations across the region were constant over time except in the Partridge River where decreases in concentration accompanied increased flows. Somewhat more limited dilutional effects were observed at peak of spring melt in the Dunka, Stony, St. Louis, and Kawishiwi River systems.

Sodium concentrations in the St. Louis and Partridge Rivers are comparable (or higher than) those in the lower Mississippi at the Twin Cities municipal water intakes (Table 11). Concentrations in the Kawishiwi River and Filson Creek (Appendix 1) are somewhat lower than in the Coeur d'Alene River, Idaho, perhaps because of the greater degree of surficial disturbance by mining in the Coeur d'Alene watershed.

Table 11

Specific conductance is a measure of water's ability to conduct electrical current, which in turn is the result of the presence of charged ionic species. In undisturbed igneous basins, characterized by insoluble rock, weathering is expected to occur slowly. This should be reflected in low concentrations of dissolved ionic species and, consequently, low conductivity levels. This pattern was observed in the Study Area. Sites downstream from disturbed areas had median specific conductance levels almost six times higher than background sites (Group C) and lakes (Table 12 and Appendix 2).

Table 12

Hardness of water is an old term related to its capacity to form insoluble compounds in the presence of soap. Historically, hardness was measured by titration

Table 11. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Sodium (Na) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.2-45.0	1.8	304
Lakes	0.8-18.0	1.8	77

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
6.2-14.0	3.16

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 12. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Specific conductance values in micro-mhos/cm at 25°C
(November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	12-1198	65	463
Lakes	24-389	65	141

Standards and Protection Guidelines in micro-ohms/cm at 25°C

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
1000-Agriculture and Wildlife	NA	NA	NA

Comparative Data in umhos/cm

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
300-463	94.4

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

with a standard soap solution. In waters where the predominant cations are calcium and magnesium and the predominant anions are carbonates, hardness is closely related to the amounts of these ions and is often measured as the sum of calcium and magnesium ions (and expressed as mg/l of $CaCO_3$). This process was followed by the Regional Study.

Based on the classification system presented in Table 13, a majority of the Study Area surface waters would be considered "soft," while waters in disturbed areas would be considered moderately hard to hard waters (Table 14 and Appendix 2).

Tables 13 and 14

Although hardness is a composite parameter and is not generally very useful in water quality studies, in the case of the Regional Study, bioassay experiments revealed that nickel was less toxic to aquatic organisms in harder waters (see Volume 4-Chapter 1).

Turbidity is a measure of suspended particulates in water. It is caused by plankton, clay, silt, detritus, or other finely divided suspended material. Increases in turbidity levels can be caused by increases in algae growth or inorganic material load. If the biomass is increasing, nutrient levels may also be increasing. An increase in nutrient levels along with concommitant increases in inorganic load could be the result of recent upstream land disturbance, such as excavation due to road construction.

Turbidity is a quick, simple, analytical method that provides important information on the general status of waters. For the Study Area, no clear differences between stream groupings were evident (Table 15 and Appendix 2).

Table 13. Classification of water by hardness content.

Conc., mg/l $CaCO_3$	Description
0- 75	soft
75-150	moderately hard
150-300	hard
300 and up	very hard

SOURCE: Sawyer 1960.

Table 14. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Hardness in mg/liter $CaCO_3$ (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	5.3-310.0	31.0	206
Lakes	9.0-142.0	28.9	92

Standards and Protection Guidelines in mg/liter $CaCO_3$

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
50-500-Industrial Consumption	NA	NA	NA

Comparative Data in mg/liter $CaCO_3$

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
150-180	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 15

Total organic carbon (TOC) provides some indication of the amount of bioproductivity in an aquatic system (including input from adjacent land areas which feed into the system). The carbon compounds that comprise TOC are: metabolic waste products, such as amino acids; detrital matter composed of dead and decaying organisms; or living matter, for example phytoplankton, zooplankton, and bacteria. Total organic carbon provides a measure of both dissolved organic carbon and particulate organic carbon.

Particulate and dissolved organic compounds can bind metals through sorption and complexation, respectively. This binding has important ramifications. Bound metals may be biologically unavailable, or more available, depending on the metal in question, the nature of the organic compound, and the pH of the water. Some toxic metals entering an aquatic system may be rendered less toxic through complexation.

It appears that in headwater lakes and streams such as Filson Creek and the Partridge River, high organic carbon concentrations are often associated with high color; conversely, downstream waters usually have less color (Table 16 and Appendix 2 and 3).

Table 16

4.3.2.2 Summary Discussion of General Parameters--Median values for the major ions in streams of the Study Area are illustrated in Figure 7. This figure shows that Study Area waters are dominated by calcium as the major cation and

Table 15. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Turbidity in Jackson Turbidity Units (JTU) (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.5–64.0	2.1	463
Lakes	0.4–7.0	2.0	135

Standards and Protection Guidelines in JTU

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
5–domestic consumption	25–fisheries and recreation	NA	NA
10–25 fisheries and recreation			

Comparative Data in JTU

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
8.5–13.0	No data available

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 16. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Total Organic Carbon (TOC) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.4-45.0	15.0	80
Lakes	4.6-38.0	14.0	142

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
No data	No data

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

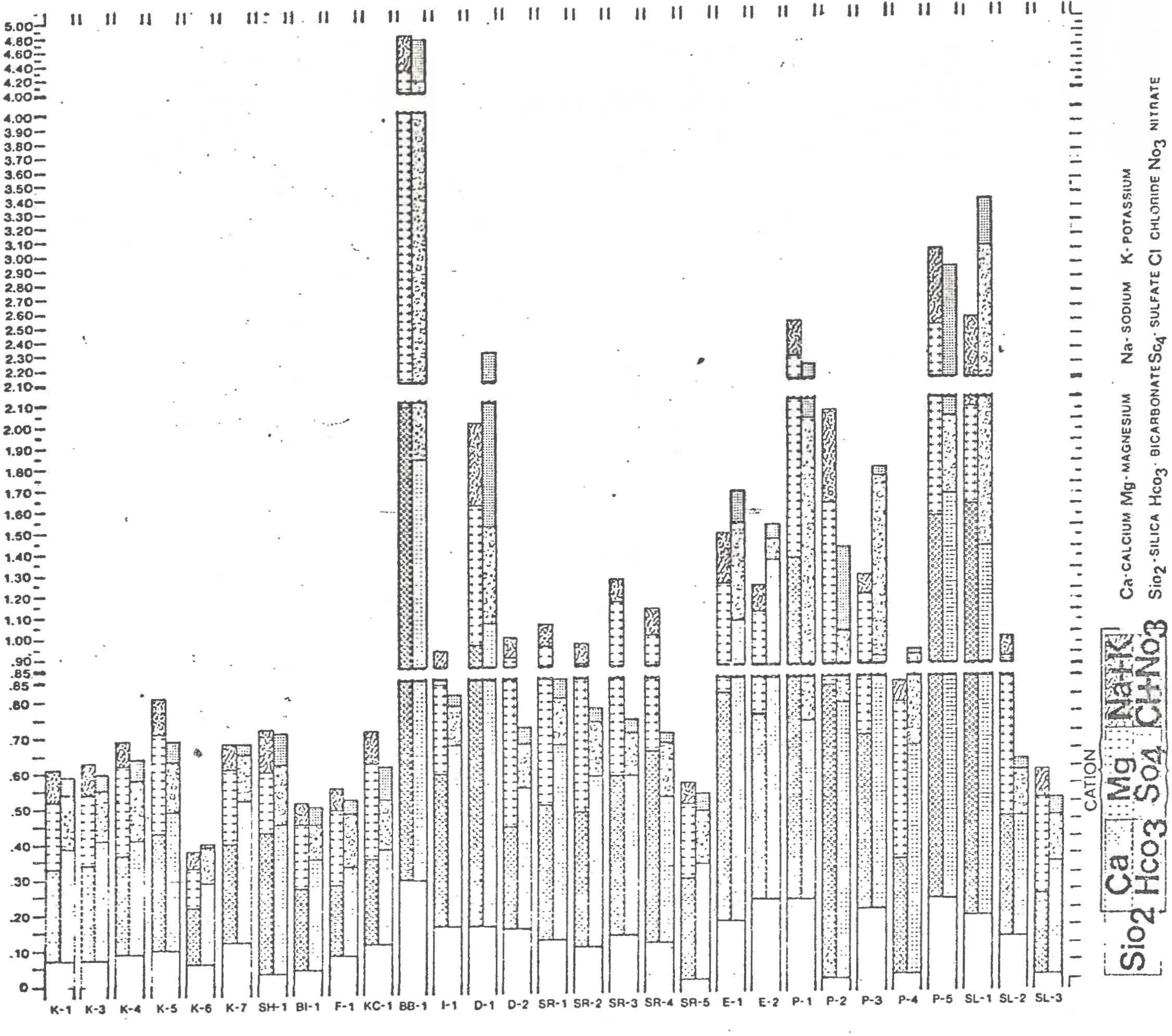
carbonates as the major anion. The sum of the concentrations of anions should be in balance with the concentration of cations. The reason that this is not the case in Figure 7 is probably because additional ions other than those considered are important in waters of the Study Area. Cations generally exceed anions in all waters studied except stations K-6, D-1, E-1, E-2, and SL-1. Figure 7 also illustrates the higher overall concentration of major ions in streams south of the Laurentian Divide than north of the Divide. Exceptions to this generalization are stations BB-1 and D-1 north of the Divide, which are downstream from mining operations.

Figure 7

As previously mentioned, the spatial variability of the stream general parameters falls into a pattern of three distinct groupings. Group A streams (Partridge River-1, St. Louis River-1, and Bob Bay-1) include drainages both north and south of the Laurentian Divide and are downstream of mining operations (Figure 5). Group B stations (Partridge River-2, Embarrss River-1, and Dunka River-1) are also downstream of mining, but generally show less elevated levels of ions than Group A stations (Figure 6), but in some cases Group B stations can have higher concentrations (e.g. Na and Cl). All remaining streams, from both north and south of the Laurentian Divide form the third group. It is apparent from a summary (Appendix 2) that the concentrations of all of the general parameters are higher in Groups A and B, the impacted stations, than in Group C, the background sites. In general, the Group A stations are higher than Group B, probably an indication of the relative amount of impact. While a clear difference in water quality of watersheds containing mining operations can be seen, sufficient data

FIGURE 7

Major Ions in Streams



to prove a direct cause and effect relationship for all parameters is not available and was not the purpose of monitoring programs conducted by the Regional Copper-Nickel Study. Stations with the highest concentrations of general parameters exhibited the greatest variability in water quality, and smaller drainage areas showed greater variability than larger ones.

Temporal variations in streams cannot be easily separated from flow-dependent relationships. Two extremes of flow conditions exist: peak flow and base flow. Peak flow may occur immediately after precipitation or during the influx of meltwaters in the spring. During "spring flush" the constituents stored throughout the season in the snowpack are released with meltwaters. This release results in elevated levels of only a few constituents.

Interrelationships between flow conditions and water chemistry take many forms. Concentrations may be: directly related to flow, as is often the case with constituents whose major input is within the watershed; inversely related so that peak flow causes dilution; or independent of flow.

Throughout most of the year the concentration of most parameters is independent of flow. Calcium and sodium concentrations at station P-1, and calcium concentrations in the St. Louis River were exceptions. In these cases a distinct dilutional effect was caused by spring runoff and storm events. In two instances (potassium at Isabella and sodium at Kawishiwi, K-5) there were slight indications that concentrations were increasing with flow.

Linear correlations for five general parameters were tested for statistical significance at the 0.05 level (Table 17). In stream waters of the Study Area, significant direct relationships were found between calcium and pH, magnesium, suspended solids, specific conductivity, and dissolved solids. This means that as the level of calcium varies, the level of these parameters (except for pH) vary proportionately. Suspended solids, dissolved solids, and specific conductance are in large part due to calcium content and therefore such a relationship is expected. Because calcium is a major cation (a cation is a positively charged (+) ion) in the Study Area surface waters, it dominates these measurements. It is also common for calcium to correlate with magnesium. Chemically these two elements behave similiarly; both occur in the same family. Although calcium is more abundant in the earth's crust, the calcium to magnesium ratio observed in water is similar to the ratio in the rock present in the Study Area.

Table 17

The relationship of pH to calcium is inverse. As pH levels decrease, calcium concentrations increase. The mobility of calcium in water is closely linked to the dynamics of dissolved carbon dioxide CO_2. At higher pH's, calcium tends to associate with bicarbonate ions (HCO_3^-) and precipitates out as $CaHCO_3$. Reducing the pH would dissolve these compounds and release the calcium to solution.

In lake water, calcium also correlates with these chemical factors, but in addition is directly related to copper, nickel, and mean depth. Why copper and nickel correlate with calcium in lakes is unknown. It could either be coincidental, or perhaps the chemistry or the lake biota that affect calcium may also affect copper and nickel in a similar fashion. Lakes can act as sinks, where elements such as these are transported, either chemically or biologically, to the bottom sediments. Generally the transport is irreversible.

Table 17. Correlations: general parameters (P 0.05).

STREAMS		LAKES	
Sp. Cond:	Ni Ca Mg Suspended solids Total dissolved solids(t) pH	Sp. Cond:	Cu Ni Suspended solids Mg Alkalinity(t) Total dissolved solids
Color:	KJD-N TOC DOC Fe(t)	Color:	Fe Tot-N KJD-N S.D.(t) TOC DOC D.O.
Ca:	pH Mg(t) Suspended solids Specific conductivity Total dissolved solids(t)	Ca:	Alkalinity Specific conductivity(t) pH Suspended solids Cu(t) Ni(t) Total dissolved solids(t) $\overline{Z}$ (t)
Mg:	Suspended solids Ca(t) Specific conductivity(t) Total dissolved solids(t)	Mg:	Cu(t) Suspended solids(t) Specific conductivity Alkalinity(t) Color(t) Dissolved solids(t)
TOC:	Color Tot-N KJD-N DIC(t) TDS(t) TON(t)	TOC:	Secchi disk Iron Color Suspended solids DO(%) KJD-N Ortho-P Zinc(t) Lead(t) Tot-N(t) D.O(%)(t) $\overline{Z}$; Zmax(t) KJD-N(t) TSI-SD(t)

(t) = log transformed data.

Specific conductance, which is based on total ionic concentration, was correlated with concentrations of the two major cations: calcium and magnesium. In addition, specific conductance was correlated with suspended and total dissolved solids, pH, and nickel. Similar patterns of correlation existed for calcium and magnesium. Both are significantly correlated with suspended solids, total dissolved solids, and specific conductance, as well as being correlated with each other. In addition, calcium concentration is correlated with pH, as might be expected because the major anion associated with calcium is carbonate, which is involved in acid-base systems. Color and total organic carbon are both correlated with each other and with Kjeldahl (organic) nitrogen. Color is also significantly correlated with dissolved organic carbon and total iron, whereas total organic carbon is correlated with dissolved inorganic carbon, total dissolved solids, total nitrogen and total organic nitrogen.

For the most part the relationships observed are not too unusual and can usually be explained. More correlations exist for lakes than for streams (Table 17). Lakes, because they act as sinks, will attenuate or equilibriate chemical concentrations. Thus correlations may exist, not because the correlated parameters are controlled similarly but because the lake tends to dampen the natural fluctuations of the chemical parameters. In this region, especially north of the Laurentian Divide, lakes are an integral part of the major river systems. Any natural or man-induced change in the concentration of any parameter will be modified by lakes, especially lakes that are deep (and which stratify) and have longer water residence times.

Spatial variabilities between lakes were less easy to test statistically because of smaller sample size than the data set for streams. Analysis of variance delineated the following trends between lakes for nine water quality parameters:

Calcium: Tofte greater than Colby, Wynne greater than others
Magnesium: Slate, Colby, Wynne greater than most others greater than Perch, One, Triangle
Potassium: Colby greater than most others greater than Wynne
Sodium: no distinct grouping
Chloride: Colby greater than most others greater than Clearwater
Silica: Gabbro, Wynne greater than most others greater than Tofte, Clearwater
Specific Conductance: Colby, Tofte, Wynne greater than all others
Color: South McDougal greater than most others greater than Clearwater, Tofte
Total Organic carbon: Colby, Sand, Wynne, Long, Whiteface, South McDougal, Greenwood, Seven Beaver greater than all others

This analysis reveals a trend, with Tofte, Wynne, and Colby lakes exhibiting elevated ionic concentrations that are reflected in their elevated specific conductance levels. Clearwater is notable for its low chloride, silica, and color levels. Temporal variations in lakes are less related to flow conditions than to the amount of oxygen and thermal properties of the water. Most major ions do not undergo temporal cycles in lakes. Small lakes downstream of flashy streams will be greatly affected by the quality of the snow pack and individual storm events, and therefore could experience significant water quality variability. For example, certain ions may occur in higher concentrations in the snow pack as compared to the average concentration in the lake. During spring flush, the water quality of the lake would be dominated by the quality of the snow melt. At other times, the concentration of the same ion in rain may be significantly lower than the lake water quality and the concentration of the ions in the lake would be diluted during significant rain events. Since the quality of individual rain events can vary significantly, rain events may not always have a dilutional effect on the water quality of small lakes. Very small bodies of water might be expected to show similar responses to an input of allochthonous organic materials such as humic leachates.

4.3.2.3 Parameters Related to Acidity and Acid Buffering--Alkalinity is defined as the capacity of a solution to neutralize acid. It is predominantly produced by the presence of anions or molecular species of weak acids which are not fully dissociated above pH 4.5 (e.g. organic acids). Under most conditions encountered in aquatic environments, these dissolved species are bicarbonate and carbonate ions; although, theoretically, any ion that reacts with strong acid can contribute to alkalinity. Alkalinity is a measure of the buffering capacity of water, and since pH has a direct effect on organisms as well as an indirect effect on the toxicity of certain other pollutants in water, the buffering capacity is important to water quality. For the most part, alkalinity measurements are a bicarbonate measurement.

Alkalinity is important for fish and other aquatic life in freshwater systems because it buffers pH changes that occur naturally as a result of the photosynthetic activity of the chlorophyll-bearing vegetation. Components of alkalinity such as carbonate and bicarbonate will complex some heavy metals and reduce their toxicity markedly. For these reasons, the National Technical Advisory Committee (1968) recommended a minimum alkalinity of 20 mg/l and the subsequent NAS report (1974) recommended that natural alkalinity not be reduced by more than 25 percent but did not place an absolute minimual value for it. The use of the 25 percent reduction avoids the problem of establishing criteria on waters where natural alkalinity is at or below 20 mg/l, as is the case for some Study Area waters (Table 18). For such waters, alkalinity should not be further reduced (EPA 1976).

Table 18

Table 18. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Alkalinity in mg/liter $CaCO_3$ (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1-190	23	457
Lakes	1-73	19	141

Standards and Protection Guidelines in mg/liter $CaCO_3$

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	Any pollutant added to the water should not reduce the alkalinity more than 25% below ambient concentrations-fisheries and recreation		NA

Comparative Data in mg/liter $CaCO_3$

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
140-180	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Typically, alkalinity is measured by titration with standardized acid to a pH value of about 4.5. Because the water solution being titrated is mixed in the presence of air, alkalinity measurements below 10 mg/liter may be suspect. Special methods have been developed to eliminate this problem, and such methods should be used in the future when the low alkalinity waters of the Study Area are measured.

Bicarbonate ion (HCO_3^-) is the the predominant form of dissolved carbon dioxide in natural waters in the pH range of 7.0 to 9.0. At pH less than 7.0 carbonic acid (H_2CO_3) becomes more common, at a pH greater than 9.0, carbonate ions (CO_3^{-2}) become more common. The ultimate source of the CO_2 is the atmosphere. The linkage between the hydrologic cycle and the carbon cycle provides the mechanism for the introduction of CO_2 into natural water. The only mineralogical source of carbon dioxide identified in Study Area rock was calcite ($CaCO_3$) (see Volume 3-Chapter 1). Calcite is an insignificant source of bicarbonate to surface waters in undisturbed watersheds because it is a minor component of the rock in those areas. The atmospheric pathways of dissolved carbon dioxide to surface waters include direct deposition via precipitation, and indirect production through photosynthetic activity.

Spatial variation in bicarbonate levels appeared to be related to anthropogenic disturbances. It is possible that mining activities have exposed more mineral surface to weathering, thereby accounting for observed increases in concentration at stations SL-1, P-2, P-5, D-1, E-1, E-2, and BB-1 (soil chemistry variabiity could also account for some of the high values measured). Levels of bicarbonate (and alkalinity) were very low in the Kawishiwi river system (Appendix 1).

Relative ranking of lakes from high to low bicarbonate concentrations indicated Tofte and Wynne to be highest, most others were intermediate, and Perch and Turtle were lowest. In the case of Tofte Lake mineralized groundwater seepage into the lake may be the reason for the elevated bicarbonate concentration. As discussed in section 4.3.5.6, the lack of bicarbonate in snow-melt water significantly affects the alkalnity levels, and consequently the pH of some streams during the snow-melt season. As with many parameters the median bicarbonate concentration in lakes approximates that of background stream sites (Table 19).

Table 19

Sulfate ($SO_4^=$) is the major form of sulfur in the aquatic environment. Sulfur is widely distributed in igneous rocks as metallic sulfides. In the Study Area, these are principally chalcopyrite, pentlandite, and pyrrhotite. The weathering process for these minerals is relatively straightforward. When aerated water comes into contact with the minerals, the reduced sulfides are oxidized to sulfates which, in turn, are carried off by the water. In oxygenated water, over a wide range of pH, sulfate is a chemically stable ion. It does, however, tend to form ion pairs with metal ions. As sulfate concentrations increase, an increasing proportion of sulfate can be expected to form these associations. Reduction of sulfate to sulfide is usually associated with biochemical processes, particularly bacterial, under anoxic conditions.

A second source of sulfur for waters is the atmospheric deposition (both anthropogenic and natural) sulfur-containing materials. The significance of this pathway on the region's water quality will be discussed in section 4.3.5.

Table 19. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Bicarbonate (HCO_3) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	6-151	25	257
Lakes	9-88	20.5	38

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
No data	No data

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.
[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.
[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.
[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.
[e]
[f]

Elevated sulfate concentrations were found in waters downstreams from areas where accelerated oxidation of excavated/exposed sulfide deposits may be occurring due to mining operations (P-1, SL-1, BB-1).

The chemical activity of sulfate in lakes is somewhat different from that in streams because of the tendency for the bottom waters of deep lakes to become anaerobic (anoxic) during periods of thermal stability. Under entirely anaerobic conditions sulfate present in the water will be reduced to H_2S or precipitated as FeS, and the water loses sulfur compounds. These conditions do not exist in streams of the Study Area because they remain oxygenated throughout the year. The addition of sulfates may result in acidification of surface waters. Waters having significantly reduced pH levels are usually characterized by a different flora and fauna than normal waters. If sulfate levels in the Study Area become high enough to overcome the buffering levels present in surface waters, then acidification of waters will occur.

Levels of sulfate in undisturbed watersheds of the Study Area (such as the Kawishiwi River and Filson Creek) are comparable to the lakes and are lower than in the Mississippi River at metropolitan water intakes (Table 20, Appendix 2). Levels of sulfate in treated Twin Cities tap water are higher than in untreated water because of the treatment process. Sulfate concentrations in St. Louis River (SL-1) water exceed those of the treated tap water.

<u>Table 20</u>

The <u>pH</u> of water is an expression of the effective concentration of free hydrogen ions (i.e. those not bound by carbonate or other bases). Most natural waters

Table 20 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Sulfate (SO_4) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1-630	7.4	434
Lakes	1-140	7.8	138

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
250-domestic consumption	250-domestic consumption	NA	NA
10-wild rise production			

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
18-33.5	NA

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

have a pH in the range of 4-9, while a pH of 6.5-8.5 is typical for unpolluted surface water. In waters where photosynthesis (CO_2 utilization) by aquatic organisms takes place, diurnal pH fluctuations, where pH values as high as 9.0 are not uncommon during daylight hours, may be observed.

Only two watersheds, Filson Creek (F-1) and Keeley Creek (KC-1), showed a distinctive difference in pH from other sites. These two basins are small (Table 1) and drain areas containing bog material. Another explanation may be the fact that both streams pass over sulfide mineral zones, which apparently results in increased copper, nickel, and sulfate levels. These factors can all contribute to the lower pH observed. In addition, the alkalinity levels were also low in these streams, which explains why the pH is not buffered upward. Acidic precipitation may also be affecting these two systems (see section 4.3.5).

Overall most of the surface water pH values measured in the Study Area to date are near the neutral point (pH=7), especially the stream sites. Future changes in regional acid deposition rates may significantly affect pH values, with the most noticeable effects in headwater areas (Table 21).

Table 21

Calcite saturation indices (CSI) were calculated for all study lakes. This index provides a measure of a lake's ability to assimilate hydrogen ions (e.g. resist a change in pH due to an acid input) (Conroy et al. 1974). Acidification of surface waters by acidic precipitation and acid mine drainage is discussed in section 4.3.5 of this chapter. The resistance to pH change is a function of the type of acid input (i.e. strong or weak acids) and the type of chemical

Table 21. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

pH in pH units (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	4.7-8.4	6.91	458
Lakes	5.7-8.8	7.11	141

Standards and Protection Guidelines in pH units

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
6.5-8.5 6.5-9.0 Fisheries & recreation 6.0-9.0- Industrial consumption 6.0-8.5- Agricultural & wildlife	6.5-9.0 Fisheries & Recreation	5-9-Domestic consumption 6.5-9.0- fisheries	NA

Comparative Data in pH units

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
7.6-8.5	——

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

components in the receiving water which can assimilate or bind the hydrogen ions. CSI relates calcium, alkalinity, hydrogen ions, and the 2nd dissociation constant of carbonic acid (H_2CO_3), viz:

$$CSI = -Log_{10}(IAP) + Log_{10}(K_2CaCo_3)$$

$$\text{where } IAP = \frac{(Ca)\ K_2\ (AlK)}{40{,}000\ (H^+)}$$

and where $Ca = mg/l$
$AlK = eq/l$
$H = eq/l$
K_2 = 2nd dissociation constantof H_2CO_3

Lakes with an index less than 3.0 are considered well buffered; lakes with an index between 3.0 and 5.0 are poorly buffered with the possibility that acidification may already be occurring; and, an index over 5.0 indicates lakes with little or no buffering ability and a strong possibility that severe acidification has already occurred.

The CSI's for the 26 lakes are presented in Table 22. Tofte Lake appears to be nearly saturated with respect to calcium carbonate, and therefore, very well buffered. The poorly buffered lakes are, with one exception, all headwater lakes. This may be explained by the fact that buffering is a function not only of atmospheric processes, but also of watershed geology. Headwater lakes, such as Greenwood, have smaller drainage areas than downstream lakes, such as Birch. The chemistry of headwater lakes often reflects that of precipitation, with watershed contributions to lake chemistry assuming secondary importance. In general, in the Study Area as one proceeds from headwater to downstream lakes, the ability of the lakes to assimilate hydrogen ions increases. In addition to Study Area Lakes, CSIs were calculated for thirty lakes located in the Boundary

Waters Canoe Area (BWCA). Data on the lakes were obtained from the U.S. Forest Service (USFS) in Duluth (Table 23). Fifty percent of the lakes were found to be poorly buffered, and with few exceptions these represented headwater lakes. This analysis indicates that the headwater areas of the region are generally not well-buffered and have limited abilities to assimilate additional and possibly present acid loading.

Tables 22 and 23

4.3.2.4 Summary Discussion of Parameters Related to Acidity and Acid Buffering--Group A streams (BB-1, SL-1, and P-1) exhibited significantly higher pH, alkalinity, and sulfate values than group B streams, and group B streams, in turn, exhibited significantly higher values for these parameters than all other streams (see Appendix 2). Unlike the general parameters discussed earlier for which elevated values and increased variability went hand-in-hand, stations with higher pH, alkalinity, bicarbonate, and sulfate, did not necessarily exhibit greater variability. Headwater areas of streams could not be distinguished statistically from downstream stations, although headwater areas of given streams (St. Louis River and Stony River) had lower median pH values than at their mouths.

Alkalinity exhibited partial dilution effects in all watersheds, except those of the Kawishiwi drainage that lie downstream of large lakes (Bear Island, Shagawa, and Kawishiwi-6 and 7). Low pH values during winter base flow at Filson Creek reflect the pH of precipitation, because samples were withdrawn from meltwaters surrounded by ice.

Determinations of sulfate concentration and pH were made for samples of surface water, groundwater, and precipitation collected from the Filson Creek watershed

Table 21. Calcite saturation index (CSI) for Regional Copper-Nickel Study lakes studies.

LAKE	CSI[a]	LOCATION[b]
Tofte	0.3	H,N
Wynne	1.1	S
Triangle	1.4	H,N
Colby	1.4	S
Bass	1.5	N
Slate	1.5	N
Bearhead	1.6	H,N
Sand	1.8	H,N
Cloquet	2.0	H,S
Birch	2.0	N
Big	2.0	
Pine	2.1	H,S
Gabbro	2.3	N
White Face	2.3	H,S
Bear Island	2.3	H,N
Fall	2.6	N
White Iron	2.6	N
Seven Beaver	2.8	H,S
South McDougal	2.9	H,N
Clearwater	3.0	H,N
August	3.1	H,N
Turtle	3.1	H,N
One	3.2	N
Greenwood	3.3	H,N
Perch	3.4	H,N
Long	4.1	H,S

[a] 0-3 well buffered; 3-5 poorly buffered; 5+ little or no buffering

[b] H = headwater lake
N = north of Divide
S = south of Divide

Table 23. Calcite saturation index (CSI) for selected BWCA lakes.

WELL BUFFERED		POORLY BUFFERED	
LAKE	CSI	LAKE	CSI
Cypress	1.5	Silver Island	3.1
North	1.5	Vernon	3.1
South	2.2	Sawbill	3.3
Magnetic	2.2	Alice	3.3
Dunkan	2.3	Karl	3.4
Splash	2.5	Kawishiwi	3.5
Seagull	2.6	Gaskin	3.5
Kekekabic	2.6	Agnes	3.6
Crooked	2.6	Stuart	3.6
Alpine	2.7	Malberg	3.7
Saganaga	2.7	Sunday	3.7
Basswood	2.8	Grace	3.7
Gabigichigami	2.9	Cherokee	4.0
LaCroix	2.9	Carp	4.0
S. Fowl	3.0	Pauness	4.1

Note: Calculated from STORET data

during November, 1976, to February, 1978 (Siegel, 1978). The samples were collected and analyzed to provide data for an evaluation of the relative contributions of sulfate to Filson Creek from acid precipitation and the oxidation of sulfide minerals associated with copper and nickel deposits. Excluding data collected during snowmelt, concentrations of sulfate in Filson Creek averaged less than 2 mg/l. During snowmelt, sulfate concentrations in Filson Creek increased to an average of 10 mg/l. Simultaneously with the increase in sulfate concentration, pH of Filson Creek decreased from an average of 6.4 to 5.8. The pH of samples from the snowpack in March, 1977, was 4.7 compared with an average pH for precipitation of 5.1. The changes in sulfate concentration and pH of Filson Creek and the lower pH of the snow suggest accumulation of sulfate acidity in the snowpack during winter, which is similar to changes reported in Scandinavia in areas subject to acid precipitation. Snowmelt contributed more than 33 percent of the annual sulfate load discharged from Filson Creek. The sulfate contribution to streamflow by groundwater was minimal compared to that contributed by precipitation and surface runoff. During baseflow, sulfate did not appreciably increase from the headwaters of Filson Creek to the mouth, even though sulfate was as much as 74 mg/l in groundwater discharging to the creek from surficial materials overlying a sulfide-bearing mineralized zone in the lower third of the watershed.

No other temporal variations were evident in streams. Sulfate concentrations were partially diluted during high flow in Filson Creek, the Bear Island River and the Dunka River in the north, and the Partridge and St. Louis rivers in the south.

Alkalinity in streams was correlated with nickel as well as with bicarbonate, dissolved inorganic carbon, pH, and sulfate (Table 24). In addition to a significant correlation with alkalinity and bicarbonate, pH was significantly correlated with calcium, copper, suspended solids, specific conductivity, and total dissolved solids. Sulfate also correlated with alkalinity, bicarbonate, and dissolved inorganic carbon.

Table 24

The buffering parameters are quite variable in lakes. Diurnal and seasonal fluctuations occur because of biological activity. For this reason, lake values presented may be less meaningful for determining baseline concentrations than values in streams because of the limited number of samples measured.

Spatial variations in these parameters appear to be related to the location of lakes in their drainage systems, with poorly buffered lakes at headwaters and better buffered lakes downstream. Headwater lakes are noted in Table 22. With respect to the individual parameters, Tofte was higher than most other lakes in alkalinity, pH, bicarbonate, and dissolved inorganic carbon, and had the lowest Calcite Saturation Index. Wynne exhibited a similar pattern of elevation for alkalinity and bicarbonate, with sulfate levels lower than Colby but higher than all others except Birch. Patterns in minimum values did not involve any one lake. Seven Beaver exhibited the lowest pH, Greenwood the lowest alkalinity, Perch and Turtle the lowest bicarbonate, Clearwater the lowest dissolved inorganic carbon, and Slate and Bear Island the lowest sulfate. Temporal variability of buffering parameters in lakes is related to biological activity with elevated pH values in productive lakes during the midsummer season of photosynthesis.

Correlations of buffering parameters with other water quality parameters in lakes were similar to those in streams. Both alkalinity and pH were significantly

Table 24. Correlations: buffering parameters. (p 0.05).

STREAMS		LAKES	
Alkalinity:	HCO_3	Alkalinity:	HCO_3
	DIC		DIC
	pH		pH
	SO_4		Ca
	Ni		Ni
			$\overline{Z}$
pH:	Alkalinity		Co(t)
	HCO_3		Mg(t)
	Ca		Spec. conductivity(t)
	Cu		
	Suspended solids	pH:	Alkalinity
	Spec. conductivity(t)		HCO_3
	Total dissolved solids(t)		Ca
			Pb
SO_4:	Alkalinity		D.O.%
	HCO_3		Co
	DIC		Fe(t)
		SO_4:	CSI(t)

(t) = log transformed data

correlated with levels of bicarbonate, calcium, and cobalt and with each other. In addition, alkalinity was correlated with dissolved inorganic carbon, nickel, magnesium, and specific conductivity, and pH with iron, lead, and dissolved oxygen. The relationship between pH and dissolved oxygen probably is related to biological productivity. In lakes, sulfate is significantly correlated only with the calcite saturation index.

4.3.2.5 Nutrients--The phosphorus-containing rock identified in the Study Area is apatite. However, upon weathering, phosphate ions tend to form new complexes with clay and/or soils, rather than remain in solution. The primary sources for dissolved phosphorus are agricultural fertilizer and sewage effluents. In solution, phosphorus forms polymeric complexes and ionic complexes, especially with metals.

Phosphorus, along with nitrogen, is an essential nutrient for aquatic plant growth. In all but the most grossly polluted waters, phosphorus is the growth limiting nutrient; in the latter case, nitrogen is the limiting factor.

To prevent the development of biological nuisances and to control accelerated or cultural eutrophication, total phosphates, as phosphorus (P), should not exceed 50 ug/l in any stream at the point where it enters the lake or reservoir, or 25 ug/l within the lake or reservoir. A desired goal for the prevention of plant nuisances in streams vs other flowing waters not discharging directly to lakes or impoundments is 100 ug/l total P (Mackenthun 1973). Most relatively uncontaminated lake districts are known to have surface waters that contain from 10 to 30 ug/l total phosphates as P (Hutchinson 1957).

Spatial and seasonal patterns were indistinct in streams and lakes, with elevated levels generally occurring in disturbed watersheds. Levels of phosphorus in the

Study Area are less than those reported by the U.S. Geological Survey for lower Mississippi River water (Table 25). No data are available from either the Minneapolis or St. Paul waterworks or from the Coeur d' Alene River, Idaho.

Table 25

Nitrate in aqueous systems is the result of biological conversion (fixation) of nitrogen by micro-organisms. There are no geologic sources of nitrogen in the Study Area. The ultimate reservoir of nitrogen is the atmosphere. In aquatic systems, blue-green algae and bacteria found in the sediments or on surfaces of aquatic plants are the main nitrogen fixers. Nitrogen entering streams as organic debris from terrestrial ecosystems may be in the form of ammonia, which is oxidized to nitrate in oxygenated waters rich in particulate matter. In addition to these natural sources of nitrate, agricultural fertilizers and blasting compounds provide an added source of nitrate to a watershed. Low concentrations of nitrate in the Study Area may reflect the absence of agricultural fertilizers. In mining areas where a fertilizer (NH_4NO_3) kerosene mixture is used as a blasting compound (ANFO), an estimated 2% of the fertilizer remains as a residue on the rocks following the explosion. This residue is subject to release during heavy runoff following a rain event, and may result in a localized nutrient problem in receiving streams.

Nitrate is an essential nutrient and an oversupply may lead to "blooms" of algae in polluted waters. However, concentrations within blasting zones of the Study Area remain far below levels required for such blooms and are only slightly in excess of measured values for the Lower Mississippi River at the Minneapolis waterworks intake. In general, values in the Study Area are comparable to Twin

Table 25. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Total phosphorus (P) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.8-2100	20.1	260
Lakes	0.8-220.0	22.9	140

Comparative Data in ug/liter

MISSISSIPPI RIVER[a] (St. Paul)	COEUR D'ALENE RIVER[b]
60-260	——

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[a]
[b]

Cities drinking water and to the Coeur d' Alene River, Idaho, where agricultural uses are mainly pasture and haylands (Table 26).

Table 26

Nitrate concentrations are generally low and remain stable throughout the season. Two exceptions are the high values observed at Bob Bay (BB-1) and the Dunka River (D-1) (Appendix 1), both areas receiving drainage from blasting zones.

Nitrogen:Phosphorus ratios (N:P) can be used to evaluate lake nutrient limitations. Lakes with N:P ratios greater than 14 are phosphorus limited; ratios less than 14 indicate nitrogen limitation. In general, only highly eutrophic lakes exhibit nitrogen limitation. For the 26 study lakes, the median ratios ranged from 14 to 60; 50 percent of the lakes had median N:P ratios greater than 25 (Appendix 3). The lakes approaching nitrogen limitation were Fall, Greenwood, One, and Long; the lake with the highest N:P ratio (most phosphorus limited) was Colby.

Trophic state indices (TSI) using total phosphorus (TP) and secchi disk (SD) values were calculated for the study lakes according to the equations developed by Carlson (1977). SD is a measure of water clarity which is a function of the standing crop of biomass and in turn relates to the nutrient status of the water.

The indices are:

$$\text{TSI (SD)} = 10\left(6 - \frac{\ln SD}{\ln 2}\right)$$

$$\text{TSI (TP)} = 10\left(6 - \frac{\ln \frac{48}{TP}}{\ln 2}\right)$$

A nutrient starved lake is called an oligotrophic lake; and conversly a nutrient rich lake is called eutrophic.

Table 26 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Nitrate ($NO_2 + NO_3$) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.01-13.00	0.1	260
Lakes	0.01-1.50	0.02	120

Total Nitrogen (N) in mg/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.01-14.1	0.91	250
Lakes	0.12-9.9	0.63	78

Standards and Protection Guidelines in mg/liter

CURRENT PCA STANDARDS[a] (NO_3)	PROPOSED PCA STANDARDS[b] (N)	EPA CRITERIA[c] (N)	CU-NI GUIDELINES[d]
45-domestic consumption	10-domestic consumption	10-domestic consumption	—

Comparative Data in mg/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
0.08-1.9	0.16

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

As a guide, for given index values, lakes can be categorized as follows:

Category	Index
Oligotrophic	15-25
Oligo-Mesotrophic	25-35
Mesotrophic	35-45
Meso-Eutrophic	45-55
Eutrophic	55-65

The results for the 26 study lakes are presented in Table 27. By the definitions given above, 7 of 26 can be considered eutrophic; an additional 16 can be considered meso-eutrophic. The least productive lake was Tofte; the most productive was South McDougal. The most fertile lakes were all headwater lakes and for the most part were shallow and surrounded by extensive bog and marsh areas.

<u>Table 27</u>

Theoretically, the index values calculated by using phosphorus and secchi disk data should be equal. This was not the case for most of the lakes and is caused in large part by the tendency of the secchi disk index to be biased high and low for highly colored and highly transparent lakes, respectively. Examples of this were Clearwater Lake (highly transparent) and Seven Beaver Lake (highly colored).

4.3.2.6 Summary Discussion of Nutrient Parameters--Phosphorus and nitrogen are the major nutrients in aquatic systems. Although producers use these elements in the form of phosphate and nitrate, conversion from one chemical species to another is constantly occurring within the ecosystem and measurements of totals reflect all forms of nutrients tied up in all forms (i.e. organic, inorganic, dissolved particulate). Concentrations of both N and P are at the low end of the range of values for streams in the United States. It should be noted that

Table 27. Median trophic state indices for Regional Copper-Nickel Study lakes.

LAKE	TSI (SD)	TSI (TP)	LOCATION[a]
Tofte	37	37	H,N
Bearhead	43	40	H,N
Triangle	42	46	H,N
Bass	42	47	N
Clearwater	39	50	H,N
Bear Island	46	47	H,N
August	51	42	H,N
Wynne	51	45	S
Pine	51	45	H,S
Colby	42	44	S
One	48	51	N
Big	54	55	H,S
Turtle	52	48	H,N
White Iron	53	48	N
Birch	53	49	N
Gabbro	54	48	N
Fall	52	51	N
Perch	52	51	H,N
Slate	53	54	N
Sand	56	55	H,N
White Face	58	53	H,S
Long	60	55	H,S
Cloquet	62	55	H,S
Seven Beaver	63	54	H,S
Greenwood	61	59	H,N
South McDougal	66	59	H,N

[a] H = headwater lake
N = north of Divide
S = south of Divide

SD = Secchi disk
TP = Total phosphorus

concentrations of phosphorus are expressed in parts per billion (ug/l) whereas nitrogen, and nitrate plus nitrite (Appendix 2) are expressed in parts per million (mg/l), these differences in scale reflect the greater concentrations of nitrogen in the Study Area.

Spatial variations in nutrient parameters exhibited no clear trends between headwater and downstream stations or between small and large watersheds. Group A and B, stations were similar to each other but higher than Group C with respect to nutrient parameters. Group C stations represent baseline values for the area. The greatest variability in phosphorus concentrations occurred in group A and B stations. Variability for phosphorus was greater than for nitrogen. Nitrogen also exhibited its highest concentrations at Group A and B stations (BB-1 and D-1), downstream from mining operations that use nitrogenous blasting compounds.

Both nutrient parameters were largely independent of flow except in the Dunka River where higher concentrations occurred during the winter of 1976-1977 and during the 1977 drought, and lower concentration occurred during periods of runoff, storm event and average baseflow.

Nutrient parameters in streams were correlated with each other. Total phosphorus was significantly correlated with total nitrogen, nitrate plus nitrite, Kjeldahl nitrogen, and dissolved oxygen. Total nitrogen was significantly correlated with total phosphorus and total organic carbon (Table 28).

Table 28

In lakes, nutrient parameters are closely associated with the activities of aquatic organisms. Higher levels of available nutrients encourage greater

Table 28. Correlations: nutrient parameters. (p 0.05)

STREAMS		LAKES	
Tot-P:	Tot-N $NO_2 + NO_3$ KJD, N D.O.	Tot-P:	Secchi disk(t) D.O.(%) (t)
Tot-N:	Tot-P TOC	Tot-N:	Color Suspended solids Secchi disk(t) TOC(t) TSI-SD(t) TDS(t)

(t) = log transformed data

biological productivity. The concentration of chlorophyll A provides a direct measure of this productivity, whereas the transparency of the water gives an indirect and less accurate measure. Reduced secchi disk measurements are often associated with highly productive waters. Photosynthetic activity releases oxygen as a byproduct and therefore may result in elevated, or at times supersaturated oxygen levels in the surface waters of productive lakes. As successive algal blooms die and sink to the bottom they are broken down by decomposers. Because such decomposition is generally an oxidative process, the bottom waters of productive lakes often become depleted of oxygen and, if the lakes are thermally stratified, may become anoxic. Evidence from the literature suggests that orthophosphate (non-organic) is released from the sediment into the bottom waters under such reducing conditions.

The supply of nutrients (phosphorus, nitrogen, or silica in the case of diatoms) is a major limiting factor for algal productivity. Overall concentrations of both nutrients were at the low end. Median values for both phosphorus and nitrogen were higher south of the Laurentian Divide than north of it, but the range of values for phosphorus was greater north of the Divide (P = 1-1220 ug/l[north], and 1-70 ug/l[south]). Variability in nitrogen concentration was greater south of the Divide (N=120-9999 ug/l) than north of it (N=300-1100 ug/l). Current loadings of phosphorus for lakes in the Study Area were calculated as a basis for understanding anthropogenic stresses. Median loading for lakes in the area was 25 kg/ha/year.

Analysis of variance for nitrogen and phosphorus in the Study Area lakes indicated no relative spatial patterns, perhaps because of the great temporal variability of both elements. Spatial differences in the N/P ratio also did not follow any pattern. Lakes most nearly limited by nitrogen are Fall, Greenwood, One, and Long, with Colby the most limited by phosphorus.

Spatial variability in Carlson's (1977) trophic state index indicates that the most eutrophic lakes are headwater lakes that are generally shallow and surrounded by extensive wetlands.

Temporal variations of nutrients differ between lakes. Surface water phosphorus concentrations should be highest in dimictic lakes at the time of spring turnover when phosphorus from bottom waters is redistributed throughout the water column. Over the summer season, total phosphorus in surface waters is likely to become depleted as it is incorporated into algae, which eventually die and sink to the bottom. In 13 lakes for which data were available, midsummer phosphorus values were 70 percent of the vernal values (variability 20%). Nearly half the lakes exhibited temporal changes in surface water phosphorus that did not seem to follow this expected pattern.

In keeping with the general patterns of relationships between productivity and nutrient parameters discussed above, phosphorus in Study Area lakes was significantly correlated with both the amount of dissolved oxygen and the secchi disk transparency. In addition to this correlation there were direct relationships between secchi disk and chlorophyll A and the concentration of phosphorus and chlorophyll A in the Study Area lakes (Mustalish et al. 1978). The variability in these relationships was probably increased by the fact that median values were used and that algal productivity generally occurs in a series of successive spurts whose occurrence is not simultaneous in all lakes. For this reason some lakes may have been sampled during blooms whereas others were not.

Correlation of total nitrogen with other parameters indicates that much of the nitrogen in aquatic systems is in an organic form. In addition to its correlation with secchi disk transparency and trophic state, total nitrogen also correlated with a group of parameters that measure in one form or another, the amount of organic material in the water, i.e. suspended solids, TOC, TDS, and color.

4.3.2.7 Mineral Fibers--Mineral fibers are a potentially serious, but presently poorly understood, environmental health hazard for the occupational and non-occupational population in both Minnesota, as evidenced by the Reserve Mining controversy, and nationwide. This poor understanding can be attributed partly to confusion over and misuse of terminology and incomplete knowledge of the mechanism by which fibers affect health. These topics will be briefly discussed below. Because of the present interest and difficulties with "state of the art" analysis, this parameter is presented in more detail than other water quality parameters presented in this section. For further information, see Volume 3-Chapter 2, Volume 5-Chapter 2, and Ashbrook (1978).

Asbestos is a collective mineralogical term encompassing the asbestiform varieties of various silicate minerals and is applied to a commercial product obtained by mining primarily asbestiform minerals. Five minerals fit this definition: chrysotile (a member of the serpentine group), and the asbestiform varieties of actinolite-tremolite, anthophyllite, cummingtonite-grunerite, and riebeckite (members of the amphibole group). Chrysotile always occurs in the asbestiform habit, amphiboles usually occur in non-asbestiform habits with the exception of riebeckite, which usually occurs in the asbestiform habit as crocidolite. Asbestiform minerals occur as fibers, which display some resemblances to organic fibers in terms of circular cross section, flexibility, silky surface luster, and other characteristics. Cleavage fragments, such as those produced from crushing and processing non-asbestiform minerals, do not satisfy this definition of fibers and should be considered "fiber-like." When asbestiform and non-asbestiform minerals are subjected to crushing and processing, the resulting fragments have minor differences in morphology and physical properties that are very difficult to distinguish under a transmission electron microscope (TEM). For this reason, when the TEM is used, fibers are defined as fragments with aspect (length to width) ratio of 3:1 or greater, even though many of these fragments may not meet the mineralogic definition of a fiber. In this report, the term "mineral fiber" will be used to denote both asbestos fibers and cleavage fragments of non-asbestiform minerals because ambient levels of mineral fibers were determined by transmission electron microscopy, which did not distinguish between these two classifications. Asbestos fiber and non-asbestiform cleavage fragments have different characteristics in terms of tensile strength, flexibility, durability, and surface properties. The extent to which these differences are related to the harmful properties of asbestos is uncertain at this time.

Mineral fibers have a number of possible sources. Fragments can be generated from both asbestiform and non-asbestiform minerals by both human activities, such as construction, drilling, blasting, transporting, and processing ore, and by natural processes such as mechanical effects from wind and water. Asbestos fibers may occur naturally; however, they are uncommon in northeast Minnesota. Mineral fibers may also be introduced to this region through sources such as insulation materials, foods, and brake linings in motor vehicles.

The Regional Copper-Nickel Study conducted a general survey of ambient fiber levels in water and air to characterize existing levels and to try to correlate these levels with suspected fiber sources near the Duluth Gabbro Contact. Samples were collected throughout 1977 in conjunction with the rest of the water sampling program. Water samples consisted of 21 stream samples, a snow sample, a lake sample, an Ely tap water sample, and a sample from the AMAX shaft water. All samples were analyzed by the Minnesota Department of Health (Ashbrook 1978). Analysis of surface waters for mineral fibers is extremely difficult because of the large amounts of intervening materials. Diatoms and other non-fiber particulates not only prevent large amounts of water from being filtered, but obscure and confuse the final preparation. Little sample to sample comparison is justified. Because a relatively small number (25) of water samples were taken during the course of the study, the results for each sample are listed in Table 29. Figure 2 shows the location of sampling sites.

Table 29

Fiber levels are reported in four categories. Amphibole fibers are defined as those fibers which give electron diffraction patterns characteristic of amphibole minerals. A fiber which clearly has a chrysotile diffraction pattern is classified as chrysotile. A mineral with a clearly non-amphibole, non-chrysotile diffraction pattern is classified as non-amphibole/non-chrysotile. Mineral fibers classified as ambiguous had diffraction patterns or chemical ratios which cannot be used to place the fiber in one of the three previous categories. Mean aspect ratios for each category were calculated by dividing the mean length by the mean width of all the fibers observed in the category.

Total fiber levels are given with and without chrysotile because the Minnesota Department of Health was uncertain whether the observed chrysotile fibers were

Table 29 continued.

LOCATION	TYPE OF SAMPLE	DATE COLLECTED	THOUSANDS OF FIBERS/LITER (mean aspect ratio)					
			Amphibole	Chrysotile	Non-amphibole Non-chrysotile	Ambiguous	Total Fibers	Total Without Chrysotile
Dunka-1 (05126000)	stream	8/18/77	582 (54.0)	1,940 (19.7)	388 (5.6)	1,360 (8.1)	4,270	2,330
Kawishiwi-4 (05126620)	stream	11/21/77	900 (37.1)	1,100 (33.5)	500 (8.3)	600 (22.0)	3,100	2,000
Kawishiwi-5 (05126210)	stream	7/25/77	256 (6.6)	3,860 (15.8)	386 (4.4)	256 (29.3)	4,760	900
Kawishiwi-5 (05126210)	stream	8/15/77	356 (15.0)	3,020 (27.8)	533 (9.0)	356 (8.5)	4,270	
Kawishiwi-5 (05126210)	stream	11/21/77	919 (30.2)	1,840 (12.8)	1,100 (5.6)	827 (12.3)	4,690	2,850
Kawishiwi-7 (05125000)	stream	8/15/77	125** —	502 (9.0)	1,130 (4.6)	251 (3.6)	1,880	1,380
Bob Bay-1 (05125730)	stream	9/27/77	420 (7.2)	2,760 (15.0)	840 (11.2)	240 (12.8)	4,260	1,500
St. Louis-1 (04016500)	stream	8/30/77	580 (6.4)	1,740 (7.6)	483 (5.6)	483 (8.0)	3,290	1,550
St. Louis-3 (04015430)	stream	9/26/77	1,110 (6.9)	3,330 (14.5)	222 (4.6)	889 (6.0)	5,560	2,220
Whiteface-2	stream	9/26/77	1,920 (5.4)	1,200 (17.6)	2,400 (5.8)	720 (8.4)	6,240	5,040

Table 29. Ambient concentration and mean aspect ratio for fibers found in water samples.

			THOUSANDS OF FIBERS/LITER (mean aspect ratio)					
LOCATION	TYPE OF SAMPLE	DATE COLLECTED	Amphibole	Chrysotile	Non-amphibole Non-chrysotile	Ambiguous	Total Fibers	Total Without Chrysotile
Partridge-1 (04015490)	stream	8/30/77	110* (3.2)	6,380 (14.9)	110* (7.4)	1,320 (15.8)	7,920	1,540
Partridge-2 (04015471)	stream	5/5/77	427 (16.7)	107* (0.0)	640 (5.4)	320 (4.4)	1,490	1,390
Partridge-2 (04015471)	stream	7/25/77	232 (6.8)	929 (8.9)	77.4* (7.4)	77.4* (17.3)	1,320	387
Partridge-2 (04015471)	stream	8/30/77	448 (9.3)	1,340 (26.2)	336 (8.7)	448 (7.6)	2,570	1,230
Partridge-2 (04015471)	stream	11/21/77	40.7 (16.7)	149 (13.9)	81.4 (7.7)	108 (10.1)	380	231
Partridge-5 (04015447)	stream	8/18/77	711 (7.1)	4,270 (17.2)	711 (13.2)	178* (4.3)	5,870	1,600
Stony River-2 (05125550)	stream	5/5/77	213* (4.0)	213** (—)	1,280 (4.9)	640 (10.9)	2,130	2,130
Stony River-2 (05125550)	stream	7/26/77	88.7** (—)	1,240 (19.4)	88.7** (—)	266 (6.8)	1,510	266
Stony River-2 (05125550)	stream	8/30/77	102* (5.5)	3,170 (16.8)	716 (7.9)	511 (8.8)	4,500	1,330
Stony River-2 (05125550)	stream	11/21/77	264 (24.8)	926 (17.4)	793 (10.7)	1,320 (14.9)	3,310	2,380
Stony River-5 (05125450)	stream	9/26/77	1,430 (7.9)	715 (17.0)	238* (3.4)	238* (6.0)	2,620	1,910

Table 29 continued.

			THOUSANDS OF FIBERS/LITER (mean aspect ratio)					
LOCATION	TYPE OF SAMPLE	DATE COLLECTED	Amphibole	Chrysotile	Non-amphibole Non-chrysotile	Ambiguous	Total Fibers	Total Without Chrysotile
Filson Creek Area	snow	11/21/77	495 (7.7)	1,130 (13.8)	2,190 (5.9)	354 (13.5)	4,170	3,040
Bear Island Lake	lake	11/21/77	212 (38.6)	636 (31.4)	1,700 (8.4)	636 (7.9)	3,180	2,550
Ely	tap water	11/21/77	244 (45.6)	610 (21.6)	1,200 (10.6)	244 (37)	2,230	1,710
AMAX-Babbitt	mine shaft	11/21/77	712,000	89,000	2,050,000	1,250,000	4,100,000	4,010,000

*Detection limit, based on one fiber observed.
**No fibers observed.

NOTE: Counting error limits are shown in Ashbrook, 1978.

artifacts from the filters or were actually present in the medium sampled. Analyses of blank filters by the Minnesota Department of Health have suggested that Millipore filters contain significant levels of chrysotile fibers and that Nuclepore filters sometimes contain amphibole fibers. Comparisons between amphibole and chrysotile concentrations and mean blank levels can be found in Ashbrook (1978). In 9 of the 25 samples, the amphibole blank fiber level was higher than the corresponding sample amphibole concentrations. Similarly, 12 of 25 chrysotile sample concentrations were less than their corresponding blank fiber level. These results suggest that, with the exception of the mine shaft sample, most of the fibers found in these samples come from sources other than the water sampled. Therefore, the fiber levels presented in Table 29 should be considered upper limits for the probable fiber concentrations in the Study Area.

Total fiber counts for stream samples ranged from 380,000 to 7,920,000 fibers per liter with a median of 3,310,000. Excluding chrysotile, total fiber levels ranged from 231,000 to 5,040,000 fibers per liter with a median of 1,540,000. Fiber levels in the Filson Creek snow sample, Ely tap water sample, and Bear Island Lake sample were similar to those in stream samples. A water sample from the AMAX mine shaft near Babbitt contained approximately four billion fibers (both with and without chrysotile). Half of these fibers were classified as non-amphibole/non-chrysotile, and thirty percent were ambiguous. These levels from the AMAX shaft water appear to be generally consistent with the results of an earlier analysis by the EPA laboratory in Duluth of a series of water samples collected from sumps and reservoirs associated with Reserve Mining Company's Peter Mitchell Pit (a taconite operation) (Cook, 1976). Reported values for total amphibole plus chrysotile fiber concentrations in the collected samples include values of 0.67×10^9, 1.5×10^9, and 9×10^9 fibers/liter. The operations taking place at Reserve's pit are generally comparable to those at Amax in that blasting, loading, and hauling operations are involved. Reserve's operation at the mine site includes primary crushing, which is not taking place in the Amax test shaft. Neither operation includes the degree of grinding which is apparently responsible for the generation of much higher fiber concentrations in tailings water (see Volume 3-Chapter 2).

Stream sampling stations receiving direct minewater discharge from taconite mines are Partridge-5 (from Reserve), Dunka-1 (from Reserve), and Bob Bay-1 (from Erie). Several stations downstream from these three stations, which may also be considered impacted, include Kawishiwi-4 and 5, Partridge-1 and 2, and St. Louis-1 (see Figure 2). Fiber levels for both disturbed and undisturbed streams showed large variations with little difference between the two stream groups. Amphibole fiber levels in the Partridge River appeared to decrease as the distance from the Reserve pit increased. This would be consistent with earlier data, cited above, indicating that the Reserve discharge is a source of fibers. However, it is not known whether Reserve was actually discharging during the sampling periods for this study. Thus, this observation may be due to natural variation. The two highest amphibole levels were found in undisturbed streams. Very high aspect ratios for amphibole fibers were found in the Dunka sample (average of 54.0) and the Kawishiwi-5 and 4 samples (30.2 and 37.1, respectively), which are downstream from the Dunka.

In conclusion, ambient water levels of fibers found in the streams of northeast Minnesota are similar to previous literature reports for other streams and rivers, as well as to levels found in beer, wine, and soft drinks. Sampling and analytical uncertainties limit the conclusions here to the statement that fiber levels in the waters of the Study Area represented by the sites sampled are not significantly elevated above detection limits. This conclusion is to be contrasted with the results of sampling of mine discharge water, in which a large elevation in levels was found. Data from this study, as well as earlier work, clearly indicate this pattern. Mine shaft water from the AMAX site near Babbitt has fiber levels two-to-three orders of magnitude above those for nearby streams, but almost three orders of magnitude below those estimated for tailings from Reserve Mining in Silver Bay. However, fiber levels in streams receiving mine water discharges appear to be similar to streams not receiving such discharges. This raises the possibility that some natural removal mechanism, such as filtration or a settling process, is operating. Due to the limited sampling program, such a possibility is purely speculative at this time and would require experimental investigation. In the absence of some natural removal process, mine dewatering, as well as other possible water discharges from a mining operation, has the clear potential of elevating ambient fiber levels above the low values presently found in the Study Area.

4.3.2.8 Metals: Aluminum is widely distributed in the minerals of the Study Area and is found in feldspars, micas, amphiboles, and altered silicates. Concentrations in natural waters rarely exceed a few tenths of a milligram per liter in spite of the ample supply. This suggests that the element's chemistry is such that the dissolution of aluminum is greatly limited in aquatic environments or that dissolved aluminum is rapidly removed from solution. When concentrations as high as one mg/l are observed it is probably caused by particulate aluminum.

Aluminum values in the Study Area were all lower than the values reported for Minneapolis tap water (Table 30).

Table 30

Except for the high concentration of aluminum observed in Filson Creek, no distinctive spatial or seasonal patterns in aluminum concentrations were observed in lakes or streams. Groups A, B, and C stream stations all had comparable aluminum concentrations.

Arsenic may occur in water as a result of mineral dissolution, industrial discharge, or from the application of certain insecticides. A possible arsenic source in this area is the pyrrhotite mineral called niccolite, a nickel arsenide. Compounds of arsenic are ubiquitous in nature, insoluble in water, and occur mostly as arsenides and arsenopyrites. Samplings from 130 water stations in the United States have shown arsenic concentrations of 5 to 536 ug/l with a mean level of 64 ug/l (Kopp 1969).

Arsenic exists in the trivalent and pentavalent states and its compounds may be either organic or inorganic. Trivalent inorganic arsenicals are more toxic than the pentavalent forms both to mammals and aquatic species.

Although arsenic is concentrated in aquatic organisms, it is evidently not progressively concentrated along the food chain. In addition, arsenic consumed as an organically bound species in flesh appears to have low toxicity (Ferguson and Gavis 1972).

There are no distinctive spatial variations in median values for arsenic, in Study Area surface waters, although downstream sites (SL-1 and K-1) seem to

Table 30 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Aluminum (Al) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	1.6-760	90	270
Lakes	4-610	77	60

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	NA

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
No data	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f].

exhibit greater variability than headwater stream sites (Appendix 1). Whiteface (WF) and Waterhen sites (extreme southern portion of Study Area), based on one sample only, show a higher level for As compared to all other sites. More samples would be needed further delineate the real levels at these sites. Arsenic does not appear to be flow dependent in the Study Area and appears in similar concentrations at Group A, B, and C stream sites (Appendix 2).

Table 31

Cadmium is uncommon in natural waters. This element is most commonly found in sulfide minerals and is closely related to zinc. Upon release the predominant form of cadmium is often as the free ion (Cd^{+2}). With increasing pH and in the presence of inorganic and organic carbon, cadmium forms complexes. Cadmium is quite toxic to aquatic organisms, at levels varying from 1 ug/l for chronic injury to 10 ug/l for acute injury.

Spatial patterns are not apparent for either lakes or streams of the Study Area. Given the lack of significant cadmium containing mineral deposits in the region, concentrations observed may largely be due to long range atmospheric sources. Cadmium concentrations were essentially flow independent except during spring melt when elevated snow-melt concentrations caused slightly elevated levels in the streams. Cadmium values in the Study Area are lower than those in the Coeur d'Alene River (Table 32), where elevated cadmium levels are considered a problem, and less than the limits of detection for Twin Cities waterworks.

Table 32

Table 3l Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Arsenic (As) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.2-5.0	0.8	185
Lakes	0.4-2.1	0.6	41

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
10-50-domestic consumption	10-domestic consumption	50-domestic consumption	10-1000 Aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
3-50	458

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 32 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Cadmium (Cd) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.01-0.45	0.03	443
Lakes	0.01-0.77	0.03	114

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
10-domestic	(see Figure __)	0.4-4-Aquatic life	1-10-Aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
7.5-10	40

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

The primary mineral source of cobalt for this region is Cattierrite, a cobalt sulfide (CoS_2). Very little cobalt is believed to enter the aquatic system from atmospheric deposition.

Cobalt is one of the few trace metals that does not readily complex with organics or inorganic anions in water. Cobalt usually exists as a free cation (positively charged species) probably surrounded closely by water molecules (aquated). Because cobalt does not readily combine with other constituents, it has mobility in the aquatic system, but it is not as mobile as nickel or zinc.

Seasonal variations in cobalt concentrations are not great. In the Kawishiwi River and Filson Creek, slight decreases were observed during peak flows in April, 1976. Cobalt concentrations were highest at Group A stations and intermediate at Group B stations (Appendix 2). Bob Bay, which receives stockpile seepage, and Filson Creek, which flows directly through the Gabbro Contact, had the highest levels. In both these cases values were one-twentieth the detection limit used by the USGS for Mississippi River water at the Twin Cities (Table 23 and Appendix 1). No further data were available for comparison of Study Area cobalt levels with those of metropolitan drinking water or the Coeur d'Alene River, Idaho.

Table 33

One major copper containing mineral in the Study Area is the sulfide chalcopyrite; it is contained in rocks of the Duluth-Gabbro complex. In natural waters copper is found in inorganic complexes (oxide, hydroxy-carbonate), and as metal-organic compounds. Because copper is an essential plant and animal

Table 33. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Cobalt (Co) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.1-11.0	0.4	410
Lakes	0.1-2.2	0.4	72

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	NA	NA	10-100-Aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
less than 50-60	No data

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

nutrient, the biota may influence or be influenced by its occurence in aquatic systems. Even thought it is an essential element, copper may be toxic to aquatic organisms in very low concentrations (10-100 ug/l).

Weathering of exposed copper-containing sulfide rock accounts for some of the high values in the Study Area. Filson Creek has high mass release rates as a result of draining a portion of the Copper-Nickel Mineral Resources Zone which contains mineral outcroppings. Overall, the mobility of copper is very low. Precipitates and binding to organics such as bog-type material, readily remove copper from solution. The level of copper observed in Groups A and B were higher than Group C and lakes were comparable to Group C (Appendix 2, Table 34). The concentrations observed appeared to be primarily a function of copper chemistry rather than the strength of the source. Surprisingly higher concentrations of copper were found in the snow-melt water (see section 4.3.5) than many of the stream sites.

Table 34

Copper concentrations in the Study Area were less than the detection limits used for Twin Cities water supplies, and the higher values at Filson Creek were half those recorded by the USGS for the lower Mississippi River. Waters of the Coeur d'Alene River, Idaho, located in an active mining area, contain ten times the copper concentration than found at Filson Creek and still are below recommended water standards for acute injury to aquatic organisms. However, current levels at Filson Creek are only 3 ug/l less than Copper-Nickel Study Guidelines for detection of chronic injury to aquatic organisms and the lower Mississippi River exceeds these guidelines by 5 ug/l.

Table 34 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Copper (Cu) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.2-12.0	1.5	447
Lakes	0.2-10.0	1.5	129

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
1000-domestic consumption	(see Figure __)	1000-domestic consumption	10-100-Aquatic life
10-fisheries & recreation		0.1 times 96 hour, LC50	

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
10-20	80

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Iron, like aluminum, is widely distributed in the minerals of the Study Area. It has been identified in feldspars, pyroxenes, neosilicates (such as olivine), micas, opaque minerals (such as chalcopyrite), pentlandite, pyrrhotite, ilmenite, magnetite (as in taconite), epidote, allanite, and cordierite. Typically the iron in these minerals is in the ferrous (Fe^{+2}) form, but, in the case of magnetite, iron can occur in the ferric (Fe^{+3}) state.

Once released into solution, iron is greatly influenced by the pH, redox potential (Eh), dissovled CO_2, and dissolved sulfur species in water. In oxygenated waters, iron is usually found either as the particulate ferric hydroxide, or complexed with dissolved or particulate organic material. In deep lakes that stratify during winter and summer, and develop an anoxic hypolimnion; greatly elevated ferrous ion concentrations may occur in the bottom waters.

Stations showing the higher concentrations were either those which drained mineralized zones (e.g. F-1, KC-1) or those in taconite mining areas (e.g. P-3, P-5) (Appendix 1). However, the fact that the St. Louis and Partridge systems as a whole did not show elevated levels reflects the aquatic chemistry of iron. The precipitation of insoluble iron hydroxides or the settling of particulate iron organics limits mass transport. The natural causes for iron release appear to be localized, rather than regional.

Table 35

Spatial variability of iron concentrations in lakes appeared to be related to increasing proportions of dissolved organics and concomitant increases in water color. The two most highly colored lakes, South McDougal and Seven Beaver were

Table 35 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Total Iron (Fe) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	99-5500	610	457
Lakes	16-2300	350	138

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
300-domestic consumption	300 (soluble)-domestic consumption	700-domestic consumption	100-1000-Aquatic life
	1000 (total)-fisheries	1000-fisheries	

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
31-645	458

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

also those with the highest iron concentrations. The lowest iron concentrations were found in Tofte, Clearwater, and Triangle lakes.

Decreased concentrations of iron with the first flush of spring meltwater were observed in both large and small watersheds (F-1, D-1 P, SL and K^{-2}), whereas limited dilution effects were observed at D-1 and K-7 (see section 4.3.5). Although significant lift-off and transport of iron occurs in the atmosphere (see Volume 3-Chapter 3) as a result of taconite mining, the atmospheric deposition of this element does not appear to significantly influence water quality. It is believed that internal sources, albeit influenced by anthropogenic disturbances, strongly influence concentrations of iron in the region's surface waters.

About one-half of the iron is associated with filterable particulate matter (Appendix 2). The filterable particulates may be inorganic, i.e. hydroxide, or organic. Streams in in Group A and B also have lower organic carbon levels (Appendix 2). Lake levels for iron were generally lower than those in streams, which again indicates the attenuating effect of lake systems on non-conservative parameters.

Lead is present at very low concentrations in the Duluth Gabbro rock. In natural waters lead is found in ionic form (Pb^{+2}). In oxidized waters as pH increases above neutrality, insoluble carbonate and sulfate complexes may form, thus controlling lead solubility. Lead is acutely toxic to aquatic organisms at 100 ug/l range, chronically toxic at 10 ug/l range, and is accumulated in primary producers but is not magnified in the food chain.

No significant spatial variations in lead concentrations have been observed in the Study Area. Automobile exhaust constitutes a major source of lead in urbanized areas. Given the lack of apparent internal sources of lead, it appears that deposition of airborne lead constitutes the principal source of the element to the Study Area. Examination of snow melt water and bulk precipitation samples support the conclusion that a significant portion of the lead for this region is derived from atmosphere deposition (see section 4.3.5).

Concentrations of lead in streams were essentially constant over time. Group A and B stations appeared to be comparable and were significantly (P less than 0.005) greater than Group C stations (Mustalish et al. 1978)

Table 36

Manganese is not contained in significant concentrations in any mineral identified in the Study Area; however, it is known to occur in a reduced form in many igneous rocks. Oxides and hydroxides of manganese are common in soils; manganese is also an essential plant nutrient.

In natural waters, the predominant form of manganese is in solution as the Mn^{+2} ion. Although the ion can form organic complexes, it is stable in water and generally remains uncomplexed. Little is known of the dynamics of manganese in biological systems except that manganese levels are depleted along the food chain.

Generally, the greater concentrations of manganese were observed in the more disturbed watersheds (Appendix 1) of the Study Area. Group A stations again appeared to be highest with Group B intermediate (Appendix 2). Manganese levels were low in the Kawishiwi River system.

Table 36. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Lead (Pb) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.1-6.4	0.5	443
Lakes	0.1-1.9	0.4	114

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
50-domestic consumption	50-domestic consumption (see Figure __)	50-domestic consumption .01 times 96 hours LC50	10-100-aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
50-77	75

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Managanese levels were also quite low in the lakes, except for a few very high measurements (1000-5400 ug/liter). Two of the high levels were found in bottom water samples from deep lakes.

Table 37

Mercury sources in the Study Area were not identified and if local sources do exist, they are likely inconsequential. However, elevated levels of mercury have been found in fish, and other organisms, in the region. It is speculated that these levels are either natural, from atmospheric deposition, or from a fungicide that was applied to the forest several years ago. Anthropogenic sources of mercury may include coal burning in power generating plants or similar combustion sources, where the mercury is released as a vapor or particulate and eventually is deposited onto land by scavenging rainfall.

The most toxic form of mercury is methylmercury, produced by bacteria under oxygen deficient conditions. This form is readily absorbed and accumulated by organisms. Higher animal forms, including humans, are the most susceptible to methylmercury poisoning because the nervous system and sensory organs are afflicted.

Mercury values in the Study Area were quite low (Appendix 1). Spatial elevations in mercury were restricted to unexplained elevated levels in the Whiteface River and Waterhen Creek. No consistent seasonal variations in surface water mercury concentrations were detected. Elevated measurements were not related to flow. Mercury values in the Study Area were lower than those reported by the U.S. Geological Survey for the lower Mississippi River but higher than levels reported

Table 37 Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Manganese (Mn) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	5-1200	50	309
Lakes	1-5400	29	135

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
50-domestic consumption	50-domestic consumption	50-domestic consumption	——

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
17-185	542

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

by the Health Department for Twin Cities tap water (less than detection levels of 0.01 ug/l). Levels of mercury in the Coeur d'Alene River, Idaho, are four times the highest levels observed in the Study Area (Table 38).

Table 38

The major nickel-containing rock in the Study Area is pentlandite, and, like copper, it occurs in the Duluth-Gabbro complex. In natural waters, the predominant form of nickel in solution is as Ni^{+2} ion. Nickel is significantly more mobile than copper and cobalt in the aquatic environment.

Two stream stations stand out above the rest for elevated nickel levels (Appendix 1). The highest concentrations occurred at Bob Bay (BB-1). The source of these high nickel levels has been traced to a series of waste piles created by Erie Mining Company and consisting of taconite and Duluth gabbro sulfide material. Accelerated weathering and leaching caused by the greatly increased rock surface area of the stockpiles, has resulted in the release of nickel that eventually is transported out of the Unnamed Creek watershed into Bob Bay of Birch Lake. A second site with elevated levels is Filson Creek (F-1). As in the case of copper, these levels are caused by water draining a highly mineralized section of the Duluth gabbro. While the concentrations are elevated over background because of the presence of the mineralized zone, they are less than at Bob Bay (which is also in the mineralized zone) because there has not been the same magnitude of anthropogenic disturbances which accelerate the weathering process. The primary source of nickel is within the watershed, i.e. geological material. Overall, Group A stations were again highest in nickel, with Group B stations intermediate.

Table 38. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Mercury (Hg) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.01-0.60	0.08	183
Lakes	0.08-0.64	0.28	96

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	2-domestic consumption	2-domestic consumption	----
	0.05-fisheries & recreation	0.05-aquatic life	

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
.01-.38	No data

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 39. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Nickel (Ni) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.2-210	1.2	447
Lakes	0.4-6.0	1.0	129

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
NA	(see Figure __)	0.01 times 96 hour LC50, aquatic life	100-1000 Aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
1.85-10	less than 100

---

[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

Table 40. Comparison of surface water quality data from the Regional Copper-Nickel Study Area to standards and impact criteria and to other rivers in the United States.

Zinc (Zn) in ug/liter (November, 1975, to April, 1977)

	RANGE	MEDIAN	SAMPLE SIZE
Streams	0.1-30.0	2.2	446
Lakes	0.2-35.5	1.8	113

Standards and Protection Guidelines in ug/liter

CURRENT PCA STANDARDS[a]	PROPOSED PCA STANDARDS[b]	EPA CRITERIA[c]	CU-NI GUIDELINES[d]
5000-domestic consumption	5000-domestic consumption (see Figure __)	5000-domestic consumption 0.01 times the 96 hour LC50	100-Aquatic life

Comparative Data in ug/liter

MISSISSIPPI RIVER[e] (St. Paul)	COEUR D'ALENE RIVER[f]
10-20	1946

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[a] Minnesota State Regulations, WPC 14 and 15, 1973 Supplement.

[b] Draft Revision of MPCA Water Quality Standards, January 26, 1979.

[c] Quality Criteria for Water, U.S. Environmental Protection Agency, July, 1976.

[d] Regional Copper-Nickel Study, Volume 4-Chapter 1, Section ____.

[e]

[f]

The only data available for nickel levels in Twin Cities tap water show that nickel is below the detection limit of 10 ug/l. Nickel levels in the Coeur d'Alene River are below a detection limit of 100 ug/l (Table 39). Some of the high levels at BB-1 are above the level where chronic toxicity to aquatic organisms has been detected in research studies (100 ug/liter) (see Volume 4-Chapter 1).

Table 39

No major zinc-containing minerals were identified in the Study Area; zinc is known, however, to be found in sulfide and carbonate rocks in igneous regions. Upon weathering, zinc ions are released. As pH increases above neutrality, zinc forms complexes with hydroxides and carbonates. Kopp and Kroner (1967) report that in 1,207 positive tests for zinc on samples from U.S. waterways, the maximum observed value was 1,183 ug/l (Cuyahoga River at Cleveland, Ohio) and the mean was 64 ug/l. Although aquatic macrophytes are known to accumulate zinc, there is no evidence of biomagnification in the food chain. Levels above 100 ug/l may cause both chronic and acute injury to aquatic organisms (Volume 4-Chapter 1). Compared to most zinc values observed for surface waters, zinc in precipitation is elevated (see section 4.3.5). Group A and B stations were comparable and both elevated above Group C sites.

Table 40

4.3.2.9 Discussion of Metal Parameters--Not all metal parameters monitored by the study are presented in this discussion. The reader is referred to Appendix 2, and the primary data files available at the Land Management Information

Center-State Planning Agency for more information. More sampling emphasis was placed on streams because stream water quality in the Study Area better reflects anthropogenic disturbances, climatic effects on water quality, and a more representative "background water quality" value. As can be seen by the data presented previously, lakes tended to dampen the variability of parameters. With respect to metals, there is little variability in the levels of arsenic, cobalt, cadmium, mercury, titanium, selenium, and silver across almost all stations.

Spatial variability of metals did not appear to be related to watershed size. As was the case for most other spatial patterns, some heavy metals varied significantly between streams in the A, B, and C groupings. In groups A and B combined, iron, manganese, copper, nickel, zinc, lead, fluoride and chromium concentrations are significantly (p less than 0.005) higher than in Group C waters (Mustalish et al. 1978).

At background stations (Group C) copper, nickel, and zinc are comparable in concentration, with median concentrations of copper and zinc in the range of 1-2 ug/l and nickel around 1 ug/l. Other toxic trace metals of biological importance (As, Cd, Co, Hg, and Pb) had median concentrations significantly below 1 ug/l (one part per billion) (Appendix 2).

Iron, aluminum, and manganese dominate the total metal values measured in the Study Area waters (Figure 8), but it is the trace metals which are of primary concern on the basis of aquatic toxicity. In streams which are presently undisturbed by mining and related activities, such as the Kawishiwi River system, Bear Island River, Isabella River, and Stony River, total trace metals (Cu, Ni, Zn, Cd, Pb, and Co) concentrations are in the 0.05 to 0.08 micromoles/liter range

(Figure 9). This is compared to watersheds presently impacted by mining activities or streams which drain areas of sulfide mineralization, such as, Filson Creek, Keeley Creek, Dunka River, Partridge River and Embarras River, which has total trace metal concentrations 2 to 33 times higher (0.013 to 1.65 micromoles/liter) than background levels.

Figures 8 and 9

Filson Creek exhibited significantly higher copper concentrations than any other station. Other metals with elevated median concentrations at Filson Creek included iron, aluminum, nickel, and cobalt (Appendix 1). Within the Filson Creek watershed, total concentrations of copper and nickel in the year 1977 generally increase from headwater locations to F-1 near Filson's point of discharge into the Kawishiwi River. Total nickel concentrations measured in headwaters were, except for one sample, less than 1 ug/liter, while mean concentrations near the mouth of the watershed were about 3 to 5 ug/l. The smaller copper and nickel concentrations at Filson Creek headwater locations reflect the smaller percentage of sulfide bearing classes in the till and the greater distance from the mineralized contact zone (Siegel 1978).

The elevated metal values measured in Filson Creek may not be completely due to natural weathering of sulfide minerals in this watershed. Considerable mineral exploration activities, including the taking of a surface bulk mineral sample, have occurred in this watershed. Following the taking of the bulk sample, a surface discharge was discovered coming from the foot of the bulk sample site having elevated metals values (10,000 to 13,000 ug/l Ni, 360 to 1000 ug/l Cu and 190 to 5300 ug/l Zn). A small tributary of Filson Creek flows past and receives

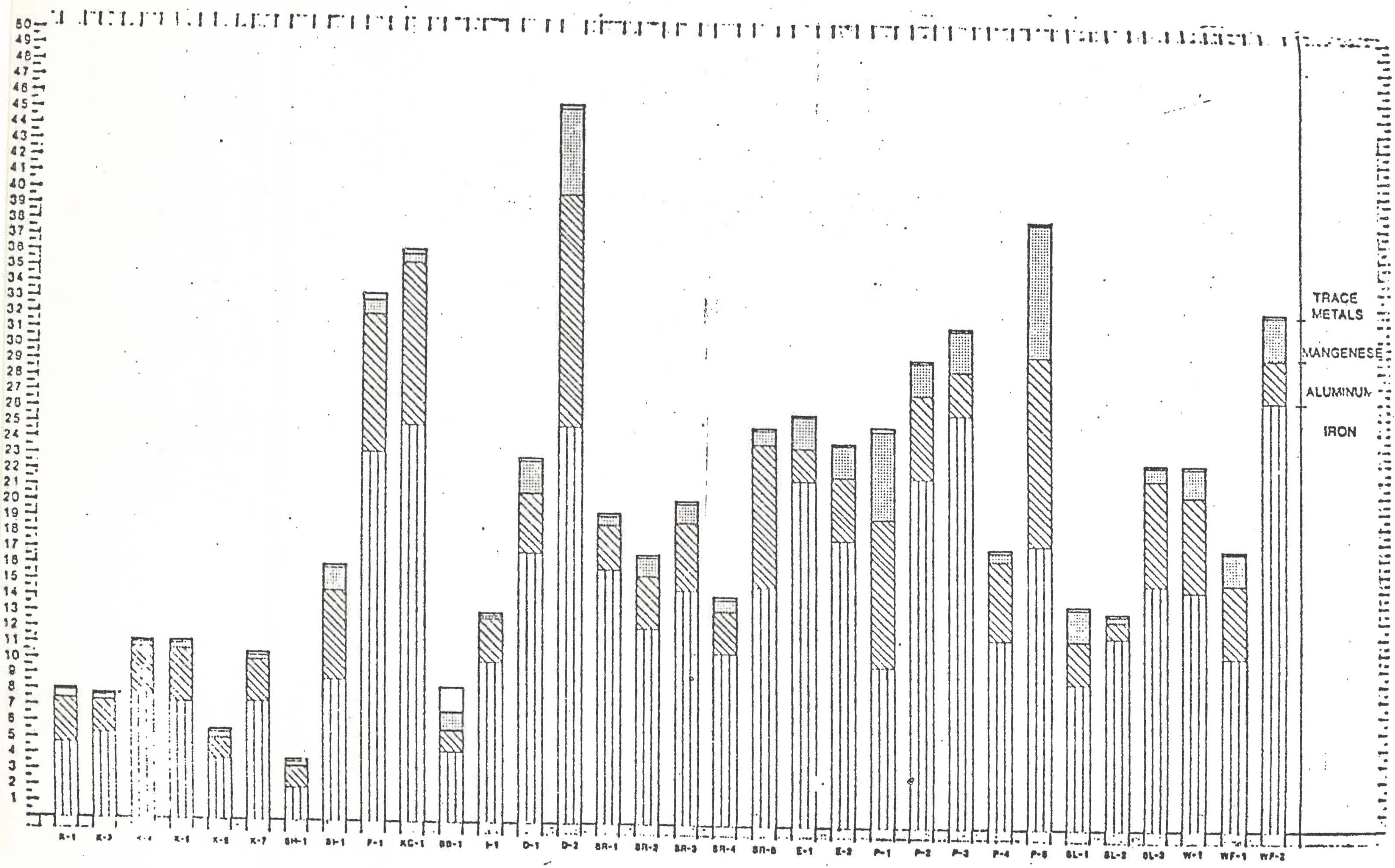
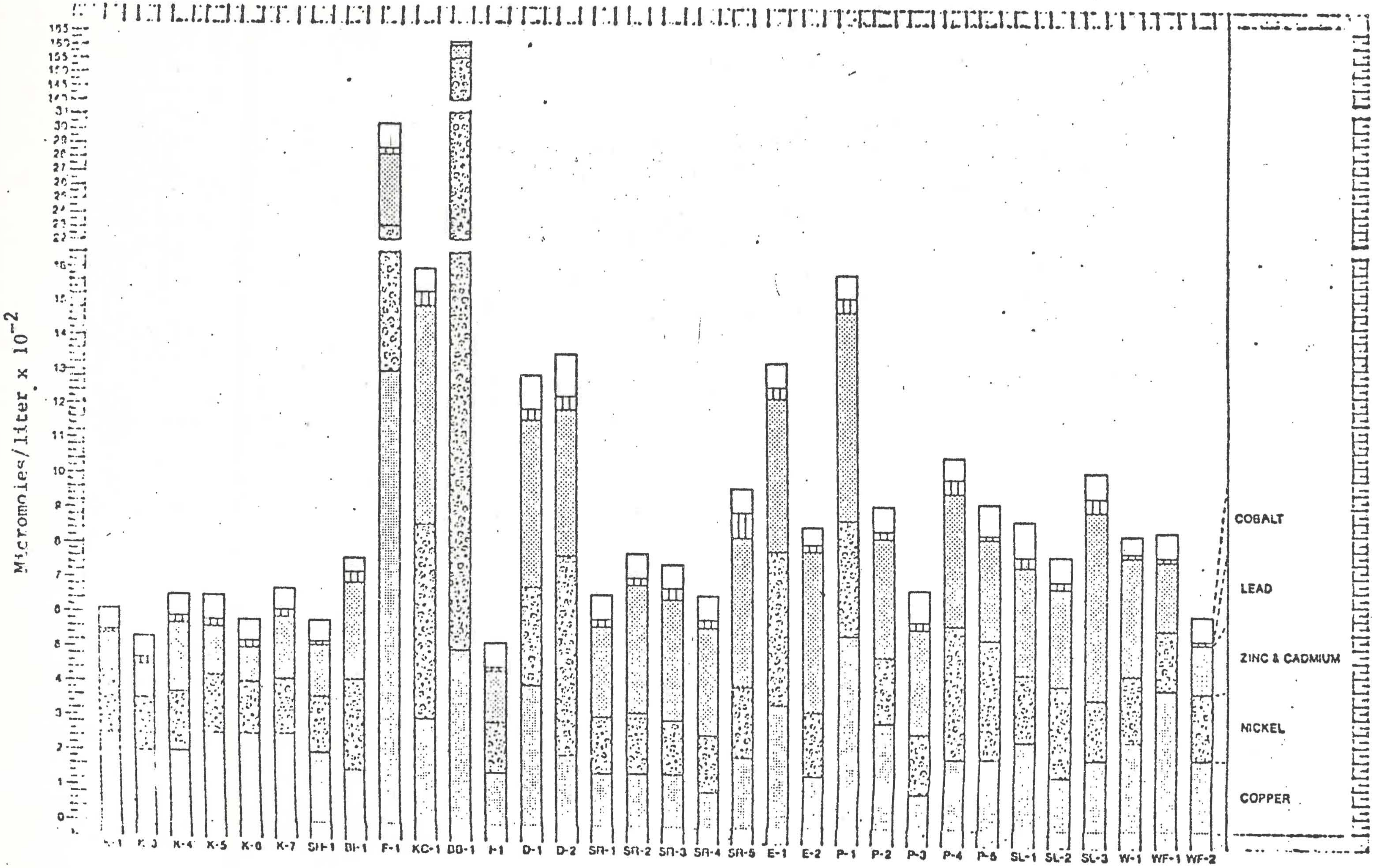


FIGURE 8

Major and trace metal proportions at stream stations.



STREAM STATION

FIGURE 19

Trace metal proportions at stream stations.

the discharge from the bulk sample site. An increase in copper and nickel concentrations as the tributary flows past the bulk sample site was apparent. A paired t-test performed on the data demonstrated that the difference in the data sets (upstream vs. downstream) was significant at the 0.05 probability level both for copper and nickel. The average increase in nickel and copper concentrations is about 9 ug/l and 5 ug/l, respectively.

Although there were fewer correlations between metals and other parameters in streams than in lakes, several relationships warrant particular note (Table 41). Higher copper concentrations were significantly correlated with lower pH values and elevated nickel concentrations. Iron was directly correlated with water color but inversely correlated with dissolved oxygen. Patterns of occurrence of toxic trace metals, cadmium, lead, and mercury were directly related.

Table 41

The dynamics of metals in lakes are somewhat different from those in streams because the large surface area of bottom sediments with its varying oxidation-reduction (redox) potential complicates the picture. Lakes can act as sinks for metals, as is the case with iron at Colby Lake, so that the chemistry of outflowing waters is different from that of inflowing waters. Large lakes may exhibit variability in the concentration of metals within the lake itself (as is the case with nickel in Birch Lake). Similar to streams, iron, aluminum and manganese were the most elevated metals in the Study Area lakes (Table 42). Copper, nickel and zinc have median values between 1 and 2 ug/l, whereas arsenic, cobalt and lead have median values of 0.6, 0.4, and 0.4 ug/l, respectively. Cadmium values were an order of magnitude lower than arsenic, cobalt and lead.

Table 41. Correlations between metal and other water quality parameters for surface waters of the Regional Copper-Nickel Study Area (P 0.05).

STREAMS

Cu:	Co pH(-) Ni(t)
Ni:	Specific conductivity DOC Co Suspended solids Cu(t)
Cd:	Hg Pb(t) Zn(t)
Zn:	DOC Suspended solids Pb(t) Cd(t)
Pb:	Hg Cd Suspended solids Zn(t) Cd(t)
	DOC D.O.%(-) Color(t)

LAKES

Cu:	Specific conductivity Ni Suspended solids(t) Mg(t) Zn(t) Ca(t) Total dissolved solids(t)
Ni:	Cu Specific conductivity Suspended solids Alkalinity Mg Ca Total dissolved solids(t)
Cd:	Pb Co Suspended solids Total dissolved solids(t)
Zn:	Pb(t) Fe(t) TOC(t) Total dissolved solids(t) Suspended solids
Pb:	Cd Co pH Fe(t) TOC(t)
Fe:	Co Color TOC DOC D.O. D.O.%(t) Zn(t) Pb(t) $\overline{Z}$ (t) Zmax(t)

(t) = log transformed data.

The greatest variabilities in concentration were exhibited by manganese, zinc, cadmium and aluminum, with arsenic the least variable metal.

Table 42

Analysis of variance for six metals revealed no spatial variations for nickel and cadmium. Of the four remaining metals lead and iron were both elevated in South McDougal Lake, lead in Greenwood, and iron in Seven Beaver. Concentrations of copper were highest in Colby and zinc in Clearwater. Triangle Lake exhibited exceptionally low values for all four metals that varied spatially. In addition, copper levels were reduced in Long and Turtle lakes, zinc was lower in Bear Island, Tofte, and Bearhead lakes, and iron was significantly less in Tofte and Clearwater. Clearwater was the only lake that exhibited elevated levels of one metal and lower levels of another. No attempt was made to analyze temporal variations of metal concentrations in lakes because of insufficient data. In general, many more parameter correlations were observed in lakes than in streams, because lakes can act on metals and dampen the variability. Suspended and dissolved solids were consistently correlated with trace metals in lakes.

Most metals were significantly correlated with other metals (Table 41): copper with nickel and zinc; nickel with copper; cadmium with lead and cobalt; zinc with lead and iron; lead with cadmium, cobalt and iron; and iron with cobalt, zinc and lead. In addition, copper, nickel, cadmium and zinc were correlated with suspended and total dissolved solids. Both copper and nickel were correlated with calcium, magnesium, and conductivity. Zinc, lead, and iron were all correlated with total organic carbon (iron with dissolved organic carbon as well). Iron was correlated with more parameters than any other metal including

Table 42 Comparison of metal parameters for Regional Copper-Nickel Study Lakes.

	RANGE ug/l	MEDIAN ug/l	COEFFICIENT OF VARIATION
Iron	16-2300	350	88%
Manganese	1-5400	29	568%
Aluminum	4-610	77	100%
Zinc	0.2-35.5	1.8	163%
Copper	0.2-10.0	1.5	80%
Nickel	0.4-6.0	1.0	75%
Arsenic	.4-2.1	.6	50%
Cobalt	.2-2.2	.4	72%
Lead	0.08-1.9	.4	77%
Cadmium	.008-0.8	.03	160%

dissolved oxygen, color, and average and maximum lake depths. Although both cadmium and lead were significantly correlated with mercury in streams, no metals were correlated with mercury in lakes.

4.3.3 Quality of Ground Waters of the Regional Copper-Nickel Study Area

Many factors, both natural and anthropogenic, affect the quality of ground waters on a spatial and temporal basis. Local and regional variations in geological material in and adjacent to ground water aquifers such as, particle size, chemical constituents, hydraulic conductivity, recharge areas, and many other factors, will affect ground water quality. Because of the extensive variability possible and the large study area size, the identification of "baseline" ground water quality conditions in the Study Area was not feasible. Therefore, the following information on the ground water quality of the Study Area should not be used as a baseline reference, but for general characterization and comparative purposes. The information adequately describes the quality of ground water at the specific location monitored and for the time period covered, and caution is advised if any comparison is made to other monitoring locations or to areas not monitored. This information provides a perspective for regional (non-site specific) impact analysis pertaining to potential copper-nickel development.

The information presented in this section is based on samples collected by the USGS during 1976-1977 water year (Siegel and Ericson 1979). Water samples were collected for chemical analysis quarterly during 1976-1977 from 12 observation wells finished in glaciofluvial sand and gravel, 11 wells finished in the Rainy Lobe till, and 2 wells finished in peaty material. An additional single sampling of the U.S. Forest Service campground wells was added during a drought period in

October, 1976, when ground water levels were extremely low. This sampling included 3 wells finished in sand and gravel, 5 wells finished in Rainy Lobe till, and 3 wells in the Duluth Complex. Three other wells in the Duluth Complex were sampled during 1976. Locations of sampled wells are given in Figure 3.

In order to relate geochemical variations with known hydrologic conditions in the Study Area, interpretations of ground water quality generally were made using only the USGS (1977) analyses. Not all wells could be sampled an equal number of times and not all analyses were complete. Interpretations of ground water quality were made using seasonal subsets of the data.

As previously discussed in section 4.2.6 of this chapter, the principal source of ground water in the region is from surficial aquifers. Bedrock across the region is generally massive and yields only small supplies of water, its occurrence being limited to joints, fractures, and faults. The best ground water supplies are obtained from stratified sand and gravel zones in glacial drift, where the saturated thickness of the drift is sufficient.

4.3.3.1 Surficial Aquifers--Summary statistics for major dissolved constituents and other properties for samples collected by the USGS during winter 1976-1977 are presented in Table 43. These samples were collected when ground water levels were declining and were least affected by dilution from recharge. The concentration range of the major dissolved constituents that characterize ground water is presented in Figure 10 for samples collected during February, 1976.

Table 43, Figure 10

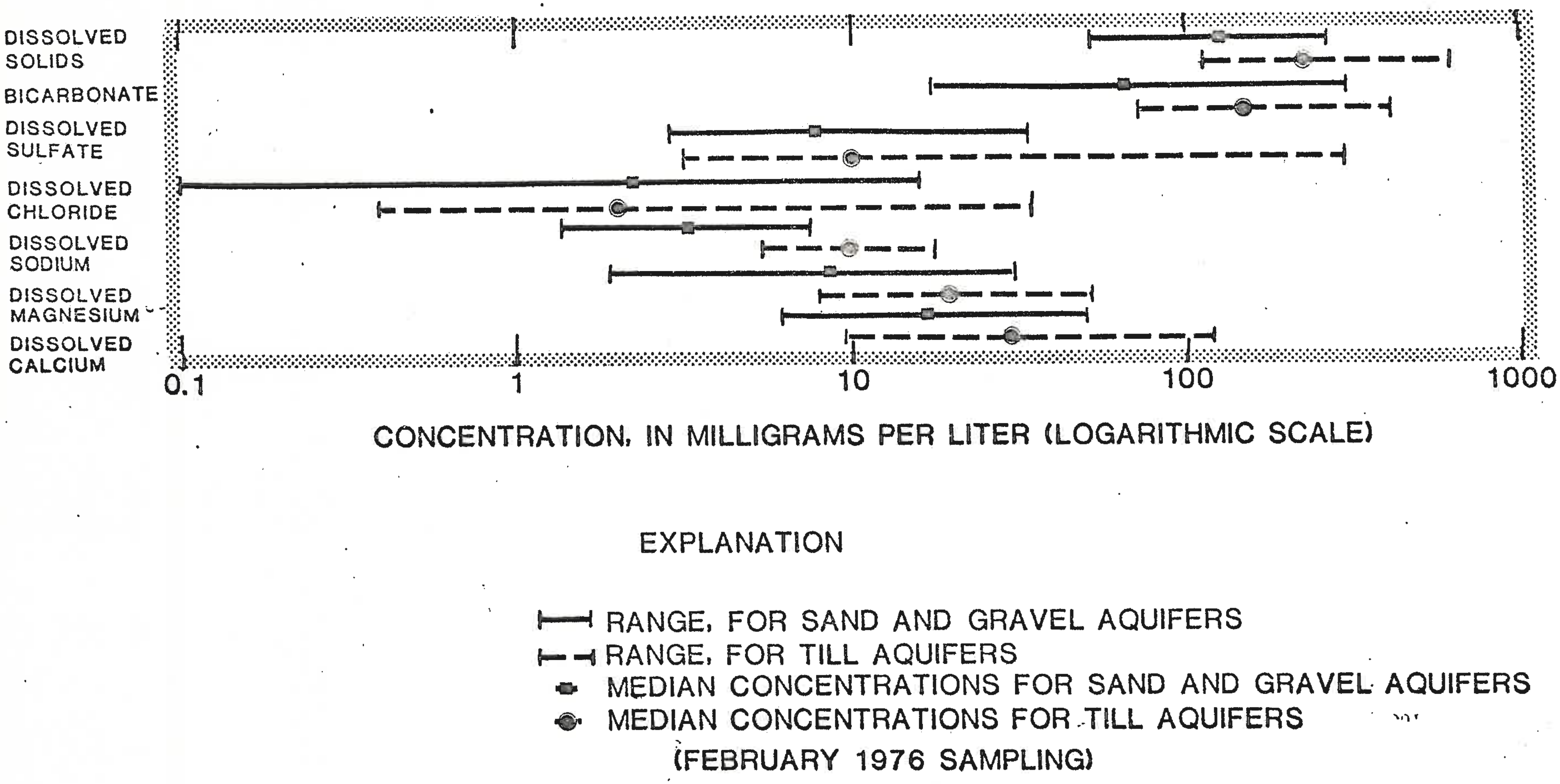
T-test results indicate that with the exception of bicarbonate, mean values of major dissolved constituents are significantly higher for ground water from Rainy

Table 43. Summary statistics for groundwater quality from surficial materials sampled during 1976. Concentrations in milligrams per liter except when designated otherwise.

	SAMPLES FROM TILL AQUIFERS					SAMPLES FROM SAND AND GRAVEL AQUIFERS				
CONSTITUENT OR PROPERTY	Number Samples	Max.	Min.	Mean	Median	Number Samples	Max.	Min.	Mean	Median
Specific Cond. (mmhos)	32	1250	120	368	251	40	577	5.5	193	166
pH (unitless)	25	8.0	5.7	6.81	6.70	28	7.1	5.7	6.33	6.35
Chemical Oxygen Demand	10	870	22	198	51	10	800	0	93	18.5
Hardness (Ca,Mg)	30	637	37	173	104	40	284	26	93	71
Dissolved Calcium	31	150	6.5	38.9	22.3	40	76	6.0	20	16
Dissolved Magnesium	31	64	5.1	18.0	14.0	41	31	1.1	10.2	7.3
Dissolved Sodium	31	18	2.1	7.7	6.9	41	7.3	1.4	3.1	2.9
Dissolved Potassium	31	9.3	.1	2.7	2.1	41	3.0	0.2	1.3	1.1
Bicarbonate	30	423	45	145	120	30	392	15	95	69
Dissolved Sulfide	11	12	0	1.5	.4	17	4	0	.9	.6
Sulfate	31	450	1.8	61	11	40	35	0.7	11	6
Chloride	31	35	.4	4	1.4	40	18	0.1	4	2.2
Silica	13	37	13	20.5	18.3	21	28	10	18.6	18
Solids (residue 180°)	13	938	97	293	187	14	284	55	148	130
Nitrate plus nitrite	11	12	0	1.5	0.4	37	10	.01	2.2	.62
Total Phosphorus	13	.07	0	.006	0.001	21	.04	0	—	—
Dissolved Organic Carbon	22	46	2.1	18	13	33	52	0.7	11.3	6.4

SOURCE: Siegel and Ericson (1979)

FIGURE 10. DIAGRAM ILLUSTRATING CONCENTRATION RANGES AND MEDIANS FOR MAJOR DISSOLVED CONSTITUENTS IN GROUND WATER.



MEDIAN CONCENTRATIONS ARE FOR THE SINGLE SAMPLING DURING FEBRUARY, 1976.

Lobe till than in ground water from outwash sand and gravel aquifers. Mean and median concentrations of the major ions, specific conductivity, and hardness in water from till aquifers are about twice that found in water from sand and gravel aquifers and about 3 to 5 times higher than water in group C (background) streams.

Concentrations of many chemical constituents are greater in till than in sand and gravel aquifers. Silt and finer-sized particles found in the till have large surface area to volume ratios, which place large areas of minerals in contact with the ground water and enhances chemical reactions. In addition, till has a much lower hydraulic conductivity than sand and gravel, and the time available for chemical reactions is at least an order of magnitude greater because of the slow ground water movement.

Water in till is classified as moderately hard to very hard (Table 13), while water in sand and gravel aquifers is classified as moderately hard to hard.

During winter 1976, the pH of water from sand and gravel aquifers ranged from 5.8 to 7.1. The pH of water from Rainy Lobe till ranged from 6.2 to 8.0. The lower range of pH in water in sand and gravel reflects rapid recharge to the aquifer from precipitation and a shorter time available for chemical reactions.

The pH of water from observation wells H10 and H33, which are finished in reed-sedge peat, ranged from 5.9 to 6.2.

Figure 11 shows that the samples collected from sand and gravel and from peat are a mixed calcium-magnesium bicarbonate type, based on predominant ions. This type of water is typical of ground waters in contact with calcic igneous minerals, as are found in the Study Area, and which have either a short residence time or have been collected in a recharge zone. Analyses plotted are of samples collected during summer 1976, when ground water levels were declining in response to drought conditions. Normal seasonal differences generally are not great enough to significantly alter the plots.

Figure 11

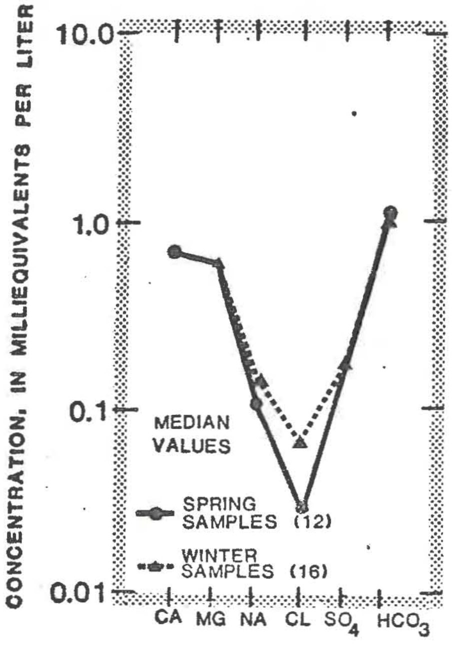
Water collected from wells in till can be classified as either a calcium magnesium bicarbonate or calcium magnesium sulfate type, based on predominant ions. The calcium magnesium sulfate water was collected from wells near the mineralized zone between the Duluth Complex and the Giants Range Granite in the northern part of the Study Area. Oxidation of sulfide minerals in the till accounts for the increase in sulfate concentration found in this water.

The curves connecting the median values for dissolved solids on the semilogarithmic graphs (Figure 11) illustrate the overall chemical similarity between water from the sand and gravel and till aquifers. Median concentrations were chosen so that the plots would not be biased with extreme values. The parallelism of the curves suggests that chemical reactions between surficial sediments and the ground water are generally the same. The slight separation between the curves indicates longer residence time for water moving through till. Consequently, water-quality differences in surficial aquifers are more a matter of relative concentrations than of differences in specific ions.

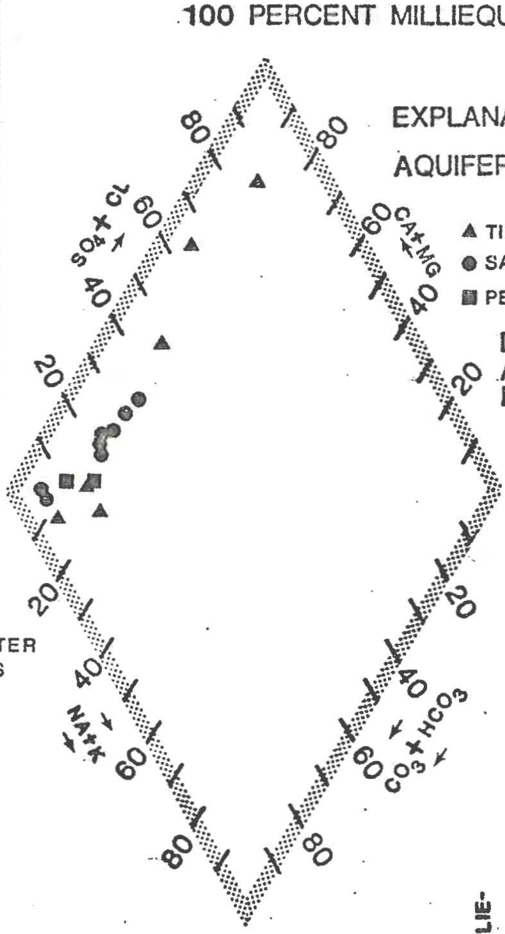
Mean values of the principal constituents in ground water from till and from sand and gravel aquifers do not vary significantly between seasons. The semilo-

FIGURE 11.

PIPER PLOT AND INDIVIDUAL SEMI-LOGARITHMIC PLOTS OF GROUND-WATER CHEMISTRY FOR MAJOR SURFICIAL AQUIFER TYPES.



SEMILOGARITHMIC PLOT OF MAJOR DISSOLVED SOLIDS IN GROUND-WATER FROM SAND AND GRAVEL AQUIFERS

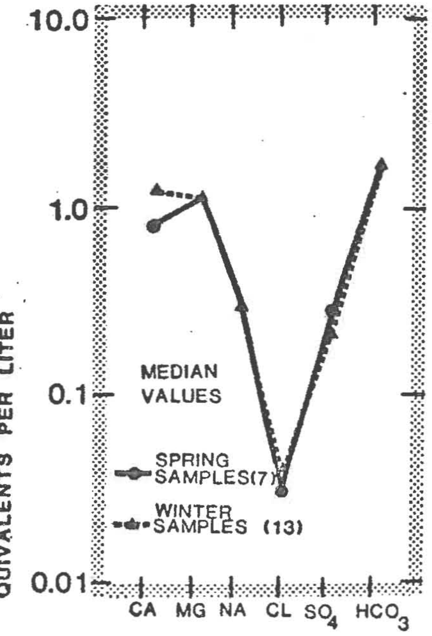


EXPLANATION

AQUIFER TYPES

- ▲ TILL (SUPERIOR LOBE)
- ● SAND AND GRAVEL
- ■ PEAT

DATA ON THE PIPER PLOT ARE FOR SAMPLES COLLECTED DURING SUMMER, 1976.



SEMILOGARITHMIC PLOT OF MAJOR DISSOLVED SOLIDS IN GROUND-WATER FROM TILL AQUIFERS garithmic plots illustrate the nearly identical concentrations between the median values for the major parameters sampled during both winter and spring.

Mean concentrations of nitrate, total phosphorus, total organic carbon, silica, and chemical oxygen demand in water from sand and gravel, peat, and till are not significantly different. Summary statistics for all samples collected from drift materials (Table 43), however, give order-of-magnitude ranges in the data, which reflect the diversity of local hydrochemical conditions and seasonal hydrologic conditions. Summary statistics for selected minor and trace metals for all samples collected from wells in till and in sand and gravel are given in Table 44.

Table 44

Concentrations of copper, cobalt, and nickel generally are less than 30 micrograms per liter, but can exceed 100 micrograms per liter in surficial material directly over the mineralized contact zone between the Duluth Complex and older rocks. These metals are probably related to oxidation of sulfide ores found at the contact zone and in the nearby glacial deposits. Concentrations of chromium, cadmium, and lead are less, generally ranging from 0 to 15 micrograms per liter. Iron is occasionally found in anomolously high concentrations ranging up to 67 milligrams per liter. These concentrations of iron are difficult to explain with the limited data base, but probably reflect local chemical conditions related to the reduction of iron in the system.

Trace and minor metal concentrations from water in two wells in peat are within the same range as found in other surficial materials.

Table 44. Summary statistics for selected trace and minor metals in surficial aquifers, (concentration in micrograms per liter).

CONSTITUENT OR PROPERTY	SAMPLES FROM TILL AQUIFERS					SAMPLES FROM SAND AND GRAVEL AQUIFERS				
	Number Samples	Max.	Min.	Mean	Median	Number Samples	Max.	Min.	Mean	Median
Cadmium	29	8.4	0.00	0.8	0.3	30	1.2	0.0	0.3	0.3
Cobalt	30	28.0	0.3	3.5	1.4	30	46.0	0.1	6.3	0.7
Chromium	30	5.5	0.00	0.9	0.6	31	3.2	0.0	0.6	0.5
Copper	30	190.0	0.6	11.7	3.8	30	45.0	0.2	7.2	4.2
Lead	30	6.4	0.1	1.8	1.3	31	18.0	0.0	1.9	1.1
Nickel	27	120.0	1.0	15.2	9.0	29	40.0	0.7	7.5	5.0
Aluminum	24	200.0	0.0	20.0	20.0	30	280.0	0.0	32.0	29.0
Zinc	30	170.0	3.9	27.6	8.9	30	620.0	0.7	56.1	14.1
Iron	30	3100.0	0.0	221.0	25.0	38	67000.0	0.0	5152.0	45.0
Manganese	31	7190.0	10.0	1268.0	330.0	38	26000.0	0.0	2140.0	45.0

SOURCE: Siegel and Ericson (1979)

The areal distribution of copper and nickel concentrations in water from surficial aquifers reflects proximity to the mineralized contact zone between the Duluth Complex and older rocks (Figures 12 and 13). Anomolous concentrations of both copper and nickel occur in zones about 5 to 10 miles wide centered on the contact. Ground water within these zones generally contains other trace metals as well, as a result of the oxidation of sulfide minerals found in the surficial deposits. Existing anthropogenic disturbances, such as mining and exploration activities can have localized effects on ground water quality. For example, copper and nickel concentrations from ground water discharging from INCO bulk-ore sample site (T.62N., R.11W., sec. 25) near Filson Creek are as great as 700 micrograms per liter. Nearby background values are less than 25 micrograms per liter. Water from observation well H-2 (excluded from regional characterization data presented in this section), finished at the base of the sample site, had copper and nickel concentrations of 370 and 3,800 micrograms per liter in April, 1976. Cobalt concentration was 440 micrograms per liter, an order of magnitude greater than general background levels.

Figures 12 and 13

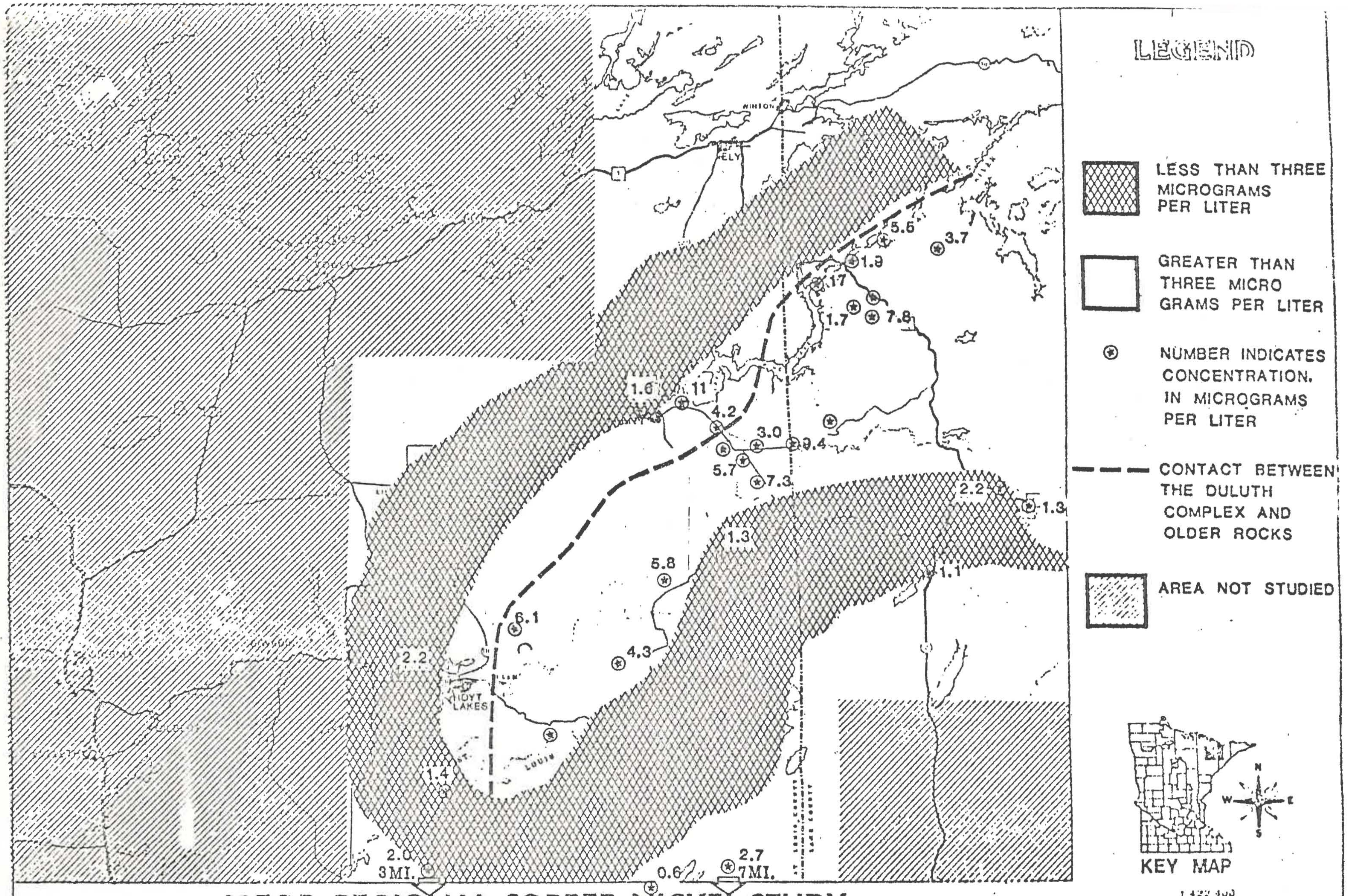
4.3.3.2 Bedrock Aquifers—Bedrock groundwater quality well locations are shown in Figure 14. Representative analyses of water samples collected from these wells are given in Table 45. Although the number of samples collected was not large enough to adequately perform statistical tests of significance, the analyses do suggest apparent differences.

Figure 14, Table 45

Table 45. Representative groundwater analyses from major bedrock units (Siegel and Ericson, USGS 1979).

PARAMETER	UNITS	1	2	3	4	5	6	7	8	9	10	11	12
Geologic Unit[a]		DCPX	DCPX	DCPX	DCPX	BBKF	BBFK	BBFK	GRNT	GRNT	GRNT	GRNT	VRGN
Total Depth of Well	feet	225	1000	125	1046	398	180	—	197	425	147	121	90
Date of sample		10/20/76	10/20/76	10/19/76	2/15/77	12/14/74	10/65	10/70	8/8/75	12/5/74	9/8/72	9/12/72	12/3/74
Specific Conductance	micro-mhos/cm	320	1300	2220	4620	380	—	—	240	143	572	237	745
pH	(units)	8.5	7.4	7.7	8.1	7.4	—	8.9	8.2	8.3	7.5	—	7.8
Hardness (Ca, Mg)	mg/l	7	150	9	1100	200	130	94	—	63	193	—	390
Dissolved Calcium (Ca)	mg/l	2.7	44	3.1	420	43	58	42	93	31	19	110	46
Dissolved Magnesium (Mg)	mg/l	0.1	9.1	0.3	2.0	22	—	—	53	9.1	6.0	10	66
Dissolved Sodium (Na)	mg/l	73	220	48	470	5	—	20	7.3	13.0	4.6	26	19
Dissolved Potassium (K)	mg/l	0.9	3.3	0.3	2.0	2.3	—	7	0.8	1.9	0.9	26	4.2
Bicarbonate (HCO_3)	mg/l	167	155	115	94	189	99	32	207	140	71	204	523
Dissolved Sulfate (SO_4)	mg/l	—	—	—	—	18	—	—	—	14	13	—	19
Dissolved Chloride (Cl)	mg/l	—	—	—	—	—	—	180	—	—	323	—	436
Dissolved Silica (SiO_2)	mg/l	3.8	45	9.6	3.6	41	47	88	17	7.3	65	13.8	22
Dissolved Solids	mg/l	5.3	310	4.3	1500	9	1.4	7.8	1.0	1.3	7.5	1.5	1.3

[a] DCPX Duluth Complex
BBKF Biwabik Iron Formation
GRNT Giantic lithologies
VRGN Virginia Formation



MEQB REGIONAL COPPER-NICKEL STUDY

FIGURE 12 GENERAL COPPER DISTRIBUTION IN SURFICIAL AQUIFERS
(DATA FROM 10-76 OR 4-76 SAMPLES)

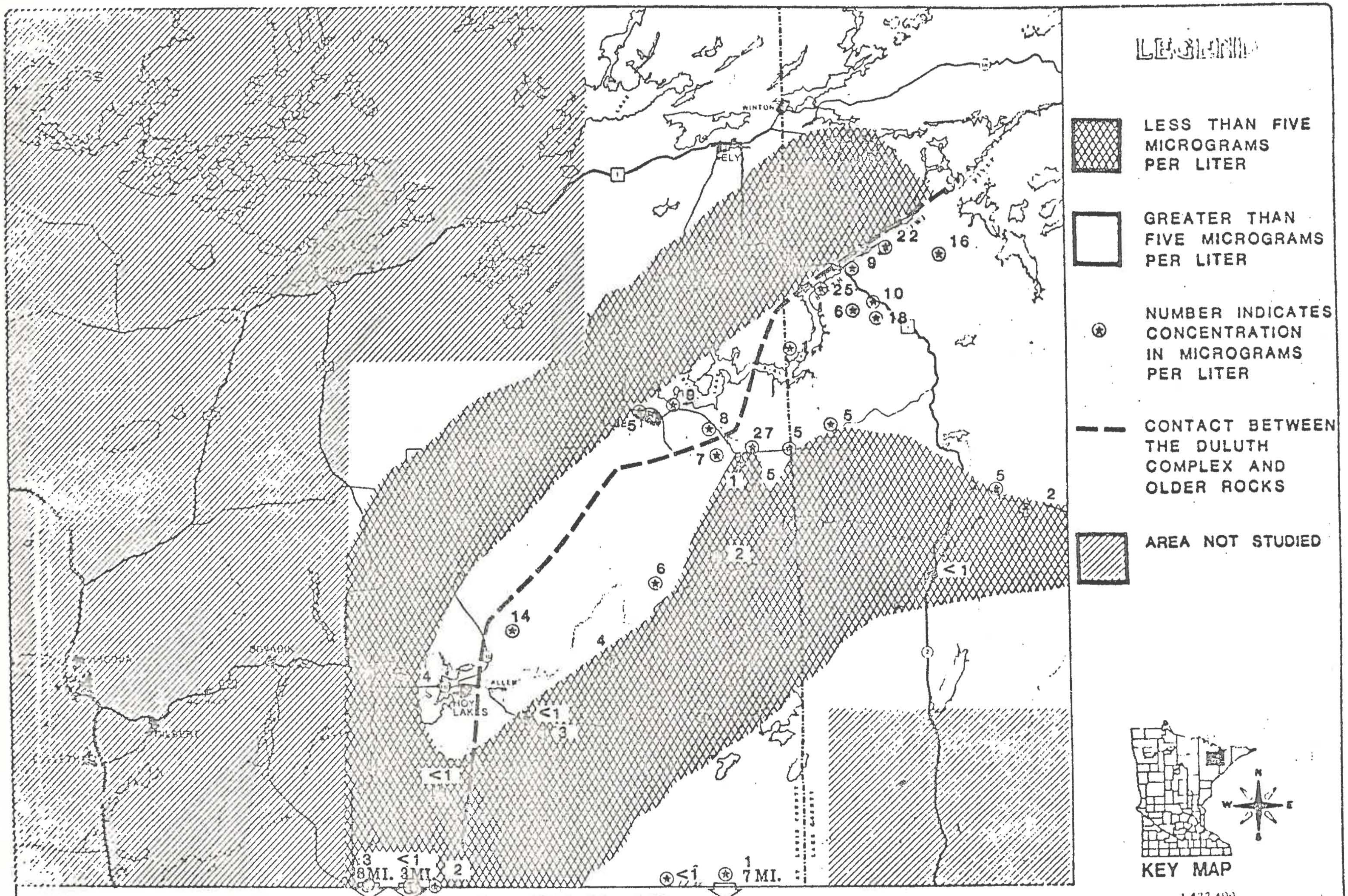
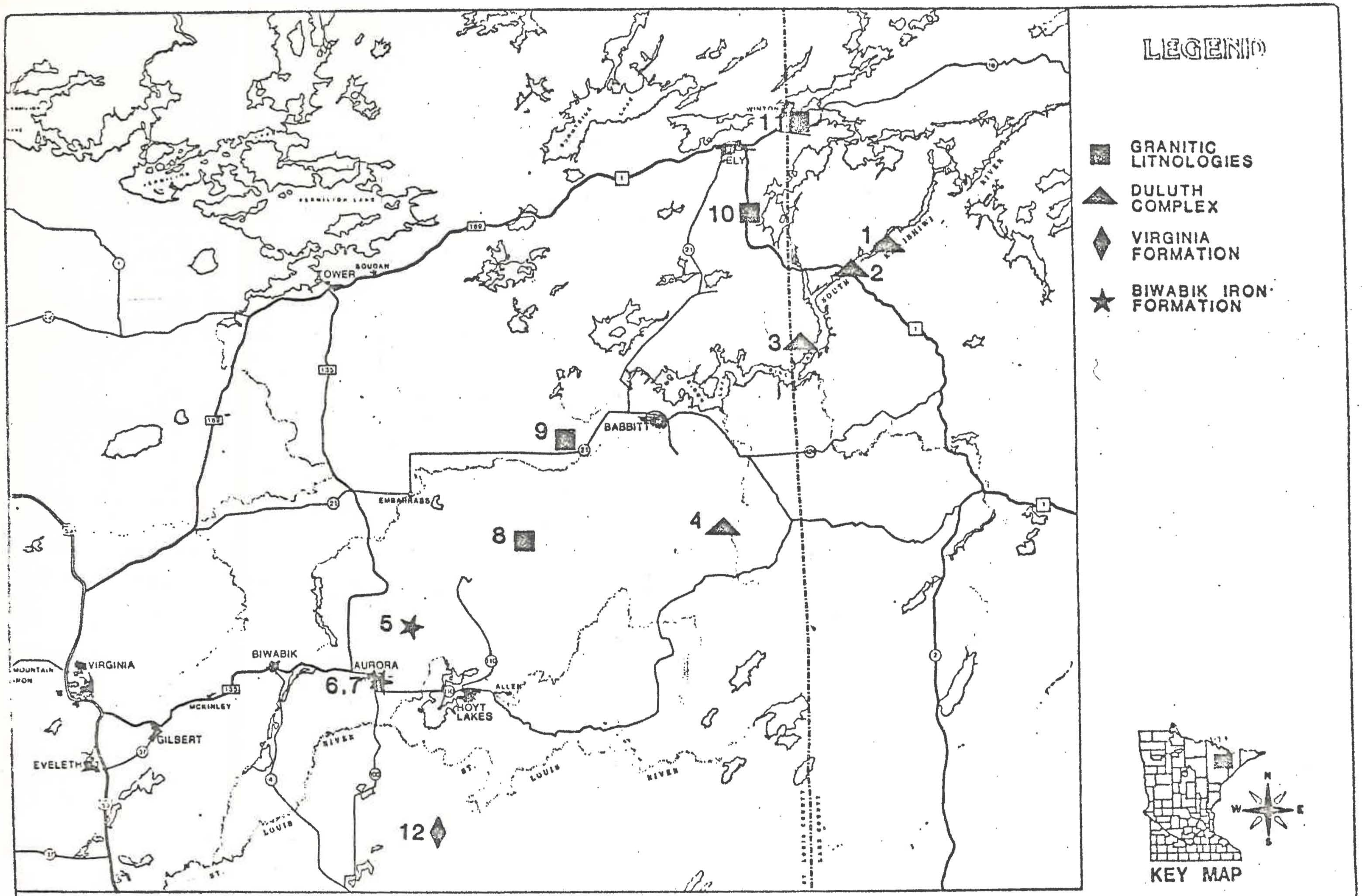


FIGURE 13 **MEQB REGIONAL COPPER-NICKEL STUDY**

GENERALIZED NICKEL DISTRIBUTION IN SURFICIAL AQUIFERS
(DATA FROM 10-76 OR 4-76 SAMPLES)



MEQB REGIONAL COPPER-NICKEL STUDY

FIGURE 14

BEDROCK GROUNDWATER QUALITY WELL LOCATIONS (U.S.G.S., 1978)

1:422,400

MILES

KILOMETERS

Concentrations of major constituents in water from the Duluth Complex are highly variable. Specific conductance, a measure of total dissolved solids, ranges from 220 to 4,[illegible] micromhos per centimeter, while chloride concentrations range from 1.3 to 1,500 milligrams per liter. Available data from six wells suggest that concentrations increase with depth, but, since water in the Duluth Complex occurs in isolated fractures and joints, the chemical composition is probably a function of local hydrogeochemical conditions rather than indicative of a trend with depth. Field pH in water from the Duluth Complex ranges from 7.0 to 8.5, generally one pH unit more basic than water from surficial lithologies in the Study Area.

Water from the Duluth Complex plotted on both Piper and semilogarithmic diagrams (Figure 15), ranges from sodium chloride to sodium bicarbonate types.

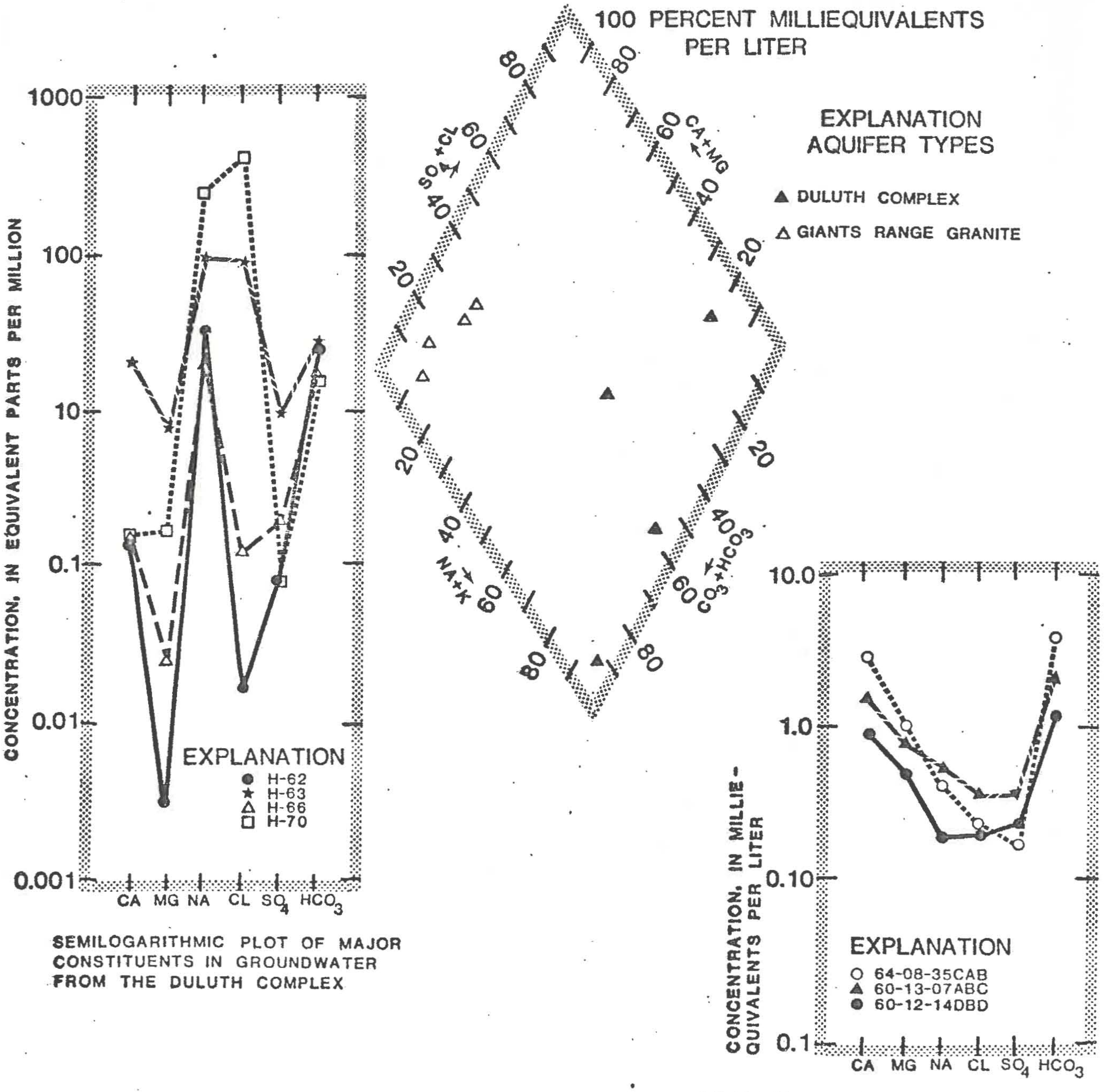
Figure 15

Waters from granite, Biwabik Iron Formation, and other non-troctolitic lithologies (Figures 15 and 16) are a mixed calcium-magnesium bicarbonate type, comparable to water from surficial materials. Water in these lithologies mainly occurs in an upper fracture zone that is in hydrologic continuity with overlying surficial sediments. As a result, wells finished near the upper surface of the granite or in fractures within the Animikie Group produce water having a chemical composition similar to that of water in surficial materials but modified by reactions with the bedrock surfaces.

Figure 16

FIGURE 15.

PIPER PLOT AND SEMILOGARITHMIC PLOTS OF MAJOR CONSTITUENTS OF GROUND WATER FROM THE DULUTH COMPLEX AND GIANTS RANGE GRANITE.

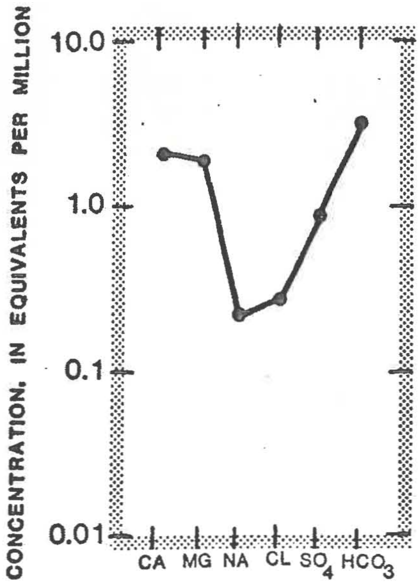


SEMILOGARITHMIC PLOT OF MAJOR CONSTITUENTS IN GROUNDWATER FROM THE DULUTH COMPLEX

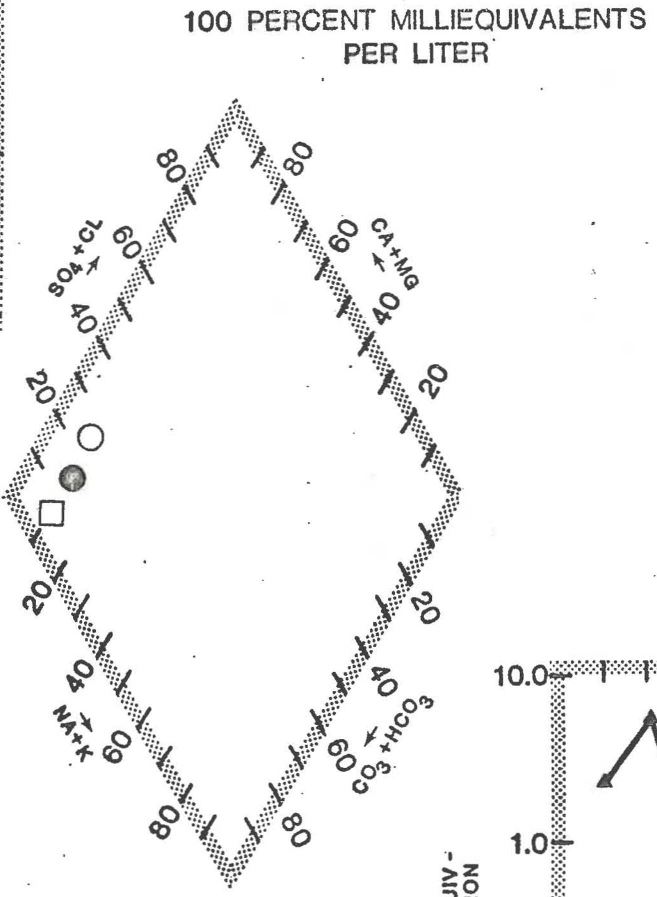
SEMILOGARITHMIC PLOT OF MAJOR CONSTITUENTS IN GROUNDWATER FROM THE GIANTS RANGE GRANITE

FIGURE 16.

PIPER PLOT AND INDIVIDUAL SEMILOGARITHMIC PLOTS OF MAJOR CONSTITUENTS OF GROUND WATER FROM THE BIWABIK IRON-FORMATION AND THE VIRGINIA ARGILLITE.



SEMILOGARITHMIC PLOT OF A GROUNDWATER SAMPLE FROM THE BIWABIK IRON FORMATION

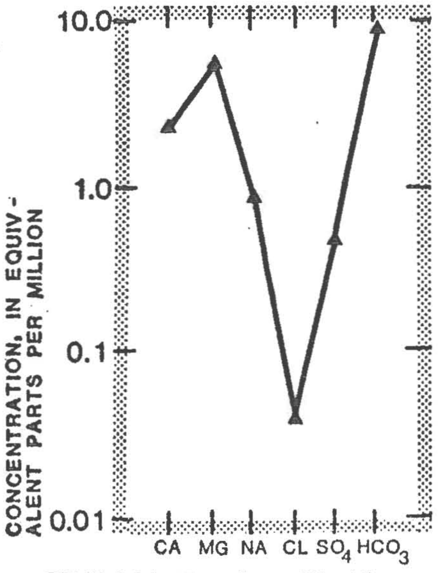


EXPLANATION

□ VIRGINIA ARGILLITE (T.56 R.14 SEC. 6 BBA)

○ BIWABIK IRON-FORMATION (T.59 R.15 SEC. 26 DAB)

● MEAN VALUE OF 15 MUNICIPAL WELLS IN BIWABIK IRON-FORMATION (COTTER)



SEMILOGARITHMIC PLOT OF A GROUNDWATER SAMPLE FROM THE VIRGINIA ARGILLITE FORMATION

Except for iron and manganese, few reliable trace and minor-metal analyses exist for water from bedrock aquifers in the Study Area. The small number of analyses available suggest that dissolved copper, nickel, cadmium, silver, mercury, and lead concentrations are less than a few micrograms per liter in water from most bedrock.

Iron and manganese concentrations in water from the Duluth Complex range from 0 to 150 and 0 to 60 micrograms per liter, respectively. Concentrations of these metals are higher in water from the Biwabik Iron Formation, ranging from 50 to about 5,000 micrograms per liter for iron and from 0 to 1,800 micrograms per liter for manganese. Data from four wells indicate iron and manganese concentrations for water in the Giants Range Granite can be as high as 500 micrograms per liter.

Evaluation of trends in bedrock ground water chemistry cannot be made with the present data base. Most variations likely reflect local complexities in the hydrogeochemical and hydrologic environment.

Fair to good correlations exist between specific conductance in surficial and bedrock aquifers and dissolved calcium, hardness, and dissolved solids for all analyses performed for this study (Figure 17). Because of this relationship, easily obtained specific conductance measurements can be used to roughly predict these constituents.

Figure 17

No significant correlations were obtained between trace metals and sulfate which might have been expected from oxidation of sulfide minerals included within drift

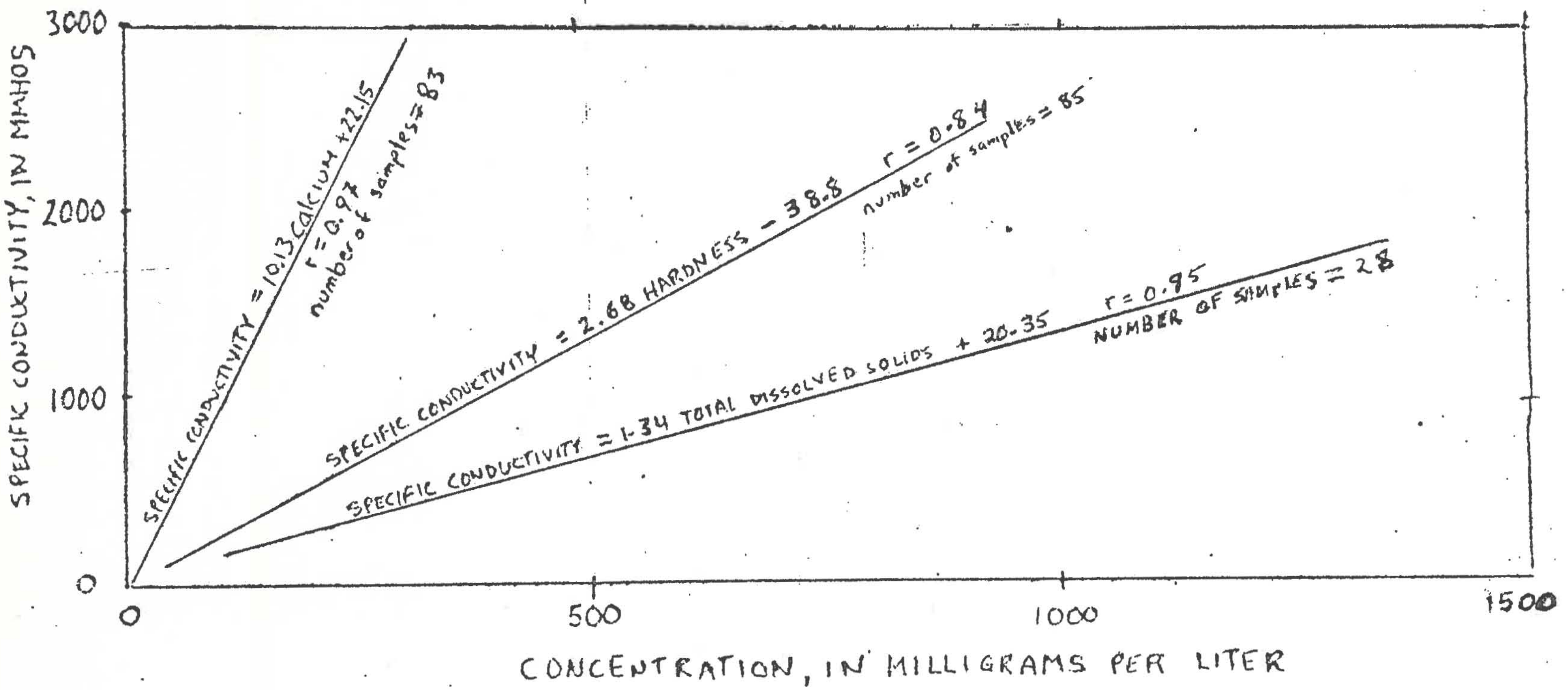


FIGURE 17 Graph showing relation between specific conductivity and selected constituents in ground water collected from the Copper-Nickel Study Area.

and bedrock, or between dissolved organic carbon and trace metals as might be expected from chelation of metals by humic or fulvic acids. The lack of these correlations highlights the complexity of local hydrogeochemical conditions. Concentrations of trace metals are controlled by inorganic and organic mechanisms that operate non-uniformly over the region. An evaluation of local trace metal concentrations requires a site-specific understanding of the local ground water flow system and the mineral and organic constituents in the glacial drift.

Highly saline water has been encountered in some bedrock areas in the Study Area (AMAX Drill Hole 303). The source and spatial distribution of this water in the Study Area is unknown. Its occurrence in significant quantities (if encountered during mining) could present significant water quality, mineral processing, and water treatment problems. Table 46 compares the analysis of a single sample of the high saline water to water from a nearby AMAX bedrock ground water monitoring well.

Table 46

4.3.4 Existing Point Water Discharges and Land-Use Activities Effecting Regional Water Qualtiy

Information presented in this chapter shows that the water quality of several watersheds cannot be explained soley on the basis of natural conditions and surroundings, and that anthropogenic factors are the likely cause of some (and in some cases, the majority) of the variability from "background" conditions. The monitoring program conducted by the Regional Copper-Nickel Study was not designed to pinpoint the cause of this variability, but comparison of water quality data to regional point discharge and land use information offers a clue to those

Table 46. Comparison of quality of highly saline bedrock ground water to water from nearby AMAX bedrock groundwater monitoring well (B-3).

	UNITS	DRILL HOLE 303	AMAX B-3 (Jan. 1975-Sept. 1977) Range	AMAX B-3 (Jan. 1975-Sept. 1977) Mean
Acidity	mg/l as $CaCO_3$	12	2	2
Alkalinity	mg/l as $CaCO_3$	6	67-95	85.8
Barium	ug/l filtered	170	2-5	2.9
Chloride	mg/l as Cl	11,000	14-212	128.9
Cobalt	ug/l filtered	2.0	1-1	1
Copper	ug/l filtered	2.9	0.2-10	1.33
Hardness	mg/l as $CaCO_3$	12,000	1-80	34.88
Iron	mg/l filtered	4.9	0.05	0.05
Lead	ug/l filtered	3.6	No data	
Manganese	mg/l filtered	0.51	0.03	0.03
Nickel	ug/l filtered	20.0	1-6	2
pH		5.8	10.2-11.0	10.4
Sodium	mg/l as Na	1,900	70-123	101.5
Specific Conductivity		32,000	504-720	606.8
Sulfate	mg/l as SO_4	2	1-7	4
Zinc	ug/l filtered	5.0	5	5

SOURCE: AMAX Data Summaries 1975-77 and L.A. Darling 8/11/76.

anthropogenic factors influencing regional water quality. The reader is cautioned that no direct cause and effect between divergence of water quality from regional background conditions and specific point discharges or land use activities has been proven, except in the case of Unnamed Creek (BB-1).

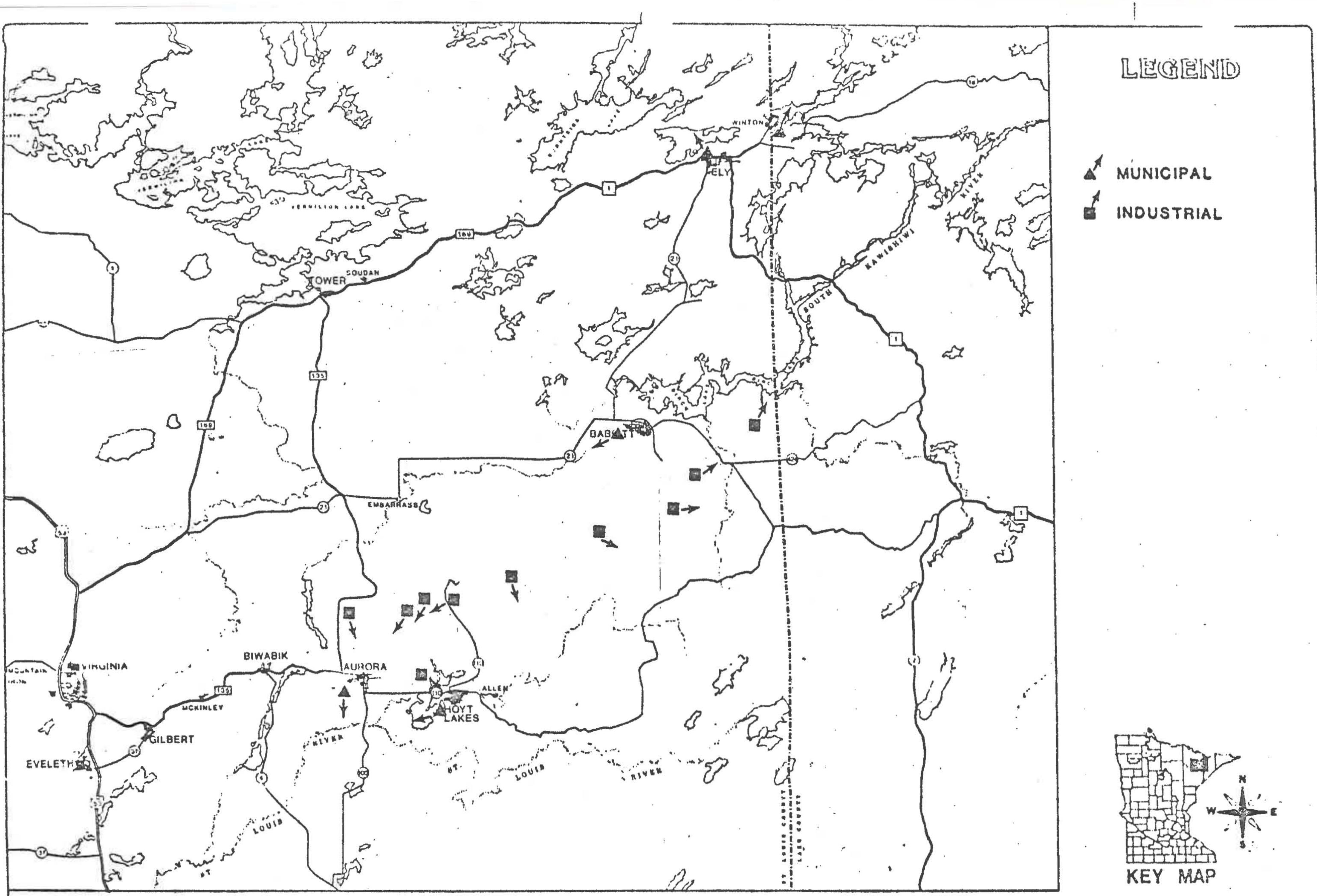
Anthropogenic factors affecting regional water quality can be grouped into two principal categories: point discharges (sources) and land-use activities (area sources). Another source receiving more and more attention by the scientific community and pollution control officials which significantly affects the quality of the region's surface waters is the atmosphere. Precipitation as a source influencing water quality is discussed in section 4.3.5.

4.3.4.1 Point Discharges--Major point discharges in the Study Area are either municipal discharges from sewage treatment plants or industrial discharges related to the iron ore and taconite industries (Figure 18, Table 47). Very limited data on the quality of these discharges is available, therefore the discussion of this subject will also be limited.

Figure 18, Table 47

There are 5 major sewage treatment plants in the area covered by surface water quality monitoring data (Table 18). The Ely and Winton plants discharge into the Kawishiwi watershed. The other treatment plants, servicing Babbitt, Hoyt Lakes and Aurora, discharge into the Embarrass, Partridge, and St. Louis (downstream of SL-1) watersheds, respectively. While the monitoring data do not pertain to the Aurora plant, it is included in Table 48 for comparative purposes.

Table 48



MEQB REGIONAL COPPER-NICKEL STUDY

FIGURE 18 MUNICIPAL AND INDUSTRIAL WATER DISCHARGES
(BASED ON MASCHWITZ, 1977)

Table 47. Point source discharges in Copper-Nickel Study Area Lake Superior Watershed (Maschwitz, 1977)

Name & Permit #	Description Of Discharge	Receiving Water	Discharge Mo/Avg MGD	Water shed
Hoyt Lakes WTP MN0043770	filter backwash untreated	Colby Lake	.25	P-1
Hoyt Lakes WWTP MN0020206	primary & secondary treatment	Whitewater Lake	.266	P-1
Aurora WTP	filter backwash and lime sludge, untreated	St. James Abandoned open pit	.008	NA
Aurora WWTP MN0020494	primary and secondary treatment	Unnamed Creek tributary to St. Louis R.	.48	*
Babbit WWTP MN0020656	primary and secondary treatment	Hay Lake to Embarrass R.	.2	E-2
Reserve Mining 002	mine dewatering	Partridge River	8.9	P-5
Erie Mining Co. MN0042552				
009	mine pit water	Wyman Creek	1.0	P-1
010	" " "	" "	1.5	P-1'
MN0042536				
001	mine pit & surface runoff water	Knox Creek	2.7	SL-1
005	" " " " "	" "	2.5	SL-1
007	" " " " "	" "	1.0	SL-1
008	" " " " "	" "	1.2	SL-1
MN0042544				
002	mine pit water	First Creek	5.7	SL-1
003	" " "	" "	.58	SL-1
004	" " "	" "	.43	SL-1
006	" " "	" "	2.2	SL-1
Pittsburgh Pacific Co. Know Mine	mine pit water treated by settling pond	Second Creek	11.5	SL-1
Erie Mining Co. WWTP MN0045756	primary & secondary treatment	drainage ditch to swamp to Knox Creek	.105	SL-1

Table 47. Point source discharges in Copper-Nickel Study Area
Rainy River Watershed (Maschwitz, 1977)

Name & Permit #	Description Of Discharge	Receiving Water	Discharge Mo/Avg MGD	Water shed
Ely WTP MN0042137	filter backwash untreated	Shagawa Laek	.018)a	K-2
Ely WWTP MN0020508	tertiary treatment	Shagawa Lake	1.59	K-2
Reserve Mining				
001	mine dewatering, sanitary septic system, shop water	Unnamed Creek to Dunka R	2.9	D-1
002	mine dewatering, sanitary water, shop water	Langley Creek	2.2	D-1
004	shopwater, sewage treatment plant, water treatment plant	Unnamed tributary Langley Creek	0.22	D-1
005	tire shop water, taconite stockpile wash & paint shops, septic system	Unnamed tributary Langely Creek	0.28	D-1
Winton WTP MN0046485	filter backwash treated	Fall Lake	.0009	K-1
Winton WWTP MN0025283	tertiary treatment	swamp to Shaqawa R. to Fall Lake	.026	K-1
Tower WWTP MN0025038	primary and secondary treatment	East two River to Vermilion Lake	$.1^c$	*
Breitung Township Soudan-MN0046507	primary and secondary	East two River to Vermilion Lake	.02	*
Erie Mining Dunka Pit MN0042579				
011	mine pit water	Unnamed Creek to Birch L	2.3	BB-1
012	" " "	" " "0	.45	BB-1

Table 47 contd.

Name & Permit #	Description Of Discharge	Receiving Water	Discharge Mo/Avg MGD	Water shed
U.S.Steel Corp. Stephen Mine, Mt. Iron MN0003336				
001	mine pit water	Second Creek	2.9	SL-1
002	" " "	" "	.39	SL-1
MN. Power & Light MN0000990				
001	ash pond effluent scrubber system blowdown and	Partridge R. & Colby Lake	eliminated Oct.,1976	P-1
002	condensor cooling water		.72,144	
003	track hopper drainage	Partridge R. & Colby Lake	elimintated Oct., 1976	
004	track hopper drainage and coal pile runoff	Partridge R. & Colby Lake	.05	

[a] Discharge once/week summer, once/month winter.
[b] Discharge every 10 days.
[c] Design flow rate
WTP = Water treatment plant
WWTP = Waste water treatment plant

Table 48. Comparison of sewage treatment plant effluents (January 1976 - December 1976)

	MONTHLY AVERAGE BOD* RANGE	(Kg/day)	DISCHARGE MGD	WATER SHED
Winton STP	3.8-26.9	9.9	.025	K-1
Babbitt STP	4.7-26.2	11.6	.321	E-2
Hoyt Lakes STP	11.1-90.3	38.0	.295	P-1
Aurora STP	49.0-118.0	79.7	.452	NA
Ely STP	2.4-24.4	8.0	.982	K-2

*Biochemical oxygen demand.

Minnesota Pollution Control Agency rules WPC14 [Sec. 115.03, Subd 5.C (6)] establish specific performance requirements for sewage treatment plants. Except for the Ely sewage treatment plant, the other four treatment plant effluents during 1976 appear not to meet the MPCA requirements for Biochemical Oxygen Demand and phosphorus. Water quality data for the Embarrass River which receives the Babbitt sewage treatment plant effluent appears to have slightly elevated total phosphorus levels (Appendix 1), but these levels have not reached concentrations which can cause plant nuisances.

The total phosphorus concentrations measured at the outlet of Shagawa Lake (K-2) alos appear to be higher when compared to other reaches of the Kawishiwi River. The testing treatment system at the Ely sewage treatment plant is very effective in reducing total phosphorus loadings to Shagawa Lake. The higher concentrations at K-2 are probably due to residual phosphorus contained in lake sediments as a result of years of inadequately treated effluents entering this watershed.

The major industrial sources of water discharges to lakes and streams in the Study Area is the taconite/iron ore mining industry (Table 47). The major activity causing these discharges is mine dewatering. Table 49 compares the quality of Reserve Mining Company discharges to tributaries of the Dunka River with the background water quality data for the Dunka River upstream of these discharges (Station D-2). This information shows that such discharges have levels of various chemical parameters significantly higher than background levels and that there are also significant variations between discharges. The impact of such discharges on the quality of Dunka River waters can be clearly seen by comparing results for the D-2 and D-1 stations in Appendix 1.

Table 49

Table 49. Comparison of mining water discharges and background surface water quality.

RESERVE MINING CO.

	DISCHARGE #001			DISCHARGE #002			DISCHARGE #004			DISCHARGE #005		
	MEAN	RANGE	#SAMPLES	MEAN	RANGE	#SAMPLES	MEAN	RANGE	#SAMPLES	MEAN	RANGE	#SAMPLES
Conductivity umhos/cm	413.3	280-800	12	394.6	210-500	12	1146.3	1090-1225	4	613.8	575-680	4
Cl mg/l	40.4	22.5-63.0	12	39.6	21.5-56.7	12	270.5	238.9-310	4	135.4	122-148	4
SO_4 mg/l	40.9	23.0-60.4	12	29.9	20.8-44.0	12	18.6	7.5-34.4	4	8.9	5.6-14.8	4
Ca mg/l	33.4	22.8-63.6	12	34.0	16.2-41.4	12	113.6	105.4-120.5	4	64.8	59-75	4
Na mg/l	15.7	9.4-36.6	12	17.4	6.8-29.3	12	39.9	30.6-48.4	4	12.4	11.3-13.5	4
K mg/l	3.2	2.1-6.8	12	4.3	2.48-5.23	12	8.4	7.1-9.5	4	3.9	2.98-4.72	4
Mg mg/l	17.3	11.6-30.9	12	16.1	8.5-19.7	12	30.1	29.3-31.8	4	19.1	18.2-20.3	4
NO_3 mg/l	4.5	1.5-8.8	12	1.2	0.1-2.1	12	0.1	0.1-0.13	4	0.1	0.1	4

DUNKA RIVER (D-2) UPSTREAM OF DISCHARGES

	MEAN	RANGE	#SAMPLES
Conductivity umhos/cm			
Cl mg/l	2.19	1.3-3.9	7
SO_4 mg/l	6.21	4.0-11.0	7
Ca mg/l	5.8	3.1-8.5	2
Na mg/l	1.8	0.9-2.7	2
K mg/l	0.65	0.5-0.8	2
Mg mg/l	5.5	3.4-7.6	2
NO_3 mg/l	no data		

The only mine dewatering discharge for which trace metals data are available, is from Erie Mining Company's Dunka Pit (Table 50). Once again background water quality is significantly different than discharge quality. Dunka Pit discharge water is likely atypical for the Minnesota taconite industry because of the occurrence of mineralized gabbro in the Erie Dunka pit. The sulfate values for Erie pit dewatering discharge No. 012 is several times greater than Reserve Mining Company discharges (compare Tables 49 and 50).

Table 50

Unnamed Creek (BB-1) receives Erie Dunka pit dewatering discharges, but this discharge is not the principal source of trace metal and other chemical parameters in this small stream. This small watershed (BB-1) in addition to receiving point discharges from mining operations also receives contaminated water from area sources. These area sources include waste piles that contain sulfide mineralization which are leaching significant quantities of trace metals and sulfates. This leachate flows into Unnamed Creek, which flows into Birch Lake.

Most of the information available on point discharges is monthly average information and does not give a good picture of the variability in the quality and quantity of such discharges. Since dewatering discharges are directly controlled by mechanical pumping operation and indirectly by precipitation events, the discharges are usually intermittent and highly variable. Measurements were taken by a continous recorder during a period when Dunka River flow conditions at D-1 were very low to compare flow with specific conductance. While traces of precipitation (less than 0.01 inch) were measured at Babbitt over this time period, the regular nature of the conductance and flow variations implied

Table 50. Comparison of mine water discharge to background water quality.

Erie Pit Dewatering Discharge	Mean of monthly values (mg/l) for 9-75 through 5-76				
	Cu	Ni	SO_4	DS	pH
012	.01	.016	260	681	8.0
011	.01	.019	85	337	8.0

Background water quality for Kawishiwi River measured at K-5 for 11-75 through 3-77.

	Mean	Range	No. Samples
Cu mg/l	0.0015	0.0011-0.002	23
Ni mg/l	0.0016	0.0009-0.0032	23
SO_4 mg/l	7.79	4.4-12.0	24
pH	7.03	6.2-7.8	14

anthropogenic control. It was interesting to note that peaks occurred at night and, due to the regular scheduling and timing of monitoring sampling times, these varitions would have gone completely undetected, if it was not for the continous recorders. During more normal stream flow conditions, such peaks could also be lost due to dilution.

The combination of source variability, monitoring program design, and lack of adequate effluent data, makes it impossible to present a clear picture of how specific discharges are affecting the region's water quality. The previous examples, give some indication of the importance of such discharges and supports the conclusion that area sources are an important factor influencing regional water quality. If future mining operations are located in watersheds affected by existing sources, then more detailed source monitoring should be performed to adequately separate potential impacts due to existing sources from impacts attributed to new sources.

4.3.4.2 Area Sources-

4.3.5 The Influence of Atmospheric Deposition on Water Quality

The atmosphere contains suspended and gaseous material as a result of natural and human activities. Dust storms, volcanic activity, sea spray, decaying processes and emissions from plants and animals are examples of some of the natural processes which contribute to the atmospheric load. Human activity exacerbates the situation by burning fossil fuel, by agriculture practices, and by various other domestic and commercial activity. The old adage "what goes up must come down" applies since atmospheric pollutants eventually deposit on land and water surfaces.

Chemical parameters considered important in atmospheric loading and ecological impacts include hydrogen ions and associated sulfur compounds, nitrates-nitrites, phosphorus (phosphate acids), trace metals such as copper, nickel, chromium, cadmium, vanadium, and other organic and inorganic particulates, for example, pesticides. Kramer (1976) suggests that pH should be considered the master variable as it affects, directly or indirectly, trace metal migration and toxicity, primary and secondary aquatic production, and land production.

In recent years the problem of acidic precipitation has been recognized. Sulfur dioxide emissions from various sources, such as coal-fired power plants and ore smelting, combine with rain to form sulfuric acid, a strong mineral acid. This acid contributes hydrogen ions, lowering the pH value of rain, and ultimately causing ecologic damage. It was once believed that acidic rain was primarily a localized problem that occurred only near the sulfur dioxide source. Evidence now shows that sulfur dioxide can travel long distances and that the problem of acid precipitation is actually world-wide.

Evidence will be presented here which shows that some lake and streams in the copper-nickel study area are more than likely now being affected by acidic precipitation. The major sources for the sulfur dioxide which causes the acidic precipitation are believed to be outside the state. This contention is, in part, speculative and further study would be required to delineate the major sources.

Other air-borne pollutants are also important, such as other acid forming pollutants, toxic metals, and nutrients. This section of the report discusses the significance of the deposition of air-borne pollutants as measured in northeastern Minnesota on land and water.

Three factors govern surface water (lakes and streams) pH: (a) the rate of strong acid input (H+ deposition); (b) the location of lakes and streams relative to the prevailing winds, which modify (a); and (c) the geochemistry of the surficial sediments and the bedrock, which determine the buffering capacity (resistance to acidic input) of the surface waters and the runoff waters entering the surface waters. Factor (c) is the most important (Kramer 1976).

4.3.5.1 Precipitation Chemistry--The presence of acids in the atmosphere can cause precipitation to be acidic. Strong acids have been found to be the most important contributors to acid precipitation, although weak acids may also contribute (Honetschlager 1978). The precursors of acid precipitation are chloride, which forms hydrochloric acid; sulfur dioxide, which is converted to sulfate and then to sulfuric acid; and nitrogen oxides, which form nitric acid. These compounds are released to the atmosphere by various natural and human activities.

Acid precipitation is of concern because of its effects on aquatic and terrestrial ecosystems (Honetschlager 1978). Acidification of lakes and streams due to acid precipitation has eliminated or severely reduced populations of aquatic plants and animals. Acid rain causes changes in the rate of leaching of elements from soils, which may affect vegetation growth and change the composition of runoff that reaches water bodies. Vegetation may also be injured by direct contact with acid precipitation. Other potential problems due to acid precipitation include effects on predator-prey relationships, effects on the metabolism of organisms, deterioration of buildings, and effects on human health.

In recent years, taller stacks have been constructed in an effort to reduce local pollution, and the areal distribution of acid precipitation has been observed to increase concommitantly. Thus, human activities are believed to be the cause of increasing acidic precipitation.

4.3.5.2 Current Level of Acidity--Increases in precipitation acidity have occurred simultaneously with increased SO_2 and NO_x emission. Natural pH is believed to be 5.7 and is caused by the dissociation of carbon dioxide in rain water:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

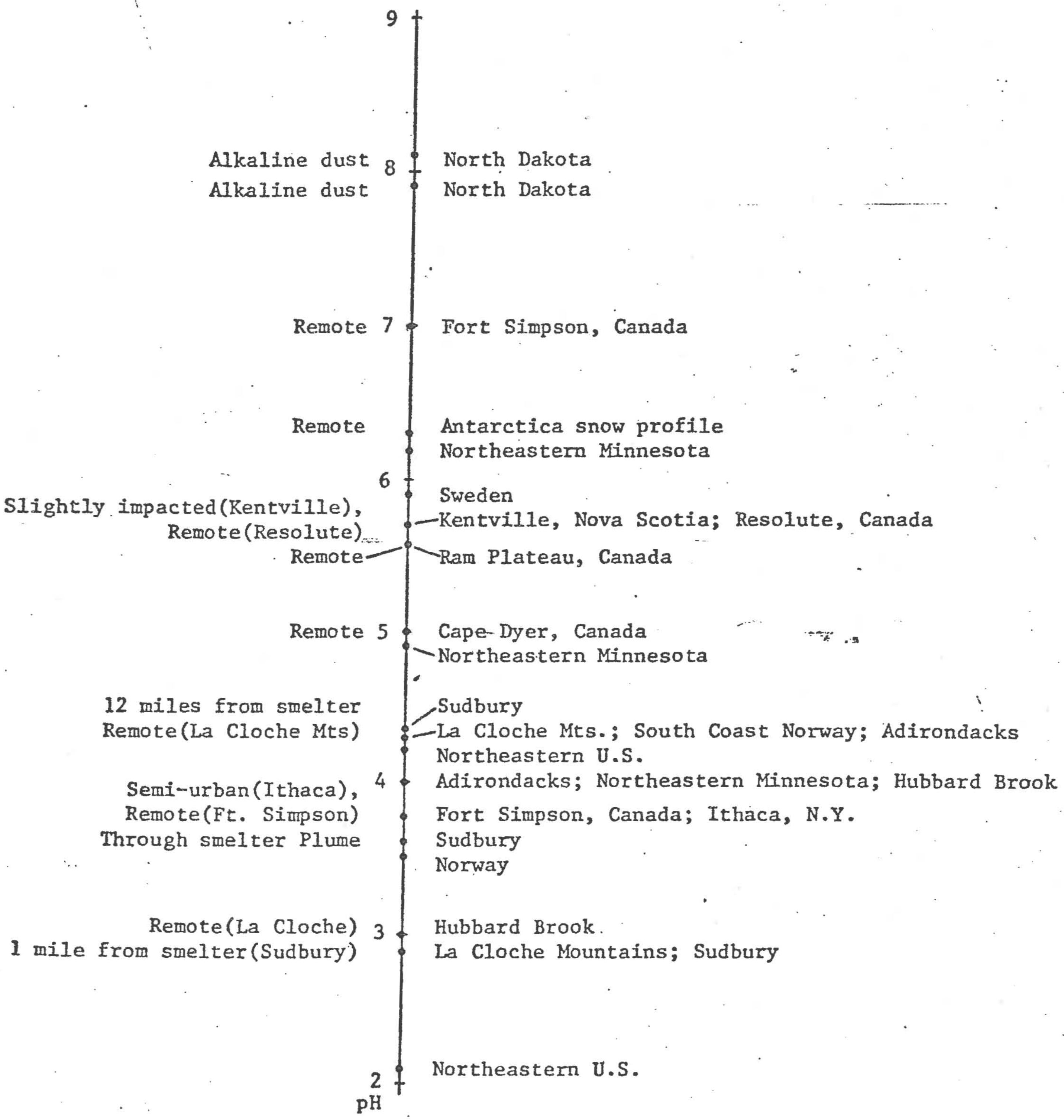
Figure 19 summarizes the pH values reported in the literature. (Additional summaries can be found in Honetschlager 1978). Areas defined by the literature as "remote" generally have pH values above 5, whereas values near 4 are not unusual in highly impacted areas. Also note the high pH (8) measured in North Dakota. This may reflect the alkaline nature of the soil in this region and/or the buffering effect of fertilizer used on the agricultural lands.

Figure 19

While pH values were once 5.7 or higher, precipitation in much of the northeastern U.S. now has an average pH of between 4.0 and 4.2. Around Sudbury, Ontario, the average precipitation pH is reported to be about 4.5 (Kramer 1976). The likely cause is the enormous INCO smelter, which emits approximately 8,000 tons/day of SO_2.

In south central Ontario, the mean pH range of bulk samples and rain-event samples was 4.06 to 4.22 and 3.95 to 4.38, respectively, for samplers located on the precambrian shield in 1976-77. For samplers located on the periphery of the shield, the mean pH range of bulk samplers was 4.78 to 5.79, and for event

Figure 7. Selected precipitation pH values.



samplers, 4.35 to 4.42. Bulk samples generally have higher pH because these samplers also collect dry fallout which can buffer pH upward. Samples collected on the shield reflect the fact that the precambrian shield is comprised of granitic bedrock that has poor buffering. Thus, when reporting or discussing pH values, it is important to note the type of sample and the location of the sampler, because the soil buffering properties of the area will affect the resultant pH.

The acidity of precipitation can be neutralized by various substances in the atmosphere. Additions of even small amounts of particulates to the atmosphere may raise the pH of precipitation because their surfaces have the ability to adsorb hydrogen ions. In areas where there is abundant windblown dust, pH values for precipitation of 7 to 8 are not uncommon (Honetschlager 1978). Bases in the atmosphere which are capable of neutralizing acid precipitation include sea spray and ammonia. Dairy farms have been suggested as sources of atmospheric ammonia.

Minnesota pH was measured on three different types of precipitation samples collected for the Regional Copper-Nickel Study: bulk, rain-event, and through-fall. Bulk samples were wet plus dry precipitation; rain-event samples were collected by bottles set out when rain occurred; and through-fall samples were collected by bottles placed beneath tree canopies (Eisenreich et al. 1978).

Bulk samples were collected from March, 1977 to March, 1978 at four sites (Tables 51 and 52). Based on general inspection of the values, most of the low pH values occurred during the months of July, August, September, October, and November. These months were also the wettest. The total hydrogen ion load per unit area of land surface is one to two orders of magnitude greater during these months as a consequence. More than likely the higher ratio of wet to dry precipitation under these circumstances accounts for the lower pH (i.e. less buffering by particulates). This is discussed in more detail later in this report.

Tables 51 and 52

Rain event pH was collected at three sites (Kawishiwi Laboratory, Ely, and Bear Island) from April, 1977 to September, 1977. Bottles were simply placed outdoors when the rain began and the pH measured soon after rainfall ceased. Twenty-one events were measured.

Four pH values were obtained from two automated sequential rain-event collectors. These two collectors were primarily for trace metal analysis and collector bottles were acidified for sample preservation. On one occasion, however, pH measurements were made at the beginning and at the end of a rain event.

The Minnesota Department of Natural Resources (MDNR) collected 15 rain samples in 1978, from June through October, at the AMAX exploration site near Babbitt. These samples were collected using a funnel to bottle arrangement. The funnel is continually exposed to the elements, and thus subject to dry fallout collecting on the surface that can be washed during rainfall. Therefore, it is likely that these pH values reflect some effects of buffering by dry fallout, similar to bulk collected samples.

Figure 20 shows a histogram of northeastern Minnesota pH values. Eighty-seven percent of the bulk samples (41) had a pH less than 5.7, which means that most of the precipitation measured can be considered acidic; and 50 percent of the samples had a pH less than 4.5. The range in pH was from 3.6 to 6.9; 14 samples

Table 51. Monthly concentration and deposition of bulk collected sulfate (SO$_4$) and hydrogen ion (H$^+$ – pH).

					SO$_4$,	LOADING RATE	
SITE & DATE	A	B	C	pH	mg/l^{-1}	SO$_4$^{D}	H + ^{E}
Fernberg							
3-15-77	29	1595	31.5	6.9	2.2	8.31	0.476
4-14	30	19	.38	–	–	—	——
5-19	35	2900	57.3	4.4	3.8	26.10	274.0
6-16	28	5500	108.6	5.7	1.8	23.50	26.0
7-20	34	5500	108.6	3.9	2.1	27.40	1640
8-17	28	750	14.8	3.9	2.1	3.73	223
9-16	30	1600	229.0	4.7	1.4	38.50	548
10-20	34	7000	138.2	3.7	-1$^{(F)}$	-16.60	3310
11-18	29	2500	49.4	4.1	-1	-5.92	471
12-16	28	2300	45.4	6.9	5	27.30	0.686
1-19-78	34	1500	29.6	4.0	5	17.8	355.0
2-15	27	500	9.9	–	–	—	——
3-20	33	1400	27.6	4.8	2.0	6.63	52.6
		TOTAL	(G)818.78	Annual Geometric mean		14.61	
Spruce Road							
3-14-77	28	1490	29.4	4.0	6.0	21.20	353
4-14	31	1160	22.9	5.2	6.1	16.80	17.3
5-19	35	1900	37.5	5.1	3.1	14.00	35.8
6-16	28	6100	120.4	4.7	1.6	23.10	288.0
7-20	34	5500	108.6	4.5	1.4	18.10	412.0
8-16	27	2250	44.4	4.1	2.9	15.50	423.0
9-16	30	8500	167.8	4.0	1.7	34.20	2010.0
10-20	34	2000	39.5	3.7	1.2	5.69	946.0
11-18	29	1000	19.7	3.7	-1	-2.37	474.0
12-16	28	1700	33.6	5.7	5	20.10	8.04
1-17-78	32	1250	24.7	4.1	5	14.80	235.0
2-16	30	550	10.9	–	–	–	——
3-22	34	1200	23.7	4.5	-1	-2.84	89.9
			653.90			12.36	

Table *5l* continued.

					SO_4,	LOADING RATE	
SITE & DATE	A	B	C	pH	mg/l^{-1}	SO_4^{D}	H + ^{E}
Dunka							
3-17-77	-	—	—	-	-	—	—
4-12	27	770	15.2	5.8	7.1	13.0	2.89
5-19	37	2500	49.4	4.9	3.1	18.4	74.60
6-16	28	5400	106.6	4.8	3.1	39.7	203.0
7-22	36	4200	82.9	4.2	2.8	27.9	628.0
8-19	28	1750	34.6	4.0	2.2	9.12	415.0
9-19	31	10600	209.3	4.0	2.0	50.2	2510.0
10-18	29	4750	93.8	3.7	-1	-11.3	2250.0
11-16	29	2500	49.4	4.2	-1	-5.92	374
12-16	30	1500	29.6	6.6	5	17.7	0.893
1-19-78	34	1300	25.7	4.2	5	15.4	194
2-16	28	400	7.9	-	-	—	—
3-20	32	900	17.8	5.2	2.0	4.26	13.5
		TOTAL	722.20	Annual Geometric mean		15.10	
Hoyt Lake							
3-16-77	29	367	7.2	4.1	-	-	69.10
4-12	27	1120	22.1	5.6	5.7	15.1	6.67
5-19	37	3500	69.1	5.1	3.8	31.5	65.90
6-16	28	425	81.4	4.5	2.1	20.5	309.0
7-22	36	4300	84.9	5.3	2.0	20.4	51.1
8-19	28	1250	24.7	4.1	2.4	7.11	235.0
9-20	32	8900	175.7	4.2	2.2	4.64	1330.0
10-19	29	5000	98.7	3.9	1.3	15.4	1490.0
11-18	30	4000	79.0	4.6	-1	-9.48	238.0
12-16	28	1900	37.5	5.1	5	22.5	35.8
1-18-78	33	1250	24.7	4.0	5	14.8	296.0
2-16	29	300	5.9	3.4	5	-	283.0
3-20	32	1450	28.6	4.8	-1	-34.4	54.6
			732.30			15.36	

A-Collection period, days.
B-Volume of precipitation collected.
C-mm of precipitation.
D-kg/ha^{-1}/yr^{-1}.
E-ueq ha^{-1} yr^{-1}.
F-Indicates less than.
G-Total precipitation for period 4-77 to 3-78, normal is about 726.

Table 52. Monthly concentration of bulk collected samples.

SITE AND DATE	SPECIFIC CONDUC. 25°C	SUSPENDED SOLIDS	TDS 180°C	NO_2, NO_3	P-TOTAL	TOTAL ORGANIC CARBON	ALKA-LINITY ($CaCO_3$)	Cl	Ca	Mg	Na	K	F	Ni	Cd	Zn	Pb	Al	Fe	As	Cu
Fernberg																					
3-15-77	(180)	8.8	-.5	-	.385	1.7	10	-.5	1.36	.5	-.5	-.5	-.1	-.1	.35	6.3	6.6	66	30	1.2	.6
4-14[a]	—	-	-	-	—	-	—	-	—	-	-	-	-	16	1.9	130	460	17000	7400	-	81
5-19	26	19	20	.51	.152	9.0	10	1.3	.72	-.2	-.5	-.5	-.1	-2	.21	9.7	16	44	40	0.7	1.4
6-16	25	5.6	3.0	.26	.021	5.0	10	0.85	.40	-.2	-.5	-.5	-.1	-2	.16	7.0	24	17	40	0.59	2.6
7-20	20	3.2	10	.30	.012	4.2	10	1.8	.56	-.2	-.5	-.5	-.1	-1	.12	3.0	5.3	19	-20	-.2	1.3
8-17	57	9.2	27	-	.012	10	10	1.8	2.0	2.0	-.5	-.5	-.1	-2	1.1	8.0	5.4	64	20	.3	3.9
9-16	17	2.4	2.0	.15	.017	1.5	-1	1.0	1.3	2.0	-.5	-.5	-.1	-1	1.0	5.6	5.0	7.5	-20	-.8	1.1
10-20	17	2.0	4.4	.18	.005	2.0	-1	1.5	2.0	2.0	-.5	-.5	-.1	-2	.85	2.2	2.9	5.5	-20	1.1	.5
11-18	46	6.4	16	.18	.001	2.0	-1	5.0	2.0	2.0	-.5	-.5	-.1	-1	.12	20	28	66	90	1.6	3.7
12-16	10	16	8.8	-	.076	1.8	-1	-.5	2.0	2.0	-.5	-.1	-.1	-1	.13	3.1	3.1	44	19	-.6	.2
1-19-78	22	8.4	0.8	-	.037	2.6	-1	-.5	2.0	2.0	-.2	-.1	-.2	-1	.55	10	36	130	90	3.7	1.6
2-15	—	-	-	-	.013	3.0	—	-	2.0	2.0	-.1	-.1	-	-1	.18	3.9	4.6	78	30	.8	.45
3-20	12	6.4	6.0	-	.006	1.8	-1	-.5	2.0	2.0	-.1	-.1	-.1	-2	.11	4.5	3.7	74	170	1.7	.2
MEAN	32	8.0	9.0	.26	.06	3.7	-10	-1.4	1.5	-2.0	-.5	-.5	-.1	-1	.57	6.9	12	51	49	1.1	1.5
Spruce Road																					
3-14-77	(320)	18	3.6	-	.053	3.2	10	4.9	1.6	0.7	-.5	-.5	-.1	2.0	.34	12	8.8	63	—	2.0	1.3
4-14	18	8.0	4.0	-	.006	1.7	10	-.5	1.3	0.3	-.5	-.5	-.1	-1	.15	7.5	9.2	140	40	1.0	1.7
5-19	18	52	2.0	-	.088	7.7	10	.8	0.9	0.3	-.5	-.5	-.1	-2	1.5	11	19	110	100	.6	3.1
6-16	20	5.2	22	.26	.006	3.3	10	-.5	0.5	0.3	-.5	-.5	-.1	-2	.17	6.3	.67	15	-20	.6	1.7
7-20	30	0.5	4.4	.19	.016	4.6	-1	1.4	0.8	-.2	-.5	-.5	0.1	-1	.12	3.9	5.3	23	-20	-.2	1.2
8-16	24	5.2	8.8	-	.02	3.9	10	20	2.0	2.0	-.5	-.5	-.1	3.0	.97	17	30	110	170	.5	9.4
9-16	23	2.8	6.0	.17	.001	2.2	-1	1.2	1.2	2.0	-.5	-.5	-.1	-1	.53	4.3	6.2	15	-20	-.8	1.0
10-20	23	4.8	2.8	-	.008	2.2	-1	1.9	2.0	2.0	-.5	-.5	-.1	-2	.85	6.2	3.4	15	80	.5	1.6
11-18	46	9.6	12	-	.017	2.6	-1	4.7	2.0	2.0	-.5	-.5	-.1	-.1	.24	10	18	54	40	1.9	1.9
12-16	12	4.4	12	-	.063	1.8	-1	-.5	2.3	2.0	-.5	-.1	-.1	-.1	.18	3.6	4.9	56	23	-.6	.6
1-17	27	13	3.6	-	.034	2.2	-1	-.5	2.0	2.0	-.3	-.1	-.1	-1	.25	17	22	230	130	1.4	1.7
2-16	—	-	-	-	.008	1.8	—	-	2.0	2.0	-.1	-.1	-.1	-1	.13	4.9	4.5	110	60	-.5	1.6
3-22	13	48	5.6	-	.018	(-1)	-1	-.5	2.0	2.0	-.1	-.1	-.1	-.2	.08	5.5	3.2	110	90	1.8	.6
MEAN	24	14	7.2	0.21	.03	3.1	-10	-3	1.6	-1.4	-.5	-.5	-.1	-.2	0.42	8.4	10.4	80.9	66	.95	2.1

Table 52 continued.

SITE AND DATE	SPECIFIC CONDUC. 25°C	SUSPENDED SOLIDS	TDS 180°C	NO_2, NO_3	P-TOTAL	TOTAL ORGANIC CARBON	ALKA-LINITY ($CaCO_3$)	Cl	Ca	Mg	Na	K	F	Ni	Cd	Zn	Pb	Al	Fe	As	Cu
Dunka																					
3-17-77	no sample																				
4-12	17	64	-.5	—	.054	2.5	-10	-.5	1.5	.5	-.5	-.5	-.1	-1	.19	7.9	8.6	290	200	2.4	1.4
5-19	26	9.6	33	—	.111	9.2	-10	1.3	1.1	.3	-.5	-.5	-.1	-2	.42	15	6.8	32	-20	.8	1.8
6-16	30	2.8	3.6	.42	.011	5.5	-10	.8	.6	.3	-.5	-.5	-.1	-2	.43	9.7	2.8	25	40	.95	1.8
7-22	20	.8	6.0	.37	.004	4.7	-1	1.6	1.8	1.0	-.5	-.5	-.1	-1	.21	5.7	7.1	25	-20	.6	1.3
8-19	41	5.6	18	—	.022	9.0	-10	6.4	2.0	20	-.5	-.5	-.1	-2	.27	4.9	12	48	60	.7	.8
9-19	23	4.4	4.5	.20	.001	2.3	-1	1.2	-1.0	20	-.5	-.5	-.1	-1	.12	3.0	73	12	-20	.8	.4
10-18	22	2.8	2.4	.22	.002	3.4	-1	1.3	2.0	2.0	-.5	-.5	-.1	-2	.09	2.4	3.7	7.9	-20	-.3	.4
11-16	64	5.6	10	.41	.01	4.1	-1	.3	2.0	2.0	-.5	-.5	-.1	-1	.79	3.3	14	30	30	.8	.6
12-16	30	6.4	8.8	—	.042	16	-1	.9	2.0	2.0	2.4	-.1	-.1	-1	.71	14	9	110	98	.6	2.1
1-19-78	30	14	17	—	.058	1.4	-1	.5	2.0	2.0	-.1	-.1	-.1	-1	.18	5.8	28	480	730	1.2	1.8
2-16	—	—	—	—	.054	2.1	—	—	2.1	2.0	-.1	-.1	—	-1	.09	4.7	5.6	400	970	1.1	1.5
3-20	8	28	4.8	—	.007	1.4	—	-.5	2	2.0	-.1	-.1	-.1	-2	.43	7.2	3.9	220	400	3.0	.7
Average	28	13	10	0.32	.031	5.3	-10	-1.4	1.7	1.5	-.5	-.5	-.1	-2	-.33	4.0	9.1	140	217	1.1	1.2
Hoyt Lakes																					
3-16-77	27	—	—	—	.116	7.0	—	—	1.0	.3	-.5	-.5	—	-1	.32	16	35	740	1600	16	2.6
4-12	17	18	-.5	—	.029	3.2	-10	-.5	1.4	.2	-.5	-.5	-.1	-1	.15	4.9	5.2	130	90	2.8	.7
5-19	22	11	26	.56	.107	9.9	-10	1.0	.9	-.2	-.5	-.5	-.1	-2	.27	12	7.1	29	40	2.5	1.8
6-16	30	5.2	5.2	.30	.022	4.8	-10	1.0	.4	.3	-.5	-.5	-.1	-2	.19	7.4	12	21	30	1.5	2.6
7-22	20	18	3.2	.37	.048	4.6	-1	1.1	2.4	1.0	-.5	-.5	-.1	-1	.85	7.0	8.8	71	70	1.2	1.4
8-19	34	12	18	—	.015	4.4	-10	2.8	2	2.0	-.5	-.5	-.1	-2	1.5	11	7.4	41	60	1.5	.8
9-20	20	3.2	32	.25	.011	2.5	-1	.9	1.4	2.0	-.5	-.5	-.1	-1	1.2	28	5.6	43	30	.8	1.1
10-19	30	2.0	26	.20	.006	2.3	-1	6.4	2	2.0	-.5	-.5	-.1	-2	.23	8.6	7.7	7.7	20	-.3	1.4
11-18	4.8	7.6	3.2	.12	.005	5.5	-1	.2	2	2.0	-.5	-.5	-.1	-1	.03	1.1	5.6	17	30	.6	.1
12-16	14	12	21	—	.04	3.0	-1	-.5	2	2.0	-.5	-.1	-.1	-1	.19	5.9	8.4	220	57	.6	.8
1-18-78	29	18	20	—	.088	2.1	-1	-.5	2	2.0	.2	-.1	-.2	-1	.36	14	26	610	500	1.5	2.1
2-16	58	—	—	—	.031	2.8	-1	3.2	2	2.0	-.1	-.1	-.2	-1	.26	7.4	18	320	500	1.8	1.3
3-20	9	46	6.8	—	.017	3.6	-1	-.5	2	2.0	-.1	-.1	-.1	-2	.09	6.1	11	450	640	7.7	.6
Average	24	14	15	0.30	.041	4.3	-10	-1.6	1.7	1.4	-.5	-.5	-.1	-2	0.47	9.9	12	208	282	3.1	1.3
Regional Average	27	12	10	.27	.04	4.1	-10	-1.9	1.6	-1.6	-.5	-.5	-.1	-2	.45	8.1	10.9	120	154	-1.6	1.5

had a pH of 3.9-4.1 (mode); and the mean pH (geometric) averaged over the four bulk sample sites was 4.6. These values are comparable to, or even less than values measured in areas of the world where ecological damage has already occurred (Figure 20).

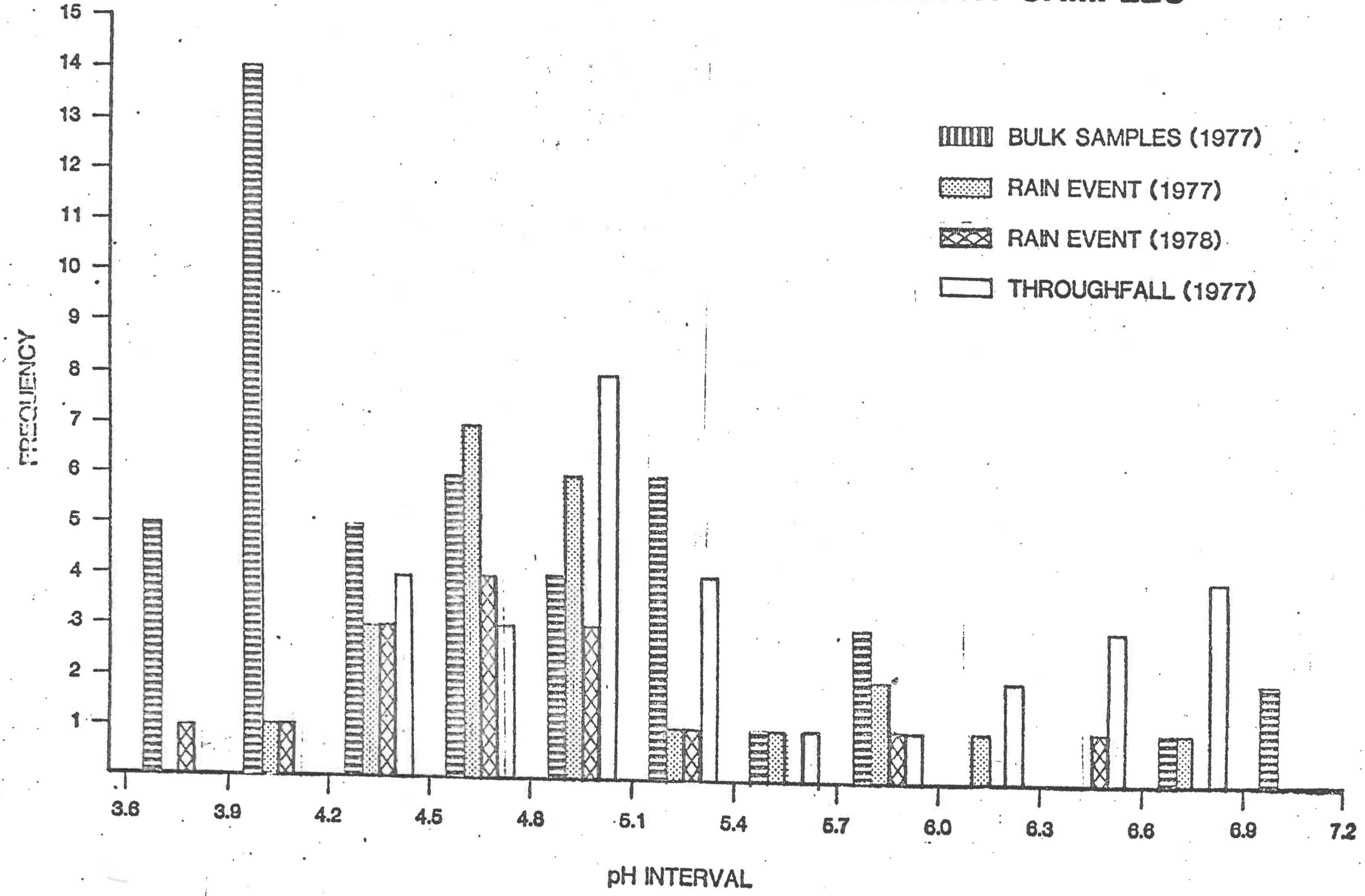
Figure 20

4.4.5.3 Current Level of Sulfate and Nitrogen Deposition--Sulfur compounds are introduced to the atmosphere by three main process: H_2S from biological decay, SO_4 from sea salt, and SO_2 from anthropogenic sources. Electric generating plant emissions account for about 60 percent of the sulfur emitted by human activities in the U.S. (U.S. EPA 1976b). Sulfur emissions from natural sources are estimated to be 133 - 152 x 10^6 metric tons per year compared to 50 - 55 x 10^6 metric tons per year from anthropogenic emissions. Although natural emissions are estimated at over twice anthropogenic emissions, natural emissions are not considered a major factor in producing acid rain because they are assumed to be in balance with natural sources of neutralizing bases (Honetschlager 1978).

Nitrogen compounds, the precursors of nitric acid, enter the atmosphere as ammonia released by biological decay processes, and as nitrogen oxides from biochemical reactions in soil and combustion processes. Annual global emissions of nitrogen oxides from natural sources have been estimated to be 150 x 10^6 metric tons. This compares to 8.1, 6.6, and 0.6 x 10^6 tons per year from combustion of coal, petroleum, and natural gas, respectively (Honetschlager 1978). Anthropogenic nitrogen emissions have been increasing due to increased use of natural gas and motor fuels, improved fossil fuel combustion techniques which use higher flame temperatures, and the increased use of nitrogen fertilizers since

FIGURE 20

HISTOGRAM OF pH VALUES IN BULK COLLECTED SAMPLES AND RAIN EVENT SAMPLES



about 1950. Although sulfuric acid remains the largest contributor to acid precipitation, nitric acid is apparently becoming more important in the northeastern U.S. and in northern Europe (Honetschlager 1978).

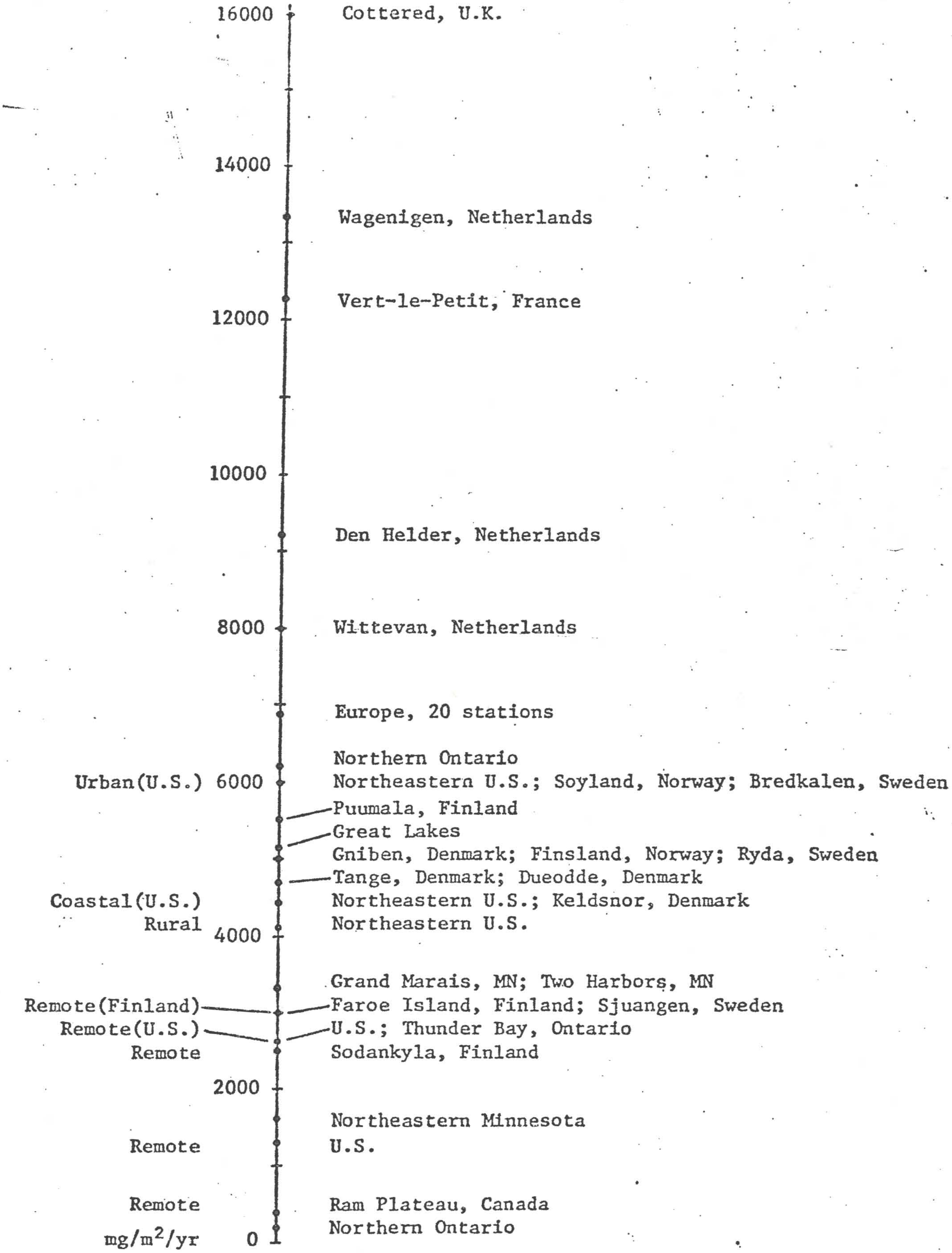
Sulfate concentrations are important in some areas of the world as a cause of acid precipitation. A level of 2.2 mg/l of sulfate in precipitation is indicative of excess sulfate. This value was exceeded often in northeastern Minnesota (Table 51).

Sulfate deposition in the Study Area was measured in bulk collected sample, rain-event samples and canopy through-fall samples. Table 51 shows the monthly results for the four bulk-samples sites. Based on the bulk collected samples the geometric annual mean for the region is about 14.4 Kg/ha/yr. The highest sulfate loadings occurred around August and September, and the second highest months were around April and May. These months also had the highest amounts of precipitation, which supports the contention that wet scavenaging of sulfate is probably more important than dry fall-out.

Figure 21 summarizes sulfate loading values reported in the literature. Remote areas of the world appear to have deposition values around 10 to 20 kg/ha/yr (1000 to 2000 mg/m^2/yr). Much higher values are reported for NE USA, Canada, and Europe. Although loading values reported by this study are not unlike remote area values, the pH values as discussed earlier are still dangerously low. The lack of buffering particles and components, or the presence of other unknown acid forming components, perhaps iron oxides, may account for the low pH measured in Minnesota.

Figure 21

Figure 2/ Sulfate loading from bulk precipitation.



4.3.5.4 Deposition Rates and Current Levels of Trace Metals, Nutrients, and Other Chemical Parameters--The copper-nickel program developed information on atmospheric concentration and deposition of trace metals, nutrients and other chemical parameters in four ways: bulk collected samples, wet-only samples, through-fall samples, and membrane filter air samples. This section will summarize the results of the bulk collected samples and the membrane samples, and discuss the importance of these findings as it pertains to the observed water quality of the region. More detailed information can be found in Eisenreich et al. (1978).

The results of the through-fall samples and the wet-only samples are comparable to the bulk collected samples (Table 52) and therefore are excluded in this report to simplify data presentation. The membrane sampler collects atmospheric particulates by drawing air through an 0.45 u membrane filter. Sampling time was 24-hours and a sample was collected every six days from late 1976 through late 1977. Samples were collected at eleven different sites, nine of which were in the Study Area. Elements determined and the sample sites are listed in Table 53.

Table 53

The dry deposition rate is a function of air concentration and deposition velocity. The dry deposition velocity of these particles is a function of particle size, particle shape and roughness, meteorological conditions and the scavenging character of the receiving surface. (For example, a forest canopy would scavage a particle differently than open surface water). Various studies have investigated these factors but much remains to be elucidated. For our purposes, Chilton's deposition velocities were used to calculate deposition rates for northeastern Minnesota.

Table 53. Mean annual dry deposition rates (in ng/m^2/sec).[a]

	SITE									
ELEMENT	Fernberg	ELC	Bearhead	Dunka	Toimi	Erie	Hoyt Lakes	Whiteface	Babbitt	Region	
Al	1.640	1.890	3.278	6.310	1.97	1.254	2.154	1.943	4.892	2.820	(.889)[b]
Cl	0.590	0.620	0.630	0.490	0.576	0.820	0.385	0.720	0.628	0.610	(.192)
V	0.010	0.005	0.014	0.014	-	-	-	0.003	0.007	0.009	(.003)
Cr	0.060	0.020	0.040	0.037	0.009	0.008	0.027	0.015	0.017	0.026	(.008)
Mn	0.050	0.050	0.090	0.150	0.062	0.108	0.066	0.062	0.146	0.087	(.027)
Fe	9.040	7.063	18.650	34.919	9.917	32.020	24.764	12.657	37.090	20.680	(6.520)
Co	0.010	0.014	0.020	0.031	0.008	0.024	0.016	0.013	0.024	0.018	(.006)
Zn	0.095	0.100	0.070	0.096	0.055	0.055	0.068	0.068	0.071	0.099	(.003)
As	0.006	0.006	0.010	0.009	0.006	0.009	0.015	0.007	0.014	0.009	(.003)
Br	0.018	0.019	0.020	0.019	0.012	0.031	0.032	0.030	0.128	0.034	(.011)
Sb	0.003	0.001	0.001	0.003	0.002	0.002	0.001	0.002	0.001	0.002	(.001)
Pb	0.058	0.057	0.064	0.065	0.040	0.100	0.103	0.092	0.408	0.109	(.034)
Cu	0.046	0.019	0.030	0.061	0.046	0.020	0.026	0.024	0.022	0.033	(.010)
S	2.123	2.027	2.108	1.966	1.400	1.066	1.888	2.248	2.088	1.883	(.594)[c]
Ni	0.035	0.018	0.020	0.056	0.005	0.010	0.016	0.017	0.036	0.024	(.007)
Cd	0.024	0.005	0.003	0.022	0.001	0.002	0.006	0.002	0.006	0.008	(.003)

[a] Using Chilton's dry deposition rates.
[b] As kg/ha/yr.
[c] 1.782 as SO_4.

Table 53 shows the mean annual dry deposition rates for the various sites by element. Most elements show a constancy in value across all sites except for aluminum, iron, and lead, where it appears that localized sources of these elements influence the sites. This is not surprising because of the existence of taconite mining in the area. Bearhead, Dunka, Erie, Hoyt Lakes, and Babbitt (all near taconite operations) show elevated levels for iron. Aluminum levels are higher at Bearhead, Dunka, and Babbitt. However, there is no ready explanation why aluminum should be elevated at these sites. Lead is elevated at Erie, Hoyt Lakes, Whiteface, and Babbitt. Vehicle traffic (combustion of leaded gasoline) in these areas could account for these levels. Lead was elevated in the surface water site near Hoyt Lakes.

Because most of the elements have similar levels at most sites, regardless of distance from various human activities, local sources are believed to be insignificant.

The loading rates from bulk collected samples are compared to the loading rate calculated from the membrane samples in Table 54. This comparison is between a wet/dry value and a dry deposition value. Of the ten comparisons that can be made, only three elements show different rates between the two methods that can be considered significant. They are sulfate and chloride, for which the bulk rates are higher, and iron, for which the bulk rates are lower. The dry deposition rate for iron is about six times higher than the wet-dry rate. It can be speculated that the mode of sampling in relationship to the source type and location may account for this difference. Most of the iron probably originates from area sources, such as haul roads, tailing basins, and stockpiles. The plume from these sources probably does not elevate to any extent, traveling perhaps only several hundred feet off the ground. The forest canopy in this area may scavenge this material effectively, and if the iron particles are relatively large, gravitational forces no doubt cause rather rapid settling.

Table 54

The membrane samplers were about 8-15 feet farther off the ground than the bulk collectors. Thus, the tree canopies may actually scavenge or screen the iron particles before they reach the bulk collectors. In fact, iron concentrations in bulk collected samples are lower in the summer months (Table 53) during the time when the deciduous trees are foliated. Since the samplers were relatively close to the sources and since the sources are relatively constant in strength, rain scavenging is probably much less important in the case of iron.

The dry deposition of sulfate is 1.78 kg/ha/yr, compared to the wet-dry rate of 14.36. One assumption made about this dry deposition rate is that the value represents sulfate. The analytical technique employed for the membrane sample only measures sulfur, not sulfate. It was assumed that the sulfur measured is sulfate.

Because the dry deposition value is low and because very little SO_2 was measured in this region (see Volume 3-Chapter 3) it is believed that most of the sulfate, as measured by the bulk samples, originates outside of this region, perhaps several hundreds of miles away in areas such as St. Louis, the Ohio valley and the East Coast area. Long-range transport of sulfate is quite feasible when large high-pressure systems are centered to the east and south of Minnesota. The large, clock-wise vortex of winds then can move sulfur compounds

Table 54. Summary comparison between air results and surface water results.

ELEMENT	BULK DEPOSITION CONCENTRATION REGIONAL MEAN	BULK DEPOSITION RATE REGIONAL AVERAGE (kg/ha/yr)	MEAN ANNUAL DRY DEPOSITION RATE (kg/ha/yr)	MEAN STREAM CONCENTRATIONS GROUP			LAKE^b CONCENTRATIONS
				A	B	C	
Al(ug/l)	51-208 (120)	.360-1.467(.846)	.889	174	127	112	4-610(114)^c
As(ug/l)	–^{a} 1.6	–.011	.003	.83	6.0	.82	.4-2.1(.7)
Ca(mg/l)	1.6	–11.3	—	32	19	6.8	1.9-46(9.5)
Cd(ug/l)	.45	.003	.003	.055	.061	.046	.008-.8(.05)
Cl(mg/l)	–1.9	–13.39	.192	11.7	22.7	2.4	.1-9.3(2.5)
Cu(ug/l)	1.5	.011	.010	3.0	2.7	4.2	0.2-10.(1.8)
Fe(ug/l)	49-282(154)	.345-1.99(1.08)	6.52	493	1241	723	16-2300(470)
F (mg/l)	–2	–.014	—	.233	.227	.158	.05-.5(.1)
K (mg/l)	–.5	–3.53	—	2.8	2.2	.61	.2-2.2(.7)
Mg(mg/l)	–1.6	–11.3	—	17.9	9.4	3.8	.65-12.2(3.5)
Na(mg/l)	–.5	–3.53	—	9.1	11.3	17.3	.9-18(2.5)
Ni(ug/l)	–2	–.014	.007	24.8	2.1	3.5	0.4-6.0(1.4)
Pb(ug/l)	10.9	.077	.034	1.08	2.4	.76	0.08-1.9(0.5)
Zn(ug/l)	8.1	.057	.003	3.6	3.8	3.2	0.2-35.5(3.1)
Alkalinity (mg/l)($CaCO_3$)	–10	–70.51	—	71	58	25	1-73(23.2)
TOC(mg/l)	4.1	28.9	—	12.1	17.6	16.9	4.6-38(16)
P-total(ug/l)	40	.28	—	102	44.7	22	
NO_2,NO_3(ug/l)	290	2.04	—	764	1100	121	
TDS(mg/l)	10	70.5	—	249	146	87	
SO_4(mg/l)^d	2.96	14.36	1.78	97	27	7.1	1-140(7.8)
pH	4.61			7.2	7.0	6.7	5.7-8.8(7.1)
Specific Conductance 25°C	27			355	230	65	24-389(78.5)
Suspended Solids (mg/l)	12			3.9	5.2	3.4	

[a] Indicates something less than.
[b] Surface values only.
[c] Range and (mean), totals.
[d] Geometric mean.

from the industrialized areas of the East to Minnesota. Under certain conditions Canadian cold-fronts can collide with this sulfur-laden, warm air mass over northeastern Minnesota causing high levels of sulfate in the precipitation. Thus, rain scavenging can be an important mechanism for deposition.

The concentration of trace elements in bulk deposition would not be expected to vary much from site to site in a region as small as the Copper-Nickel study area if localized deposition were minimal and rainfall amounts were not significantly different throughout the region. During brief but intense rainstorm one bulk sampler may experience considerable rainfall while other bulk samplers may not. Table 51 shows that rainfall was variable for each of the bulk samplers. For example, in October the Fernberg site received 138.2 mm of precipitation; Spruce Rd. 39.5; Dunka 93.8; and Hoyt Lakes 99.7. For elements that are scavenged efficiently by rain (sulfate for example) this has a large effect on the loading rate.

Except for aluminum, iron, and perhaps sulfate, all elements measured show similar mean annual concentration at all four bulk sample sites. For some elements, the concentrations were near detection limit (e.g. fluoride and nickel) and thus the average value is uncertain.

Alkalinity is listed as "something less than 10 mg/l." The actual alkalinity is probably closer to zero. The analytical technique employed grossly overestimates at low alkalinity levels. Analysis of snow-pack alkalinity (Table 55--bicarbonate) shows zero. Rainfall alkalinity, in any case, is probably very low. It is likely that the source of alkalinity, as low as it is, is caused by the suspended solids, which average 12 mg/l annually (Table 52).

Table 55

Table 56 presents a summary comparison of deposition rates, derived from the bulk collected samples, to rates observed over Lake Superior and Lake Michigan, and to the area around Atikokan, Ontario. Iron is the only element that could safely be considered to occur at rates significantly higher than the other nearby areas used for comparison. Uncertainty in the calcium and magnesium measurement precludes close comparison and for all practical purposes can be considered the same.

Table 56

In summation the deposition rate of all parameters measured are not unusual for a remote region such as northeastern Minnesota, except for iron. The taconite mines certainly influence the quality of air in this region. Based on the sameness of values across all membrane sample sites and the bulk sample sites, it is believed that the origin of most of the parameters lie outside of the region. There is some evidence to suggest that there are local sources for sulfates, in addition to iron, aluminum, lead, and chloride. Although there are local sources of sulfur (Ritchie 1978), it is believed that the majority of the sulfur measured, as sulfate, originates outside of the region.

No attempt was made to ascertain the character and level of the strong and weak acids present in the precipitation to account for the low pH's observed. However, because there is so little buffering in the precipitation, the amount of sulfate was usually sufficient to account for the low pH. Other acids that can

Table 55. Chemical composition of snow pack, Filson Creek Watershed.

PARAMETER		EPA(1)	U.S. FOREST SERVICE, 24 March 1976 Sample 1	2	3	x	Siegel 9 March, 1977
Acidity as H^+ (Mg/l)		0.0151	.01	.01	.03	.016	
Bicarbonate (Mg/l)			0	0	0	0	
Cadmium (ug/l)	Dis		0.25	0.05	0.15	0.15	
	Tot		0.13	0.14	0.49	0.25	0.24
Calcium (Mg/l)	Dis		0.6	0.3	0.4	0.43	
	Tot		0.8	0.7	0.6	0.7	
Carbon, Tot org.(Mg/l)			2.7	4.1	4.3	3.7	1.2
Carbonate (Mg/l)			0	0	0	0	
Chloride (Mg/l)		0.2	0.7	0.3	0	0.3	
Chromium (ug/l)	Dis	5.0	1.7	0.3	0.3	0.8	
	Tot		0.5	0.5	0.7	0.6	
Cobalt (ug/l)	Dis		0.6	-0.2	-0.2	-0.3	
	Tot		0.2	-0.2	-0.2	-0.2	-0.5
Copper (ug/l)	Dis		2.6	0.8	2.2	1.9	
	Tot		6.6	0.8	7.7	5.0	1.1
Fluoride (Mg/l)	Dis	0.023	0.1	0.1	0.1	0.1	
	Sus		0	0.0	0	0	
	Tot		0.1	0.1	0.1	0.1	
Hardness (ug/l)	None		2	1	1	1.3	
	Tot		2	1	1	1.3	
Iron (ug/l)	Tot		360	350	270	327	
Lead (ug/l)	Dis		3.2	1.8	5.2	3.4	
	Tot		14.0	5.6	8.3	9.3	1.7
Magnesium (Mg/l)	Dis		0	0	0.1	0.03	
	Tot		0.2	0.2	0.3	0.2	
Nickel (ug/l)	Dis		5	1	1	2.3	
	Tot		1	1	1	1.0	-1

Table 55 continued.

PARAMETER	EPA(1)	U.S. FOREST SERVICE, 24 March 1976 Sample 1	2	3	x	Siegel 9 March, 1977
N - NO_2 as N (Mg/l)		0	0.03	0	0.01	
N - NO_3 as N (Mg/l)	0.29	1.1	0.70	1.5	1.1	
N - NO_3 as N (Mg/l)	0.099	0.15	0.14	0.13	0.14	
N - org Tot (Mg/l)		1.7	0.25	0.25	0.73	
N - KJD as N (Mg/l)	--	0.57	0.39	0.38	0.45	
pH (measured)		4.3	4.6	4.6	4.5	
(free acidity)	4.82	4.0	4.0	3.52	4	
p - orth as P (Mg/l)		0	0	0	0	
p - tot as P (Mg/l)		0.04	0.02	0.02	0.03	
Potassium (Mg/l) Dis		0	0	0	0	
Tot		0.1	0.1	0	0.07	
Residue - 110c (Mg/l) Sus		29	49	NA	37.5	
Silica (Mg/l) Dis		0	0	0	0	
Silver (ug/l) Dis		-0.02	-0.02	-0.02	-.02	
Sodium (Mg/l) Tot		0.1	0.2	0.2	0.17	
Specific cond 25c FLd (us		31	15	12	19.3	
Sulfate (Mg/l) Dis	1.53	1.5	1.9	2.0	1.8	-1.0
Turbidity (JTU)		3	6	5	4.7	
Zinc (ug/l) Dis		13	3.3	9.2	8.2	17
Tot		14	18	18	16.7	
Water Content (mm) (Based on 10 samples)					114.3	

- Indicates less than
1 Unpublished data 1978 (Gary Glass, EPA-ERL Duluth)
Note - runoff for wy 76 was 8.36"

Table 56. Summary comaprison of atmospheric deposition of trace elements (kg/ha/yr).

ELEMENT	N.E. MINNESOTA	LAKE SUPERIOR		ATIKOKAN	LAKE MICHIGAN
	A	B	A	C	D
Al	.85	1.2	1.6	—	.86
Fe	1.08^2	—	1.9	.39–.55	.48
Zn	.057	—		.22–.32	.19
Cu	.011	.045	.097	.02–.03	.021
Ni	.014	0.15	.024	.015–.022	—
Mn	—	—	.079	—	.11
Pb	.077	.079	.17	.022–.033	.11
Cd	.003	.007	.006	.007–.011	.002
As	.011	—	—	—	—
Ca	11.3	4.0	4.2	3.4	14
Mg	11.3	.68	1.0	.37–.73	2.7
Na	3.5	1.8	—	.37	1.9
K	3.5	1.6	—	.37–.44	1.1
Cl	13^2	—	—	4.0–4.2	
SO_4	14.4^2	27	—	4.3–10.4	15

A-Eisenreich, et al. (1978)
B-IJC (1977)
C-Ontario Hydro (1977)
D-Eisenreich, to be published
1-Based on bulk collected samples.
2-Dry deposition rates are significantly different, see Table 31.

contribute to acidity would be organics, nitrate/nitrite, phosphate, chloride and possibly iron. Because there is so little buffering in the precipitation only small amounts of acid forming species are needed to lower pH. For impact analysis purposes this means that small increments in acid forming air effluents could cause a serious further decrease in pH.

Total phosphorus measurements included both organic and inorganic phosphorus. No attempt was made to differentiate analytically the different forms because the bulk samples were collected over a 30-day period. During this interval biotic activity in the sampler can change the phosphorus forms. The annual average concentration over the four sites was .04 mg/l. This value is similar to values reported for northeastern Minnesota and Lake Michigan (Eisenreich et al. 1978).

Few measurements were made for nitrate and nitrite. These forms of nitrogen are biotically very reactive and thus the absolute value reported probably does not reflect the true value in the original precipitation. The value of the number lies principally in comparing it to values reported elsewhere in the literature where the collection method used was the same. The mean annual average for NO_2/NO_3 (four sites) concentration is .27 mg/l, a value typical for this type of region.

4.3.5.5 Seasonal Effects of Atmospheric Deposition on Water Quality--
Periodically, extreme acid precipitation events occur and large amounts of acid are deposited in lakes and streams over short periods of time. Spring snowmelt also supplies large amounts of acid and other pollutants to lakes and streams over a short time interval. Studies have shown that concentrations of H^+, SO_4, NO_3, and heavy metals are two to three times greater in the first 30

percent meltwater than in snow. This amounts to about 40 to 80 percent of the total parameter content in the snow. Because the soils are frozen, there is no selective retention of any of the parameters.

Thus, the impacts of atmospheric deposition of air pollutants on surface water quality occur under two distinct sets of climate conditions, summer and winter. During the winter months, when the ground is frozen and overland runoff is nonexistent, air pollutants are deposited onto the snow-pack, stored, and later released over a very short time interval during spring melt. The time interval over which the pollutants are released into the surface water may be on the order of a few hours to several days. The time interval is a function of watershed size (small watersheds respond quicker), and the suddenness of the spring thaw.

During summer the deposition of air pollutants is a function of the type of storm, and the level and type of pollutant in question. Pollutants such as sulfate appear to be more affected by rain scavenging than others. In northeastern Minnesota the level of pollutants in the air, except for iron, appears to be a function of long-range transport from sources out-of-state. Weather systems from Canada contain less pollutants than systems which transport pollutants from the heavily industrial areas to the south or east of Minnesota.

Although sulfate and hydrogen ions are deposited most heavily during the wet months, and less so during the winter months, the spring-melt may be the most critical in terms of impacts. Certainly this is true over the short-run. Over the long-run the total picture of atmospheric deposition is important.

4.4.5.6 Chemical Composition of Snow-pack, Filson Creek Watershed--In northeastern Minnesota the snow season can range from three to six months, averaging about four months. Spring thaw occurs usually in late March or April, and sometimes as late as May. At Babbitt the deepest snow depth generally occurs around February 8, and at Winton this occurs around March 7. At both locations the average peak depth is about 450 millimeters (18 inches). This represents about 17 percent of the average annual precipitation of 726 mm (as water), or 123 mm (5 inches) (Watson, 1978). On March 24, 1976, the chemical composition of the Snow-Pack in the Filson Creek Watershed (Figure 22) was determined (U.S. Forest Service 1976).

Figure 22

Table 56 presents the results of the chemical analysis of the snow pack. The water equivalent of the snow pack was 114.3 mm (4.5 inches), which is about 90 percent of normal. Information from two other sources is similiar to the results obtained by the USFS (Table 56).

As part of the EPA study a snow-melt enrichment test was run (Table 57). Approximately 50 to 70 percent of the six parameters analyzed are contained in the first 40 percent of the melt-water.

Table 57

Table 58 provides a summary comparison between the Filson Creek snow-pack concentration and five stream site concentrations, at low-flow, immeditately prior to spring flow, and to the highest concentrations observed. It is assumed, for purposes of comparing snow-pack levels to stream levels, that snow-pack levels are homogeneous throughout the region. This, of course, is not true since forest

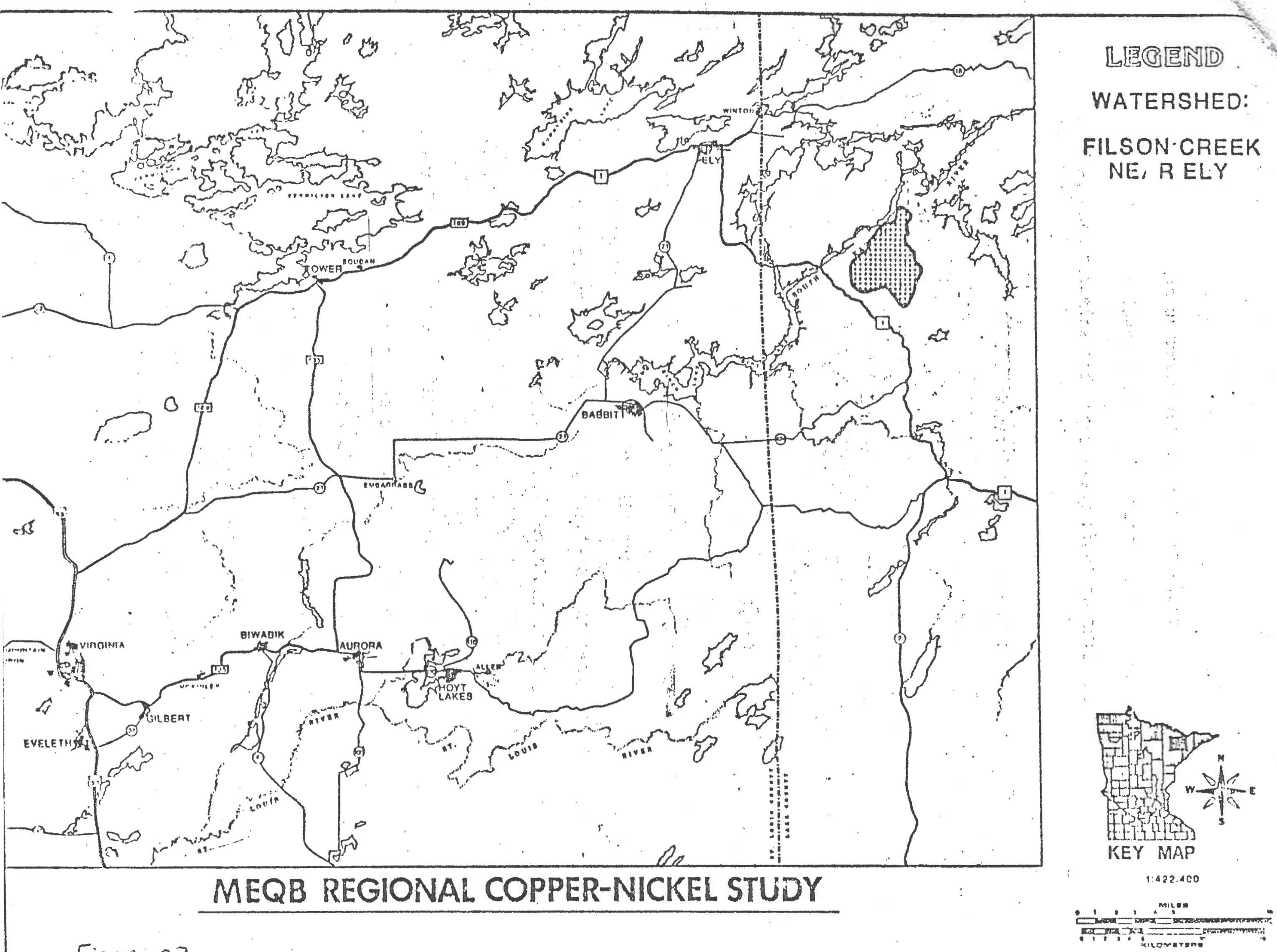


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Figure 22

Table 57. Snow-melt enrichment of dissolved components; percent of total mass found in melted snow was a function of percent melted, average of three sites.[1]

PERCENT SNOW MELT	% OF TOTAL MASS OF COMPONENTS FOUND IN MELTED SNOW											
	H^+		NH_4^+		$SO_4^=$		NO_3^-		Cl^-		F^-	
10	18		19		21		17		14		17	
20	18		18		22		19		14		16	
30	16		15		19		17		13		15	
40	10	62[2]	9	61	10	72	10	63	10	51	11	59
50	7		7		5		7		8		7	
60	6		7		4		6		7		7	
70	5		6		3		6		7		6	
80	5		6		3		5		7		6	
90	5		6		3		5		7		6	
100	4		5		3		4		6		6	

[1] Unpublished data, G. Glass, 1978, Duluth EPA.

[2] Cumulative percent.

type, cover type, and geographic location can effect the scavenging and deposition of chemical parameters.

Table 58

The following chemical elements are higher in concentration in the snow-pack water than observed in the receiving stream concentration: cadmium, lead, nitrate-nitrite, and zinc. Cadmium in snow-pack is an order of magnitude higher than the average concentration found in any of the three groups of streams, A, B, and C (Appendix 2); lead on the average is about twice as high; nitrate-nitrite is an order of magnitude higher than background streams (Group C) and about the same for streams in groups A and B; and zinc is about three times higher than average stream concentrations. Conversely, pH is about 2.2-2.7 units lower in snow-melt water than the streams in the three groupings.

To reiterate, during spring-melt the concentrations of some elements can increase 2-3 fold, due to the physical leaching of elements from between ice crystals, and some elements during spring-melt than can be higher than the concentrations normally found in the streams, particularly background streams. Most elements, however, are of low concentration in the snow-pack and would not cause an increase in the stream waters during the snow-melt period. In fact the reverse is true; during the snow-melt period the streams become diluted with respect to most elements (Table 58).

Probably the most important consideration, however, is pH and/or the buffering capacities of the two waters; i.e., snowmelt and the streams. Snowpack pH is low, about 4.5. No bicarbonate was measured, indicating little (if any) buf-

Table 58. Summary comparison between snowpack concentration and stream concentrations at low-flow, spring flow and highest concentration observed.

ELEMENT	SNOW PACK CONCEN.	SPRING-PERIOD CONCENTRATION					LOW-FLOW CONCENTRATION STATIONS					HIGHEST CONCENTRATION				
		F-1	P-1	D-1	SR-2	K-6	F-1	P-1	D-1	SR-2	K-6	F-1	P-1	D-1	SR-2	K-1
Acidity, H$^+$ (mg/l)	.016	.20	—	—	—	.10	—	.10	.20	.10	—	0.70	1.0	1.0	1.0	7.0
pH	4.5	5.9	7.3	6.8	5.8	6.4	7.3	6.6	7.1	6.8	6.5	7.3	7.3	7.7	7.5	7.0
Bicarbonate (mg/l)	0	8.0	39	26	14	16	25	17	104	60	14	25	66	117	60	18
Alkalinity-CaCO^3	-	7.0	32	21	11	13	21	14	85	49	11	21	92	110	85	15
Cadmium (ug/l)	0.25	.05	.08	.05	.04	.12	.02	.43	.08	.02	.03	.18	.18	.15	.15	.13
Calcium (mg/l)	0.70	2.6	22	9.2	3.2	2.3	5.7	62	23	10	2.9	37	80	53	13	7.0
Carbon, Tot. Org. (mg/l)	3.7	21.0	—	—	—	8.8	—	4.7	11	16	—	36	28	35	30	26
Chloride (mg/l)	0.3	.9	5.6	13	1.0	.5	1.3	7.6	27.0	1.3	.2	2.7	12	88	8.8	1.8
Chromium (ug/l)	0.6	.4	.4	-	.4	.4	—	.5	.7	.3	—	1.7	1.0	.8	1.2	1.7
Cobalt (ug/l)	.2	1.5	.3	.8	.7	.4	—	3.8	1.5	.3	.2	2.0	3.8	2.0	.7	.9
Copper (ug/l)	5.0	8.7	4.0	2.3	2.8	1.6	5.5	4.0	1.7	.6	1.8	12	5.9	6.1	2.8	2.0
Fluoride (ug/l)	0.1	.10	300	300	.10	.10	—	1400	1200	600	100	700	1400	1200	600	400
Iron (ug/l) tot	327	760	820	840	750	300	2300	60	2000	930	230	3100	1300	2200	1300	400
Lead (ug/l)	9.3	1.2	.7	1.0	.9	2.4	.7	.4	.6	.4	.3	6.4	2.6	46	31	2.4

Table 58 continued.

	SNOW PACK	SPRING-PERIOD CONCENTRATION					LOW-FLOW CONCENTRATION STATIONS					HIGHEST CONCENTRATION				
ELEMENT	CONCEN.	F-1	P-1	D-1	SR-2	K-6	F-1	P-1	D-1	SR-2	K-6	F-1	P-1	D-1	SR-2	K-6
Magnesium (mg/l)	.03	1.9	7.7	5.4	2.7	2.0	3.3	15	8.4	7.6	1.3	23	22	26	12	2.0
Nickel (ug/l)	2.3	8.0	6.0	2.0	2.0	4.0	6.0	7.0	2.0	2.0	2.0	8.0	7.0	10.0	3.0	4.0
NO_2, NO_3, -N(mg/l)	1.1	.15	-	-	-	.11	-	.57	34	.24	-	.99	.57	13	.29	.12
P-total (mg/l)	.03	10	-	-	-	1.0	-	10	-	.02	-	61	45	119	69	20
Potassium (mg/l)	.07	.7	1.5	1.5	.7	.5	1.6	2.0	2.6	.6	.6	3.2	2.3	5.2	.9	.6
Sodium (mg/l)	.17	1.0	1.1	1.0	.2	.3	1.9	1.5	1.8	2.4	.4	1.9	6.8	35	3.7	2.6
Specific Conductance, 25°C	19.3	29	199	104	36	28	46	433	238	93	29	55	568	655	163	42
Sulfate (mg/l)	1.8	7.9	63	9.5	6.5	4.0	5.4	190	13	5.5	3.7	15.0	260	70.0	14	7.2
Turbidity (NTU)	4.7	2.0	5.4	2.6	2.0	3.5	3.0	4.1	10	3.0	1.2	11.0	13.0	18	5.5	3.5
Zinc (ug/l)	16.7	3.20	5.0	3.1	6.5	8.70	3.8	11.0	30	2.4	.9	12.5	13.0	30.0	16.0	8.7
Color (Co-pT)	-	100	50	80	100	45	200	5	90	130	40	500	150	400	250	100
Peak flow date 1976		4/10	4/19	4/18	4/19	4/24										
Low flow prior to spring flush & date sample 1976							3/17	3/19	3/18	3/10	4/10					
Date of sample closest to peak flow	1976	4/06	4/07	4/06	4/15	4/21										

fering in snowpack water. Thus, snow-melt is acidic in character. In large systems (e.g. the Kawishiwi at K-6), there is sufficient receiving water, and subsequently buffering, to neutralize the effects of acidic snow-melt. In small systems (e.g. the Filson Creek at F-1), snow-melt may account for the major portion of stream flow. Thus organisms in this stream are exposed to a very low and sudden pH drop. This occurrence has been recorded in streams in the northeastern United States, and apparently is happening in the Study Area to some degree. This needs to be documented by further study.

4.3.5.7 Buffering Effects of Soils--As part of the plant pathology and terrestrial biology program, the physical, chemical, and typological characteristics of soils of the Study Area were mapped (Volume 3-Chapter 1). Five major till types have been recognized in the Study Area; and 32 named and 5 unnamed soil series, distributed among 23 soil associations.

The physical and chemical nature of the surficial material, and the areal distribution of these materials have a direct bearing on the manifestation of the impacts caused by acidic precipitation. The thicker deposits that are generally found in the southern portion of the Study Area contain calcareous and clayey materials, which can buffer acid input. Conversely, in the northern part of the Study Area, not only is the soil covering very sparse, but the soil is also acidic. The reasons for the acidic nature of the soil are three-fold: there is a paucity of calcareous material in the till; the area is underlain by granitic bedrock, a rock that is acid in nature; and, the predominance of coniferous trees and their litter, which contribute to acidity.

The surficial material in the Study Area is the result of weathering of rock and of the glacial material deposited during the various ice ages. Within the Study

Area, 9 physiographic provinces (Figure 23) have been described, 8 of which are of glacial origin, and one which includes the general area of taconite mining (Olcott and Siegel 1979).

Figure 23

Most of the surficial material was deposited by the St. Croix and automba phase of Wisconsin Glaciation. South of the Laurentian Divide are the oldest identifiable deposits, called the Toimi Drumlin Field. North of the Divide, the retreating glacier left stagnant blocks of ice and glaciofluvial deposits of sand and gravel.

The thickness of unconsolidated material in the Toimi Drumlin Field ranges from about 20 to 75 feet. North of the Divide, the topography is characterized by exposed ridges and mounds of bedrock, thin soil covering (0-10 ft), and numerous lakes, rivers, and wetlands. In general terms, the northern-eastern region of the Study Area, referred to as the Shallow Bedrock-Morain area (province C), and the Seven Beaver-Sand Lake Wetland area (province D) are the most susceptible areas to acidic precipitation. These areas also contain most of the lakes and rivers of the area.

During the summer months, atmospheric pollutants deposit on vegetation, soils, and surface waters directly. If the precipitation is acidic, it is usually neutralized in the watershed, that is, the runoff reaching surface waters is less acidic.

The effects of acid precipitation on soils and vegetation are not well understood. Experiments have shown, however, that acid deposition can cause

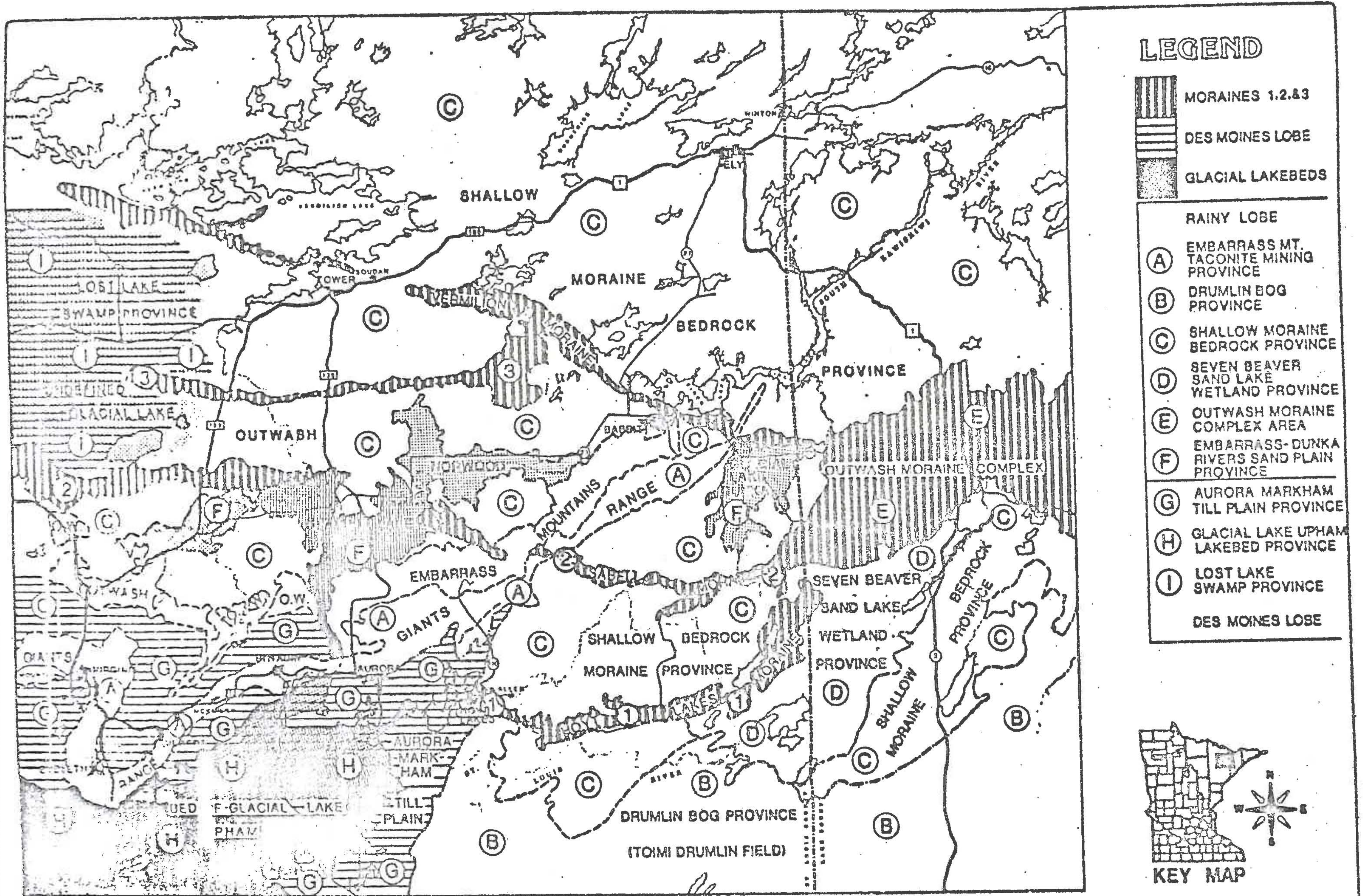

FIGURE 23

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PHYSIOGRAPHIC PROVINCES & GLACIAL FEATURES increased leaching of cations from soils and vegetation; increases or decreases in plant diseases; other plant injury such as stunting plant growth; and inhibitation of the nitrogen-fixing activities of legumes (Volume 4-Chapter 2). The acid effects are generally pronounced only in soils which have a pH of less than 5.5, especially unbuffered sandy soils and loams which have little or no base exchange capacity.

Soils that have low pH and are well supplied with bases are most susceptible to base loss. As base saturation and buffering fall to low levels, continued acid precipitation will cause leaching of H^+ and Al^{3+} ions rather than bases. This transition between base loss vs H^+ and Al^{3+} loss occurs at about 20% base saturation level in the soil. If the soils have a capacity for sulfate sorption, this capacity must be satisfied before base leaching (e.g. Ca, Mg or K) will occur (U.S. EPA 1978).

Model studies developed to simulate the long-term effects of acidic rainfall on acid soil show that soils similar to those in northeastern Minnesota may begin to show the effects of acidic precipitation within 5 to 10 years (U.S. EPA 1978). The model also showed that this soil has little buffering capacity, and within a short period of time, rainfall constituents (such as H^+ or $SO_4^=$) would not sorb into the soil, but simply move through the system and eventually into the surface waters.

The soil associations described above were entered into the Minnesota Land Management Information System along with watershed boundaries as well as other land-use information. Distribution of various soil types were calculated on a watershed basis. The chemical information of the top layer of soil (0-6 in.) was used to obtain mean weight values for each parameter for each watershed. Table 59 gives the tabulated results for watersheds in the Study Area.

Table 59

For all sub-watersheds, the pH value can be considered low (i.e. most of the values are between 5.0 and 5.5). It is not possible to determine whether these values are natural or a result of present acidic precipitation. These acidic soils combined with the observed acidic rainfall suggest that soils in the Study Area have an extremely limited ability to buffer rainfall before it reaches surface waters.

The other factor of concern is the base saturation index. Much of the soil north of the Laurentian Divide (e.g. the Kawishiwi system, Filson Creek, Keeley Creek, etc.) have base saturation values under 40 percent. When base saturation approaches 20 the soil has effectively lost its buffering capacity, not only for acidic input, but for other anions and cations also. Hydrogen ions (H^+) and sulfate ions ($SO_4^=$) deposited by precipitation will simply move through the soil system into the surface waters of the area. Thus, the surface waters of the area are either losing, or have lost, most of their external buffering.

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Table 59. Mean weighted chemical character of top soil layer (0.6 inches) by watershed.

	C.E.C (meg/100g)	Base Saturation %	pH	SO_4	Ca	Mg	F	Mn	Cu	Fe	Zn	Ni	Cd	Co	Pb
									PPM						
North of Laurentian Divide															
Filson Creek	34	26	5.0	29	1350	450	8.0	37	1	280	2	1.0	.01	.2	1
Keeley Creek	31	4	5.0	24	1130	290	8.0	29	1	230	2	0.8	.01	.2	1
Bear Island	37	34	5.1	36	1790	650	8.0	51	1	360	4	1.3	.04	.1	2
Kawishiwi															
k-6	34	29	5.2	31	1520	540	5.8	42	1	300	3	1.1	.02	.2	1
k-7	35	30	5.2	33	1610	580	7.5	45	1	310	3	1.2	.02	.2	1
k-5	36	31	5.2	34	1660	610	7.5	47	1	320	3	2.1	.02	.2	1
k-4	36	32	5.2	35	1690	630	7.5	48	1	330	3	1.2	.02	.2	1
k-3	27	30	5.5	22	1240	300	6.3	30	.5	170	2	0.5	.01	.2	1
k-1	32	27	5.1	28	1360	420	7.4	36	1	260	3	0.9	.01	.2	1
Shagawa River	32	25	5.0	26	1210	340	7.7	32	1	240	2	0.9	.1	.18	1
Unnamed Creek	36	27	5.1	33	1500	550	7.7	42	1	310	3	1.2	.02	.2	1.2
Stoney River															
sr-5	49	46	5.4	57	2830	1350	8.2	89	2.0	570	5	2.4	.07	.06	1.9
sr-4	49	45	5.4	55	2800	1280	8.3	81	1	540	5	2.2	.08	.03	1.7
sr-3	46	43	5.4	52	2600	1200	7.8	78	1	510	4	2.1	.06	.07	1.6
sr-2	46	43	5.4	51	2600	1180	7.7	76	1	500	4	2.0	.06	.08	1.6
sr-1	44	41	5.4	49	2400	1090	7.6	72	1	470	4	1.9	.05	.09	1.5
Dunka															
d-2	43	39	5.3	46	2250	990	8.0	70	1	450	4	1.8	.05	.11	1.6
d-1	38	34	5.2	39	1900	770	7.5	56	1	370	3	1.4	.03	.14	1.4
Isabella															
Little	32	34	5.5	30	1640	540	6.8	44	1	260	3	0.9	.02	.15	1.1
i-1	33	30	5.2	29	1450	460	7.2	38	1	260	3	0.9	.01	.17	1.1

Table 59 continued.

	C.E.C (meq/100g)	Base Saturation %	pH	SO_4	Ca	Mg	F	Mn	Cu	Fe	Zn	Ni	Cd	Co	Pb
									PPM						
South of Laurentian Divide															
St. Louis															
sl-3	56	49	5.5	68	3260	1690	8.2	105	2	690	5	3	.08	.04	2.0
sl-2	53	49	5.5	63	3090	1550	8.3	100	2	640	5	3	.08	.05	2.0
sl-1	45	44	5.3	49	2530	1120	8.3	80	1	500	5	2	.06	.08	1.8
Partridge River															
p-5	54	39	5.2	62	2700	1440	7.8	86	2	620	3	2.5	.05	.10	.17
p-4	38	45	5.4	39	2300	870	8.6	73	1	410	5	1.7	.06	.07	.18
p-3	40	45	5.4	42	2370	950	8.4	75	1	430	5	1.8	.06	.08	1.8
p-2	41	41	5.3	44	2280	960	8.3	72	1	440	4	1.8	.05	.10	1.7
p-1	40	41	5.3	42	2200	890	8.2	69	1	420	4	1.7	.05	.10	1.7
Embarrass															
e-2	46	33	5.0	49	2150	1010	8.0	64	1.6	500	3	1.9	.05	.13	1.6
e-1	56	36	4.8	64	2640	1300	8.6	76	1.8	670	4	2.5	.09	.09	1.9
Whiteface River															
wf-2	44	46	5.3	48	2580	1100	8.6	82	1.3	500	5.3	2.0	.07	.06	1.9
wf-1	33	44	5.4	31	2020	630	8.7	64	0.9	320	5.5	1.3	.05	.08	1.7
Waterhen Creek	44	44	5.3	49	2490	1100	8.5	82	1.4	500	4.8	2.1	.06	.09	1.8
World-wide (average)								500-1000	15-40		50-100	20-30			15-25
(range)								T-10,000	T-250		T-900	T-500			T-1,200

SOURCE: Patterson and Aaseng (1978).

a – soils of the Study Area, Regional Copper-Nickel Study

APPENDIX 1

Box Plots of Stream Parameters

- -general parameters
- -buffering parameters
- -nutrients
- -metals
- -miscellaneous

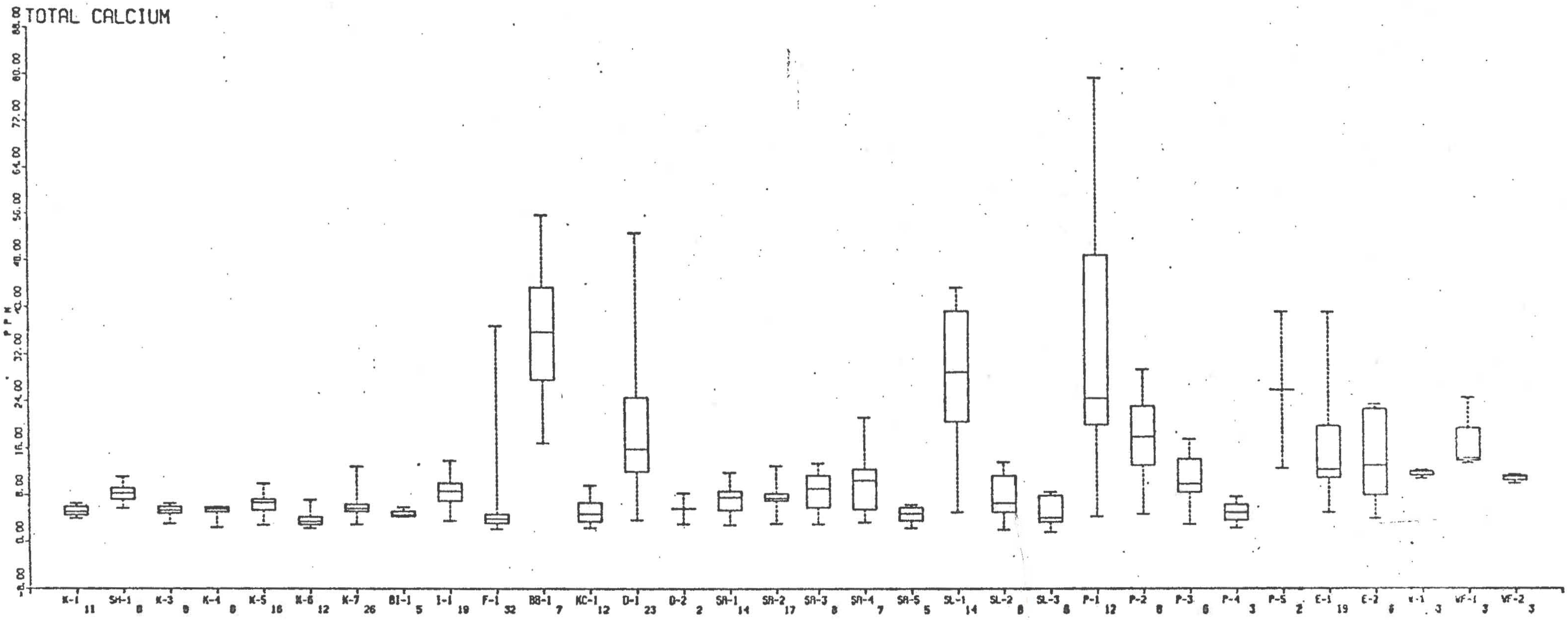


Figure 25. Box plots of summary statisitcs, general parameters.

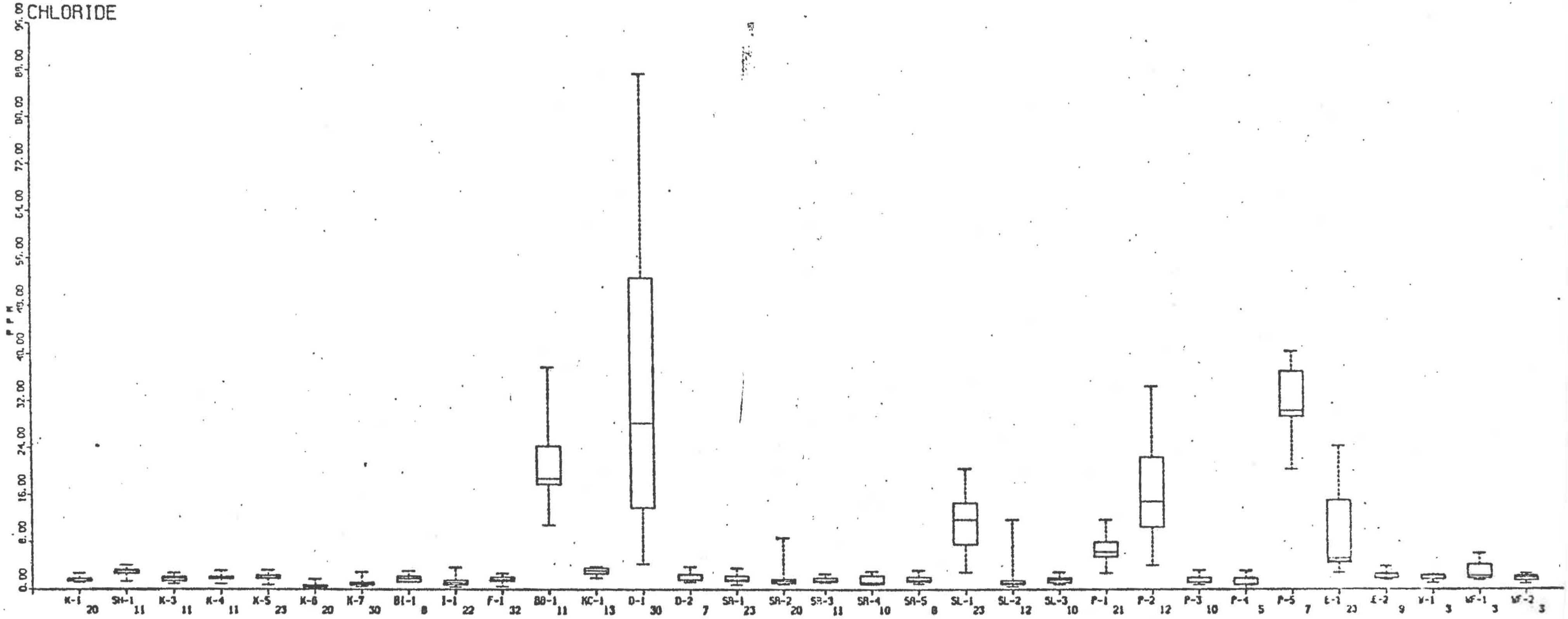


Figure 25. (Contd.)

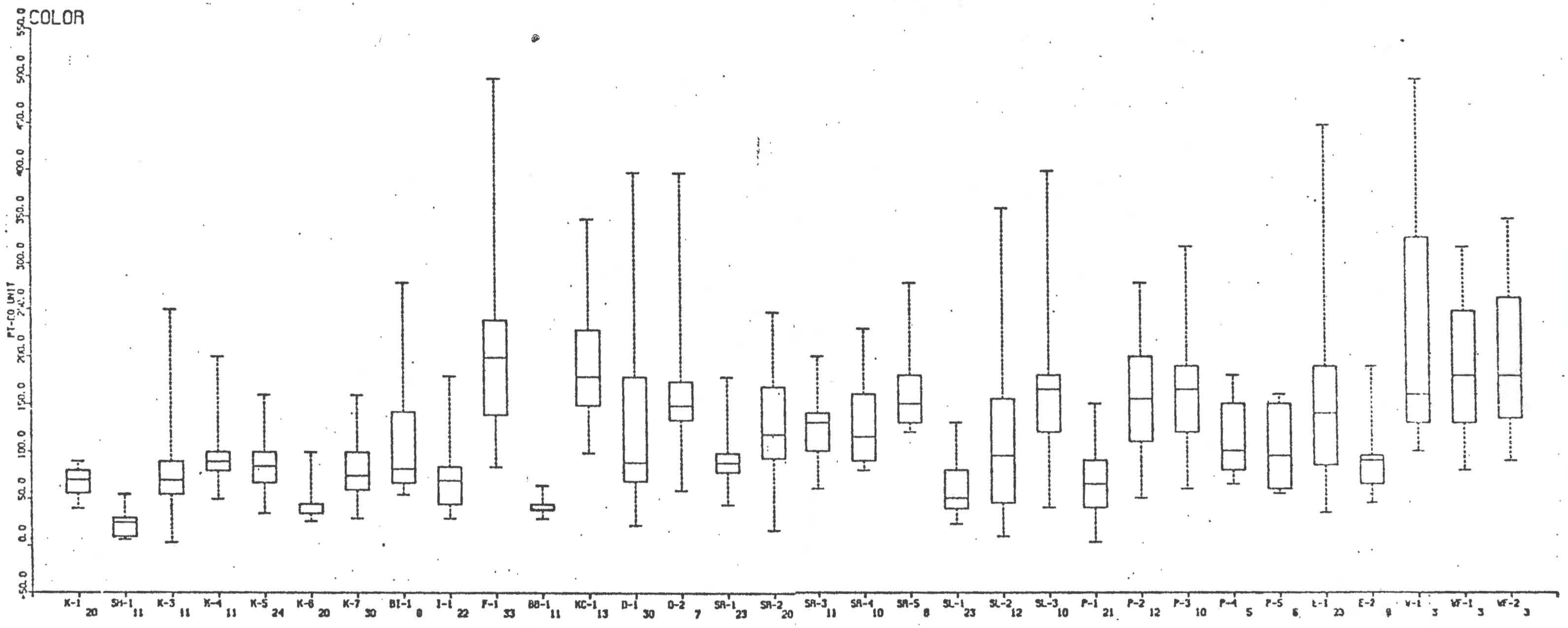


Figure 25. (Contd.)

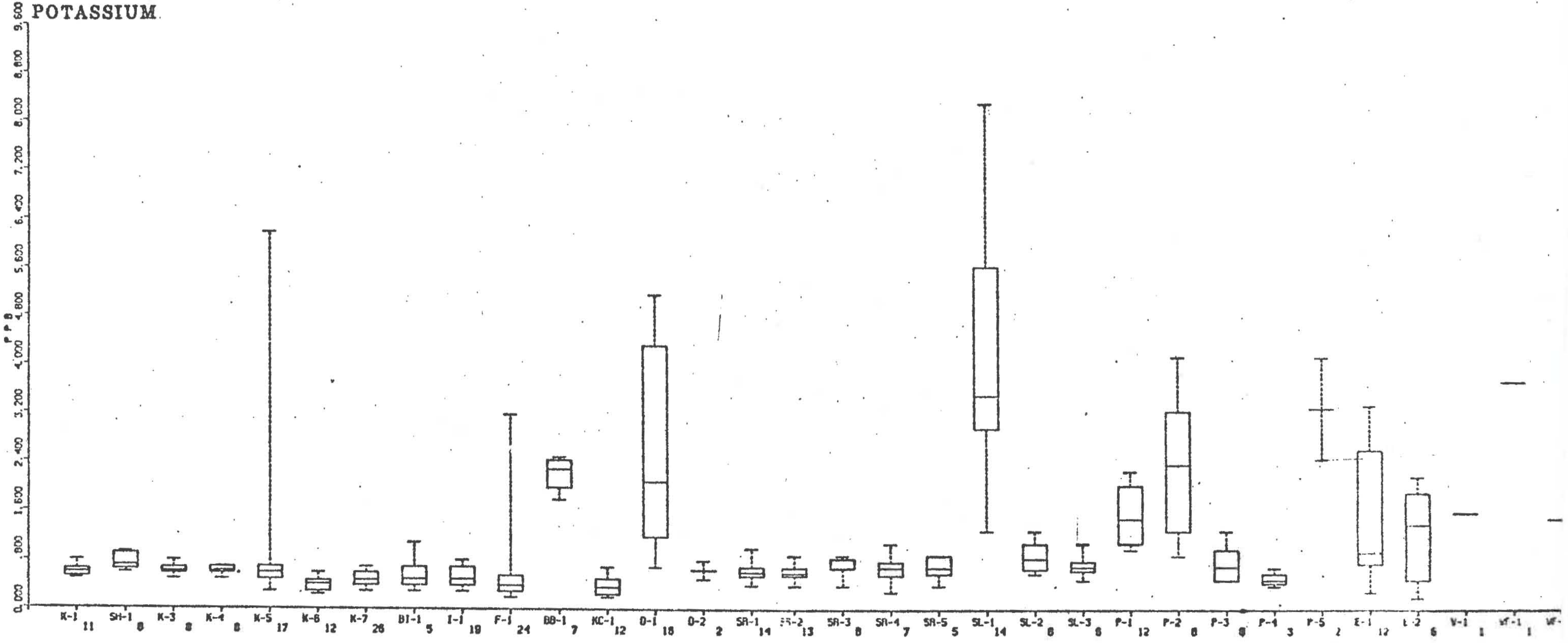


Figure 25. (Contd.)

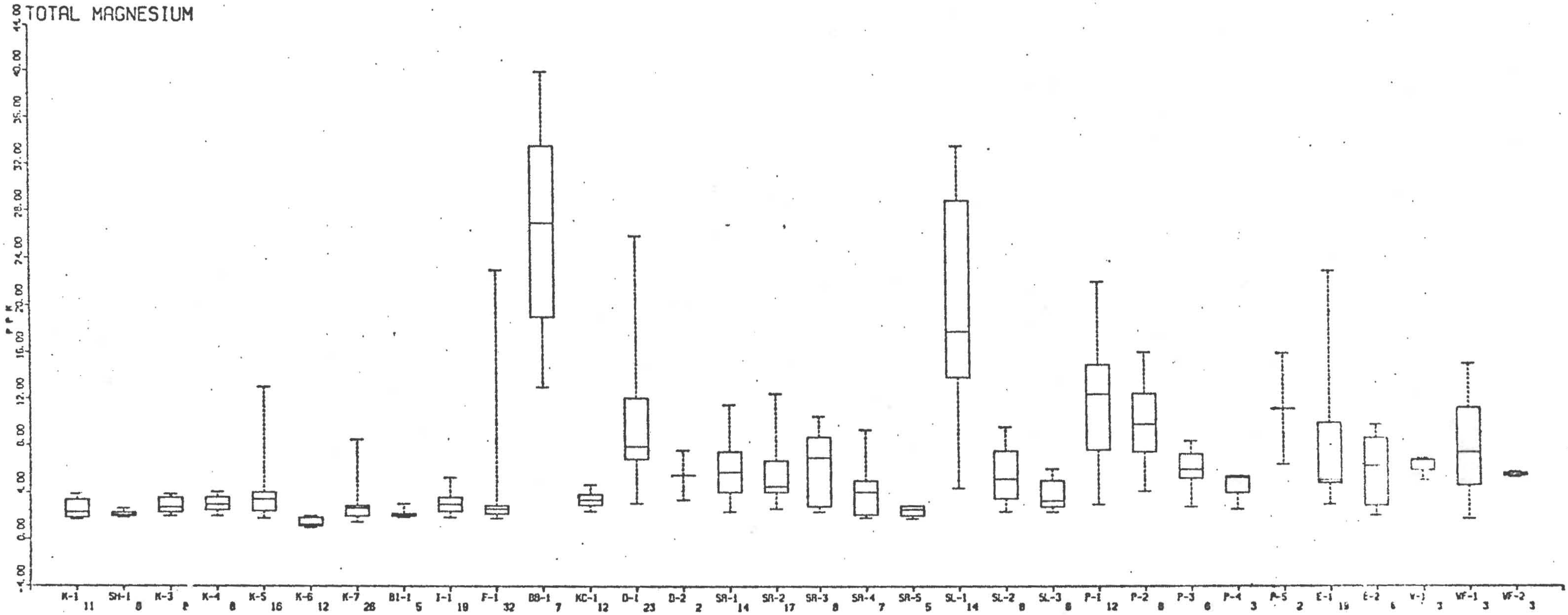


Figure 25. (Contd.)

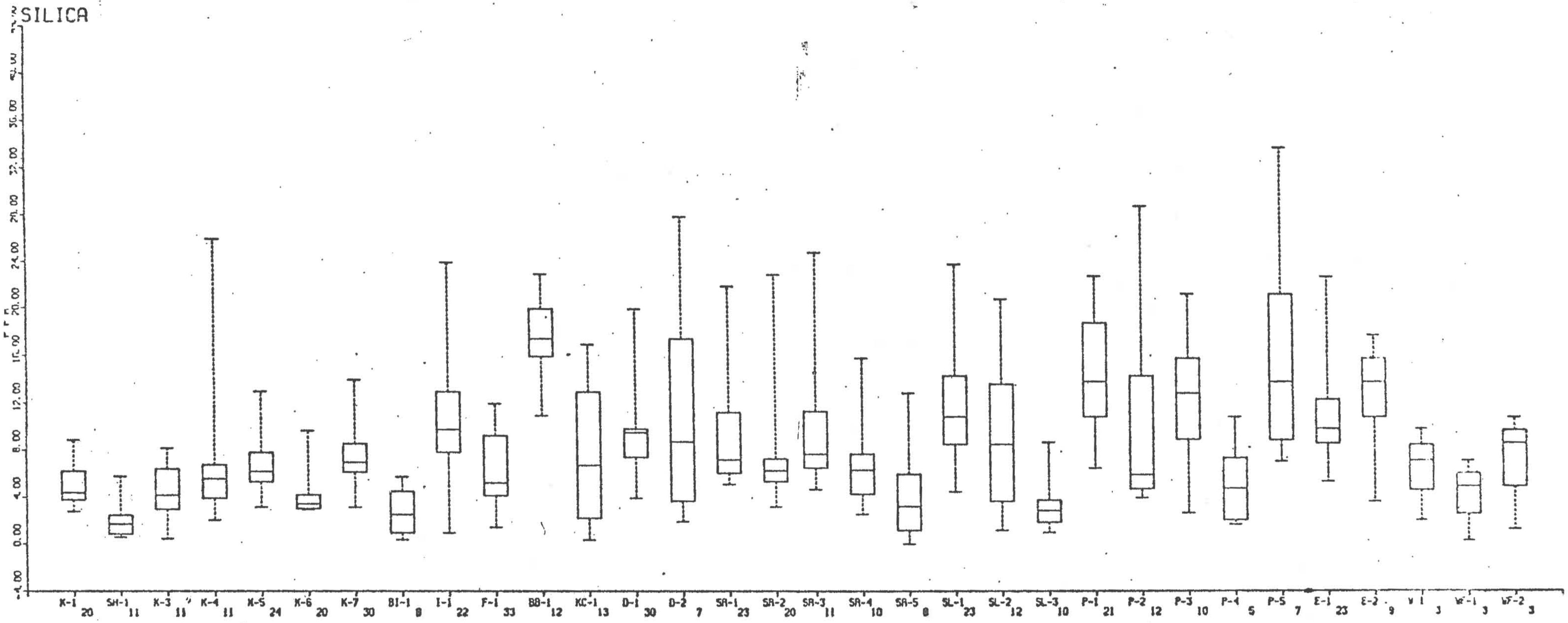


Figure 25. (Contd.)

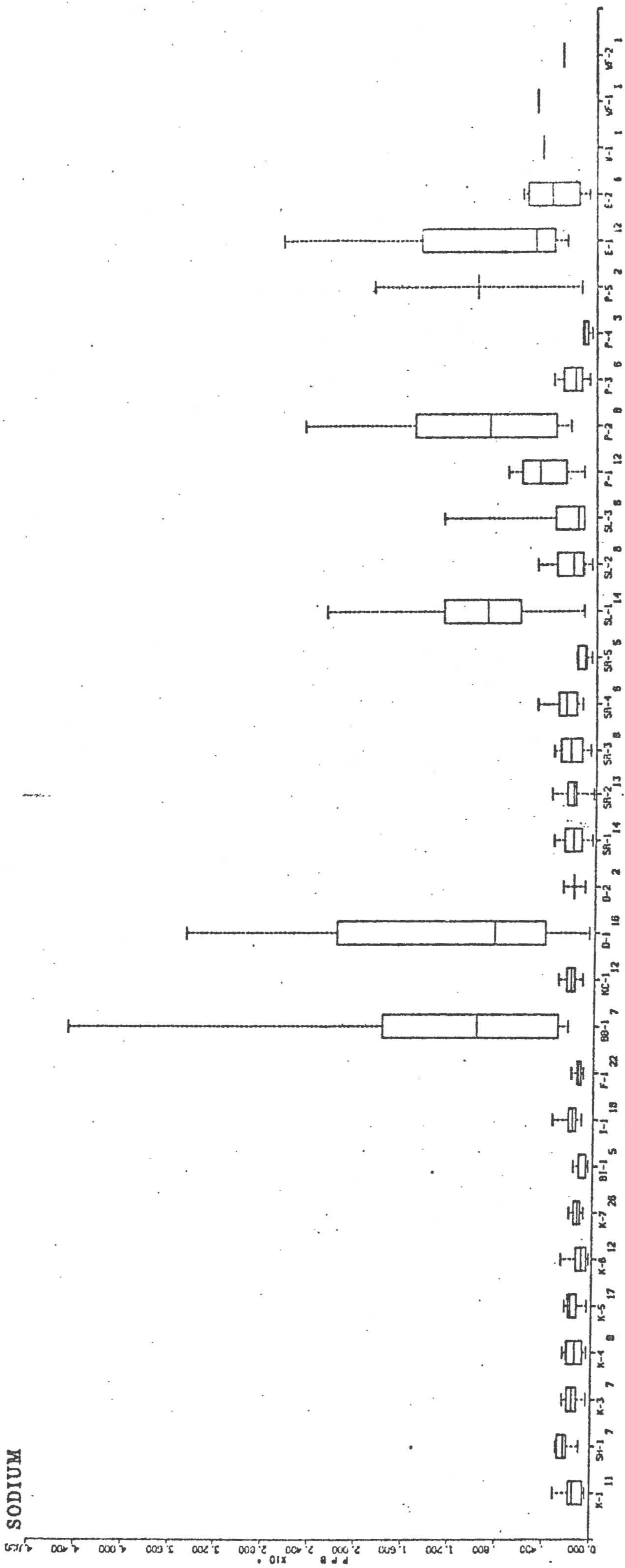


Figure 25. (Contd.)

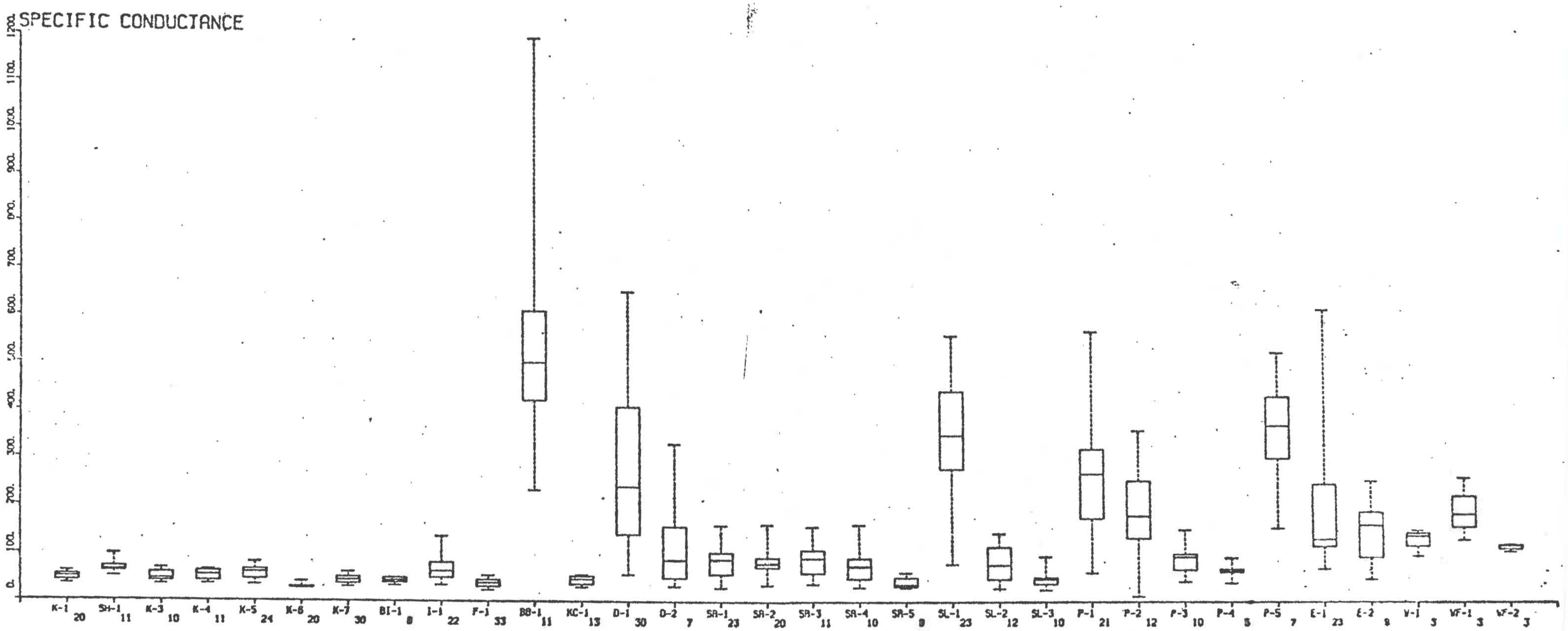


Figure 25. (Contd.)

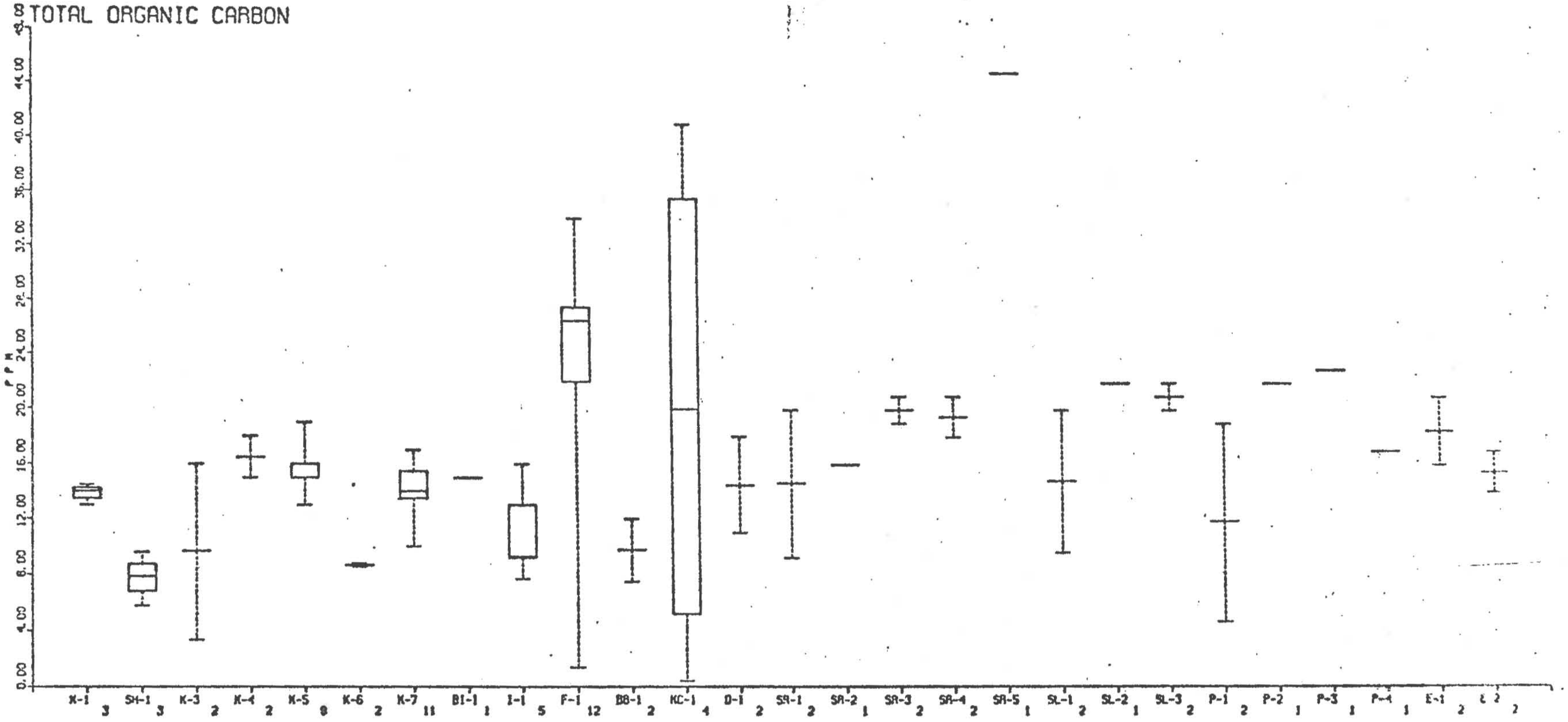


Figure 25. (Contd.)

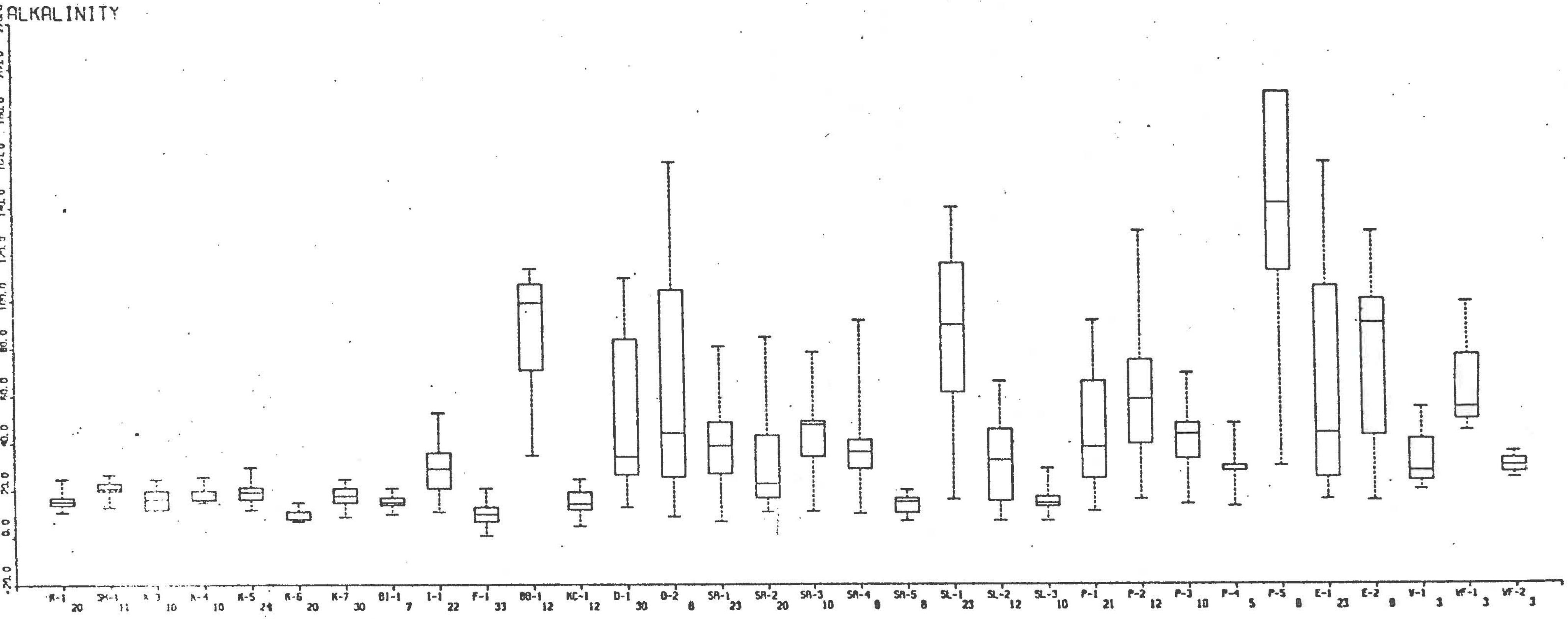


Figure 26. Box plots of summary statistics, buffering parameters.

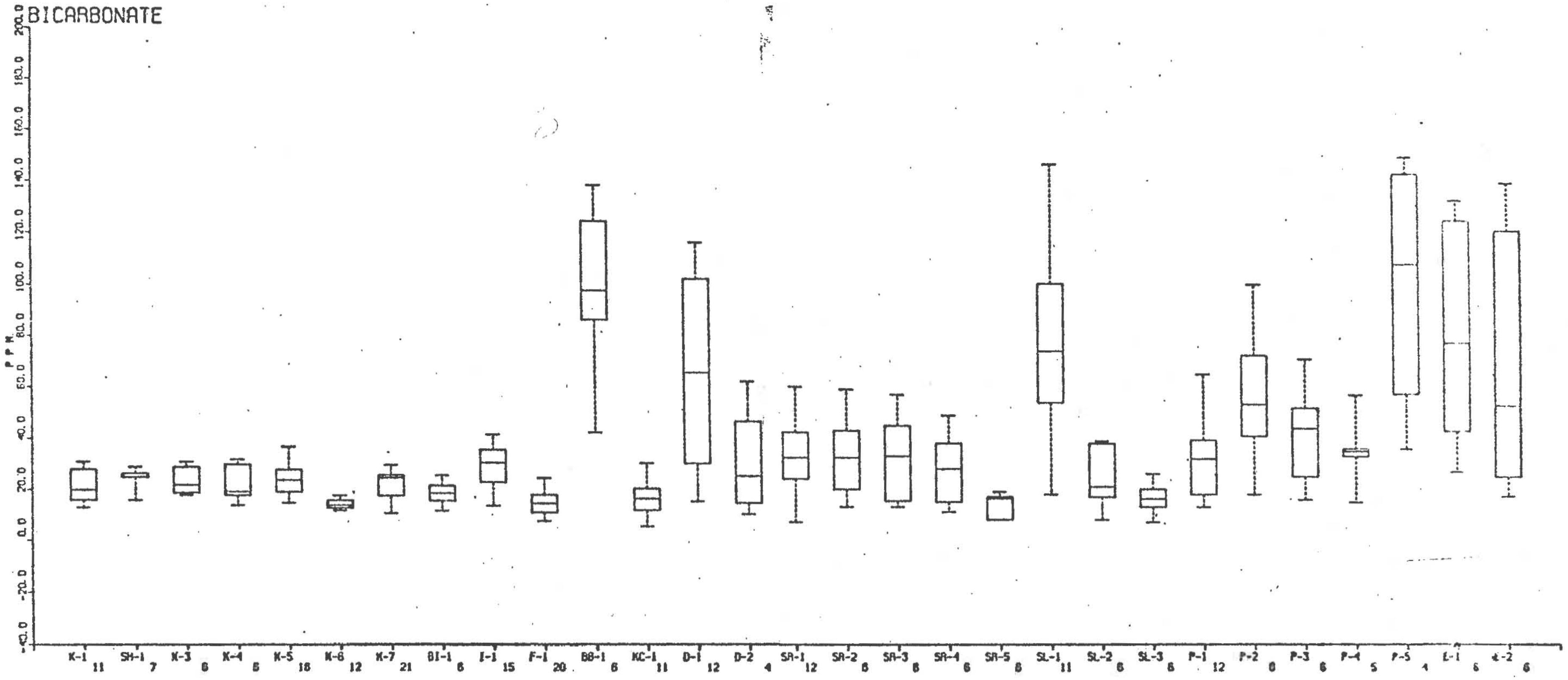


Figure 26. (Contd.)

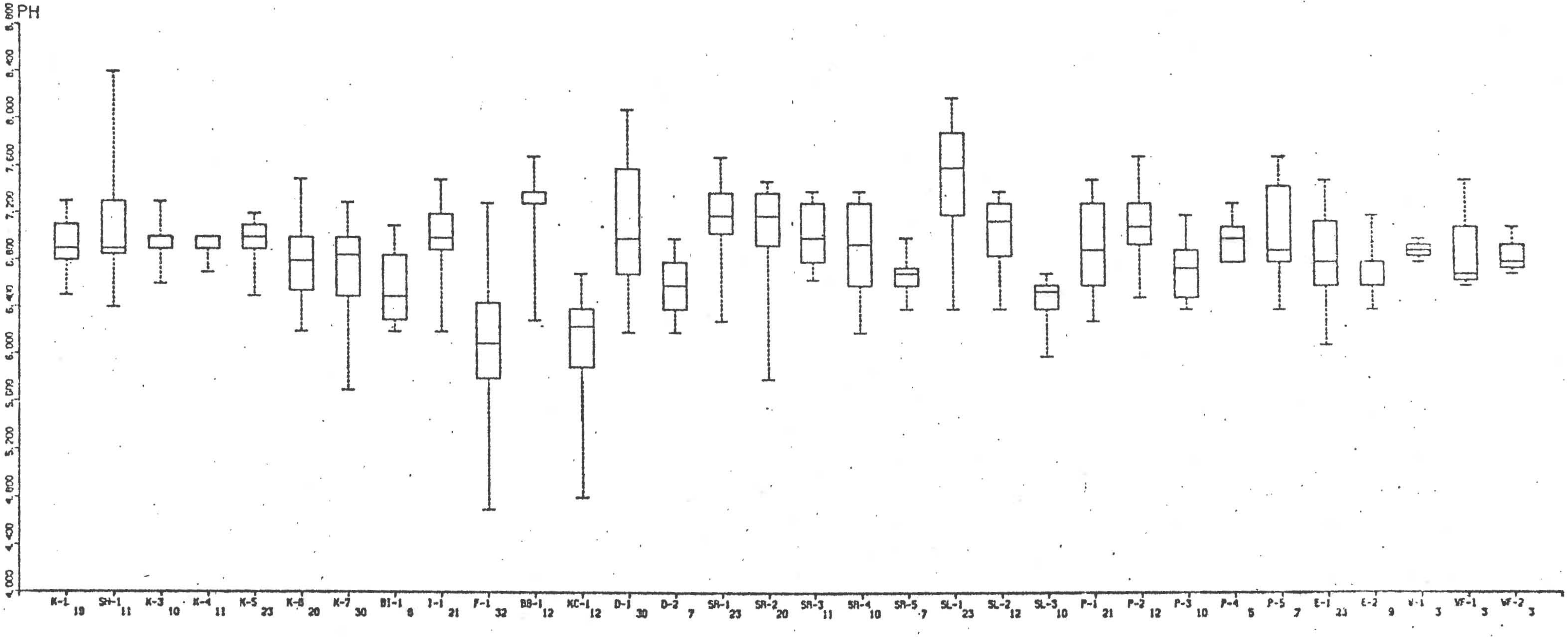


Figure 26. (Contd.)

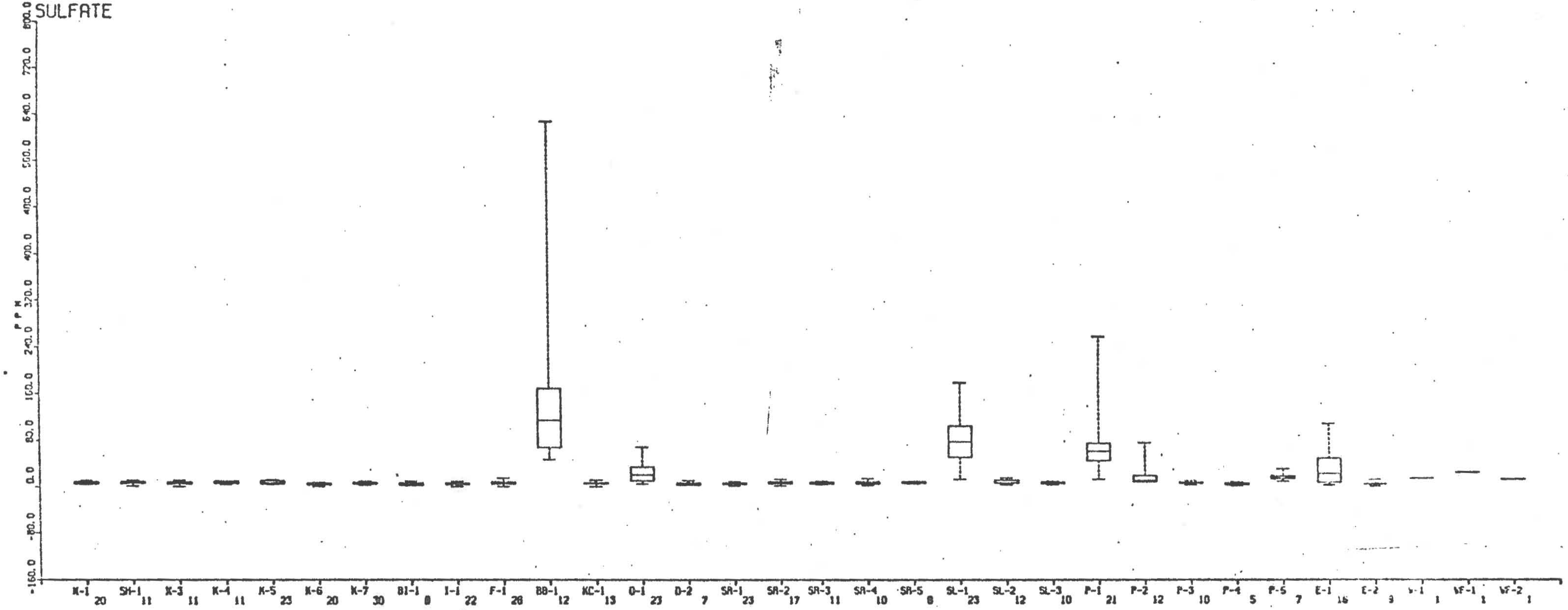


Figure 26. (Contd.)

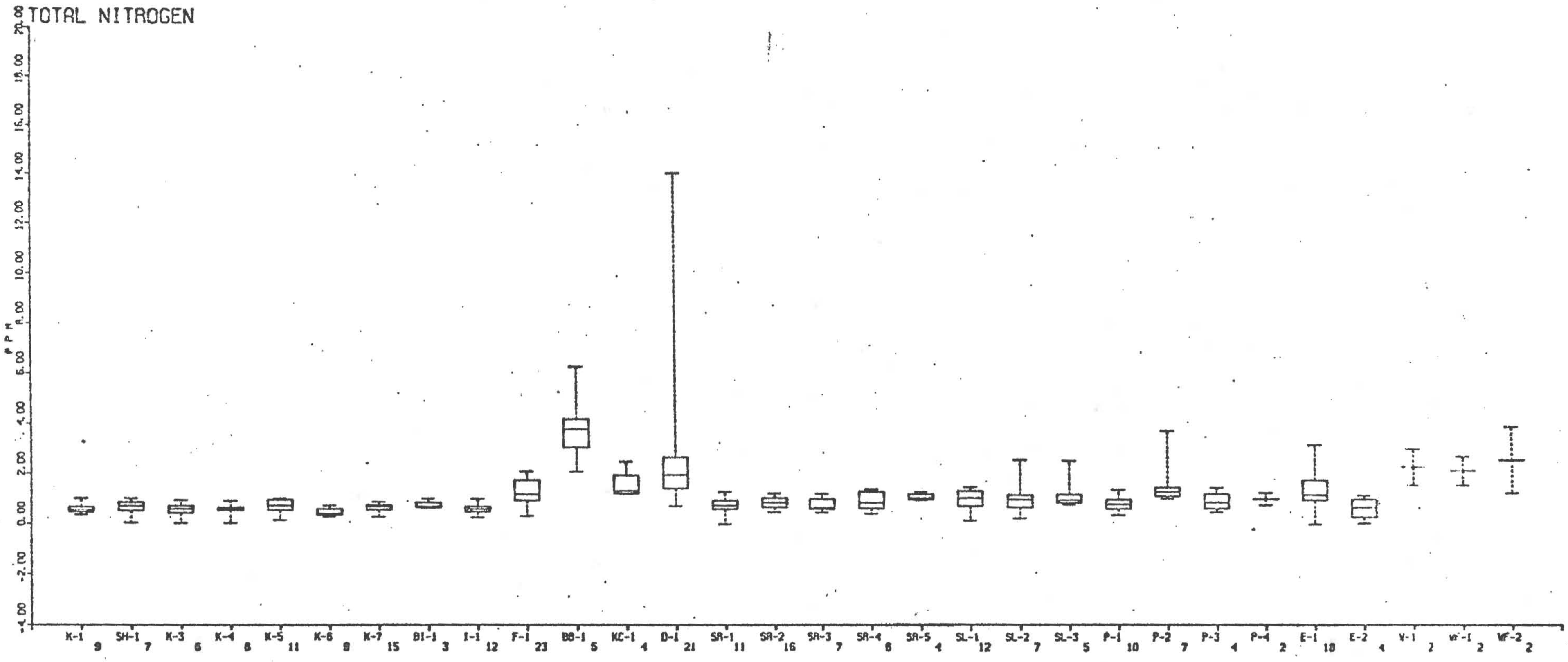


Figure 27. Box plots of summary statistics, nutrient parameters.

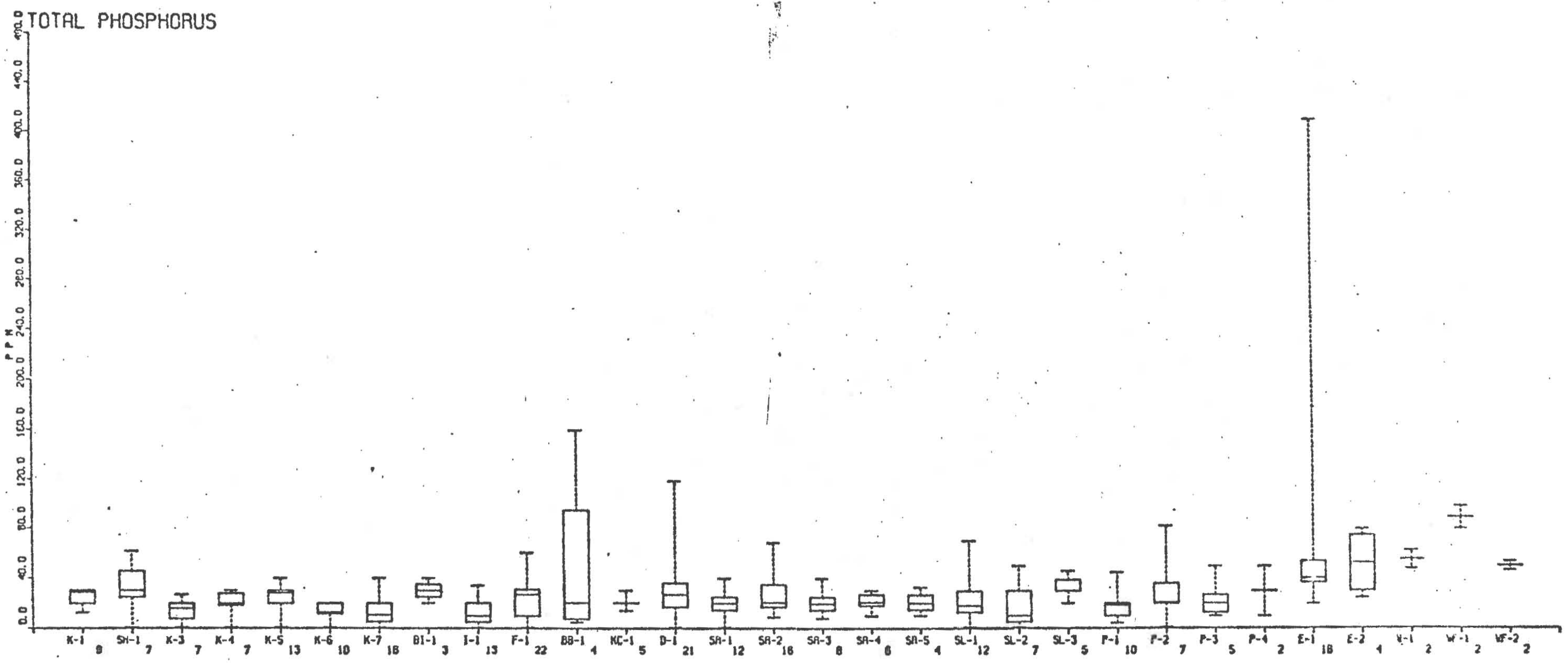


Figure 27. (Contd.)

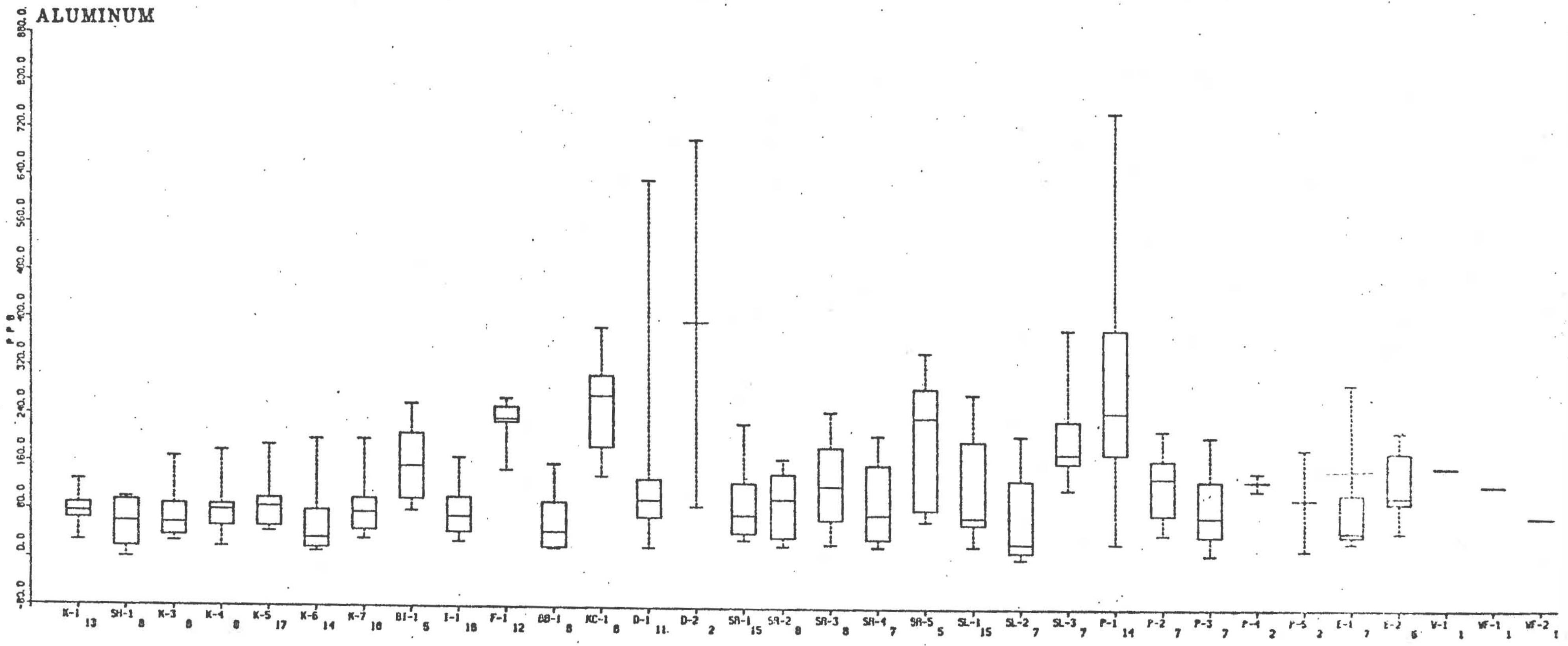


Figure 28. Box plots of summary statistics, metal parameters.

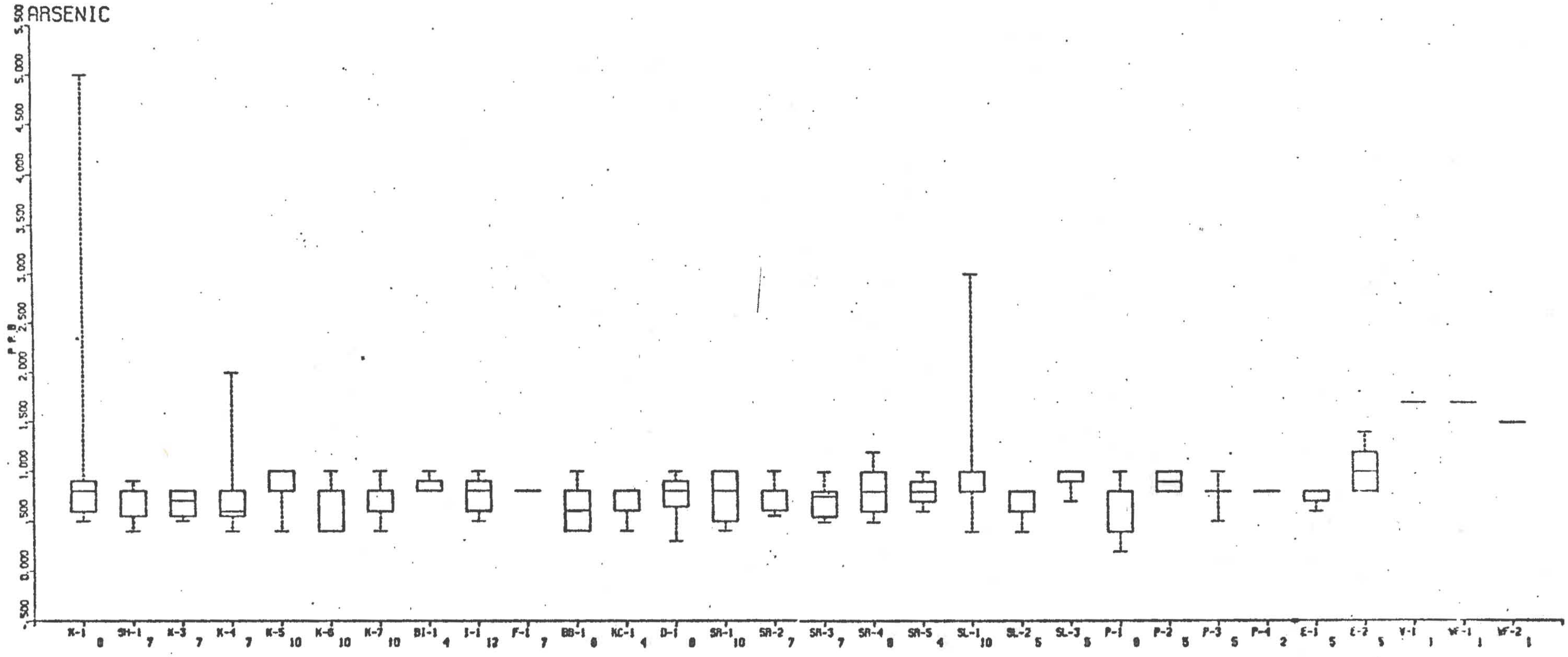


Figure 28. (Contd.)

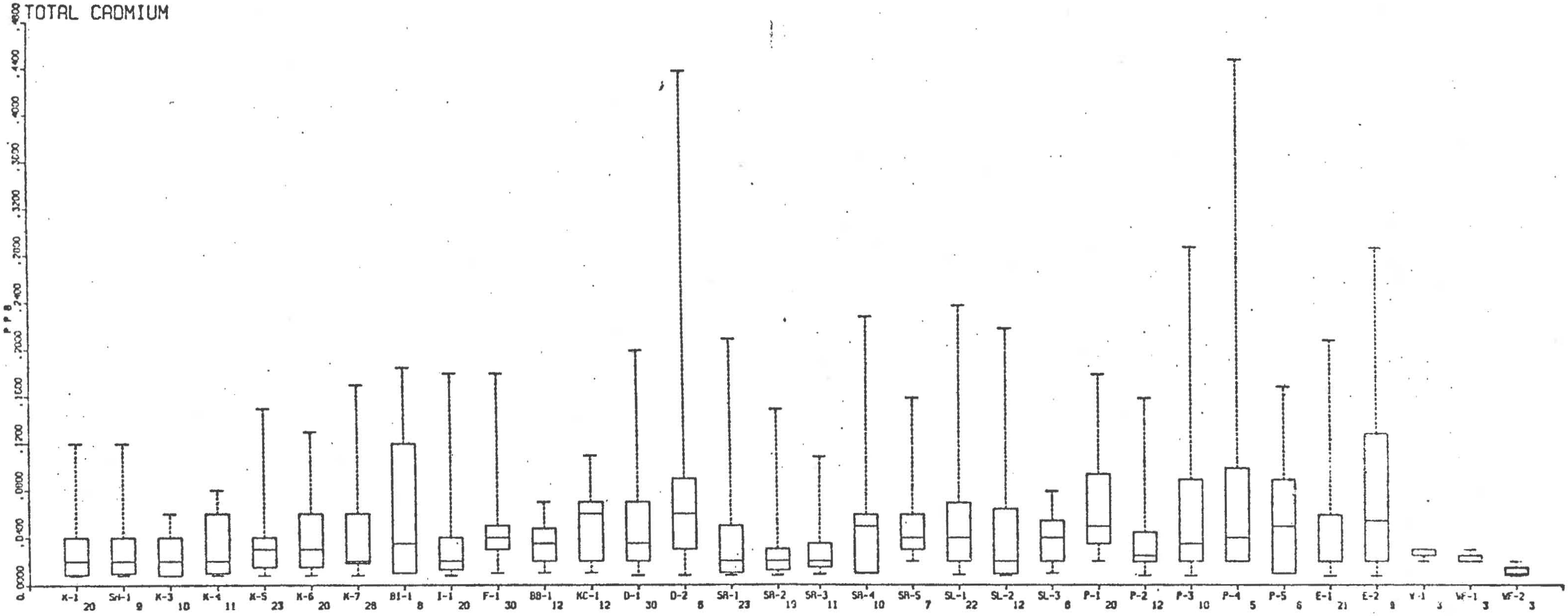


Figure 28. (Contd.)

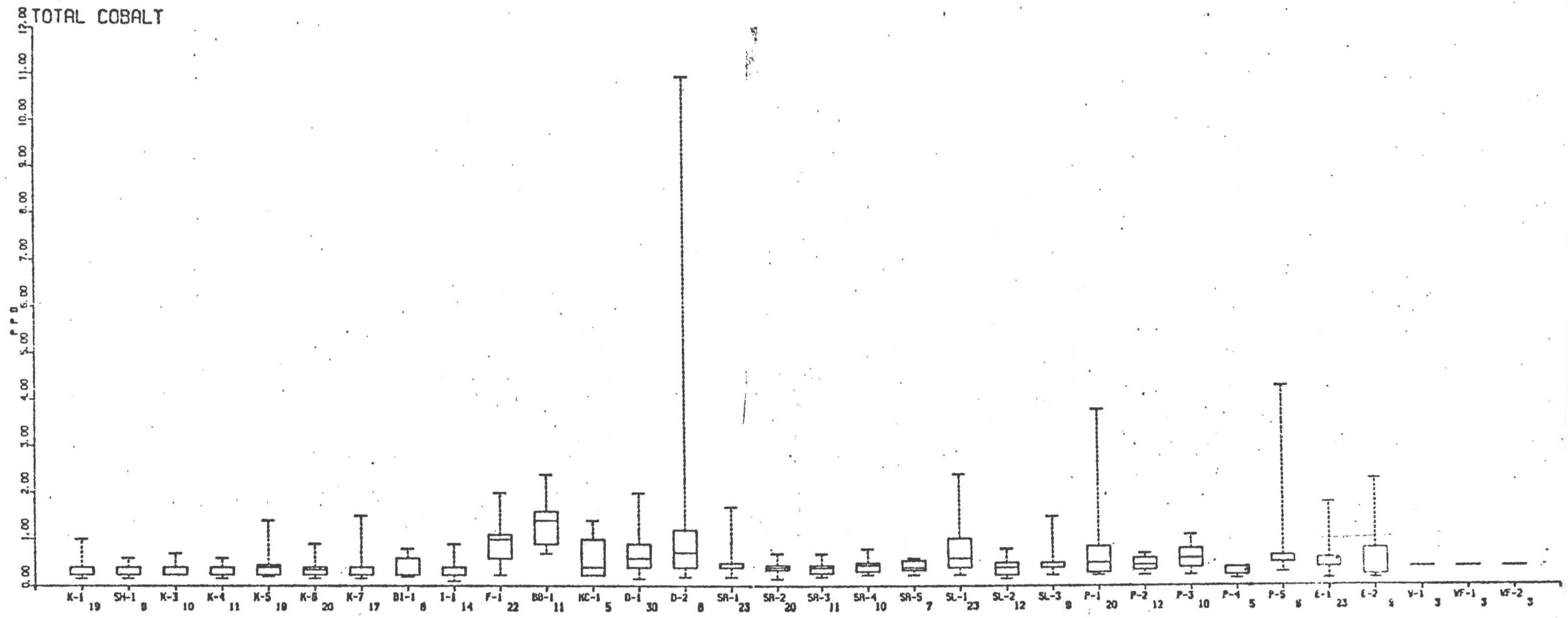


Figure 28. (Contd.)

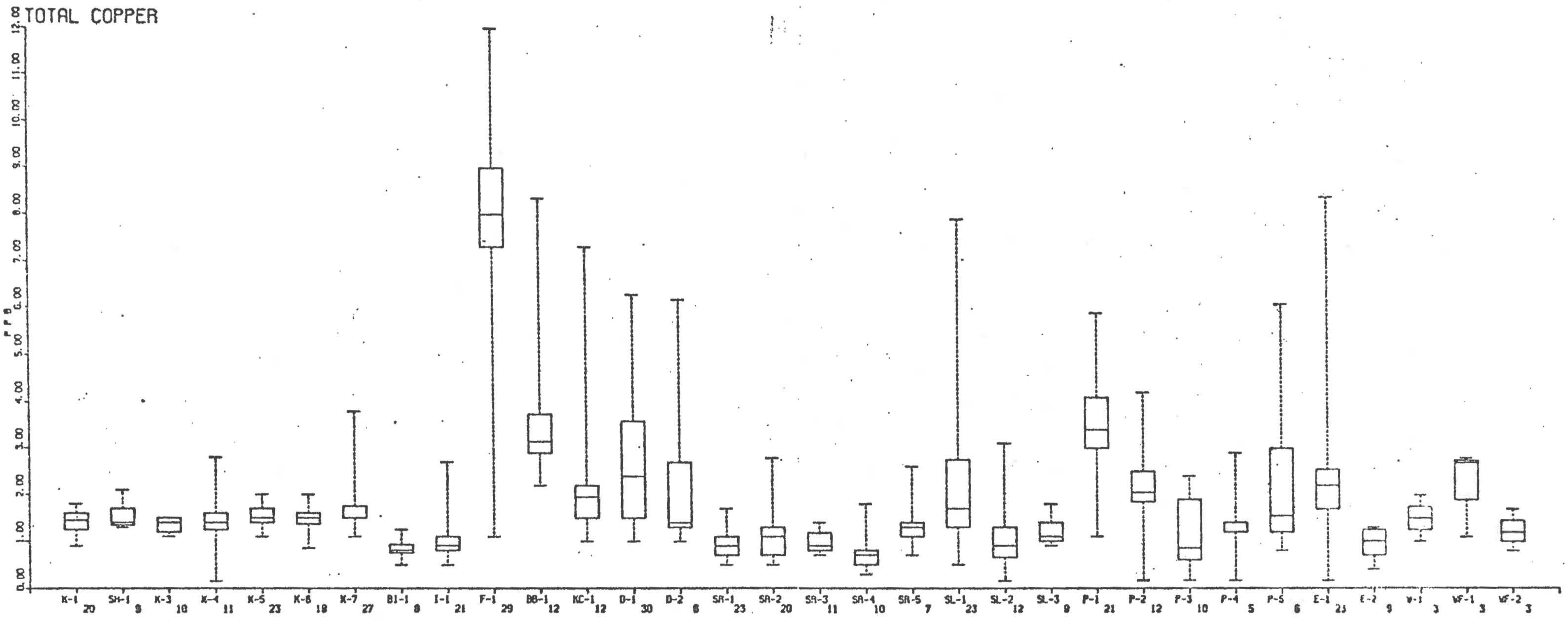


Figure 28. (Contd.)

OTAL IRON

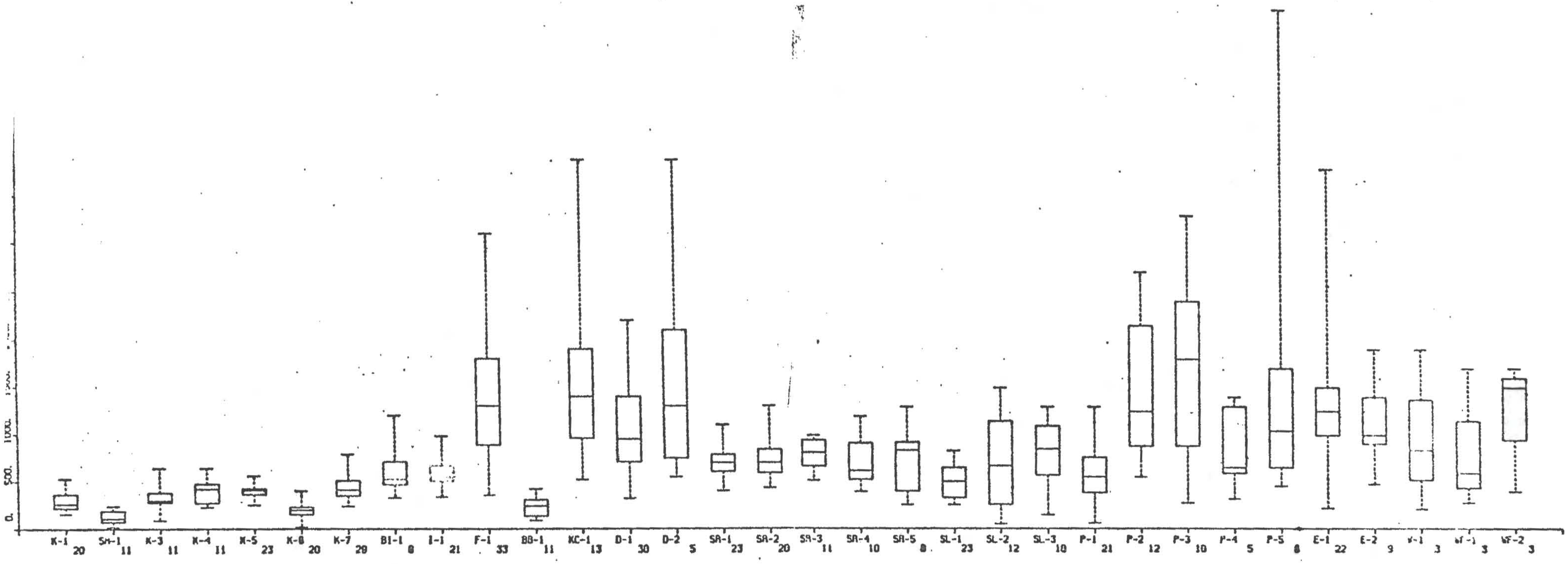


Figure 28. (Contd.)

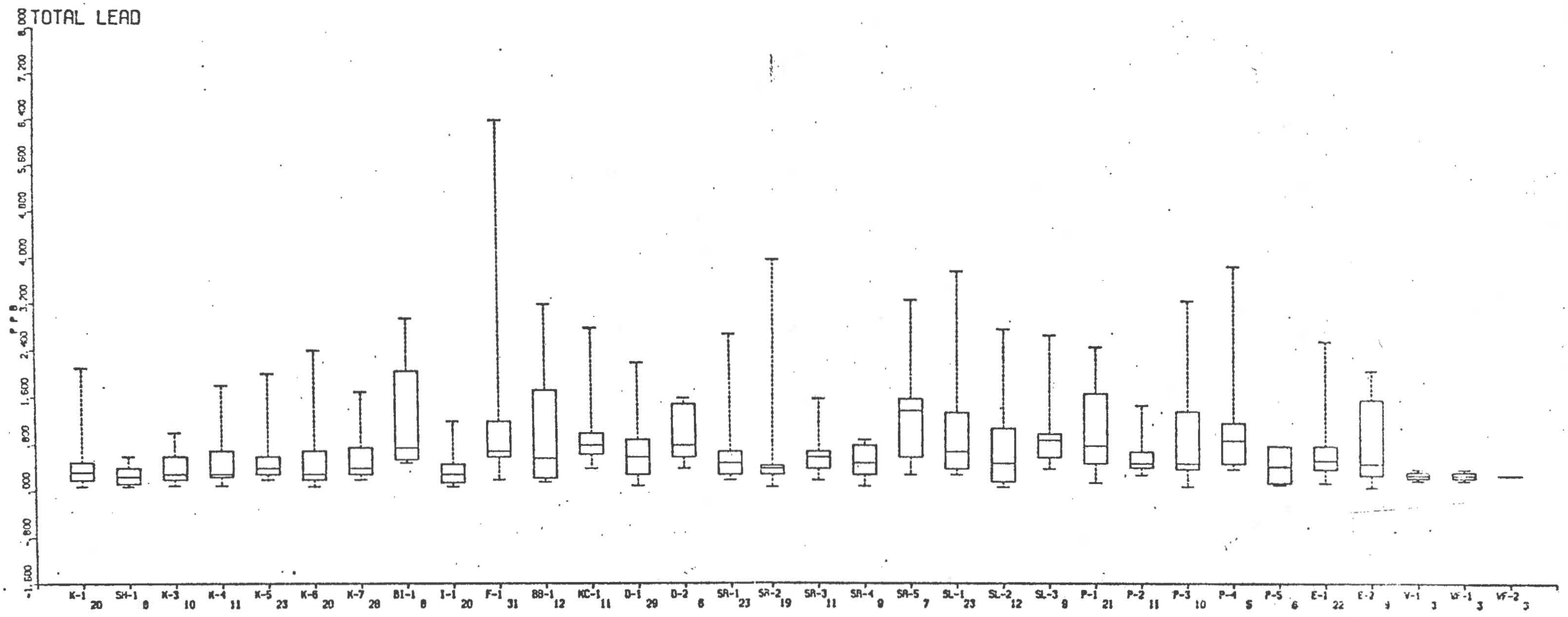


Figure 28. (Contd.)

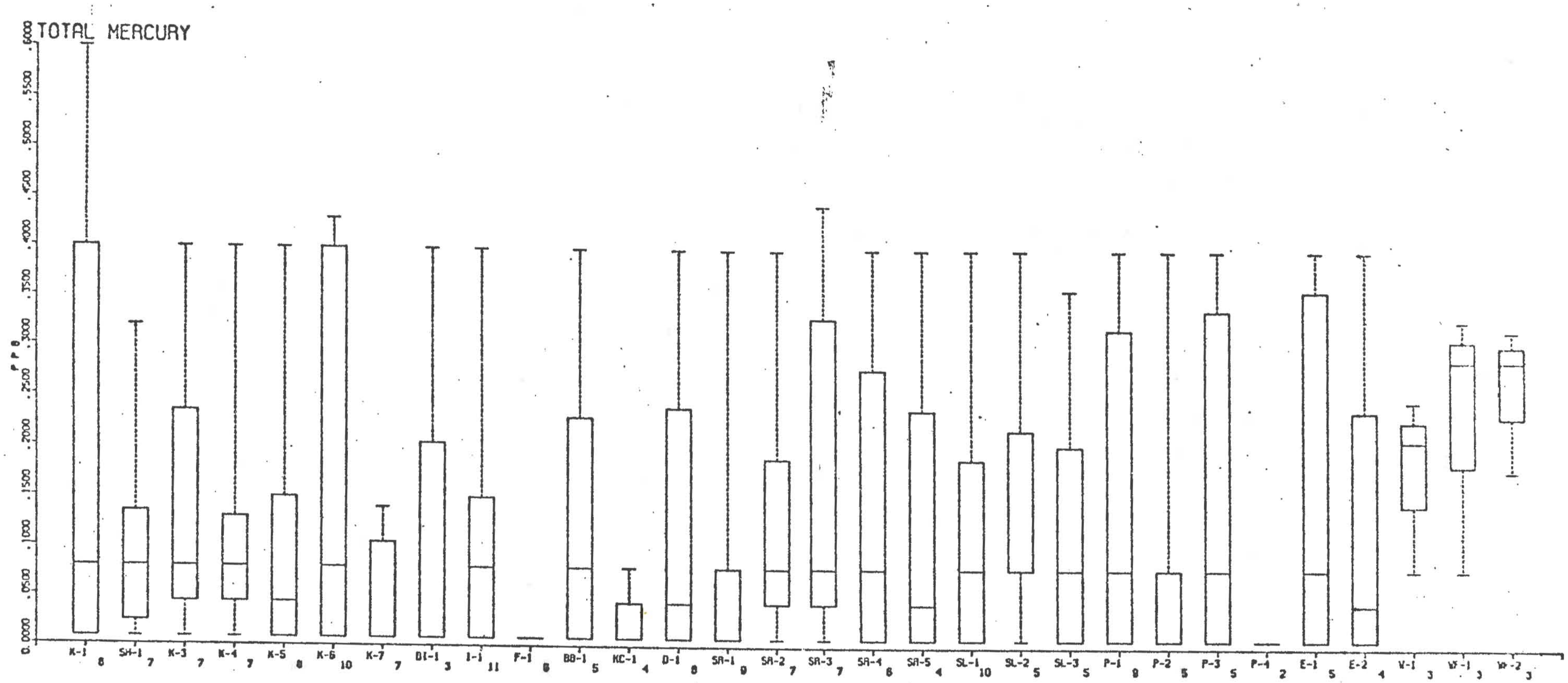


Figure 28. (Contd.)

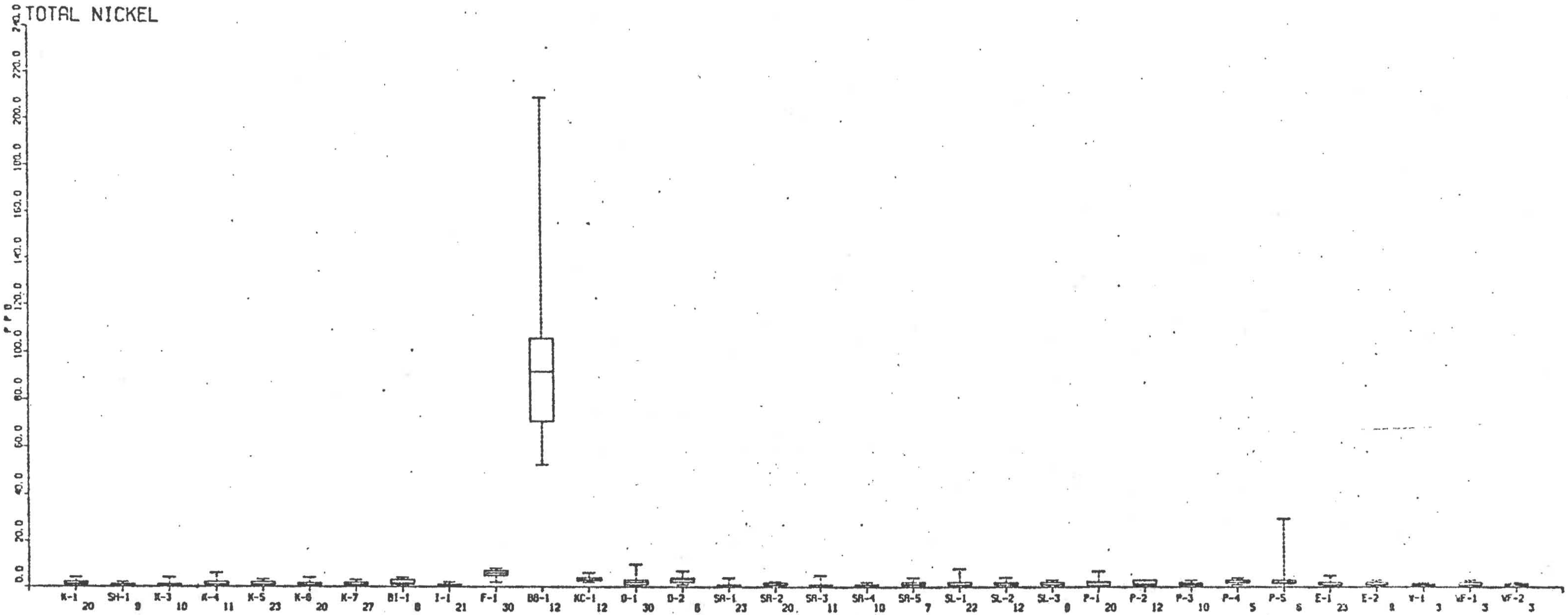


Figure 28. (Contd.)

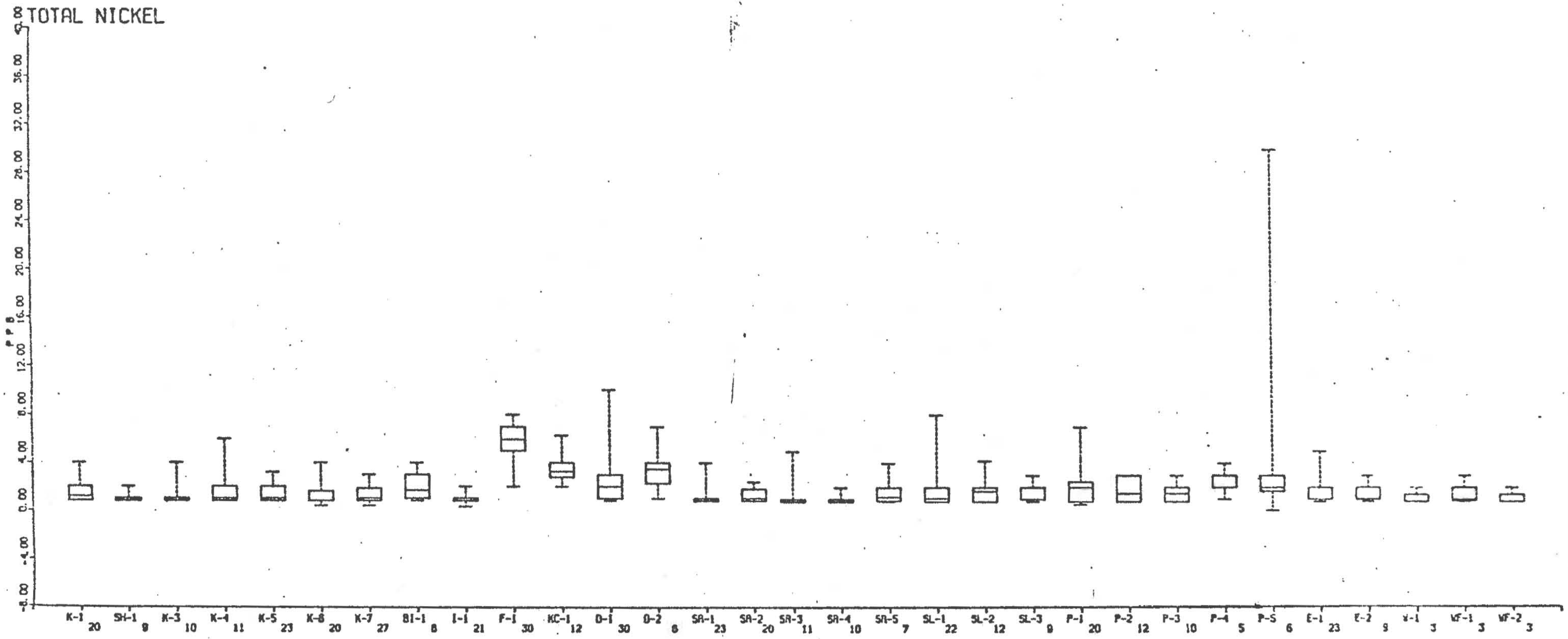
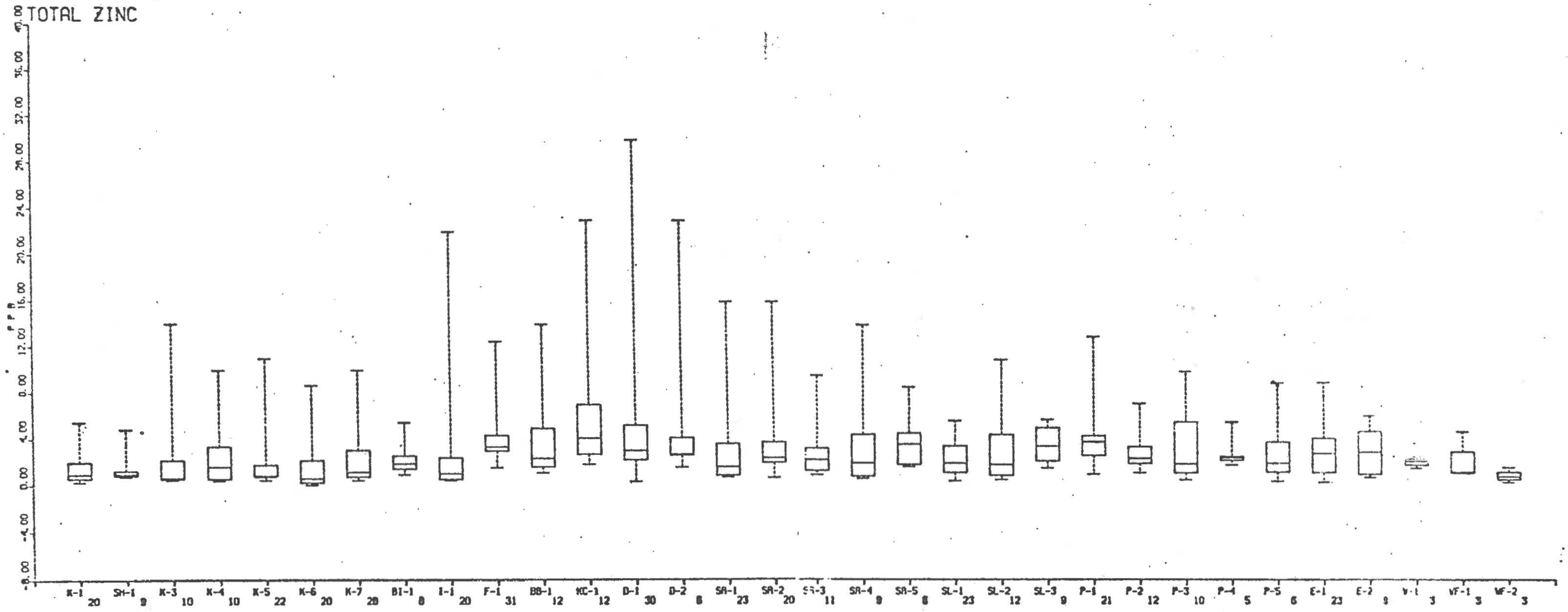


Figure 28. (Contd.)



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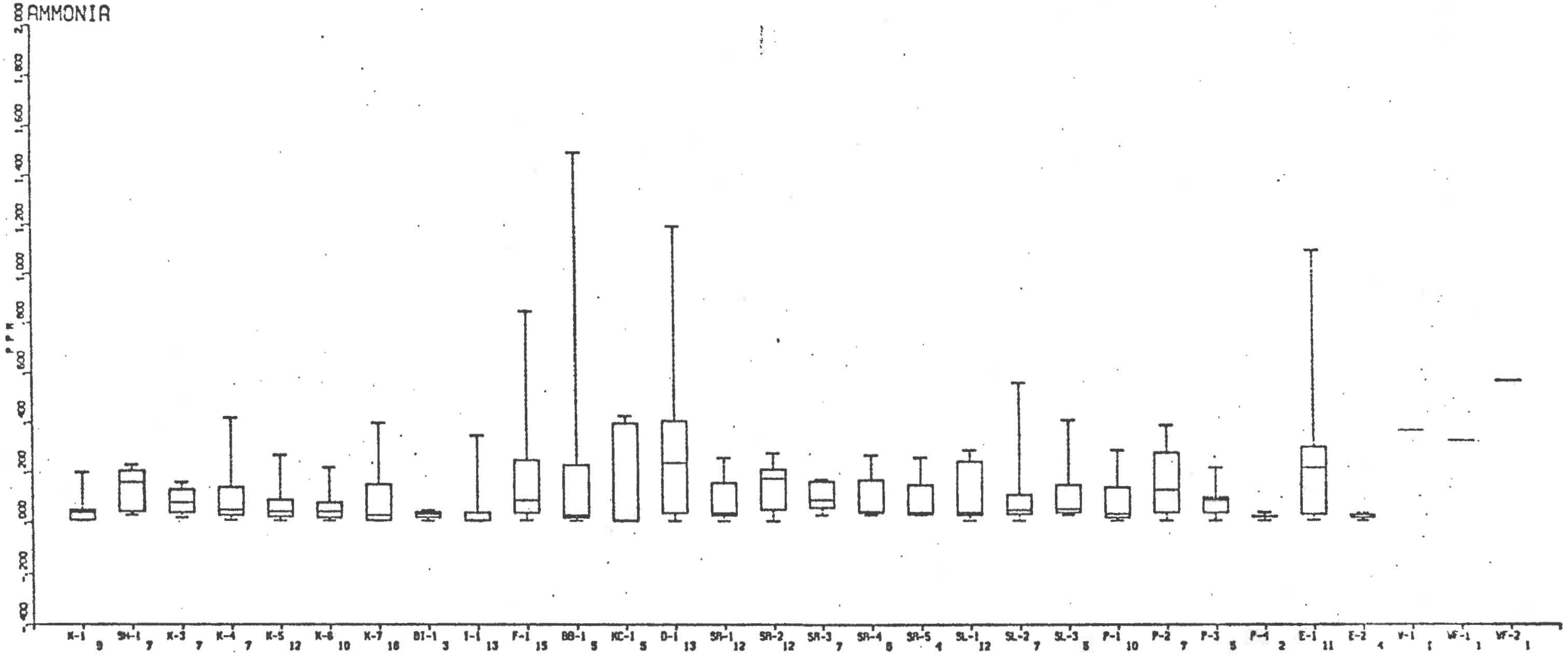
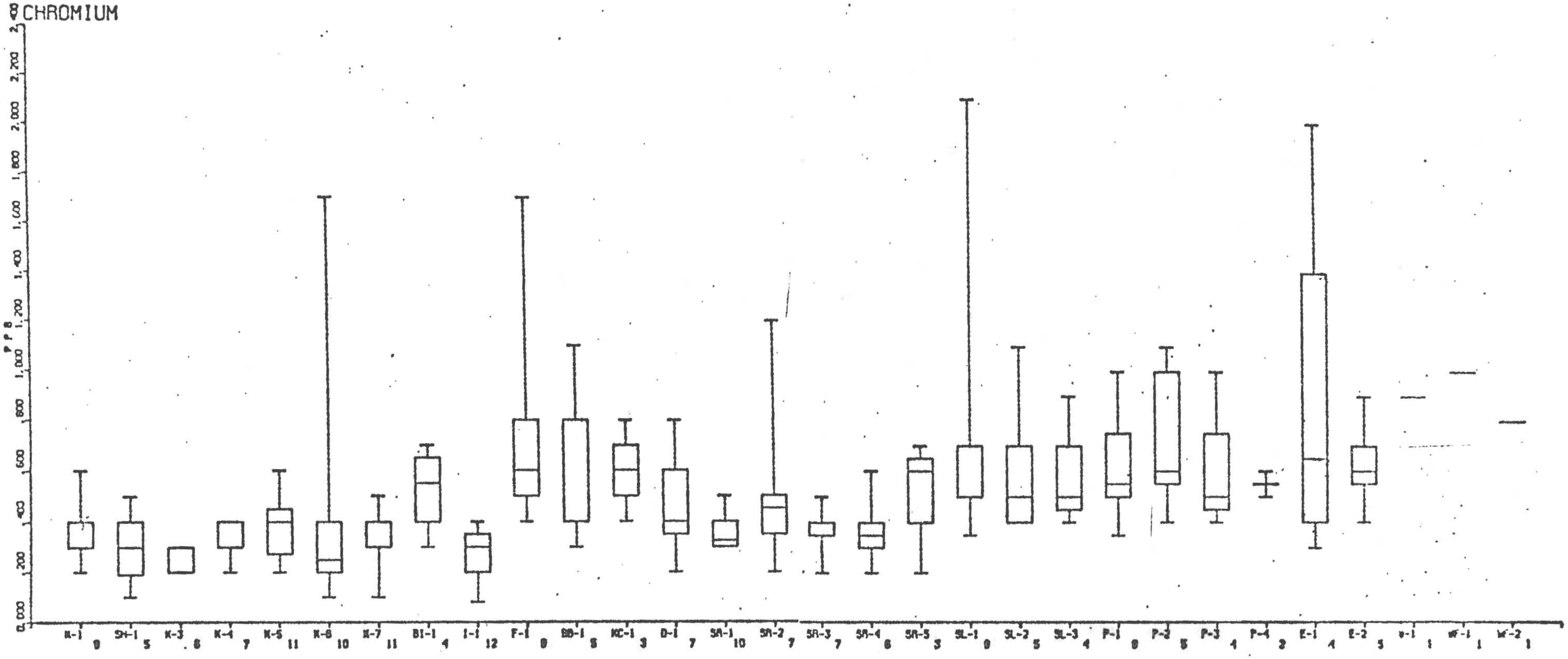
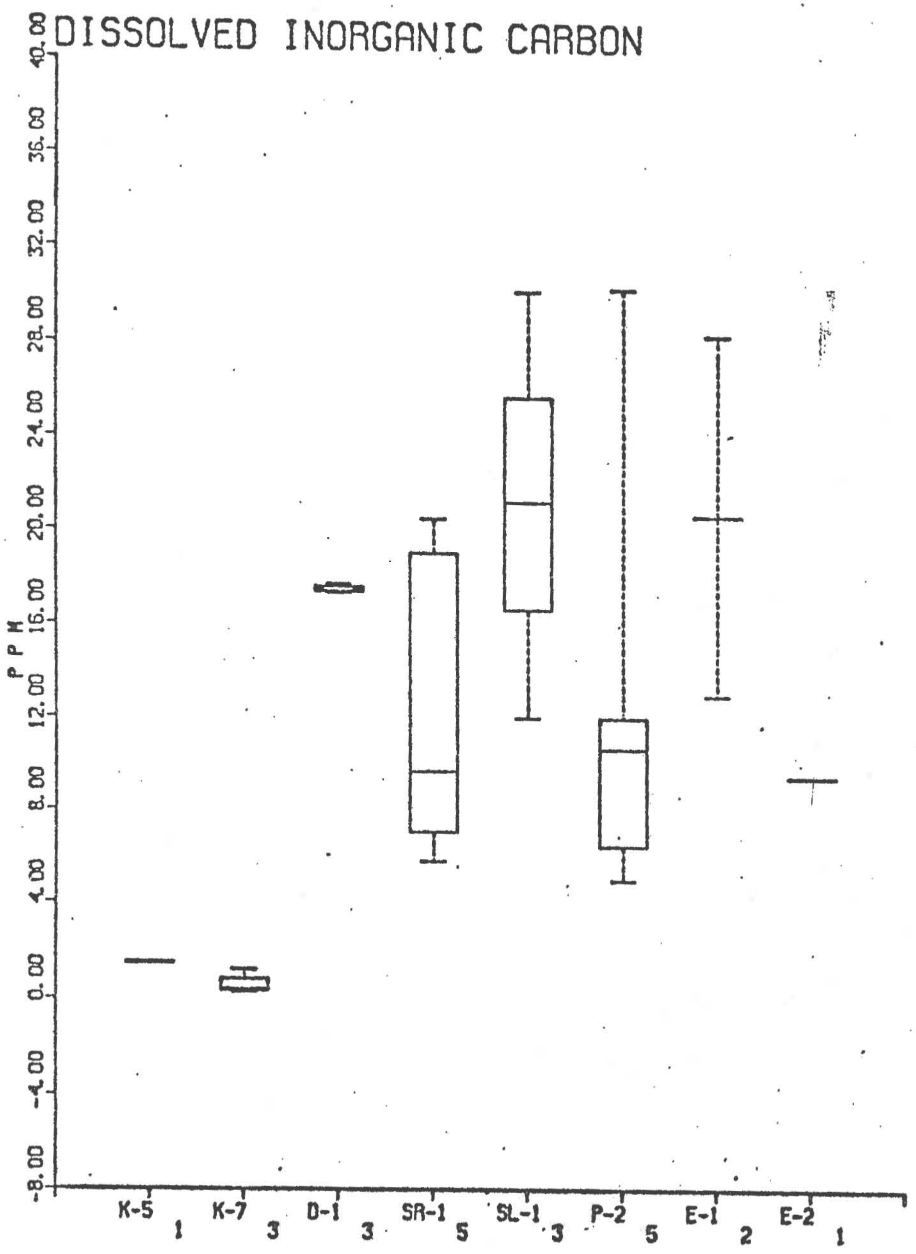
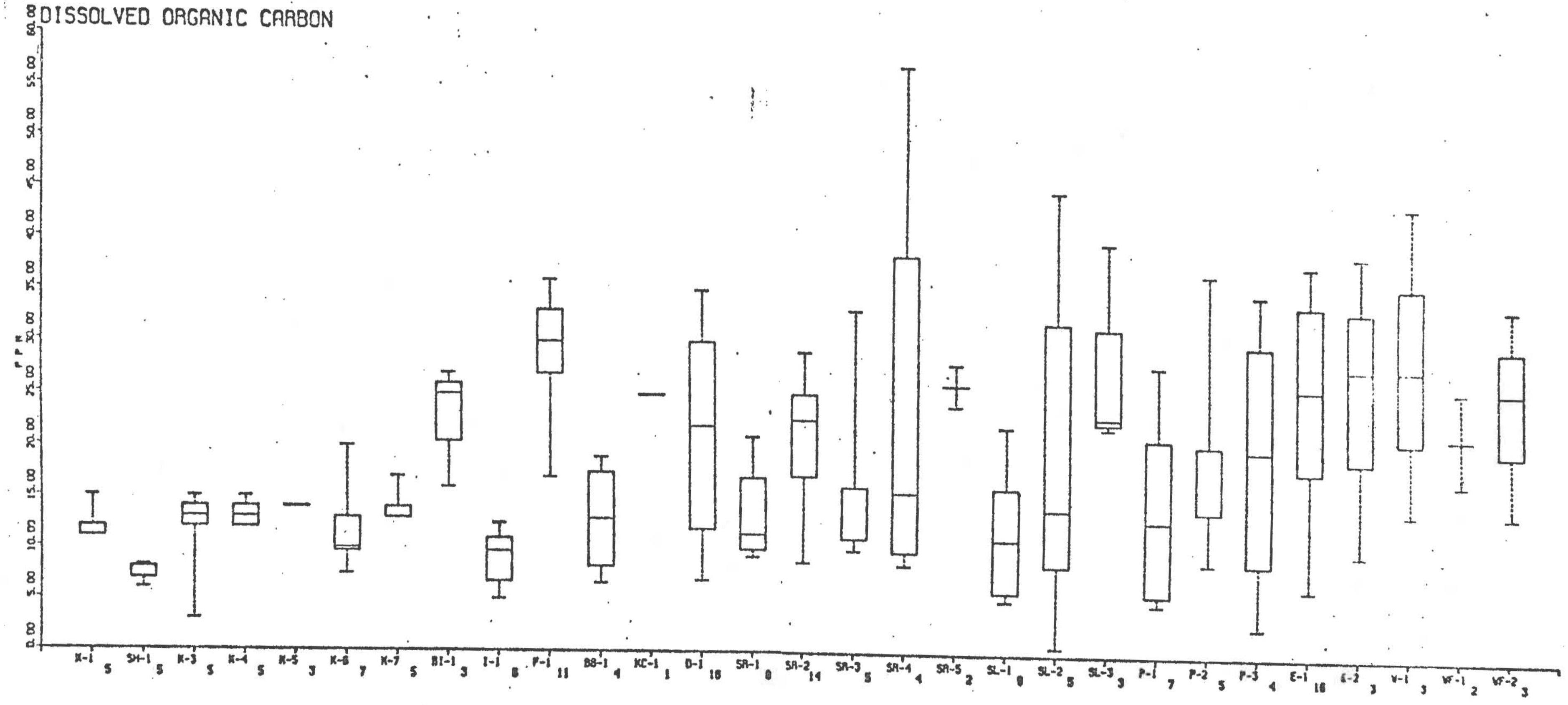
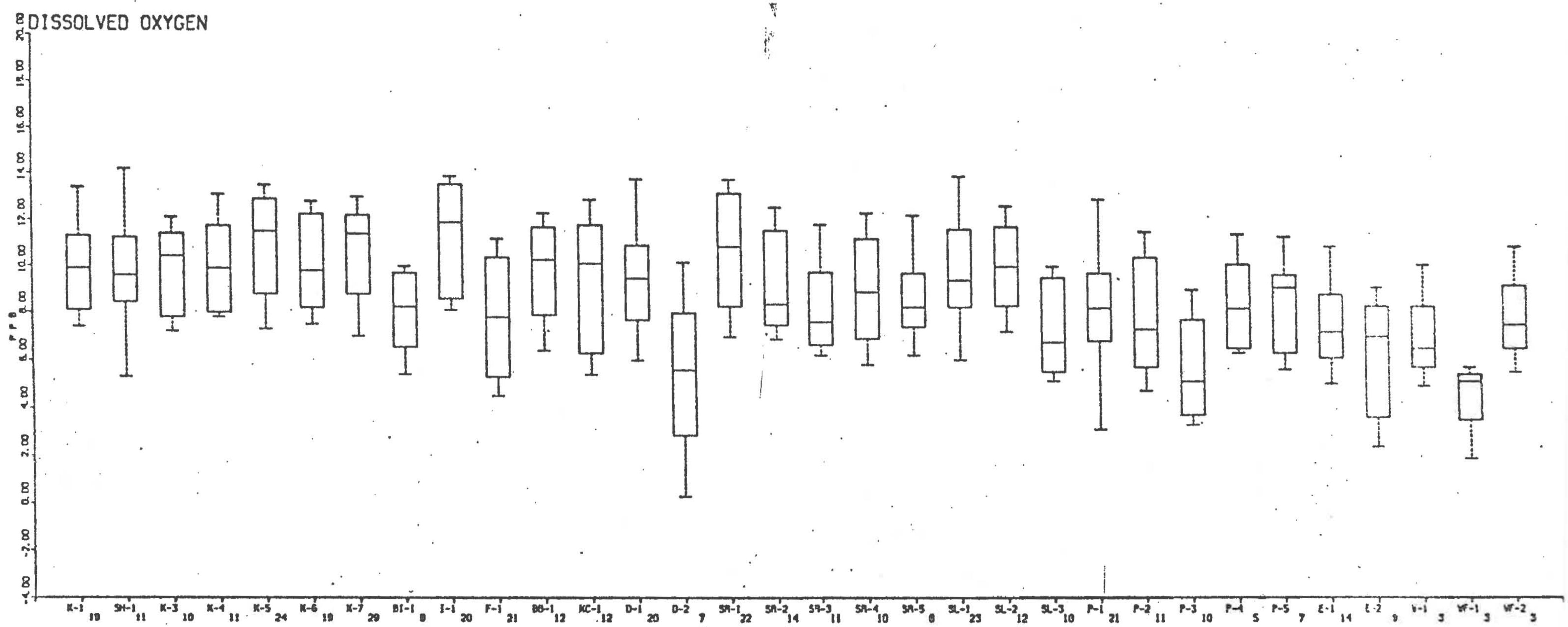
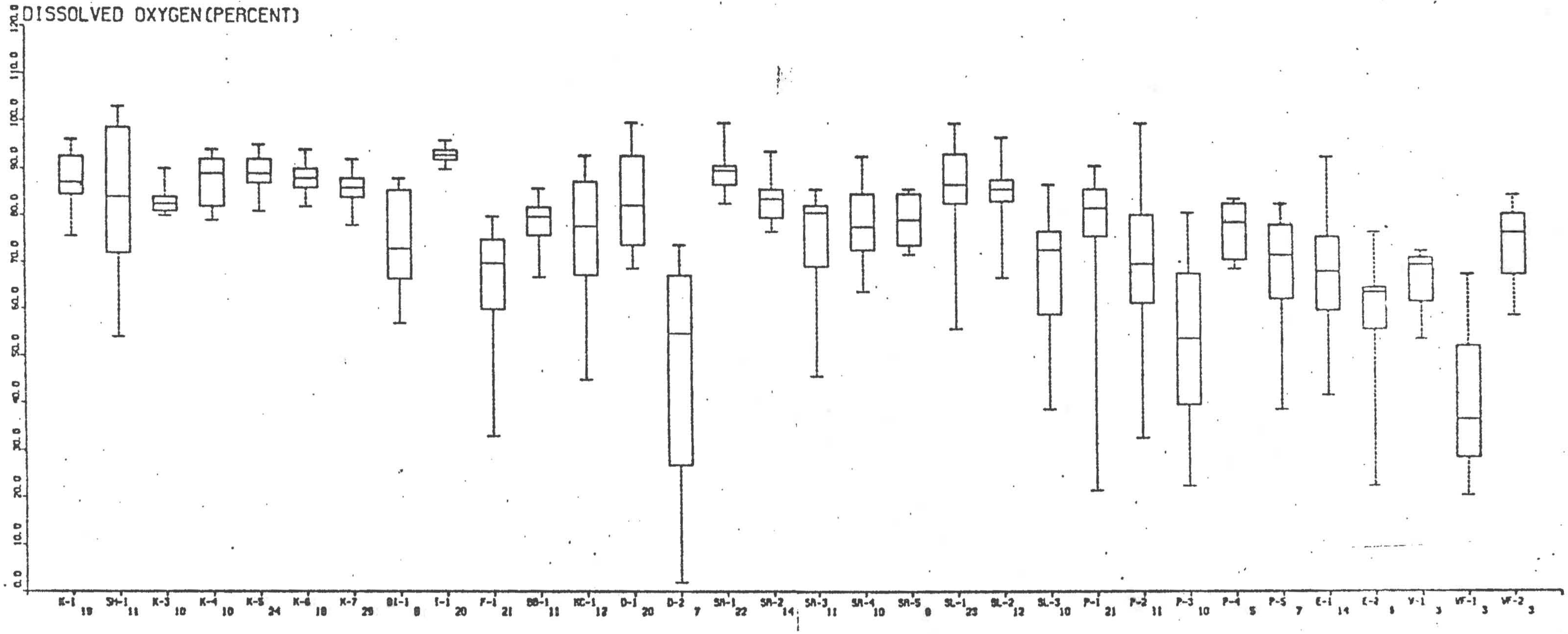
AMMONIA
2,000
1,800
1,600
1,400
1,200
1,000
800
600
400
200
000
-200
-400
P P M
K-1 9
SH-1 7
K-3 7
K-4 7
K-5 12
K-6 10
K-7 16
BI-1 3
I-1 13
F-1 15
BB-1 5
KC-1 5
D-1 13
SR-1 12
SR-2 12
SR-3 7
SR-4 8
SR-5 4
SL-1 12
SL-2 7
SL-3 8
P-1 10
P-2 7
P-3 5
P-4 2
E-1 11
E-2 4
V-1 1
VF-1 1
VF-2 1

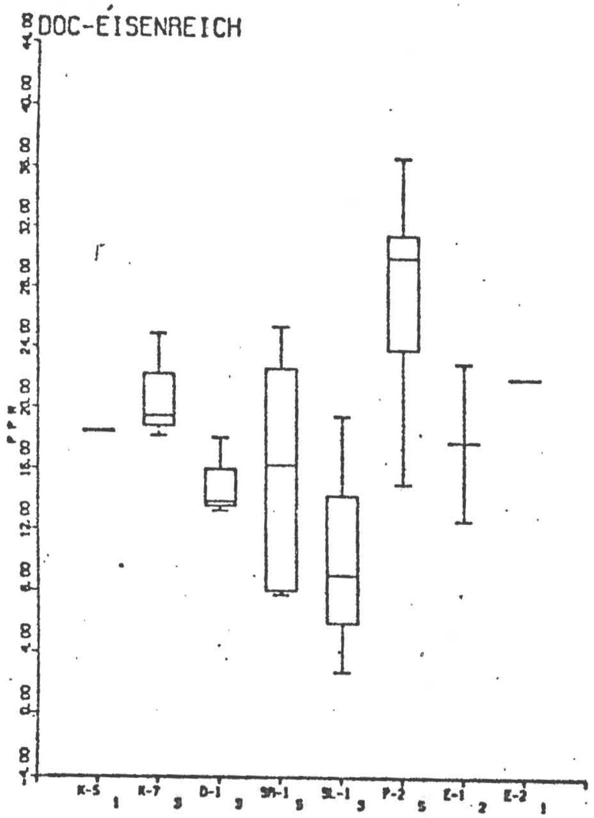
CHROMIUM
P P B
0.000
200
400
600
800
1,000
1,200
1,400
1,600
1,800
2,000
2,200
2,4
K-1 9
SH-1 5
K-3 6
K-4 7
K-5 11
K-6 10
K-7 11
BI-1 4
I-1 12
F-1 9
BB-1 5
KC-1 3
D-1 7
SA-1 10
SA-2 7
SA-3 7
SA-4 6
SA-5 3
SL-1 9
SL-2 5
SL-3 4
P-1 9
P-2 5
P-3 4
P-4 2
E-1 4
E-2 3
V-1 1
WF-1 1
W-2 1

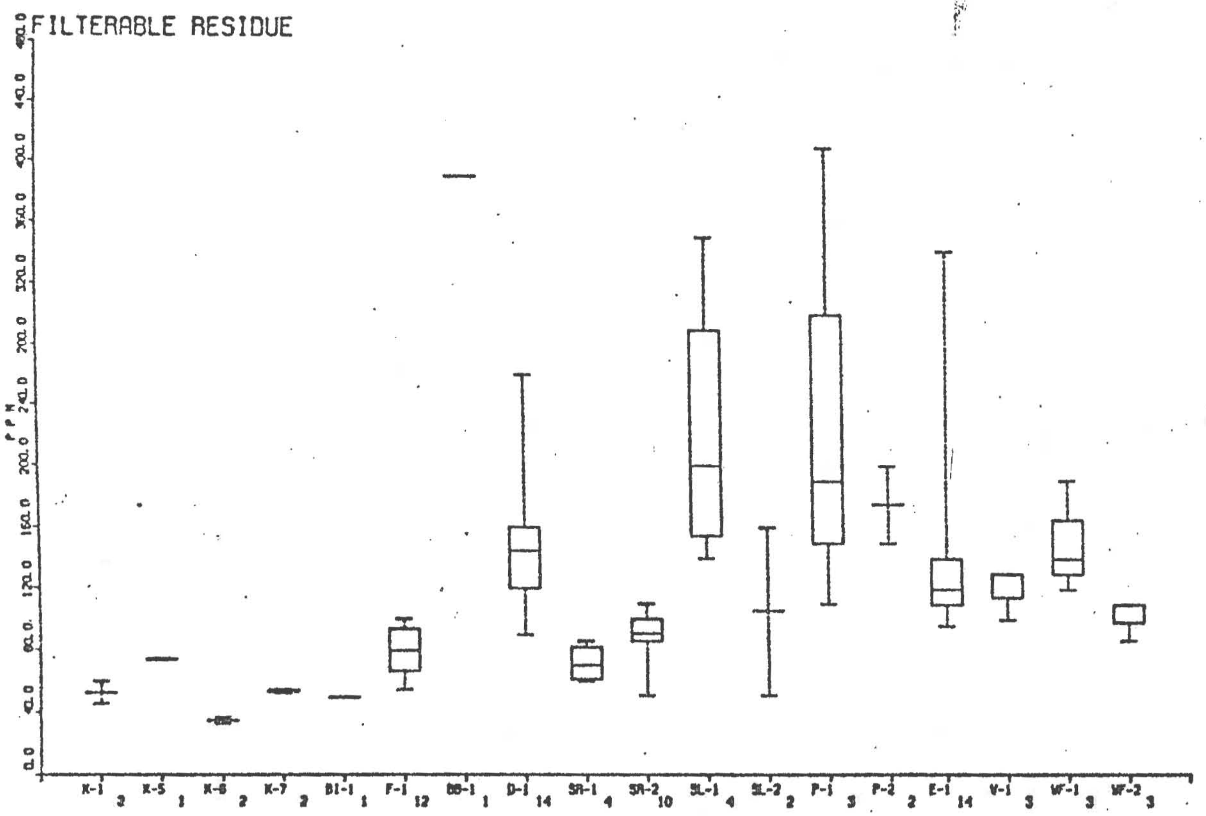

DISSOLVED INORGANIC CARBON

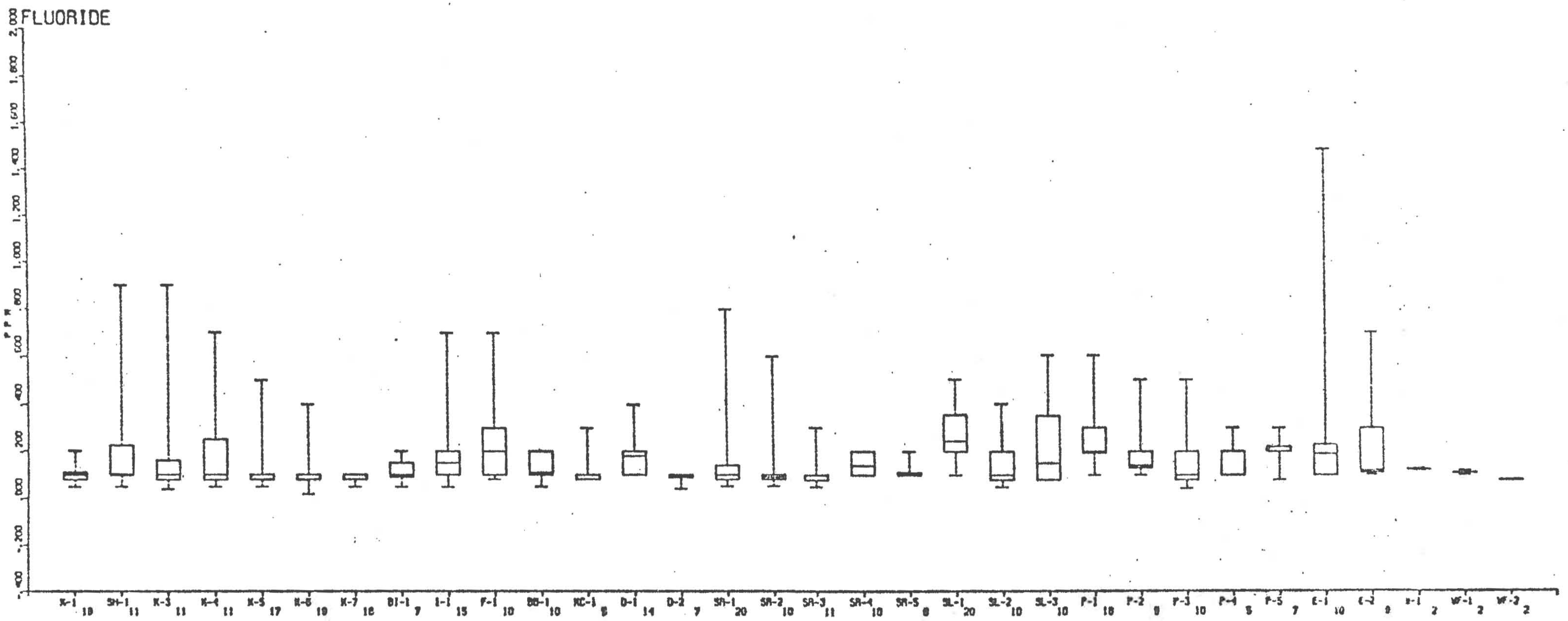

DISSOLVED ORGANIC CARBON
P P M
60.00
55.00
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
K-1 5
SH-1 5
K-3 5
K-4 5
K-5 3
K-6 7
K-7 5
BI-1 3
I-1 8
F-1 11
BB-1 4
KC-1 1
D-1 18
SA-1 8
SA-2 14
SA-3 5
SA-4 4
SA-5 2
SL-1 8
SL-2 5
SL-3 3
P-1 7
P-2 5
P-3 4
E-1 18
E-2 3
V-1 3
VF-1 2
VF-2 3


DISSOLVED OXYGEN
P P M
20.00
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
-2.00
-4.00
K-1 19
SH-1 11
K-3 10
K-4 11
K-5 24
K-6 19
K-7 29
BI-1 8
I-1 20
F-1 21
BB-1 12
KC-1 12
D-1 20
D-2 7
SA-1 22
SA-2 14
SA-3 11
SA-4 10
SA-5 8
SL-1 23
SL-2 12
SL-3 10
P-1 21
P-2 11
P-3 10
P-4 5
P-5 7
E-1 14
E-2 9
V-1 3
WF-1 3
WF-2 3

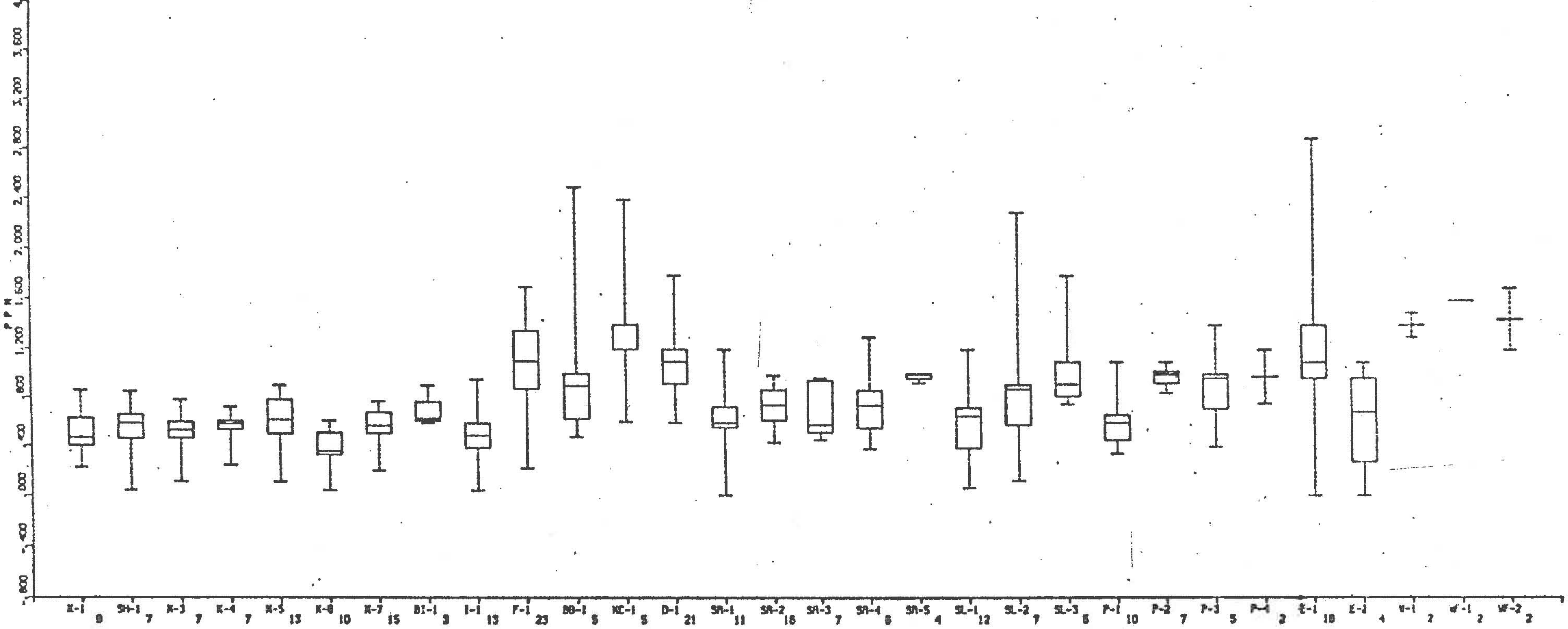

DISSOLVED OXYGEN (PERCENT)
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
K-1 19
SH-1 11
K-3 10
K-4 10
K-5 24
K-6 18
K-7 29
BI-1 8
I-1 20
F-1 21
BB-1 11
KC-1 12
D-1 20
D-2 7
SA-1 22
SA-2 14
SA-3 11
SA-4 10
SA-5 8
SL-1 23
SL-2 12
SL-3 10
P-1 21
P-2 11
P-3 10
P-4 5
P-5 7
E-1 14
E-2 8
V-1 3
VF-1 3
VF-2 3

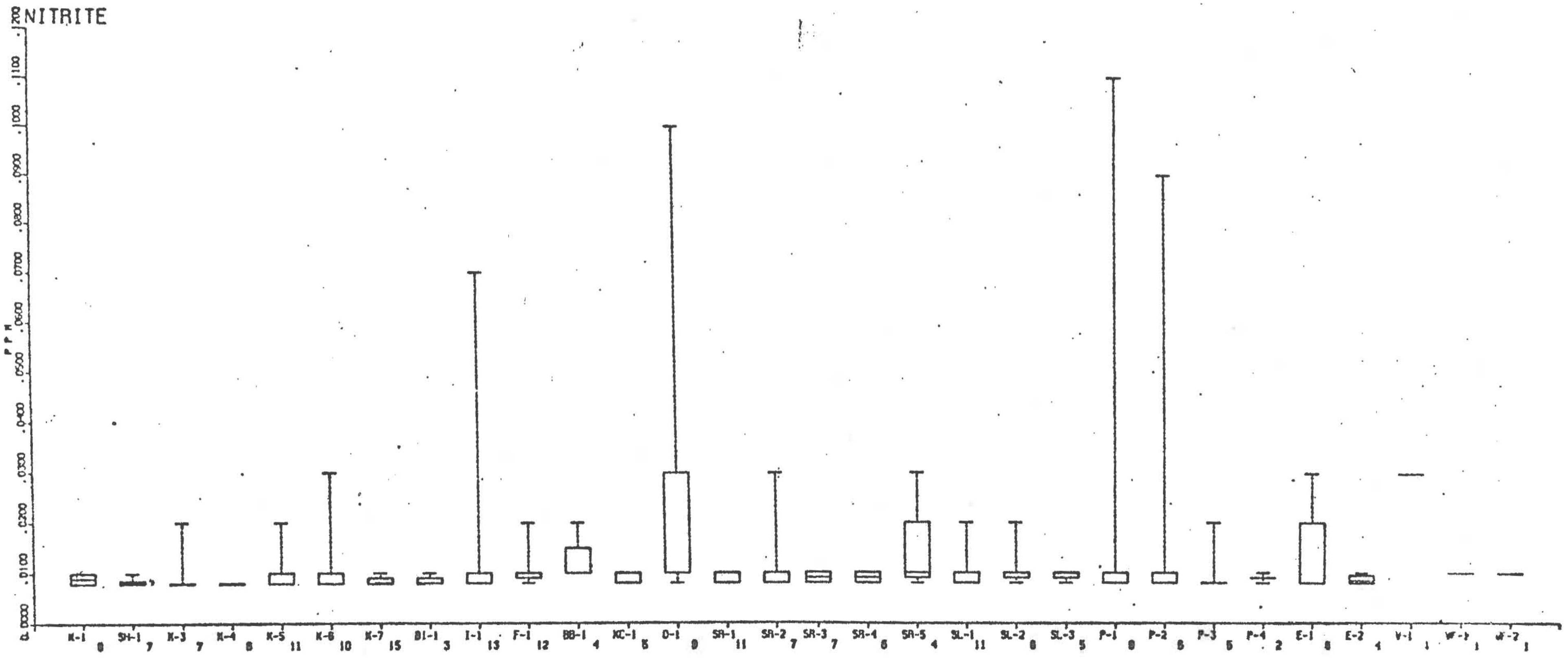

DOC-EISENREICH
44.00
40.00
36.00
32.00
28.00
24.00
20.00
16.00
12.00
8.00
4.00
0.00
-4.00
PPM
K-5
1
K-7
5
D-1
3
SM-1
5
SL-1
3
P-2
5
E-1
2
E-2
1


FILTERABLE RESIDUE
P P M
0.0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
360.0
400.0
440.0
480.0
K-1 2
K-5 1
K-6 2
K-7 2
BI-1 1
F-1 12
BB-1 1
D-1 14
SA-1 4
SA-2 10
SL-1 4
SL-2 2
P-1 3
P-2 2
E-1 14
V-1 3
WF-1 3
WF-2 3

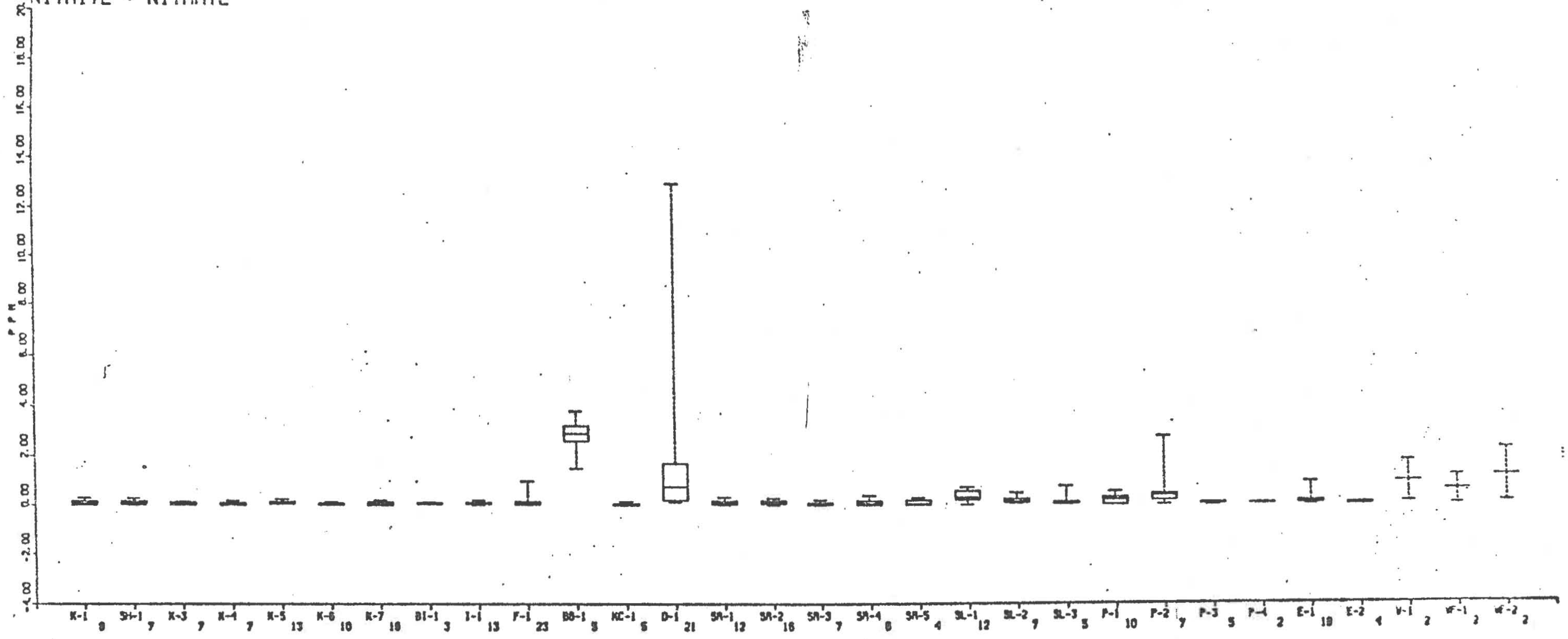

FLUORIDE
PPM
2.000
1.800
1.600
1.400
1.200
1.000
.800
.600
.400
.200
.000
-.200
-.400
K-1 10
SH-1 11
K-3 11
K-4 11
K-5 17
K-6 10
K-7 10
BI-1 7
I-1 15
F-1 10
BB-1 10
KC-1 5
D-1 14
D-2 7
SA-1 20
SA-2 10
SA-3 11
SA-4 10
SA-5 8
SL-1 20
SL-2 10
SL-3 10
P-1 10
P-2 8
P-3 10
P-4 5
P-5 7
E-1 10
E-2 8
H-1 2
WF-1 2
WF-2 2

KJELDAHL NITROGEN

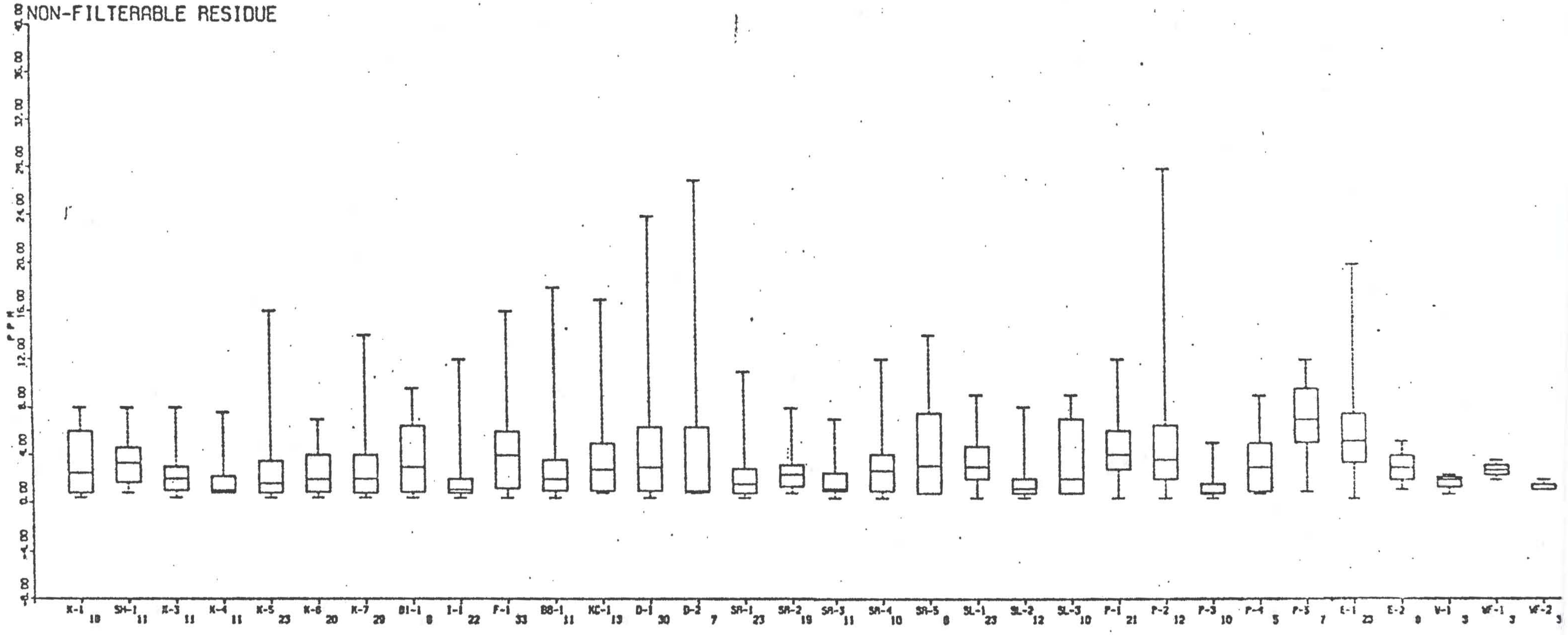


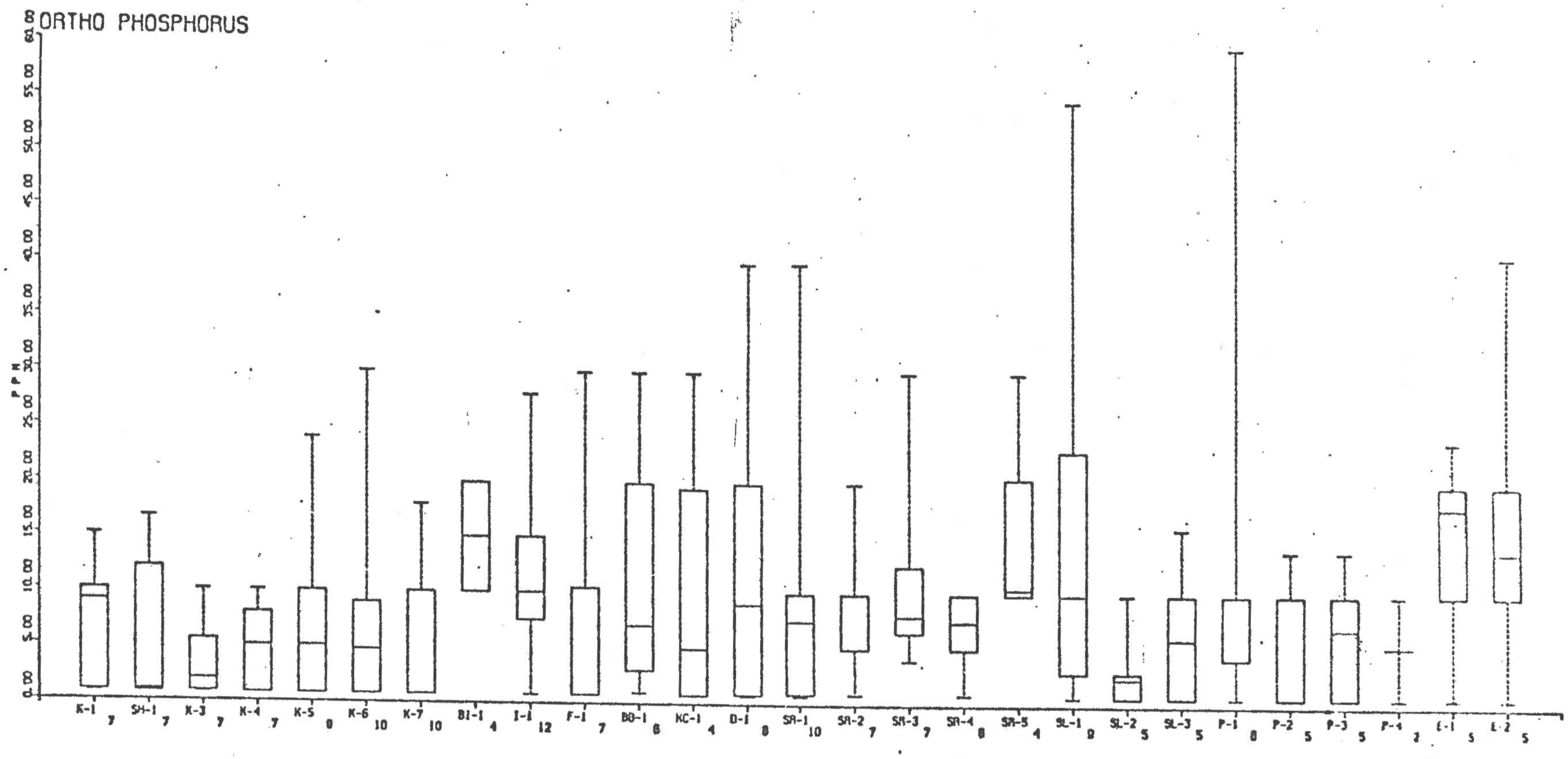
NITRITE
PPM
.0000
.0100
.0200
.0300
.0400
.0500
.0600
.0700
.0800
.0900
.1000
.1100
.1200
K-1 8
SH-1 7
K-3 7
K-4 8
K-5 11
K-6 10
K-7 15
BI-1 3
I-1 13
F-1 12
BB-1 4
KC-1 5
O-1 9
SR-1 11
SR-2 7
SR-3 7
SR-4 6
SR-5 4
SL-1 11
SL-2 8
SL-3 5
P-1 9
P-2 8
P-3 5
P-4 2
E-1 8
E-2 4
V-1 1
WF-1 1
WF-2 1

NITRITE + NITRATE



NON-FILTERABLE RESIDUE



ORTHO PHOSPHORUS
P P M
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50.00
55.00
60.00
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K-3 7
K-4 7
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K-6 10
K-7 10
BI-1 4
I-1 12
F-1 7
BB-1 6
KC-1 4
D-1 8
SR-1 10
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SR-4 8
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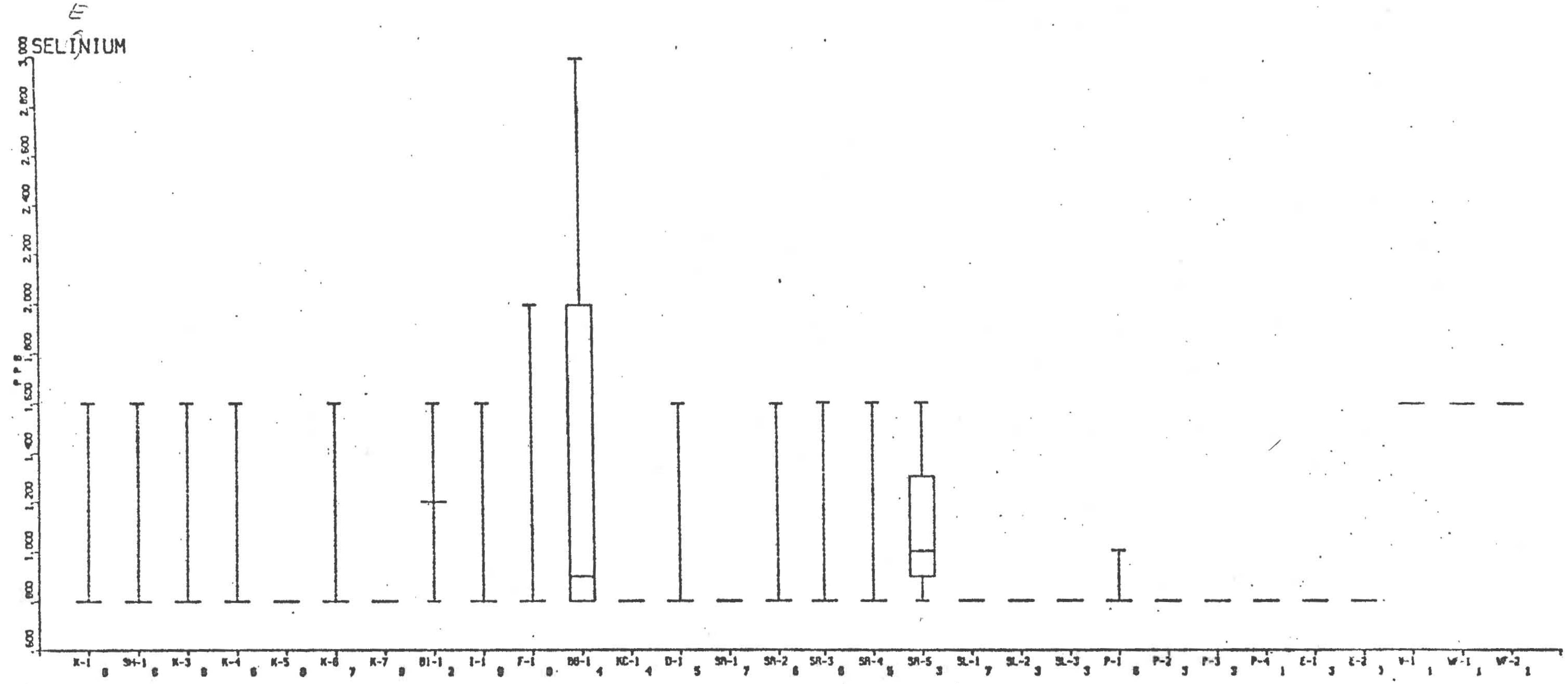
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1,000
800
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K-4 6
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K-7 8
BI-1 2
I-1 8
F-1 8
BB-1 4
KC-1 4
D-1 5
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SR-4 5
SR-5 3
SL-1 7
SL-2 3
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E-1 3
E-2 3
V-1 1
WF-1 1
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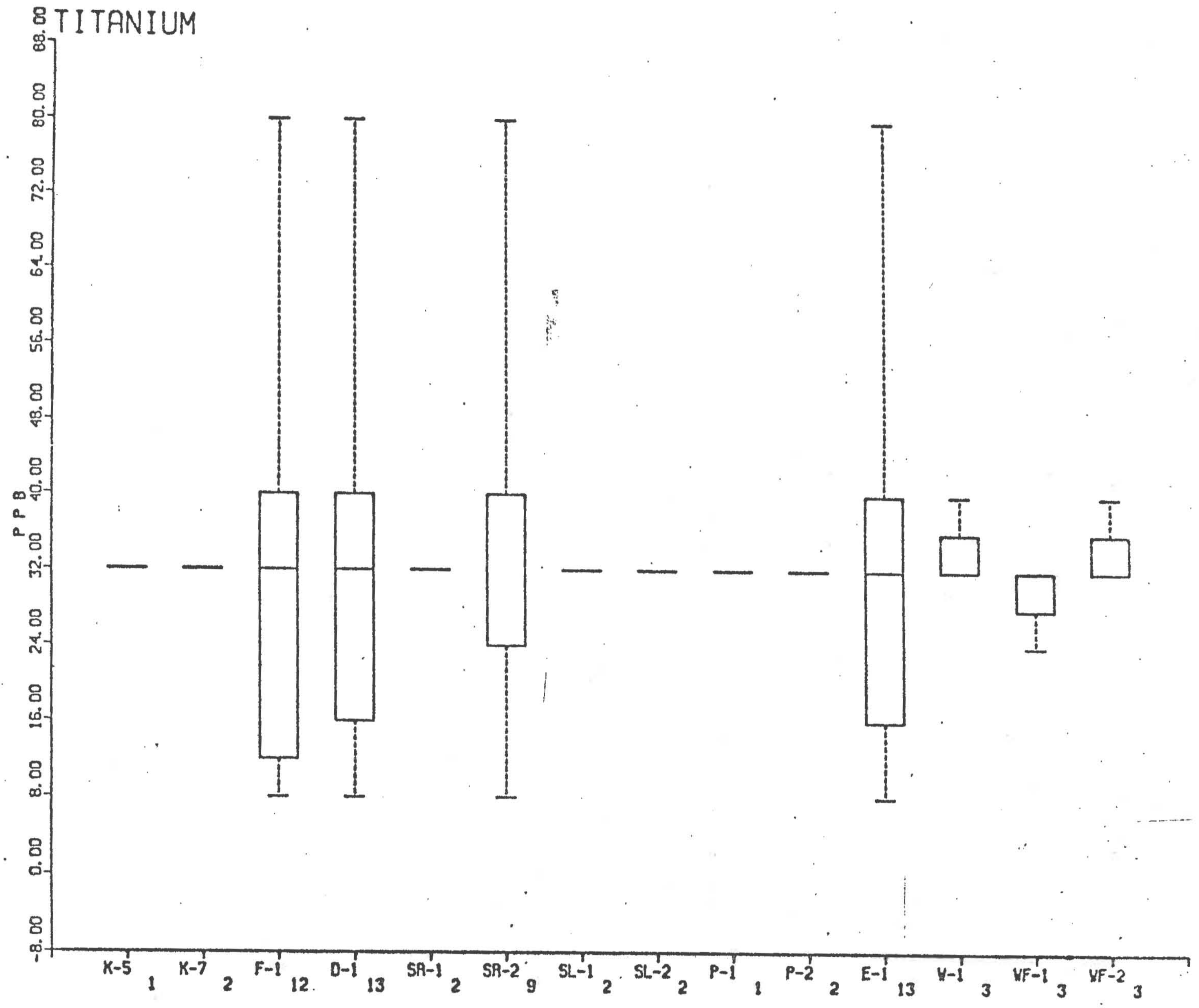
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0.00
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K-7 2
F-1 12
D-1 13
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VF-1 3
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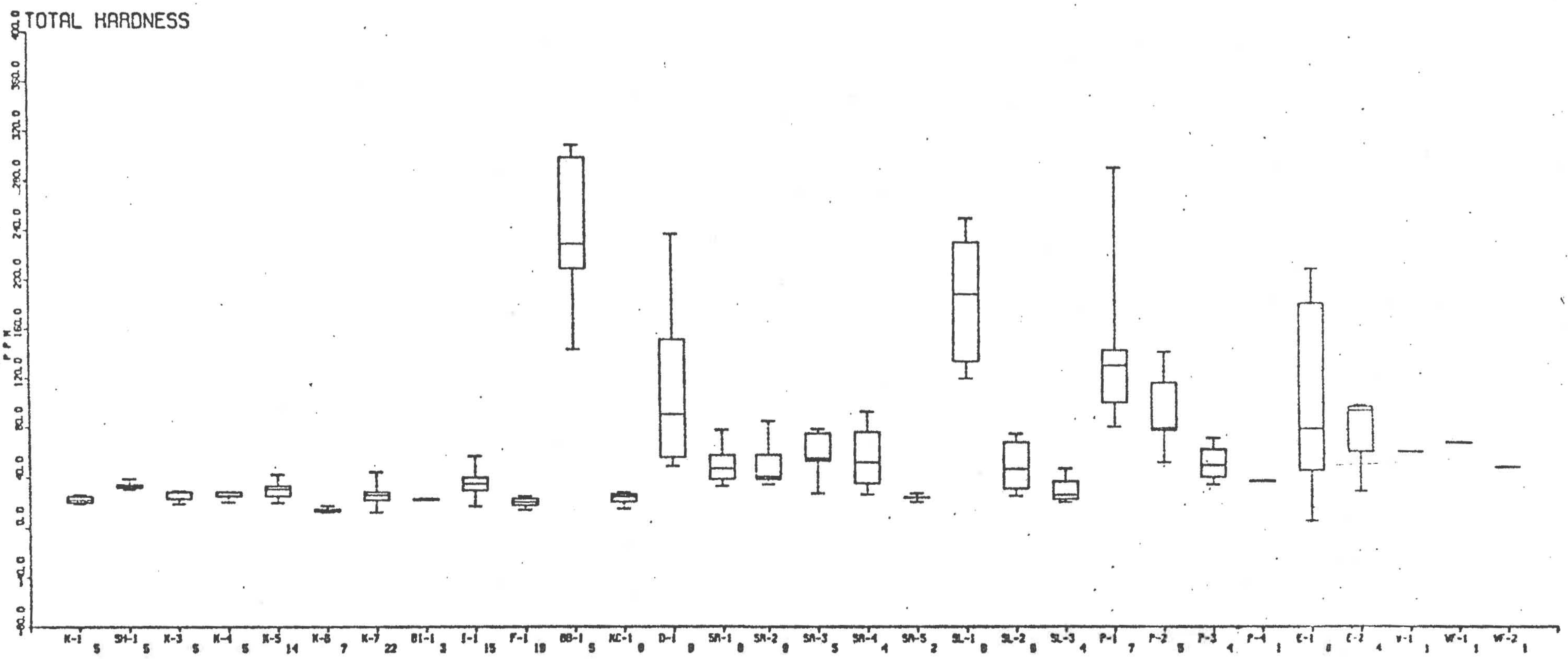
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-80.0
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SH-1 5
K-3 5
K-4 5
K-5 14
K-6 7
K-7 22
BI-1 3
I-1 15
F-1 19
BB-1 5
KC-1 8
D-1 9
SA-1 8
SA-2 9
SA-3 5
SA-4 4
SA-5 2
SL-1 8
SL-2 8
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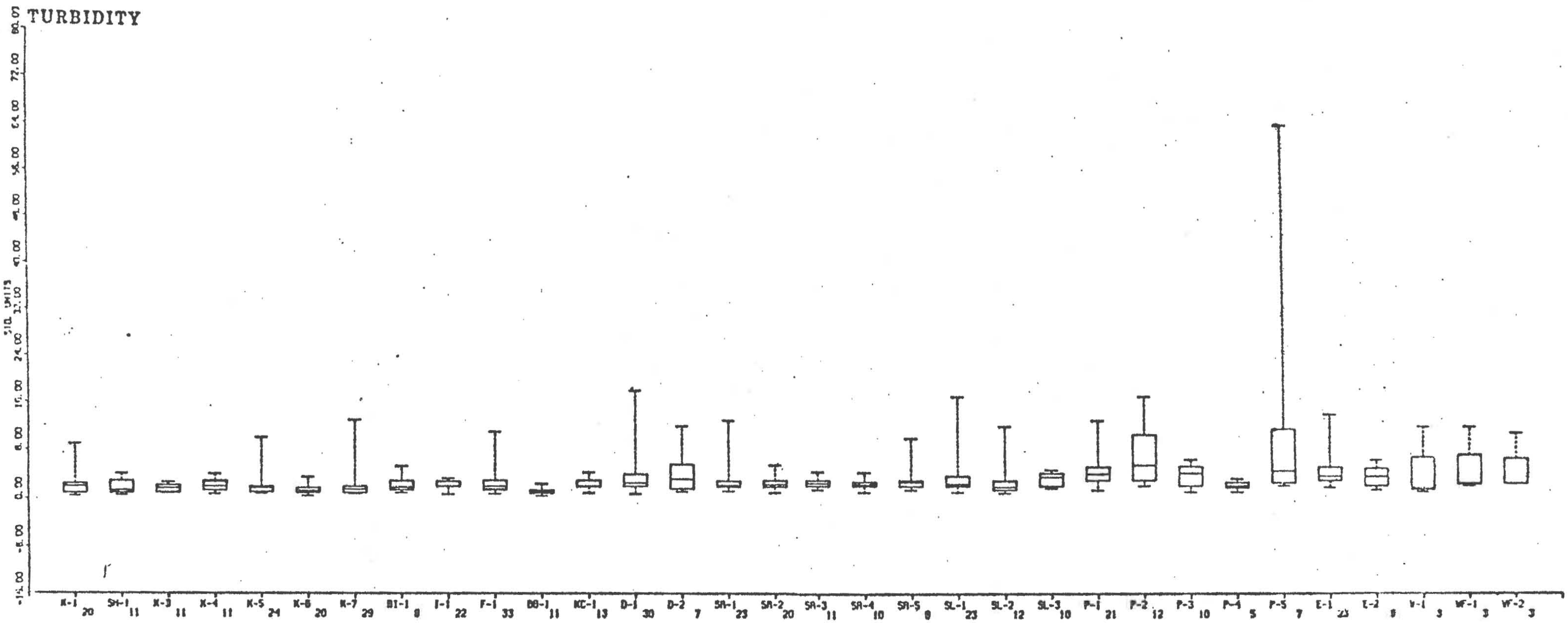

TURBIDITY

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8.00
0.00
-8.00
-16.00
K-1 20
SH-1 11
K-3 11
K-4 11
K-5 24
K-6 20
K-7 29
BI-1 8
I-1 22
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D-1 30
D-2 7
SA-1 23
SA-2 20
SA-3 11
SA-4 10
SA-5 8
SL-1 23
SL-2 12
SL-3 10
P-1 21
P-2 12
P-3 10
P-4 5
P-5 7
E-1 23
E-2 8
V-1 3
WF-1 3
WF-2 3

APPENDIX 2

Summary Comparisons of Stream Monitoring Results

Table . Comparison of general water quality paramters for three groups of streams in the Regional Copper-Nickel Study Area (November, 1975, to April, 1977).

MONITORING STATIONS GROUPINGS*			A			B			C	
Parameter	Units	Range	Median	N	Range	Median	N	Range	Median	N
Calcium (Ca)	mg/l	4.5-80	29	33	3.8-53	15	50	1.8-40	6.0	250
Chloride (Cl)	mg/l	2.8-38	9.1	55	2.9-88	17	65	0.08-41	1.6	342
Color	Pt-Co units	4-150	50	55	23-450	130	65	4-500	90.2	343
Magnesium (Mg)	mg/l	3-40	15	33	3-26	8	50	1-23	3	250
Potassium (K)	mg/l	1.0-8.4	2.3	33	0.3-5.2	1.6	36	0.2-6.2	0.6	241
Silica (Si)	mg/l	4.6-24	14	56	4.0-29	9.5	65	0.1-34	6.3	344
Sodium (Na)	mg/l	1.1-45	6.5	33	0.5-35	8.1	36	0.2-19	1.6	235
Specific conductance	micro-ohms/cm at 25°C	61-1198	323	55	12-655	181	65	24-524	55	343
Hardness	mg/l($CaCO_3$)	81-310	152	20	5.3-238	81.5	22	12-99	27.1	164
Turbidity	Jackson Turbidity Units	0.5-17	2.4	55	0.8-18	3.4	65	0.5-64	2.0	343
Total Carbon (TOC)	mg/l	4.7-20	10.1	6	11-22	18	5	0.4-45	15	69

*Group A stations	Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations	Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations	Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

Table . Comparison of water quality paramters related to acidity and acid buffering for three groups of streams in the Regional Copper-Nickel Study Area (November, 1976, to April, 1977).

MONITORING STATIONS GROUPINGS*			A			B			C	
Parameter	Units	Range	Median	N	Range	Median	N	Range	Median	N
Alkalinity	mg/1 $CaCO_3$	11-140	71	56	13-160	45	65	1.0-190	19	336
Bicarbonate (HCO_3)	mg/1	14-148	54	29	16-134	65	24	6-151	22	204
Sulfate (SO_4)	mg/1	13-630	70	56	3.5-110	14	51	0.8-31	6.6	327
pH	$-\log_{10}[H^+]$	6.3-8.2	7.3	56	6.1-8.1	7.0	65	4.7-8.4	6.9	337

*Group A stations Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

Table . Comparison of nutrient water quality paramters for three groups of streams in the Regional Copper-Nickel Study Area (November, 1975, to April, 1977).

MONITORING STATIONS GROUPINGS* Parameter	Units	A Range	A Median	A N	B Range	B Median	B N	C Range	C Median	C N
Nitrate	mg/l(NO_2+NO_3)	0.02-3.8	0.32	27	0.01-13	0.2	46	0.01-2.3	0.08	187
Total Nitrogen (N)	mg/l	0.17-6.3	1.05	27	0.04-14.1	1.42	46	0.01-4.0	0.79	177
Total (P)	ug/l	0.8-2100	19.6	27	0.8-413	32.1	46	0.8-99	20.0	187

*Group A stations	Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations	Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations	Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

Table . Comparison of radioactive isotopes in surface waters of three groups of streams and all stations monitored in the Regional Copper-Nickel Study Area (November, 1975, to September, 1977).

MONITORING STATION GROUPINGS*			A			B			C			ALL STATIONS	
Parameter	Units	Range	Median	N	Range	Median	N	Range	Median	N	Range	Median	N
Alpha-D-Uranium	Pci/L	1.36-4.24	1.60	5	1.36-1.7	1.53	2	0.32-0.96	0.4	7	0.32-4.24	1.0	14
Alpha-S-Uranium	Pci/L	0.32-0.32	0.32	5	0.32-0.32	0.32	2	0.32-0.6	0.34	7	0.32-0.6	0.33	14
Beta-D-Cesium 137	Pci/L	3.3-9.5	4.3	5	3.2-3.9	3.55	2	2.7-3.4	2.9	7	2.7-9.5	3.28	14
Beta-D-Strontium 90	Pci/L	2.7-7.6	3.6	5	2.7-3.1	2.9	2	2.2-2.8	2.3	7	2.2-7.6	2.7	14
Beta-S-Cesium 137	Pci/L	0.32-0.5	0.34	5	0.32-0.5	0.41	2	0.32-0.7	0.39	7	0.32-0.7	0.37	14
Beta-S-Strontium 90	Pci/L	0.32-0.4	0.33	5	0.32-0.4	0.36	2	0.32-0.6	0.35	7	0.32-0.6	0.34	14
Dissolved Potassium 40	Pci/L	0.9-4.8	1.2	4	——	—	-	0.2-0.4	0.35	6	0.2-4.8	0.45	10
Total Gross Alpha	Pci/L	1.6-4.0	3.0	5	4.0	4.0	1	0.8-2.0	0.97	11	0.8-4.0	1.6	17
Total Gross Beta	Pci/L	3.0-10.0	5.0	5	5.0	5.0	1	1.6-6.0	2.9	11	1.6-10	3.08	17

*Group A stations	Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations	Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations	Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

Table . Comparison of metal water quality paramters for three groups of stream stations in the Regional Copper-Nickel Study Area (November, 1975, to April, 1977).

MONITORING STATION GROUPINGS*		A			B			C		
Parameter	Units	Range	Median	N	Range	Median	N	Range	Median	N
Aluminum (Al)	ug/l	19-760	120	37	22-640	100	25	1.6-710	90	208
Arsenic (As)	ug/l	0.2-3.0	0.8	25	0.3-1.0	0.8	18	0.4-5.0	0.8	148
Cadmium (Cd)	ug/l	0.01-0.24	0.04	54	0.01-0.21	0.03	63	0.01-0.45	0.03	326
Cobalt (Co)	ug/l	0.24-3.8	0.70	54	0.16-2.0	0.5	65	0.1-11	0.4	291
Copper (Cu)	ug/l	0.5-8.4	3.1	56	0.16-8.4	2.2	65	0.16-12	1.3	326
Total Iron (Fe)	ug/l	60-1300	453	55	220-3800	1197	64	19.2-5500	560	338
Dissolved Iron	ug/l	20-580	152	36	30-1500	553	41	10-3550	310	171
Lead (Pb)	ug/l	0.16-3.8	0.7	56	0.1-2.6	0.6	62	0.08-6.4	0.5	325
Manganese (Mn)	ug/l	30-1200	140	40	30-810	120	53	5-860	35	228
Mercury (Hg)	ug/l	0.01-0.4	0.07	24	0.01-0.4	0.07	18	0.01-0.6	0.08	141
Nickel (Ni)	ug/l	0.6-210	2.0	54	0.8-10	2.0	65	0.08-30	1.0	328
Zinc (Zn)	ug/l	0.5-14	2.8	56	0.4-30	3.0	65	0.1-23	2.0	325

*Group A stations	Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations	Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations	Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

Table . Comparison of miscellaneous water quality parameters for three groups of streams and all stations monitored in the Regional Copper-Nickel Study Area (November, 1975, to September, 1977).

MONITORING STATION GROUPINGS*			A			B			C			ALL STATIONS	
Parameter	Unit	Range	Median	N	Range	Median	N	Range	Median	N	Range	Median	N
Silver (Ag)	ug/l	0.02-0.1	0.036	22	0.02-0.04	0.034	16	0.008-0.04	0.032	134	0.008-0.10	0.032	172
Titanium (Ti)	ug/l	32-32	32	3	8-80	32	28	8-80	32.8	26	8-80	32.5	57
Fluoride (F)	mg/l	0.05-0.6	0.20	48	0.1-1.5	0.18	33	0.02-0.9	0.10	266	0.02-1.5	0.10	347
Chromium (Cr)	ug/l	0.3-2.1	0.52	22	0.2-2.0	0.53	16	0.08-1.7	0.40	146	0.08-2.1	0.40	184
Selenium (Se)	ug/l	0.8-3.0	0.82	17	0.8-1.6	0.84	11	0.8-2.0	0.82	117	0.8-3.0	0.82	145
Acidity (H^+)	meq/l	0.08-1.5	0.20	24	0.1-0.8	0.25	18	0.08-18	0.15	155	0.08-18.0	0.20	197
Cyanide (CN)	ug/l	0.8-9.0	0.87	10	0.8-0.8	0.80	3	0.8-10	0.85	18	0.8-10	0.85	31
Barium (Ba)	ug/l	0.8-100	18.0	11	0.8-100	65	3	0.8-100	4.4	18	0.8-100	4.7	32
Dissolved Organic Carbon (DOC)	mg/l	2.8-19.5	9.1	3	12.7-36.6	18.4	10	7.8-25.4	18.7	10	2.8-36.6	18.5	23
Dissolved Inorganic Carbon (DIC)	mg/l	12-30.1	21.2	3	5-30.2	13.1	10	0.3-20.5	5.9	10	0.3-30.2	12.0	23
Filtrable Residue	mg/l			8			30			45			83
Non-filtrable Residue	mg/l	0.4-18	3	55	0.4-28	4.4	65	0.4-27	2.0	339	0.4-28	2.0	459
Dissolved Oxygen	ppm	3.2-14	9.4	56	4.8-13.8	8.4	45	0.3-14.2	9.3	318	0.3-14.2	9.3	419
Dissolved Oxygen	%	22-100	83	55	33-100	74.3	45	2-100	84.2	316	2-100	83.8	416
Chemical Oxygen Demand (COD)	mg/l	10-69	24	24	20-110	41.5	18	4-110	38.9	155	4-110	38.9	197
Biological Oxygen Demand (BOD)	mg/l	0.8-2.0	1.4	8	1.0-1.0	1.0	3	0.8-2.0	0.89	17	0.8-2.0	0.93	28
Fecal Coliforms	No./100ml	0-256	28	9	8-78	43	3	0-125	2.0	23	0-256	5.7	35
Phenols	ug/l	0.8-12	1.9	10	1.0-2.0	1.6	3	0.8-18	1.73	17	0.8-18	1.7	30
Total Kjeldahl Nitrogen N	mg/l	0.07-2.5	0.63	27	0.01-2.9	1.1	46	0.01-2.4	0.65	185	.01-2.9	0.73	258
Ortho-phosphorus	ug/l	0.8-60	9.9	23	0.8-40	10.0	18	0.8-41	6.1	140	0.8-60	8.1	181

*Group A stations	Bob Bay-1, St. Louis R.-1, Partridge R.-1.
Group B stations	Dunka R.-1, Partridge R.-2, Embarrass R.-1.
Group C stations	Kawishiwi R.1-7, Bear Island R.-1, Isabella R-1, Filson Creek-1, Keeley Creek-1, Dunka R.-2, Stoney R.-5, St. Louis R-2 and 3, Partridge R.3-5, Embarrass R.-2, Whiteface R.-1 and 2, Water Hen Creek.

APPENDIX 3

Summary of Lake
Water Quality Data

Table __. Regional Copper-Nickel Study Lake Water Quality Data (1976-7)

Lakes	Cu ug/l				Ni ug/l				Pb ug/l				Zn ug/l				Cd ug/l			
	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N
August																				
LA-1	1.5-1.7	1.6	9%	3	0.8-0.9	0.8	9%	3	0.3-0.6	0.4	35%	3	1.3-7.4	2.2	90%	3	0.01-0.05	0.02	81%	3
LA-2	1.0-1.7	1.3	26%	3	0.4-1.0	0.8	42%	3					0.5-4.2	1.1	103%	3	0.01-0.11	0.03	106%	3
Bass	0.9-1.7	1.2	26%	5	1.1-4.0	2.2	46%	5	0.08-0.4	0.1	90%	4	0.2-2.0	0.9	75%	4	0.005-0.03	0.02	46%	4
Bearhead	0.2-1.5	0.4	78%	4	0.8-1.0	0.8	12%	4	0.1-0.2	0.2	35%	3	0.4-2.0	0.8	98%	3	.008-0.1	0.02	117%	3
Bear Island																				
LBI-1	0.7-1.0	0.8	15%	4	0.8-1.1	0.9	13%	4	0.1-0.2	0.2	36%	3	0.5-0.8	0.7	23%	3	0.01-0.04	0.02	65%	3
LBI-2	0.5-0.8	0.7	25%	3	0.8-1.2	0.9	25%	3	0.08-0.2	0.1	61%	2	0.6-0.7	0.6	11%	2	0.01-0.04	0.02	85%	2
Big	0.5-1.2	0.8	58%	2	0.8-1.0	0.9	16%	2		0.2		1		0.6		1		0.02		1
Birch																				
LBH-1	1.2-5.4	1.6	67%	7	1.0-3.0	2.8	31%	7	0.3-1.4	0.4	77%	7	0.6-10.0	7.7	87%	7	.01-.2	0.03	42%	7
LBH-2	1.1-2.7	2.6	33%	5	2.0-5.0	3.2	33%	5	0.2-1.6	0.3	100%	5	0.7-7.0	1.9	83%	5	0.01-0.1	0.07	71%	5
LBH-3	0.5-10.0	1.5	26%	6	0.8-3.0	1.0	61%	6	0.2-1.0	0.3	77%	6	0.9-5.1	1.2	80%	6	.02-.09	0.02	84%	6
LBH-4	1.3-2.5	1.5	32%	4	1.0-2.0	1.2	40%	4	0.3-1.1	0.4	58%	4	0.5-5.6	0.6	121%	4	.02-.09	0.04	65%	4
Clearwater		1.0		1		0.8		1		0.4		1		29*		1		0.02		1
Colby																				
LCy-1	1.6-4.8	3.8	32%	6	1.0-5.7	2.0	69%	6	0.2-1.7	0.6	64%	6	1.0-35.5*	2.0	154%	6	0.03-0.2	0.04	89%	6
LCy-2	3.2-7.3	4.2	35%	4	0.8-6.0	2.0	84%	4	0.2-1.4	0.6	73%	4	1.2-4.4	2.0	58%	4	.02-.2	0.04	88%	4
Cloquet	0.4-1.0	0.8	25%	2	0.8-0.8	0.8	0%	2		0.7		1		3.3		1		0.03		1
Fall		1.4		1		0.8		1		0.3		1		1.3		1		0.01		1
Gabbro																				
LG01	1.8-2.6	2.1	15%	4	0.8-1.2	0.9	22%	4	0.5-1.3	0.8	38%	4	1.7-28.1	2.0	143%	3	0.03-0.34	0.06	123%	4
LG02	1.6-2.9	2.0	26%	4	0.8-0.8	0.8	0%	4	0.4-1.9	0.6	83%	4	1.8-3.9	2.0	40%	3	0.02-0.15	0.04	84%	4
Greenwood	1.3-2.2	1.4	24%	4	0.8-1.2	1.0	16%	4	0.8-1.5	0.9	35%	3	3.6-5.6	3.8	25%	3	0.02-0.11	0.05	78%	3
Lake One		1.8		1		0.8		1		0.3		1		7.1		1		0.008		1
Long		0.4		1		1.0		1		No data				No Data				No Data		

Perch	0.6-1.0	0.9	20%	5	0.6-1.2	0.8	28%	5	0.4-1.0	0.6	34%	4	1.5-2.0	1.6	13%	4	0.03-0.05	0.04	21%	4
Pine	0.7-1.5	1.2	29%	5	0.8-2.0	0.9	47%	5	0.3-0.6	0.4	35%	4	0.8-2.3	1.2	47%	4	0.02-0.11	0.04	81%	4
Sand	0.7-1.5	1.1	28%	5	0.8-2.0	1.0	39%	5	0.4-0.7	0.6	22%	4	0.8-3.3	1.1	64%	4	0.02-0.04	0.04	29%	4
Seven Beaver																				
LSB1	0.6-2.9	1.5	56%	5	0.6-1.3	1.0	29%	5	0.6-1.2	0.6	36%	5	1.9-8.7	3.6	61%	5	0.01-0.09	0.25	61%	5
LSB2	1.6-2.8	2.2	39%	2	0.7-1.0	0.8	25%	2	0.7-1.0	0.8	25%	2	4.5-6.5	5.3	21%	2	0.02-0.05	0.04	61%	2
Slate	0.8-0.8	0.8	0%	2	0.8-2.0	1.4	61%	2		0.7		1		2.0		1	-	0.02		1
S. McDougal	0.9-2.3	1.6	62%	2		1.0		1		1.6		1		4.9		1		0.04		1
Tofte	0.7-2.1	1.2	43%	3	0.56-2.0	1.0	49%	5	0.1-0.6	.22	71%	5	0.30-1.1	0.6	47%	5	0.008-0.06	0.02	80%	5
Triangle		.40		1		0.80		1		0.08		1		0.70		1		0.01		1
Turtle	0.2-0.6	0.6	45%	4	0.8-1.2	0.9	22%	2	0.5-1.0	0.6	38%	3	0.5-3.5	0.7	107%	3	0.008-.04	.02	71%	3
White Face	1.3-1.6	1.4	10%	3	0.8-0.9	0.8	9%	3	0.3-0.4	0.4	22%	3	1.5-2.1	1.6	49%	3	0.01-0.03	0.02	55%	3
White Iron																				
LWI-1	1.4-4.1	2.0	45%	7	0.8-1.4	1.0	24%	7	0.2-1.0	0.3	67%	7	0.6-2.6	1.9	41%	7	0.008-0.8	0.02	215%	7
LWI-2	1.6-2.3	2.0	15%	4	0.7-1.0	0.8	15%	4	0.2-1.0	0.4	71%	4	1.0-2.4	1.3	40%	4	0.02-0.07	0.02	68%	4
Wynne	1.0-6.0	1.9	78%	5	0.8-5.0	2.0	66%	5	0.2-0.4	0.3	27%	4	1.4-3.5	1.7	44%	4	.02-0.2	0.04	107%	4
Region	0.2-10.0	1.5	80%	129	0.4-6.0	1.0	74%	129	0.08-1.9	0.4	72%	114	0.2-35.5	1.8	163%	113	0.008-0.8	0.03	160%	114

Table continued

		Fe	ug/l			Co	ug/l			Hg	ug/l			As	ug/l			l	ug/l	
Lakes	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N	Range	M	CV	N
August																				
LA-1	160-230	200	15%	4	.2-.4	.3	25%	3	.23-.63	.45	38%	4		No data			32-73	42	44%	3
LA-2	220-300	235	17%	3	.2-.4	.4	27%	1	.23-.40	.32	27%	3		No data			20-44	36	29%	2
Bass	16-130	60	71%	5		.5		1	.3-.4	.3	10%	3	.4-.7	.6	27%	3		38		1
Bearhead	110-160	125	17%	4		.2		1	.08-.36	.22	90%	2	.4-.8	.6	47%	2		12		1
Bear Island																				
LBI-1	70-170	85	42%	4		.2		1	.15-.24	.20	33%	2	.4-.7	.6	39%	2		30		1
LBI-2	180-280	200	31%	3		.2		1		.21		1		.6		1		26		1
Big	65-140	102	52%	2		.2		1		No data				No data				10		1
Birch																				
LBH-1	210-800	370	51%	7	.2-.4	.3	29%	4	.08-.44	.1	80%	7	.4-.8	.7	35%	3	20-100	92	62%	3
LBH-2	170-525	350	44%	5	.2-.5	.3	37%	4	.08-.40	.2	58%	5		.4		1	19-100	74	64%	3
LBH-3	80-420	308	50%	6	.2-.5	.3	34%	4	.08-.4	.19	61%	6	.5-.6	.6	17%	2	13-140	78	82%	3
LBH-4	110-400	345	43%	4	.2-.4	.3	29%	4	.08-.4	.12	83%	4		No data			13-100	67	73%	3
Clearwater	50-70	60	24%	2		.2		1		No data				No data				13		1
Colby																				
LCy-1	190-2300	410	91%	6	.2-.5	.3	46%	3	.08-.4	.14	60%	6	.4-2.1	1.4	66%	3	220-400	310	41%	2
LCy-2	340-510	355	21%	4	.2-.4	.3	29%	4	.08-.4	.12	70%	4		No data			180-470	190	59%	3
Cloquet	440-530	510	6%	2		.2		1		No data				No data				180		1
Fall	230-300	265	19%	2		.2		1		No data				No data				70		1
Gabbro																				
LG01	450-850	465	32%	4	.2-.4	.3	26%	4	.08-.6	.4	55%	4		No data			37-120	110	51%	3
LG02	390-910	535	39%	4	.2-.4	.3	29%	4	.08-.5	.4	51%	4		No data			34-160	120	62%	3
Greenwood	610-1300	865	32%	4		.4		1	.24-.36	.30	28%	2	.6-.9	.8	24%	2		400		1
Lake One	220-230	225	3%	2		.2		1		No data				No data				32		1
Long		1260		1		No data				No data				No data				No data		
Perch	490-1040	590	34%	5		.2		1	.15-.32	.31	37%	3	.4-.6	.6	24%	3		92		1
Pine	60-270	140	63%	5		.2		1	.18-.49	.21	58%	3	.4-.6	.6	24%	3		79		1
Sand	410-880	750	26%	5		.4		1	.08-.33	.32	58%	3	.4-.8	.6	33%	3		160		1

Seven Beaver																				
LSB1	740-1300	922	25%	6	.4-.5	.4	16%	2	.30-.64	.40	31%	5	.5-1.2	1.1	40%	3	226-260	243	10%	2
LSB2	730-1700	1540	31%	3	.4-.4	.4	0%	2	.28-.40	.34	75%	2	No data				270-326	298	13%	2
Slate	800-1000	900	16%	2		1.3		1	No data				No data					180		1
S. McDougal	920-1400	1410	49%	2		.5		1	No data				No data					610		1
Tofte	16-70	32	59%	6	.2-1.6	.9	105%	2	.08-.31	.25	56%	3	.6-.8	.6	16%	3	4-14	9	56%	3
Triangle	60-80	70	20%	2		.2		1	No data				No data				No data			
Turtle	120-300	195	38%	4		.2		1	.18-.34	.26	44%	2	.6-.7	.7	6%	2		22		1
White Face	680-1100	968	19%	4	.4-.6	.4	21%	3	.11-.40	.15	63%	4	No data				76-135	130	29%	3
White Iron																				
LWI-1	200-840	370	57%	7	.2-.4	.3	21%	4	.08-.4	.3	52%	7	.4-.7	.6	27%	3	44-100	67	40%	3
LWI-2	360-480	415	13%	4	.2-.6	.4	36%	4	.08-.4	.3	52%	4	No data				63-150	130	40%	3
Wynne	270-1400	390	72%	5		2.2		1	.19-.43	.39	38%	3	.5-1.5	1.2	47%	3		33		1
Region	16-2300	350	88%	138	.2-2.2	.4	77%	72	.08-.64	.28	53%	96	.4-2.1	.6	50%	41	4-610	76	106%	60

Table continued

	Tot-P ug/l					Tot-N ug/l				secchi disk -m				N:P
Lakes	Range	M	Pv	CV	N	Range	M	CV	N	Range	M	CV	N	Ratio
August														
LA-1	2-20	14	20	62%	4	310-500	405	33%	2	1.5-2.0	1.9	12%	4	30
LA-2	1-30	14	30	98%	3	330-435	383	19%	2	1.8-1.9	1.9	3%		27
Bass	11-38	19		47%	5	430-470	460	5%	3	2.5-6.0	3.4	39%	4	24
Bearhead	6-20	12		48%	4	460-940	700	48%	2	1.8-3.8	3.3	35%	3	58
Bear Island														
LBI-1	14-30	19		33%	4	340-590	465	38%	2	2.0-3.0	2.5	17%	4	24
LBI-2	15-64	20		82%	3		500		1	2.2-3.0	2.6	22%	2	25
Big	30-36	33		13%	2		530		1	2.9-3.0	3.0	2%	2	16
Birch														
LBH-1	9-67	16	20	86%	7	610-1030	650	30%	3	1.5-1.8	1.6	9%	5	41
LBH-2	17-220	21	30	144%	5	660-770	715	11%	2	1.2-1.7	1.3	15%	5	34
LBH-3	8-70	25		72%	6	410-650	445	26%	3	1.3-3.5	1.6	43%	4	24
LBH-4	7-40	25		56%	4	520-660	590	17%	2	1.7-1.9	1.8	5%	4	24
Clearwater	11-50	30		90%	2		580		1	4.0-4.5	4.2	8%	2	19
Colby														
LCy-1	1-34	14	30	67%	6	870-2230	1065	44%	4	0.6-6.0	1.8	78%	6	76
LCy-2	17-24	20	20	15%	4	880-910	895	2%	2	1.2-2.1	1.6	23%	4	45
Cloquet	30-40	35		20%	2		750		1		0.9		1	21
Fall	22-30	26		22%	2		360		1		1.8	0%	2	14
Gabbro														
LG01	20-46	22	20	44%	4	330-800	675	26%	2	1.1-1.8	1.2	23%	4	31
LG02	10-25	21	20	34%	4		600	0%	2	1.1-1.8	1.6	20%	4	29
Greenwood	26-56	44		30%	4	300-950	625	79%	2	0.4-1.1	0.8	40%	4	14
Lake One	16-40	28		61%	2		390		1	2.2-2.4	2.3	6%	2	14
Long	28-70	34		52%	3	120-850	485	100%	2		1.0		1	14
Perch	19-40	26		28%	5	550-1100	790	34%	3	0.8-2.5	1.8	41%	4	30
Pine	1-30	17		68%	5	500-680	620	15%	3	1.2-2.8	1.9	36%	5	36
Sand	17-40	33		33%	5	590-710	680	9%	3	0.8-1.5	1.3	22%	5	21

Seven Beaver														
LSB1	27-40	30	40	17%	6	890-2110	1010	43%	5	0.4-0.9	0.8	27%	5	34
LSB2	23-44	40	40	40%	31	840-1000	920	12%	2	0.7-0.8	0.7	8%	3	23
Slate	20-50	35		61%	2		650		1		1.6		1	27
S. McDougal	40-53	46		20%	2				0	0.5-0.9	0.7	40%	2	
Tofte	8-23	10		49%	6	340-420	360	13%	3	4.2-5.6	4.8	10%	6	36
Triangle	17-20	18		11%	1		360		1	3.1-3.8	3.4	14%	2	20
Turtle	17-28	22		22%	4	630-690	660	6%	2	1.5-1.8	1.8	9%	4	30
White Face		30	40	24%	4	900-1400	1020	24%	3	0.9-1.3	1.0	17%	4	34
White Iron														
LWI-1	14-43	23	40	39%	7	370-630	505	23%	4	1.3-2.0	1.6	17%	6	22
LWI-2	11-30	21	30	39%	4	590-730	640	11%	3	1.3-2.0	1.4	20%	4	30
Wynne	5-30	17		53%	5	630-9999	885	143%	4	0.7-2.5	1.8	37%	5	52
NORTH	1-220	21		90%	100	300-1100	588	33%	51	0.4-6.0	1.8	54%	90	
SOUTH	1-70	28		49%	40	120-9999	900	136%	27	0.4-6.0	1.4	66%	36	
Region	1-220	23		80%	140	120-9999	633	133%	78	0.4-6.0	1.8	58%	126	

Table continued

	Color				TOC				SP. Cond			
Lakes	Range	M	CV	N	Range	M.	CV	N	Range	M	CV	N
August												
LA-1	40-80	55	33%	4	12-15	12.5	11%	4	41-57	49	13%	4
LA-2	48-80	72	27%	3	12-14	13.	8%	3	42-67	51	24%	3
Bass	3-30	12	72%	5	6.0-7.3	7.0	8%	5	73-86	85	8%	5
Bearhead	2-50	6	122%	4	5.8-16	6.5	56%	4	33-103	39	60%	4
Bear Island												
LBI-1	35,75	45	35%	4	10-14	11.	15%	4	43-52	49	8%	4
LBI-2	39-70	60	28%	3	12-12	12	0%	3	42-56	48	14%	3
Big	14-30	22	51%	2	6.3-11	8.8	36%	2	62-71	66	10%	2
Birch												
LBH-1	35-280	72	73%	8	8.4-28	14.5	36%	8	59-107	74	19%	8
LBH-2	30-100	62	41%	5	13-16	14.	8%	5	24-109	88	42%	5
LBH-3	5-100	75	51%	6	7.1-17	14.2	25%	6	42-123	85	31%	6
LBH-4	46-90	70	26%	4	13-14	13.8	4%	4	83-127	84	21%	4
Clearwater	2-10	6	94	2	6.7-8.4	7.6	16%	2	38-39	38	2%	2
Colby												
LCy-1	35-360	88	82%	6	11-35	17.	49%	6	74-328	169	48%	6
LCy-2	60-170	78	52%	4	11-20	14.	26%	4	170-389	192	51%	4
Cloquet	90-120	105	20%	2	14-22	18.	31%	2	54-79	66	27%	2
Fall	45-160	102	79%	2	13-14	13.5	5%	2	43-53	48	15%	2
Gabbro												
LG01	46-160	130	43%	4	10-16	13.5	20%	4	42-87	50	34%	4
LG02	55-160	130	38%	4	11-16	13.5	16%	4	48-101	58	36%	4
Greenwood	160-360	195	36%	5	16-38	25	33%	5	36-64	42	24%	5
Lake One	27-70	48	63%	2	16 38	25	0%	2	27-33	30	14%	2
Long		180		1	20-25	22.5	16%	2		46		
Perch	45-100	80	30%	5	11-17	14.	18%	5	25-38	30	16%	5
Pine	30-80	45	38%	5	13-28	15.	35%	5	54-67	58	10%	5
Sand	60-180	95	44%	5	16-36	19.	38%	5	52-79	70	15%	5

Seven Beaver												
LSB1	85-400	162	67%	6	17-38	30.5	25%	6	25-88	54	34%	6
LSB2	110-280	200	43%	3	27-30	35.	15%	3	34-90	51	49%	3
Slate	90-180	135	47%	2	12-27	19.5	54%	2	51-107	79	50%	2
S. McDougal	260-320	290	15%	2	23-28	25.5	14%	2	36-49	42	27%	2
Tofte	21-25	5	109%	6	4.6-7.6	50.	20%	6	146-166	150	5%	6
Triangle	2-30	16	124%	2	6.6-8.3	7.4	16%	2	65-76	70	11%	2
Turtle	25-40	32	20%	4	11-14	11.5	13%	4	25-29	26	6%	4
White Face	105-350	165	54%	4	17-37	18.5	31%	4	50-80	60	16%	4
White Iron												
LWI-1	53-140	89	34%	7	12-21	14.2	19%	7	39-76	64	21%	7
LWI-2	75-120	90	20%	4	13-16	13.5	10%	4	41-74	56	25%	4
Wynne	80-320	130	62%	5	14-29	22.	29%	5	112-232	161	27%	5
North of Divide	1-360	70	82%	103	4.6-38	14.	45%	103				
South of Divide	14-400	107	136%	38	6.5-38	20.	40%	39				
Region	1-400	80	85%	141	4.6-38	14.	50%	142	24-389	65	68%	141

Table continued

Lakes	pH Range	M	CV	N	Alkalinity mg/l Range	M	CV	N	Sulfate mg/l Range	M	CV	N
August												
LA-1	6.3-7.0	6.7	4%	4	14-16	16	6%	4	4.1-11.0	4.2	49%	4
LA-2	6.2-7.0	6.5	7%	3	15-21	16	18%	3	4.4-10.0	7.9	38%	3
Bass	6.9-8.2	7.6	7%	5	27-34	30	10%	5	2.7-11.0	10.7	40%	5
Bearhead	7.2-8.1	7.5	5%	4	10-31	14	53%	4	4.0-12.0	4.9	59%	4
Bear Island												
LBI-1	7.1-7.6	7.4	3%	4	11-16	14	15%	4	2.3-7.6	5.8	42%	4
LBI-2	7.0-7.2	7.1	1%	3	14-16	15	7%	3	4.0-4.3	3.9	64%	3
Big	7.4-7.6	7.5	2%	2	23-24	25	6%	2	5.5-6.0	5.8	6%	2
Birch												
LBH-1	6.4-7.7	7.0	6%	8	16-32	70	23%	8	5.8-14.0	11.2	23%	7
LBH-2	6.4-7.7	7.2	7%	5	21-36	24	24%	5	7.7-14.0	12.2	20%	5
LBH-3	6.2-7.6	7.2	7%	6	13-34	26	27%	6	3.4-12.5	10.4	36%	6
LBH-4	6.6-7.7	7.1	6%	4	25-37	26	19%	4	7.0-12.0	10.0	24%	4
Clearwater	6.7-6.9	6.8	2%	2	10-16	13	33%	2	4.0-5.5	4.8	22%	2
Colby												
LCby-1	6.8-7.8	7.2	5%	6	16-38	34	29%	6	8.7-55.0	28.0	53%	6
LCby-2	6.8-7.5	7.0	4%	4	33-37	36	6%	4	22.0-140.0	47.5	81%	4
Cloquet	7.2-7.2	7.2	0%	2	21-21	21	0%	2	5.6-8.0	6.8	25%	2
Fall	6.7-7.0	6.8	3%	2	13-16	14	15%	2	5.4-7.5	6.4	23%	2
Gabbro												
LGO-1	6.9-7.2	7.0	2%	4	16-37	18	46%	4	2.8-8.2	4.2	48%	4
LGO-2	6.8-7.3	7.0	4%	4	18-45	20	49%	4	2.8-8.0	7.9	39%	4
Greenwood	6.4-6.9	6.6	3%	5	2-11	6	53%	5	4.1-12.0	7.0	44%	4
Lake One	6.7-6.8	6.8	1%	2	6-15	10	61%	2	4.2-6.0	5.1	25%	2
Long		7.1		1		18		1		8.1		1
Perch	6.3-7.0	6.6	4%	5	3-24	8	77%	5	2.1-13.0	3.8	87%	5
Pine	7.1-7.9	7.6	4%	5	14-19	17	12%	5	4.6-15.0	9.0	40%	5
Sand	6.9-7.8	7.6	5%	5	17-23	22	11%	5	1.4-11.0	7.0	56%	5

Seven Beaver												
LSB-1	5.7-7.4	7.0	10%	6	1-36	13	79%	6	1.0-10.0	5.2	57%	6
LSB-2	5.7-7.0	6.1	11%	3	14-44	15	70%	3	3.2-4.9	4.7	22%	3
Slate	6.8-7.4	7.1	6%	2	21-43	32	49%	2	1.0-5.6	3.2	106%	2
S. McDougal	6.7-7.0	6.8	3%	2	9-11	10	14%	2	6.0-14.0	10.0	57%	2
Tofte	7.3-8.8	7.8	6%	6	64-72	70	5%	6	1.0-10.0	6.9	48%	6
Triangle	7.3-7.7	7.5	4%	2	30-34	32	9%	2	4.3-5.0	4.6	11%	2
Turtle	6.5-7.5	7.0	6%	4	6-9	6	21%	4	1.0-6.0	5.0	53%	4
White Face	6.8-7.3	6.9	3%	4	19-25	20	13%	4	9.6-11.0	10.2	7%	4
White Iron												
LWI-1	6.4-7.5	6.9	6%	7	14-20	16	14%	7	1.0-10.4	9.4	46%	7
LWI-2	6.3-7.3	6.8	6%	4	16-23	18	16%	4	1.5-11.0	7.7	58%	4
Wynne	6.8-7.6	7.4	4%	5	42-73	43	26%	5	8.7-35.0	27.0	45%	5
North	6.2-8.8	7.1	7%	103	2-72	18	66%	103	1.0-14.0	7.0	49%	100
South	5.7-7.9	7.2	7%	38	1-73	22	53%	38	1.0-140.0	9.6	127%	38
Region	5.7-8.8	7.1	7%	141	1-73	19	62%	141	1.0-140.0	7.8	136%	138