PRECIPITATION CHEMISTRY AND ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN NORHEASTERN MINNESOTA

1978

File Copy

PRECIPITATION CHEMISTRY AND ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS IN NORTHEASTERN MINNESOTA

by

S. J. Eisenreich
G. J. Hollod
S. Langevin

Environmental Engineering Program
Department of Civil and Mineral Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Prepared for

Minnesota Environmental Quality Council
and
Minnesota State Planning Agency

1978

Table of Contents

Conclusions

1. Bulk deposition of chemical components was uniform generally throughout the study area.
2. Bulk deposition of nutrients, anions, cations and trace metals in the study area was typical of remote, mid-continental areas, with the exception of Fe.
3. N.E. Minnesota exists in an atmospheric deposition "crease" where loading values were higher generally to the north, south, east and west. The primary cause is the absence of upwind pollutional sources.
4. Canopy throughfall deposition was not significantly different from bulk deposition, with the exception of TOC and perhaps SO_4.
5. Wet-only precipitation concentrations were typical of remote areas, and wet deposition accounted for 30-100% of bulk deposition.
6. Atmospheric particulate concentrations were typical of remote, mid-continental areas, and dry deposition accounted for 10-100% of bulk deposition. Iron and Al deposition in bulk collectors was underestimated by a factor of up to 5 times.
7. Elements which favor a vapor phase at some temperature were significantly enriched in air particulates. Elements exhibiting high enrichment factors are likely anthropogenic, water-soluble and biologically toxic.
8. The taconite iron industry in N.E. Minnesota affects significantly the atmospheric concentrations and deposition of Fe for much of the region.

List of Figures

List of Tables

I. Introduction

Northeastern Minnesota (N.E. Minnesota) is a heavily forested area consisting primarily of conifers, where 7-15% of the land area is covered by water, and the granitic bedrock is exposed in many locations (i.e., shallow soil depth). Although the Minnesota Pollution Control Agency has labelled the region an air quality "non-attainment area" with respect to total suspended solids (TSP), little is known of the quality of wet and dry precipitation. Gorham (1977), Wright (1974) and Comerford and White (1976) have reported on the acidity, major cation and anion and nutrient content of precipitation in N.E. Minnesota, while Schindler (1978) has documented precipitation chemistry for the Experimental Lakes Area of Ontario from 1971-1977. Krupa (1977) has investigated the cation, anion, acidity and nutrient components in wet-only precipitation for east-central Minnesota in the vicinity of a coal-fired power plant.

Outside of the immediate area, Ontario Hydro (1977) has determined the loading rates of nutrients, cations, anions and trace metals derived from bulk deposition to an area ∿ 50 Km north of the U.S.-Canadian border and near the Boundary Waters Canoe Area. Kramer (1975) and the International Joint Commission (IJC, 1977) reported the loading rates of major cations, anions,nutrients and trace metals to Lake Superior, while Eisenreich, et al. (1977) and Eisenreich (1978) have obtained similar data for the north and south basins of Lake Michigan. Gorham and Munger (1978) are investigating presently the chemistry of precipitation and dustfall in a west-east transect across North Dakota and Minnesota. Langevin, et al. (1978) have determined the trace metal content of air particulates and rain over Lake Superior and Eisenreich, et al. (1978) are conducting ongoing studies of atmospheric PCB input to Lake Superior.

Insufficient chemical data is available presently from past investigations to describe the background (existing) precipitation (wet, dry) characteristics of the region or the atmospheric deposition of chemical components such as nutrients, cations, anions and trace metals. The objective of the present project was to determine the chemical nature of precipitation in the region and to estimate atmospheric deposition. The data discussed in this report relate to this primary objective, as well as provide needed information required to assess future changes. In addition, the atmospheric data provides an important addition to the global data base for remote, mid-continental areas. This report describes the concentrations and deposition of nutrients, cations, anions and trace metals in atmospheric bulk deposition, canopy throughfall deposition, wet-only precipitation and suspended particulates.

II. Techniques of Sampling and Analysis

II-1. Sampling Sites

The atmospheric sampling stations were operated in rural, semi-rural, semi-urban and urban environments in northeastern Minnesota (N.E. Minnesota) under the auspices of the Minnesota Pollution Control Agency (MPCA) and the Copper-Nickel Regional Study Staff. Twenty-eight sampling stations were in operation during 1976 and 1977 although all instrumentation was not operable during the entire period. The sites were chosen to correspond to existing monitoring stations of the Minnesota PCA and new ones were constructed to adequately improve coverage of the regional and remote areas of N.E. Minnesota. The Fernberg Road site (7001) was chosen to represent remote, background air quality characteristics of the region. It is important to note that the Fernberg site was located immediately adjacent to and surrounded by the Boundary Waters Canoe Area (BWCA) and as such, represents the largest body of air quality data yet generated in that remote, pristene area. The air quality stations at Toimi (7007) and Kawishiwi-Spruce Road may also be viewed as sites representative of regional air quality.

Table 1 is a complete listing of air quality stations within and without the Cu-Ni Study Area that were monitored for various air parameters during the course of the study. Also included in Table 1 is a listing of the instrumentation located at each site and the date of initiation of air quality record. Figure 1(a,b,c,d) show the exact locations of the sampling sites and Figure 2 depicts the Cu-Ni Study Area.

The sites of interest to this report vary according to the mode of atmospheric occurrence for selected elements. Bulk deposition samplers were located at Fernberg (7001), Spruce Rd. (7003), Dunka Road (7006) and Hoyt Lakes (7010). Event wet-only precipitation collectors were located at Spruce Rd. (7003) and Hoyt Lakes (7010) while membrane samplers were operated during

Table 1

- **7001** Fernberg Road
  - Hi-vol 2/6/77
  - Membrane sampler 2/6/77
  - Continuous SO_2 2/12/77
  - Bulk deposition sampler 2/14/77
  - Continuous ozone 5/14/77
- **7002** Ely High School (previously site 7517 on ground at courthouse)
  - Hi-vol 11/2/76
  - Bubbler (SO_2 and NO_2) 2/6/77
- **7003** Kawishiwi Lab
  - Hi-vol 10/9/76
  - Bubbler (SO_2 and NO_2) 2/6/77
  - Cascade Impactor
- Spruce Road
  - Bulk deposition sampler 2/14/77
  - Event rain sampler 5/29/77
- **7004** Environmental Learning Center, Isabella
  - Membrane sampler 10/15/76
  - Bubbler (SO_2 and NO_2) 3/14/77-7/30/77
- **7005** Bear Head Lake State Park
  - Membrane sampler 10/15/76
  - Bubbler (SO_2 and NO_2) 2/6/77-7/30/77
- **7006** Dunka Road
  - Hi-vol 11/8/76
  - Membrane sampler 11/8/76
  - Bubbler (SO_2 and NO_2) 2/6/77
  - Bulk deposition sampler 3/16/77
- **7007** Toimi
  - Hi-vol 12/11/76
  - Membrane sampler 12/14/76
  - Bubbler (SO_2 and NO_2) 2/6/77-7/30/77
- **7008** Erie Mining Office
  - Hi-vol 10/9/76
  - Membrane sampler 10/9/76
  - Fluoride double tape sampler 4/6/77
- **7009** Hoyt Lakes Police Dept. (previously site 7520 on ground)
  - Hi-vol 1/13/77
  - Bubbler (SO_2 and NO_2) 2/6/77

7010 Hoyt Lakes Golf Course
  Hi-vol 10/9/76
  Membrane sampler 10/9/76
  Bubbler (SO_2 and NO_2) 2/6/77-7/30/77
  Bulk deposition sampler 2/15/77
  Event rain sampler 5/20/77
  Cascade Impactor

7011 Whiteface
  Membrane sampler 1/31/77
  Bubbler (SO_2 and NO_2) 2/6/77-7/30/77

7514 Mountain Iron Post Office
  Hi-vol 5/69
  Fluoride double tape sampler 9/77

1300 Virginia City Hall
  Hi-vol 9/68

7516 Hibbing Court House
  Hi-vol 5/69

7013 Babbitt City Hall
  Membrane sampler 2/24/77

7012 Minnamax Office
  Continuous SO_2 12/14/76-3/10/77

7412 Scanlon (Cloquette)
  Hi-vol 8/74
  Bubbler (SO_2) 8/74
  Membrane sampler 2/18/77

7501 107th Ave. West, Duluth
  Hi-vol 9/68
  Bubbler (SO_2) 9/68

7502 88th Ave. West, Duluth
  Hi-vol 8/70

7504 1628 West Superior St., Duluth (Ryland Ford)
  Hi-vol 11/68
  Bubbler (SO_2) 11/68

7505 4424 Regent
  Hi-vol 11/68

7506 Duluth Airport
  Hi-vol 9/68
  Bubbler (SO_2 and NO_2) 1/77

7512 Duluth City Hall
  Hi-vol 9/68
  Bubbler (SO_2 and NO_2) 9/68

7523	425 West Superior St., Duluth (KDAL) **Hi-vol** 1/75 (daily)
7527	39th Ave. West, Duluth (West End) **Hi-vol** 10/27/76 **Membrane** 10/27/76 **Bubbler** (SO_2 and NO_2) 10/27/76
7522 and 7526	314 West Superior St., Duluth (Torrey Building) **Continuous** SO_2 1975 (incomplete data set) Smoke spot sampler 1975 (incomplete data set) **Continuous** CO 1975 (incomplete data set)
7528	Floodwood **Hi-vol** 4/77

Figure 1

Air Quality Site Locations

Figure 1a

AIR QUALITY SITE LOCATIONS

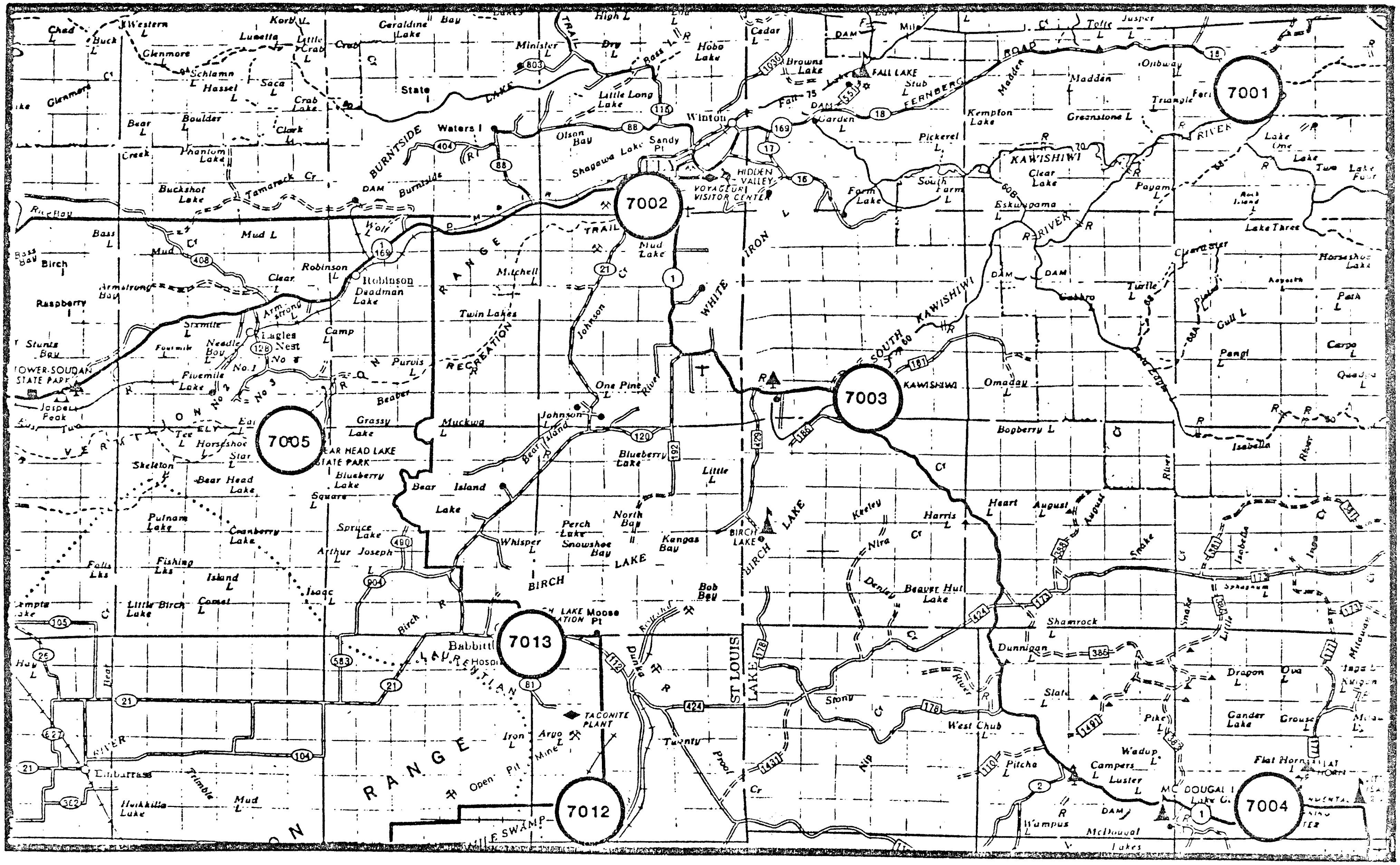


Figure 1b

AIR QUALITY SITE LOCATIONS

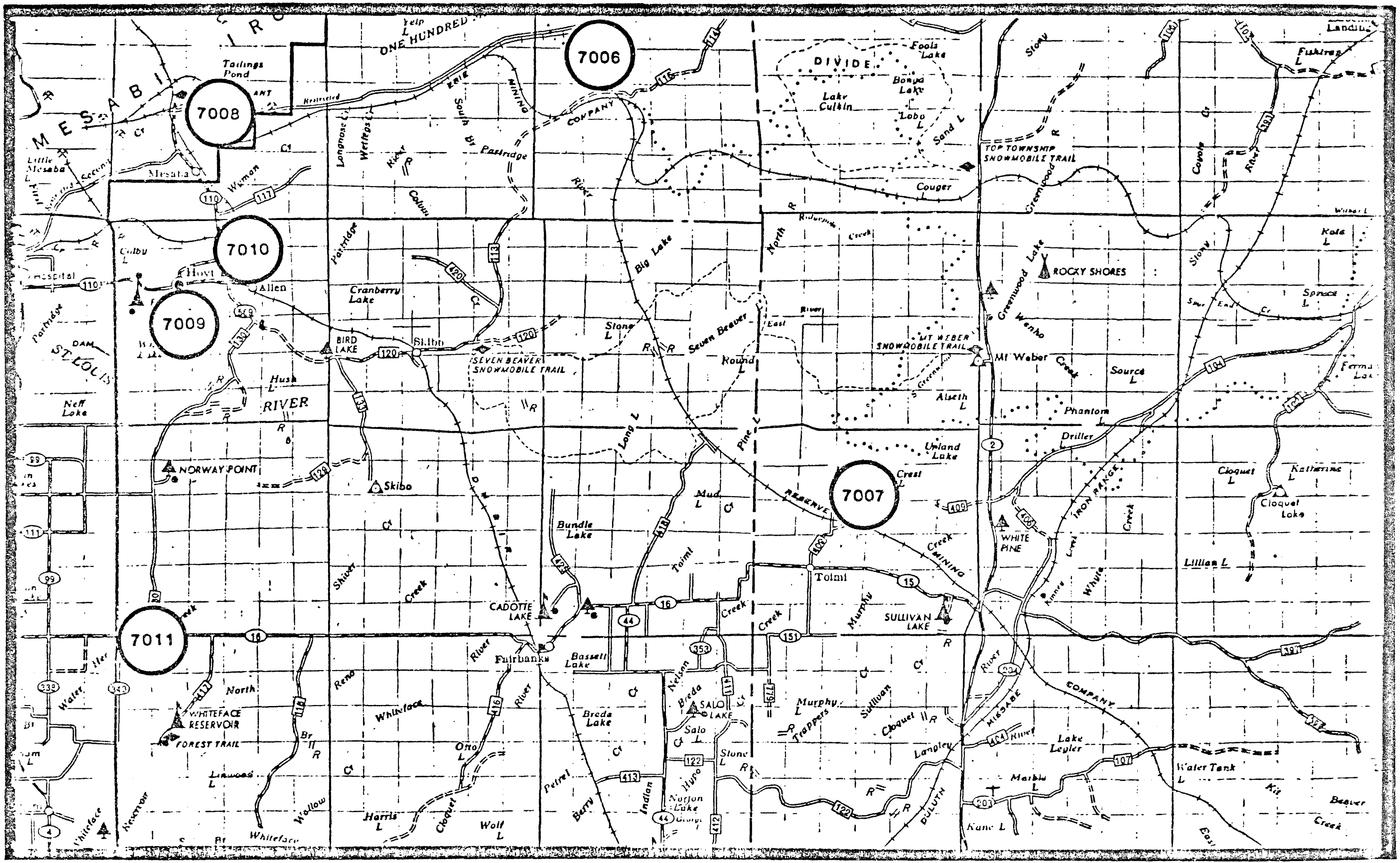
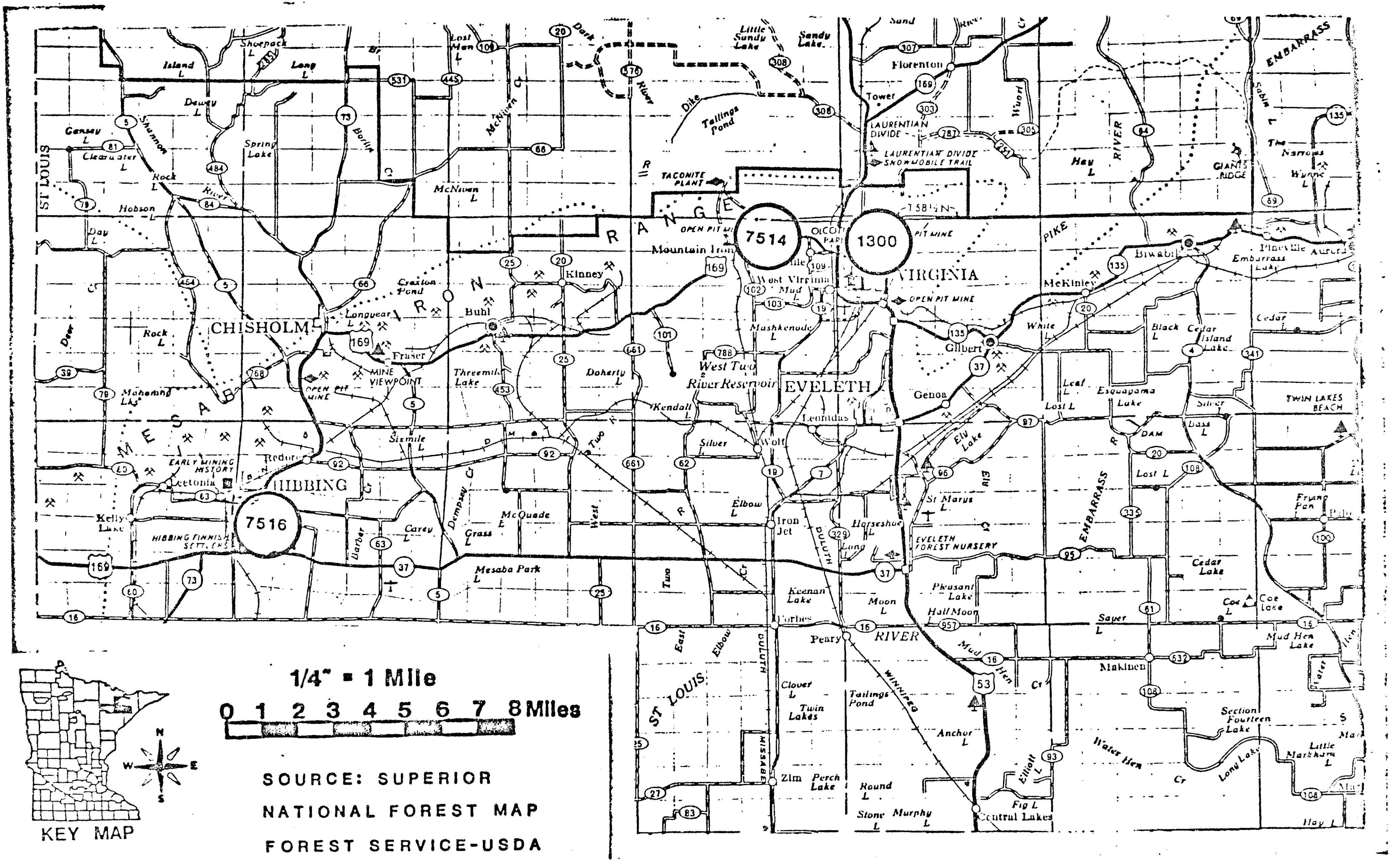


Figure 1c

AIR QUALITY SITE LOCATIONS



SOURCE: SUPERIOR NATIONAL FOREST MAP FOREST SERVICE-USDA DULUTH, MINN. 1972

Figure 1d

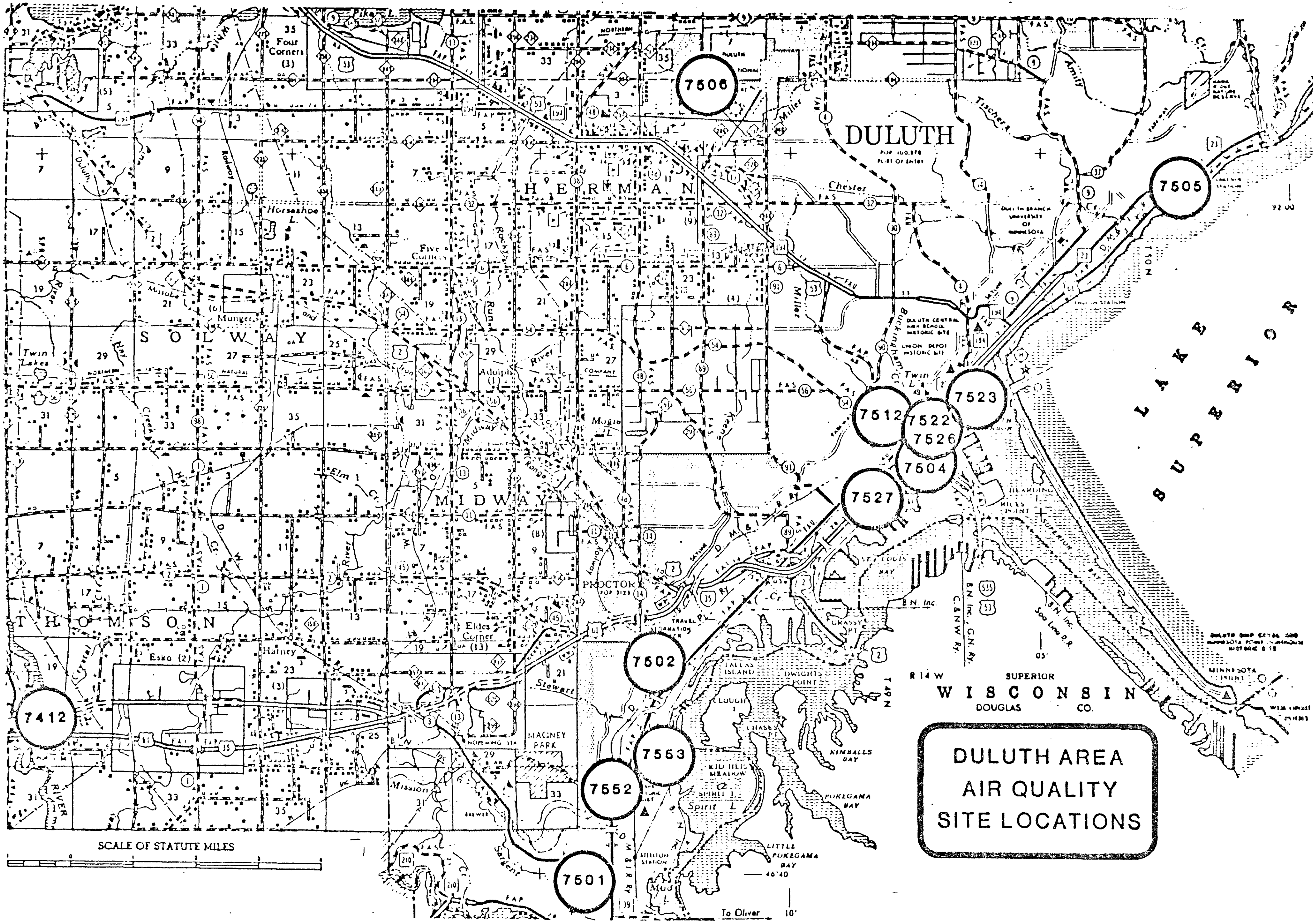
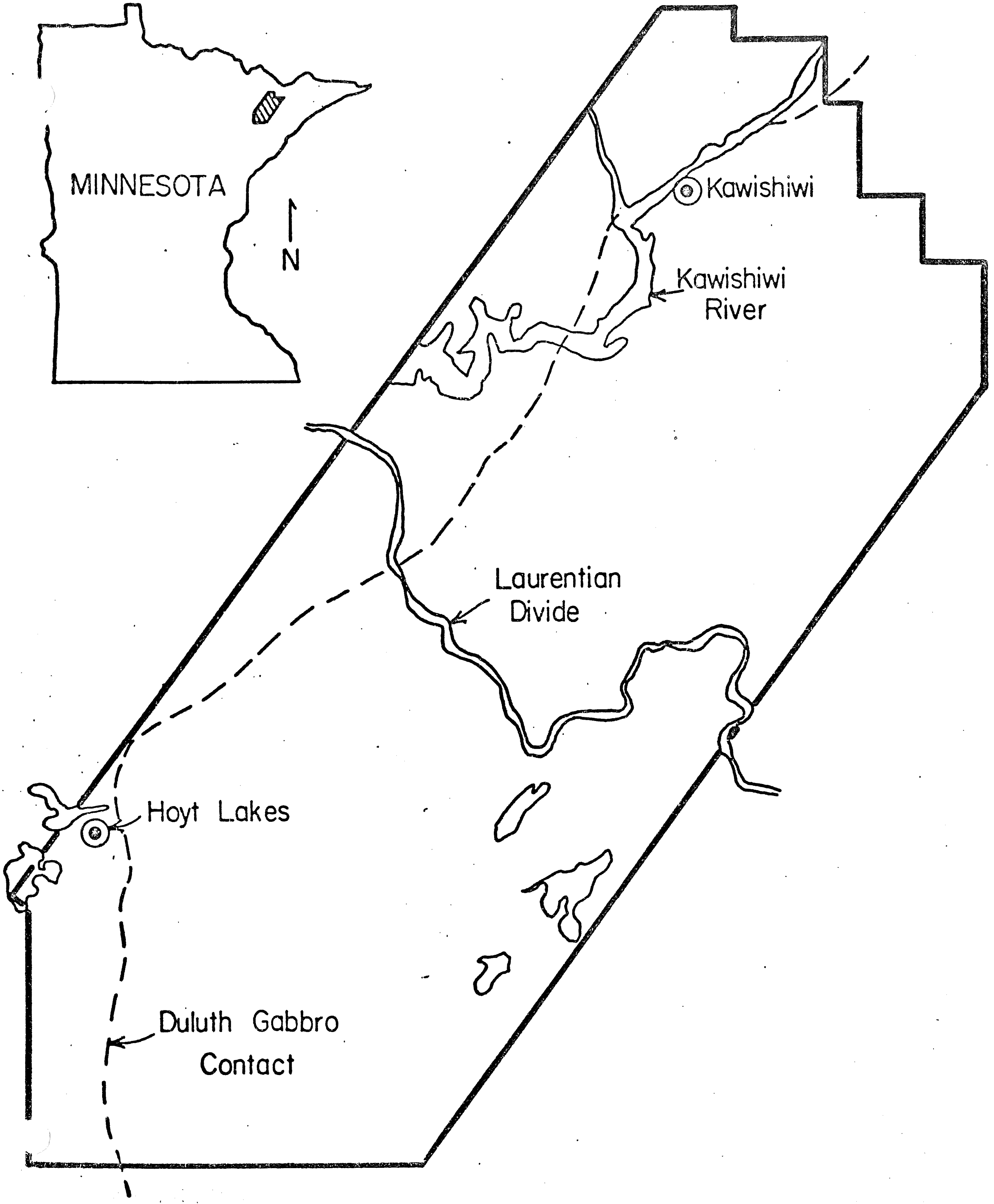

DULUTH AREA
AIR QUALITY
SITE LOCATIONS
7506
7505
7512
7522
7523
7526
7504
7527
7502
7553
7552
7501
7412
DULUTH
HERMAN
SOLWAY
MIDWAY
THOMSON
PROCTOR
LAKE SUPERIOR
WISCONSIN
SUPERIOR
DOUGLAS CO.
Four Corners
Five Corners
Horseshoe L.
Munger
Adolph
Esko
Harney
Eldes Corner
Twin Lakes
Magney Park
St. Louis Bay
Spirit L.
Pokegama Bay
Kimballs Bay
Little Pokegama Bay
To Oliver
SCALE OF STATUTE MILES

Figure 2

Cu-Ni Study Area



MINNESOTA
N
Kawishiwi
Kawishiwi River
Laurentian Divide
Hoyt Lakes
Duluth Gabbro Contact

1977 at eleven sites throughout the region representing remote rural, semi-rural, semi-urban and urban environments (Table 1). However, the membrane data collected at only four sites was thought to be typical of regional air quality and were located at Dunka Rd. (7006), Isabella (7004), Toimi (7007) and Fernberg (7001). The data from these sites were used to estimate dry deposition to N.E. Minnesota. Cascade impactor measurements for determination of particle size were obtained at Kawishiwi (7003) and Hoyt Lakes (7010) to correspond to sites of intensive air sampling for other parameters and to discern regional differences in particle size behavior if present.

II-2. Sampling of Bulk Deposition, Canopy Throughfall, Wet-Only Precipitation and Atmospheric Particulates

II- 2-1. Sampling of Bulk Deposition

Bulk deposition was collected at four sites in N.E. Minnesota from February through December, 1977. The four sites were: Fernberg Rd. (7001), Spruce Rd. (7003), Dunka Rd. (7006) and Hoyt Lakes (7010). These sites were chosen to give adequate coverage to the regional characterization of atmospheric deposition. The bulk collector used was similar to that used by Kramer (CCIW, 1975; IJC, 1976) and the same samplers used by Eisenreich et al., (1977) to determine bulk deposition of nutrients and trace elements to Lake Michigan. The bulk collector consisted of a central collection standpipe (25 cm diameter, 506.45 cm^2 surface area) surrounded by an Alter windshield and a bird-off to limit sample contamination. The standpipe collector was designed originally as a rain sampler which also operates effectively as a snow sampler with minor modification (Eisenreich et al., 1977).

Bulk deposition was collected in an inner liner made of 4-ml thickness polyethylene. In the summer, a 0.5 mm, Nytex Nylon screen was placed in the liner to limit introduction of coarse debris and large insects. In addition, a polyethylene funnel was placed at 0.3 m above the bottom of the liner and the liner restricted by tying at the funnel outlet to limit evaporation. Summer evaporative losses with the modified system were limited to less than 4% under even extreme temperature conditions.

Bulk deposition was collected on a monthly basis by staff personnel at all stations. The data resulting from such a sampling represents total loadings over a one month period. Although event, weekly or bi-weekly sampling is preferred to increase time resolution of loading, monthly samples were selected to 1) permit comparison of our data with recent atmospheric loading studies conducted with similar samplers and frequency and 2) require as little attention as possible in remote stations.

Precipitation samples were collected each month and delivered to the Minnesota State Health Department in Minneapolis, Minnesota for chemical analysis. All samples were collected according to the same procedure with special emphasis on sample homogeneity and contamination problems. Occasionally, samples were lost due to bag leakage or collapse which was avoided in the latter stages of the project by using a double-bag sampling.

II-2-2. Sampling of Canopy Throughfall Deposition

Canopy throughfall deposition measurements were initiated at six sites in the Cu-Ni Study Area in the summer of 1977. The throughfall deposition is of importance in determining the effects of forest canopies on throughfall quantity and quality. The data is necessary to evaluate the changes in foliar heavy metal burdens resulting from dust input and subsequent rainfall washing.

Fifteen samplers patterned after those used by Eaton et al., (1973) were placed at each of six sites. Sites were located north and south of the Laurentian divide in stands of upland hardwoods (aspen), upland conifers (red or jack pine) and lowland conifers (black spruce). Samples were collected every 2-3 weeks from mid-May to late September, 1977 and sent to the Minnesota State Health Department for pH, anion and trace element analysis.

The throughfall deposition sampler consists of an outer polyethylene funnel (20 cm diameter) separated from an inner polyethylene funnel of the same dimensions by cleaned filter paper. The funnels were connected to a polyethylene collection bottle by tygon tubing.

Table 2 lists the site number, vegetation type and soil type for each of the six collection sites. The site number refers to the designation code of the Biological Characterization Study and should be consulted for exact locations.

Table 2

THROUGHFALL DEPOSITION COLLECTION SITES

Site	Vegetation	Soil	Location
G44	Pole Black Spruce	Bog	N-Amax
G09	Pole-Saw Aspen	Sl/Rainy Mor.	N-Kawishiwi
G21	Pole-Saw Red Pine	Sl/Rainy Mor.	N-Dunka
G10	Sapling Aspen	ℓ/Rainy Drum.	S
G30	Pole Jack Pine	ℓ/Rainy Drum.	S
G42	Pole Birch-Fir	ℓ/Rainy Drum.	S

N ≡ North of Laurentian Divide

S ≡ South of Laurentian Divide

II-2-3. Sampling of Wet-Only Precipitation

Two event, wet-only precipitation samplers were operated at Spruce Road and Hoyt Lakes. The rain samplers were designed by Dr. S. Krupa of the Department of Plant Sciences, University of Minnesota. The two samplers were operated in the unit sampling mode and collected the first 0.28 cm. of rain falling in a given storm. Additional rainfall passed through the overflow and was not collected. The collector surface area was open only during periods of rainfall, and covered automatically when rainfall intensity and duration was less than pre-designed criteria. Fugitive dust entering during dry periods was reported not to be significant (S. Krupa, personal communication, 1977).

Samples were collected in 473-ml, acid washed Nalgene bottles made of linear polyethylene, with eight bottles devoted to each sampler. Rain samples were retrieved within several days of a major rain event, acidified with Ultrex HNO_3 and sent to the Minnesota Health Department for analysis. Unfortunately, pH and/or acidity measurements were not performed.

II-2-4. Sampling of Atmospheric Particulates

Atmospheric particulates were collected at eleven sites in late 1976 through late 1977 in N.E. Minnesota. (Table 1). Air particles were collected by drawing air through 0.45 μm membrane filters (Millipore) having a diameter of 102 mm. The air particulate membrane samplers were calibrated using an anemometer and magnehelic gauge in the field at least twice per month. The pumps were of the brushless variety to avoid Cu contamination and the entire unit was housed in an aluminum shell to limit direct atmospheric fallout. Timers on the pumping system permitted sampling for 24-hours every sixth day. Membrane filters were changed once per week using teflon forceps and special care was taken to avoid contamination. Pre-weighed filters were used to determine the total suspended particulate load in air.

II-3. Sampling of Atmospheric Particulates for Differentiation By Particle Size

Size differentration of atmospheric particulates was accomplished using a Delron Cascade Impactor Model DCI-6. The impactor is a critical orifice, round, single-jet of the Battele design consisting of six stages and a back-up filter. Particle size cutoffs are 16, 8, 4, 2, 1 and 0.5 μm equivalent aerodynamic diameter. The back-up filter collects particles passing the first six stages and less than 0.5 μm diameter. Air is drawn through the cascade impactor at a flow rate of ∿ 12.5ℓ/min. The impaction surface is a 37 mm glass slide fitted with a 0.4 μm nuclepore filter coated with a thin layer of Apiezon L silicone grease.

Cascade impactor samples were obtained at Kawishiwi (7003) and Hoyt Lakes (7010) on numerous occasions from September, 1976 to December, 1977. Sampling times were normally 24-110 hours at each site. Details of the sampling and analysis procedures and particle size results can be obtained by consulting Eisenreich et al., (1978).

II-4. Analytical Measurements

II-4-1. Bulk Deposition, Wet-Only Precipitation, Throughfall

Bulk deposition (wet-plus dry), wet-only precipitation and throughfall were analyzed for a variety of nutrients and trace elements by the Minnesota State Health Department. Elemental concentrations of Cu, Ni, Cd, Zn, Pb, Al, Fe, As, Ca, Mg, Na and K were determined by flame or flameless atomic absorption spectrophotometry (Perkin-Elmer AAS). Other parameters analyzed for include TP, o-PO_4, TOC, Cl, F, SO_4, NO_3-NO_2, pH, specific conductance, alkalinity, suspended solids, and total dissolved solids. Specific analytical procedures, detection limits, and quality control procedures can be obtained by consulting the Operations Manual of the Minnesota State Health Department.

II-4-2. Atmospheric Particulates

Atmospheric particulates collected by membrane filtration were analyzed by x-ray fluorescence at the analytical research facility of the Environmental Protection Agency in Research Triangle Park, Maryland under the direction of K. Dzubay.

The membrane filters were prepared for analysis by David Pui of the Mechanical Engineering Department at the University of Minnesota under the direction of Drs. K. Whitby, V. Marple and B. Liu. A center section of membrane filter (69.4 cm^2) was mounted in a polyethylene holder and carried by David Pui to the analytical facility in Maryland for analysis by x-ray fluorescence. Elements determined in air particulates were Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Zn, Co, Ni, Cu, Br, Sn, Ga, Ge, As, Se, Rb, Sr, Cd, Sb, Ba, W, Hg and Pb. Results are expressed in terms of ng/m^3 and ng/cm^2 filter surface area. Specific details of the measurement and quality control procedures can be obtained from the Operations Manual of the Cu-Ni Regional Study.

III. Results and Discussion

The primary objective of the air quality program associated with the Copper-Nickel Regional Study was to determine existing background information of air and precipitation chemistry, and deposition in the regional characterization. Thus, the emphasis of this report will be placed primarily on analysis of regional rather than site-specific data. To satisfy this objective, bulk deposition, throughfall deposition, wet-only precipitation and air particulates were collected, analyzed and interpreted as to controlling chemical conditions and sources, as well as to determine deposition to soil, vegetation and water surfaces.

III.-1. Bulk Deposition

Bulk deposition samplers collect wet plus dry loading to a surface. Kramer (CCIW, 1975) and Eisenreich et al. (1977) have used the standpipe collector to measure deposition of trace elements and nutrients to the Great Lakes. However, the bulk deposition samplers are significantly different from a water surface, a forest canopy or a soil surface. Deposition is a flux measurement which means that it is a measurement of deposition resulting from a net accumulation of material. The bulk deposition sampler is effective in collecting rainfall (> 90%) and snowfall (> 75%) but may underestimate dry and gaseous fallout by a significant and unpredictable factor. Thus, bulk deposition data need be interpreted in light of bulk deposition elsewhere and compared to measurements (or estimates) of wet and dry loading determined separately.

Bulk deposition rates were calculated by multiplying the analytical concentration of a monthly-collected sample by the volume of precipitation and dividing by the collector surface area.

$$\text{Loading Rate} = \frac{\text{Conc. (mg/}\ell\text{) x Volume (}\ell\text{)}}{506.45\ \text{cm}^2}$$

This value represented a monthly loading rate in units of $mg/cm^2.mo$. A geometric mean monthly loading rate was calculated for each site in 1977 and averaged to obtain a regional loading rate. An annual loading rate was calculated as

$$\underset{Kg/ha.yr}{\text{Annual Loading Rate}} = \underset{mg/cm^2.mo}{\text{Monthly Loading Rate}} \times 12\ mo/yr \times \underset{\times 10^{-8}\ cm^2/ha}{10^{-6}\ Kg/mg}$$

All values for loading or deposition rates were expressed on a common scale of Kg/ha.yr where 1 hectare (ha) is equivalent to 10^4 m^2.

III.-1-1. Concentrations

The concentrations of trace elements and pH measured in monthly-collected bulk deposition at Fernberg, Spruce Road, Dunka and Hoyt Lakes are shown in Tables 3 and 4. Table 5 summarizes the bulk deposition concentrations at each site for their respective sampling periods in 1977. Concentrations of nutrients, anions and general water quality parameters are shown in Table 6 for the four sites sampled.

The concentrations of trace elements in bulk deposition would not be expected to vary from site-to-site in a region as small as the Cu-Ni Study area if localized deposition were minimal and rainfall amounts were not significantly different throughout the region. Based on gemoetric mean concentrations of trace elements (Table 5) in bulk deposition at the four sites, the sites can be ranked according to magnitude of concentration:

Fernberg < Dunka < Hoyt Lakes < Spruce

This ranking is qualitative in nature and is based primarily on concentrations of elements which are associated primarily with coarse particles in the atmosphere: Fe, Al, Ca, Mg, etc. Fernberg Road exhibited the lowest

Table 3.

Metal Concentrations in Bulk Precipitation

	Cu	Ni	Cd	Zn	Pb	Al	Fe	As	Ca	Mg	Na	K	pH
	μg/ℓ								mg/ℓ				
							Fernberg Road						
March	0.6	<1	.35	6.3	6.6	66	30	1.2	1.36	.53	<.5	<.5	6.9
April[a]	81	16	1.9	130	460	17000	7400	-	-	-	-	-	-
May	1.4	<2	.21	9.7	16	44	40	0.7	.72	<.24	<.5	<.5	4.4
June	2.6	<2	.16	7.0	24	17	40	.59	<.4	<.24	<.5	<.5	5.7
July	1.3	<1	.12	3.0	5.3	19	<20	<.2	.56	<.24	<.5	<.5	3.9
Aug	3.9	<2	1.1	8.0	5.4	64	20	0.3	<.8	<.48	<.5	<.5	4.1
Sept	1.1	<1	1.0	5.6	5.0	7.5	<20	<.8	.52	<.48	<.5	<.5	4.7
Oct	0.5	<2	0.85	2.2	2.9	5.5	<20	1.1	<0.8	<.48	<.5	<.5	3.7
Nov	3.7	<1	0.12	20	28	66	90	1.6	<0.8	<.48	<.5	<.5	4.1
Dec	0.2	<1	0.13	3.1	3.1	44	19	<.6	<0.8	<.48	<.05	.06	6.9
							Spruce Road						
March	1.3	2.0	.34	12	8.8	63	-	2.0	1.64	.67	<.5	<.5	4.0
April	1.7	<1	.15	7.5	9.2	140	40	1.0	1.32	.26	<.5	<.5	5.2
May	3.1	<2	1.5	11	19	110	100	0.6	0.88	.29	<.5	<.5	5.1
June	1.7	<2	.17	6.3	.67	15	<20	0.6	0.52	.29	<.5	<.5	4.7
July	1.2	<1	.12	3.9	5.3	23	<20	<.2	0.84	<.24	<.5	<.5	4.5
Aug	4.4	3.0	.47	17	30	110	170	0.5	<.8	<.48	<.5	<.5	3.9
Sept[a]	1.0	<1	.53	4.3	6.2	15	<20	<.8	1.2	<.48	<.5	<.5	4.0
Oct[a]	1.6	<2	.85	6.2	3.4	15	80	0.5	<0.8	<.48	<.5	<.5	3.7
Nov	1.9	<1	.24	10	18	54	40	1.9	<8	<.48	<.05	<.5	3.7
Dec	0.6	<1	.18	3.6	4.7	56	23	<.6	0.9	<.48	<.05	.04	5.7

Table 4.

Metal Concentrations in Bulk Precipitation

	Cu	Ni	Cd	Zn	Pb	Al	Fe	As	Ca	Mg	Na	K	pH
	μg/ℓ								mg/ℓ				
						Dunka							
March[a]	-	-	-	-	-	-	-	-	-	-	-	-	-
April	1.4	<1	.19	7.9	8.6	290	200	2.4	1.52	.48	<.5	<.5	5.8
May	1.8	<2	.42	15	6.8	32	<20	0.8	1.12	.34	<.5	<.5	4.9
June	1.8	<2	.43	9.7	2.8	25	40	1.0	0.60	.29	<.5	<.5	4.8
July	1.3	<1	.21	5.7	7.1	25	20	0.6	0.72	<.24	<.5	<.5	4.2
Aug	0.8	<2	.27	4.9	12	48	60	0.7	<.8	<.48	<.5	<.5	4.0
Sept	0.4	<1	.12	3.0	7.3	12	<20	<.8	<1	<.48	<.5	<.5	4.0
Oct	0.4	<2	.09	2.4	3.7	7.9	<20	<.3	<.8	<.48	<.5	<.5	3.7
Nov	0.6	<1	.79	3.3	14	30	30	0.8	<.8	<.48	<.5	0.8	4.2
Dec	2.1	<1	.71	14	9.0	110	98	<6	<8	<.48	2.4	0.08	6.6
						Hoyt Lakes							
March[a]	2.6	<1	.32	16	35	740	1600	16	1.00	.29	<.5	<.5	4.1
April	0.7	<1	.15	4.9	5.2	130	90	2.8	1.44	.16	<.5	<.5	5.6
May	1.8	<2	.27	12	7.1	29	40	2.5	0.92	<.24	<.5	<.5	5.1
June	2.6	<2	.19	7.4	12	21	30	1.5	0.44	.29	<.5	<.5	4.5
July	1.4	<1	.85	7.0	7.8	71	70	1.2	0.96	<.24	<.5	<.5	5.3
Aug	0.8	<2	1.5	11	7.4	41	60	1.5	<.8	<.48	<.5	<.5	4.1
Sept[a]	1.1	<1	1.2	28	5.6	43	30	<.8	1.4	<.48	<.5	<.5	4.2
Oct	1.4	<2	0.23	8.6	7.7	7.7	<20	<.3	<.8	< .48	<.5	<.5	3.9
Nov	0.1	<1	0.03	1.1	5.6	17	30	<0.6	<8	<.48	<5	<.5	4.6
Dec	0.8	<1	.19	5.9	8.4	220	57	0.6	<8	<.48	<.5	.07	5.1

Table 5

Trace Element Concentrations in Bulk Depositon

	µg/ℓ								mg/ℓ				
	Cu	Ni	Cd	Zn	Pb	Al	Fe	As	Ca	Mg	Na	K	pH
						Dunka							
$\overline{x}$g	1.0	<1.4	.28	6.0	7.1	35	39	0.8	0.88	<.4	< .6	<.43	4.7
σg	1.9	1.4	2.1	2.0	1.7	3.0	2.3	1.7	1.3	1.3	1.7	1.9	--
						Hoyt Lakes							
$\overline{x}$g	0.9	<1.4	.18	6.1	7.4	40	45	1.1	0.93	<.3	.5	0.4	4.8
σg	2.7	1.5	2.5	2.1	1.3	3.0	1.7	2.2	1.4	1.5	1.0	2.0	--
						Spruce Road							
$\overline{x}$g	1.7	4.5	.27	7.9	7.8	57	42	0.7	0.91	0.4	<.3	.4	4.6
σg	1.8	1.6	2.3	1.7	3.3	2.2	2.3	2.1	1.4	1.5	2.9	2.4	--
						Fernberg Road							
$\overline{x}$g	1.2	1.4	.30	5.8	7.7	27	29	0.7	0.71	<.4	<.4	<4	4.9
σg	2.7	1.4	2.6	2.0	2.3	2.6	1.7	1.9	1.4	1.4	2.2	2.0	--

$\overline{x}$g: Geometric mean monthly concentration

σg: Geometric standard deviation (in log units)

Table 6

Nutrient and General Parameter Concentrations in Bulk Deposition[a]

SITE	TP	TOC	Cl	SO_4	F	SS	TDS	Alk[b]	Spec. Cond.
	mg/ℓ								
Dunka	.023	2.7	< 1.1	< 1.5	.1	4.0	3.2	< 10	29
Hoyt Lakes	.018	4.3	< 2.0	3.0	.1	7.5	6.5	< 10	39
Spruce Road	.010	4.6	< 1.4	2.6	.1	4.7	4.2	< 10	25
Fernberg Road	.026	4.4	< 1.5	2.6	.1	8.7	4.7	< 10	25

[a] Geometric mean concentrations, 1977.

[b] Units are mg/ℓ as $CaCO_3$.

concentrations of these elements but was not statistically different from the other collection sites for the trace metals Cu, Ni, Cd, Zn, Pb and As. This behavior serves to support the hypothesis that the atmospheric loading of trace elements to N.E. Minnesota is a regional phenomena not influenced strongly by local sources with the possible exception of Fe. In general, the concentrations of trace metals were typical of remote, mid-continental bulk deposition influenced by regional sources (Table D-1).

Measurement of pH in bulk deposition is not meaningful with respect to evaluation of acid-forming species. However, the geometric mean values ranged from 4.6-4.9 for the region, and were likely lower by 0.1 to 0.5 units for precipitation not in contact with the neutralizing components of dry fallout. The relatively acidic values may indicate that precipitation is acidic naturally in N.E. Minnesota (1st International Symposium on Acidic Precipitation, 1976).

The geometric mean concentration of Pb in bulk deposition ranged from 7.1-7.7 μg/ℓ at the four sites. These values were significantly lower than the 41 μg/ℓ found by Cawse (1974), the 34 μg/ℓ measured by Lazrus et al. (1970) at 32 stations in the U.S.A. and the 40 μg/ℓ averages reported by Chow (1970) for LaJolla, California. Pb concentrations reported above for the Cu-Ni Study Region were for bulk deposition while those reported after were for event precipitation. The lower concentrations of nearly all elements in N.E. Minnesota compared to Cawse (1974), Lazrus et al. (1970) and CCIW (1975) are again indicative of the remote nature of the area. Eisenreich (1978) found that the geometric mean Pb concentration in bulk deposition in the north and south basin of Lake Michigan was 13 and 39 μg/ℓ, respectively.

Table 7 compares the trace element concentrations in bulk deposition expressed as geometric means for N.E. Minnesota to those from the north and south basin of Lake Michigan. The north basin of Lake Michigan should be somewhat similar to the area of N.E. Minnesota although population density and soil differences are noted. Therefore, comparison of the data from N.E. Minnesota to the north basin of Lake Michigan should provide interesting comparisons. For all elements determined, the geometric mean concentrations in N.E. Minnesota represent 20 to 80% of the values reported for northern Lake Michigan, again indicating the remote character of the study area.

III.-1-2. Bulk Deposition - Loading

Bulk deposition is a measure of the amount of material deposited to the bulk collector in approximately one month's time in the form of precipitation (wet) and dust fallout (dry). Gaseous or vapor phase deposition to the bulk collector is minimal. Bulk deposition for a variety of elements was determined at four sites in N.E. Minnesota: Hoyt Lakes (7010), Dunka (7006), Spruce (7003) and Fernberg (7001). The latter site represents the remote, background site for the study area and is immediately adjacent to the BWCA. Bulk deposition at each site was calculated on the basis of the geometric mean bulk loading rate over the study period and then averaged over the four sites to obtain a regional value. Table 8 lists the mean atmospheric loading rates derived from bulk deposition in N.E. Minnesota. The loading rates calculated for the study areas do not vary excessively from site-so-site and thus were pooled to arrive at a regional loading rate.

The loading rates presented in Table 9 can be compared to loading rates to the Great Lakes derived from bulk deposition using similar collectors (IJC, 1977; Eisenreich, 1978). In general, the trace element loading rates

Table 7

Comparison of Elemental Concentrations in Bulk Deposition in N.E. Minnesota to Lake Michigan Basin

ELEMENT	N.E. MINNESOTA (Range)	LAKE MICHIGAN[a]	
		North	South
	µg/ℓ		
Al	25-35	119	282
Fe	29-45	66	157
Zn	5.8-7.9	33	57
Cu	0.9-1.7	3	6
Ni	<1.4	___	___
Mn	___	15	37
Pb	7.1-7.8	13	39
Cd	.18-.30	.4	.6
Ca	710-910	2100	4300
Mg	< 400	540	740
Na	< 600	330	550
K	< 400	220	300

[a] Eisenreich (1978)

TABLE 8

ATMOSPHERIC MEAN LOADING RATES DERIVED FROM BULK DEPOSITION IN NORTHEASTERN MINNESOTA-1977[a]

COMPONENT	HOYT LAKES	DUNKA	SPRUCE	FERNBERG	NORTHEASTERN MINNESOTA[b]
	kg/ha/yr				
Cu	0.005	0.007	0.008	0.011	0.008
Ni	<.010	<.012	<.007	<.012	<.010
Cd	0.001	0.002	0.001	0.003	0.003
Zn	0.036	0.042	0.035	0.052	0.041
Pb	0.047	0.050	0.035	0.068	0.050
Al	0.30	0.25	0.26	0.24	0.26
Fe	0.37	0.28	0.19	0.26	0.28
As	0.008	0.005	0.003	0.008	0.006
Ca	<4.5	<6.1	<4.1	<6.3	<5.3
Mg	<1.7	<3.0	<1.7	<3.4	<2.4
Na	<2.1	<4.8	<1.9	<4.7	<3.3
K	<2.1	<2.3	<1.6	<3.5	<2.5
TP	0.18	0.085	0.093	0.37	0.18
TOC	31	36	16	26	27
Cl	6.7	6.0	7.4	11	8.2
SO_4	16	18	13	18	16
N	2.6	3.6	3.1	2.8	3.0

[a] Loading Rates Represent Geometric Means Of Monthly Loading Rates

[b] Mean Loading Rates For Region Based On Four Sites

Table 9

ATMOSPHERIC LOADING OF TRACE ELEMENTS[a] TO THE GREAT LAKES

ELEMENT	SUPERIOR	MICHIGAN	HURON	ERIE	ONTARIO
	Kg ha^{-1} yr^{-1}				
Al	-	.86	-	-	-
Fe	1.18	.48	.77	2.3	.27
Mn	-	.11	-	-	-
Zn	-	.19	-	-	-
Cu	.045	.021	.13	.13	.037
Pb	.079	.11	.13	.85	.14
Cd	.007	.002	.013	.058	.023
Co	-	.004	-	-	-
Ca	4.0	14	47	8.9	16
Mg	.68	2.7	1.4	2.6	2.1
Na	1.8	1.9	7.6	5.0	9.7
K	1.6	1.1	5.4	8.5	1.7
P	.056	.22	.086	.31	.25
SO_4	27	15	39	47	45

[a] IJC (1977); Eisenreich (1978)

to N.E. Minnesota were equal to or less than values reported for the five Great Lakes. The loading rates reported for N.E. Minnesota were most similar to those determined in the Lake Superior and northern Lake Michigan basin. Increased loadings for Lake Superior relative to Lake Michigan were thought to be due to concentrated mineral sulfide smelting operations in Ontario north of Lake Superior (CCIW, 1975).

Bulk deposition of Fe in N.E. Minnesota might be expected to be influenced by taconite iron mining and processing in the region. However, bulk loading rates for Fe were equal to or less than Fe loading in the Great Lakes Basin. Evidence will be presented later in this report that bulk deposition of Fe and Al may be underestimated by a factor of 10x in N.E. Minnesota. Bulk loading of Ca, Mg, Na and K to N.E. Minnesota cannot be readily compared to Great Lakes loading rates due to insufficient analytical sensitivity for the former. The loading of phosphorus (TP) to the study area was in the same range as reported to the Great Lakes. There is some indication that insects and soil may be the most significant contributors to TP loading (Eisenreich, et al., 1977). Sulfate loading to N.E. Minnesota (16 $Kg.ha^{-1}.yr^{-1}$) was less than the value reported for Lake Superior but the latter was based on few sample collection points. For the remaining basins, SO_4 loading was greater than for N.E. Minnesota by up to 2.5 times.

The loading of Cu to N.E. Minnesota derived from bulk depositon data was $\sim$ 8 $g.ha^{-1}.yr^{-1}$ compared to remote values reported by Andren and Lindberg (1977) of 230 $g.ha^{-1}.yr^{-1}$ for Tennessee, and Struempler (1976) of 18 $g.ha^{-1}.yr^{-1}$ for Nebraska. Kramer (1975) has reported a Cu loading value from rain of $\sim$ 10 $g.ha^{-1}$ $yr.^{-1}$ for the Northwest Territories of Canada while Hutchinson and White (1975) have measured Cu loadings around Sudbury, Ontario as high as 2900 $g.ha^{-1}.yr.^{-1}$. Bulk loading of Ni to N.E. Minnesota was < 10 $g.ha^{-1}.yr^{-1}$ as compared to a Great Lakes loading of 37 $g.ha^{-1}.yr^{-1}$, (IJC, 1977), Northwest Territories of Canada loading of 3 $g.ha^{-1}.yr^{-1}$, (Kramer, 1975) and a Sudbury, Ontario loading of 2100 $g.ha^{-1}.yr$. These data represent strong evidence that present day Cu and Ni loading from the atmosphere to N.E. Minnesota is typical of remote, mid-continental deposition (see Table E-1).

Phosphorus loading from the atmosphere to the study area ranged from 85 to 370 $g.ha^{-1}.yr^{-1}$ (average, 180 $g.ha^{-1}.yr^{-1}$) compared to other values for northern Minnesota of 258 $g.ha^{-1}.yr^{-1}$ (Commerford and White, 1976) and 140 $g.ha^{-1}.yr^{-1}$ (Wright, 1976). In contrast, bulk loading of atmospheric P (TP) to Lake Superior (IJC, 1977) and northern Lake Michigan was 56 and 50 $g.ha^{-1}.yr^{-1}$, respectively. Thus, nutrient loading from the atmosphere to N.E. Minnesota appears to be ∿ 3 times greater than corresponding areas to the east. This phenomena may be due to soil injection into the atmosphere in the western plains.

III.-1-3. Bulk Deposition - Seasonal Variations

Seasonal variations in trace element loading from the atmosphere derived from bulk deposition measurements are shown in Figure 3 and summarized in Table 10. Also, the monthly precipitation amount is given at the bottom of Figure 3. Two distinctive features of the seasonal behavior of atmospheric loading are evident: 1) With the exception of P and Al, atmospheric loading was greatest in late spring, summer and fall and minimal during winter, i.e., during periods of snow cover; and 2) atmospheric loading was maximum during months of greatest precipitation. These two data suggest that snow cover inhibits transport of soil-derived elements and that rainfall is important in scavenging elemental components from the atmosphere. These conclusions are essentially the same as those reached by Eisenreich, et al. (1977) for deposition to Lake Michigan and by Kramer (CCIW, 1975) for deposition to the Upper Great Lakes. The data also indicates that Al, Fe and P have more than one atmospheric source because their peak loading months were not coincident. In addition, atmospheric loading of Pb, Zn, Cu, SO_4 and TOC exhibit peak behavior coincident with months of greatest precipitation.

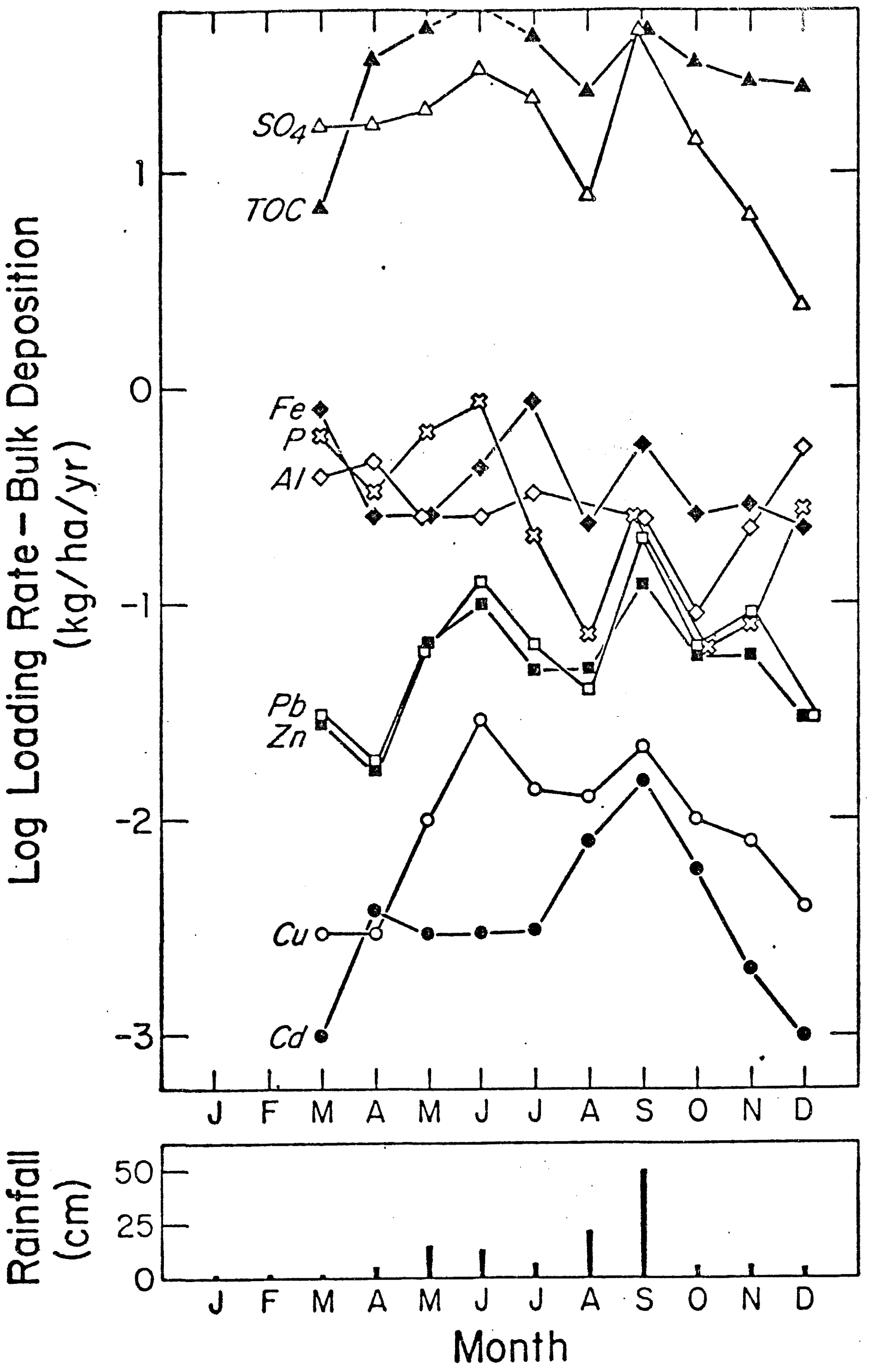
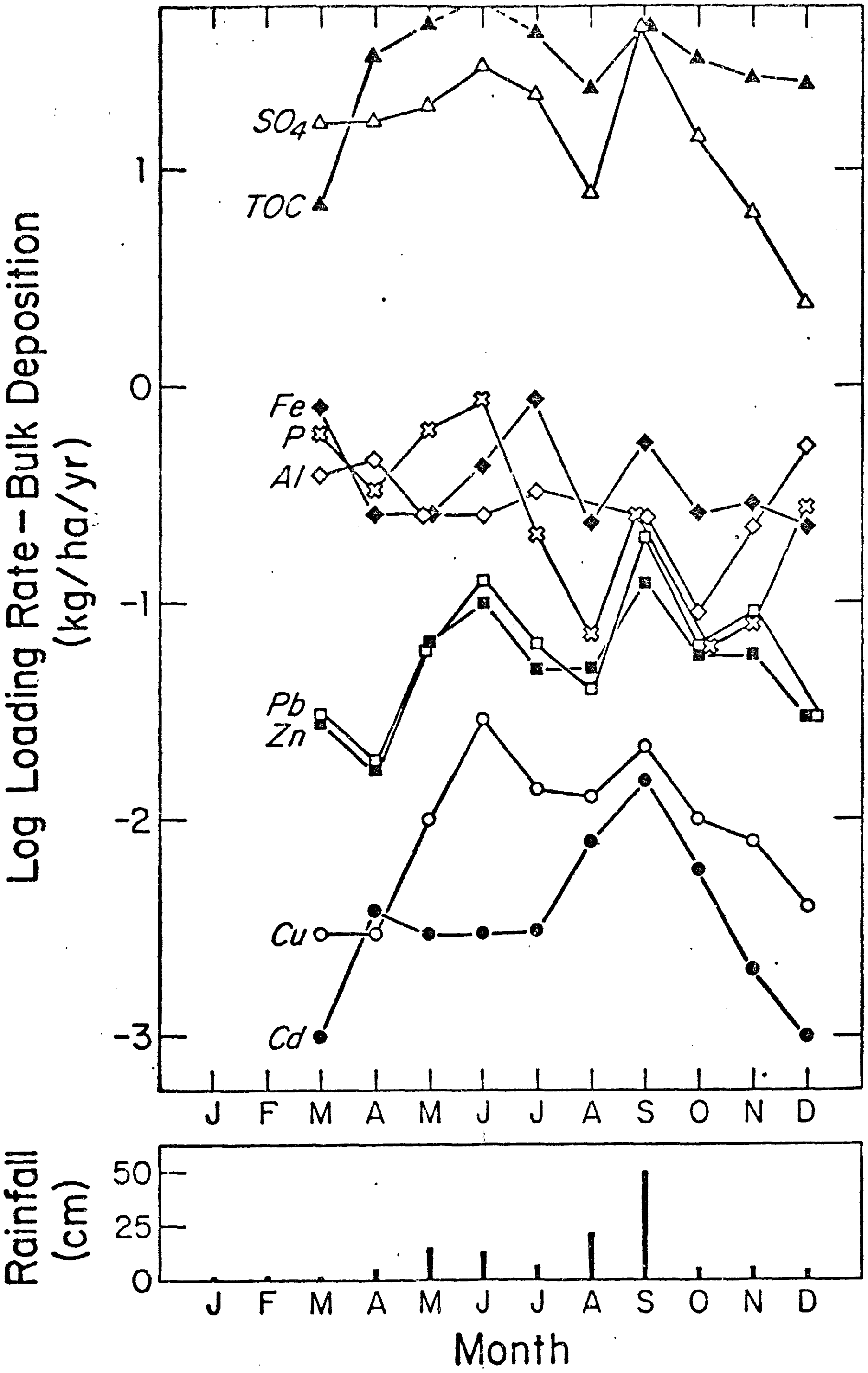

Log Loading Rate – Bulk Deposition (kg/ha/yr)
1
0
-1
-2
-3
SO4
TOC
Fe
P
Al
Pb
Zn
Cu
Cd
J
F
M
A
M
J
J
A
S
O
N
D
Rainfall (cm)
50
25
0
J
F
M
A
M
J
J
A
S
O
N
D
Month

Figure 3

Seasonal Variations in Trace Element Loading
Derived from Bulk Deposition



SO4
TOC
Fe
P
Al
Pb
Zn
Cu
Cd
1
0
-1
-2
-3
Log Loading Rate – Bulk Deposition (kg/ha/yr)
J
F
M
A
M
J
J
A
S
O
N
D
Rainfall (cm)
50
25
0
Month

TABLE 10

SEASONAL VARIATIONS IN ATMOSPHERIC BULK LOADING RATES FOR NORTHEASTERN MINNESOTA-1977[a]

	Cu	Ni	Cd	Zn	Pb	Al	Fe	As	Ca	Mg	Na	K	T.P	TOC	Cl	SO_4	N
							kg/ha/yr										
rch	0.003	<.004	0.001	0.029	0.031	0.39	0.79	0.023	<4.2	<1.6	<1.5	<1.5	0.61	6.8	9.4	16	-
	(.002)	(.003)	(.001)	(.016)	(.004)	(.25)	(.95)	(.021)	(2.9)	(1.2)	(0.9)	(0.9)	(.79)	(5.4)	(10)	(10)	
ril	0.003	<.003	0.004	0.017	0.019	0.45	0.26	0.005	<13	<0.7	<2.3	<1.3	0.33	35	3.1	16	-
	(.001)	(.0005)	(.001)	(.003)	(.005)	(.12)	(.15)	(.003)	(16)	(0.3)	(1.5)	(0.2)	(.47)	(52)	(2.8)	(1.3)	
y	0.010	<.011	0.003	0.064	0.063	0.26	0.25	0.007	<4.9	<2.4	<3.5	<2.7	0.63	49	5.9	19	
	(.002)	(.003)	(.002)	(.017)	(.028)	(.12)	(.12)	(.007)	(1.2)	(2.0)	(1.0)	(0.6)	(.24)	(16)	(2.0)	(6.4)	
ne	0.029	<.027	0.003	0.10	0.13	0.26	0.44	0.012	<6.7	<3.8	<6.8	<6.8	0.86	63	10	29	4.4
	(.005)	(.004)	(.002)	(.023)	(.15)	(.06)	(.14)	(.003)	(1.8)	(0.6)	(1.0)	(1.1)	(.14)	(13)	(1.9)	(9.5)	(1.2)
ly	0.014	<.010	0.003	0.049	0.064	0.34	0.85	0.005	<7.9	<2.5	<5.2	<5.2	0.20	47	15	21	3.1
	(.002)	(.002)	(.003)	(.012)	(.004)	(.21)	(1.0)	(.004)	(1.7)	(0.4)	(0.7)	(0.8)	(.17)	(5.7)	(4.6)	(4.4)	(0.6)
gust	0.012	<.008	0.008	0.049	0.042	0.23	0.23	0.003	<3.1	<0.7	<1.9	<1.9	0.07	24	25	8.9	-
	(.010)	(.003)	(.010)	(.011)	(.018)	(.10)	(.10)	(.002)	(1.3)	(0.7)	(0.8)	(0.8)	(.04)	(11)	(13)	(2.7)	
pt.	0.021	<.026	0.015	0.12	0.20	0.25	0.53	0.021	<20	<13	<13	<13	0.25	49	29	44	4.5
	(.014)	(.002)	(.017)	(.058)	(.03)	(.06)	(.05)	(.003)	(7.2)	(1.2)	(1.1)	(1.1)	(.32)	(11)	(1.2)	(7.3)	(0.6
t.	0.010	<.026	0.006	0.056	0.061	0.09	0.26	0.008	<10	<6.3	<6.5	<6.5	0.06	33	39	14	2.6
	(.007)	(.003)	(.006)	(.044)	(.032)	(.008)	(.003)	(.007)	(1.3)	(0.8)	(0.8)	(0.8)	(.03)	(6.4)	(35)	(2.2)	(0.1)
v.	0.008	<.006	0.002	0.056	0.090	0.22	0.29	0.006	<5.0	<2.9	<3.1	<3.1	0.08	25	12	6.2	1.6
	(.010)	(.003)	(.002)	(.048)	(.059)	(.13)	(.20)	(.002)	(2.4)	(1.4)	(1.5)	(1.5)	(.04)	(21)	(14)	(3.0)	(0.8)
c.	0.004	<.005	0.001	0.029	0.029	0.50	0.22	<0.003	<3.9	<2.3	<2.5	<0.3	0.27	24	<2.8	2.4	-
	(.003)	(.0001)	(.001)	(.017)	(.011)	(.39)	(.14)	(.001)	(.67)	(0.4)	(0.5)	(.08)	(.13)	(26)	(0.5)	(4.4)	

---

[a] Monthly Loading Rates Represent Arithmetic Means Of Average Bulk Deposition At Four Sites In Northeastern Minnesota; Numbers In Parenthesis Represent One Standard Deviation

III.-2 Canopy Throughfall Deposition

Forest canopies are efficient scavengers of dust and aerosol from the atmosphere (Eaton, et al, 1973) and may act to concentrate atmospheric trace elements and pollutants. Depending on the reactivity, size and chemical nature of the deposited material, subsequent rainfall events may wash the component off the leaf surface and transfer it to the forest floor. Until recently, little work has been reported on the deposition of aerosol particles to vegetation surfaces, and subsequent ecological consequences.

Chamberlain (1966) has reported on the transport of spores to grassy surfaces in a wind tunnel and in the field. Gregory (1961) performed similar experiments on smooth and rough surfaces. Sehmel (1973) and Sehmel et al. (1973) investigated the deposition of monodisperse particles to a number of surfaces in a wind tunnel.

Filtration models for aerosol scavenging by vegetation have been developed by Gregory (1961), Davies (1966), Hidy (1972), Slinn (1976) and Hidy and Heisler (1977). Chamberlain (1975) has invoked a convective diffusion model to predict transport of small particles and gases to vegetation in wind tunnel experiments.

Recently, Davidson (1977) developed a model for dry deposition of aerosol particles on fields of vegetation. The model includes the processes of diffusion, sedimentation and impaction as transport mechanisms for aerosol metals depositing on a wild oat grass. Davidson described dry deposition as a two-step process involving the transport of aerosol from the open atmosphere into the vegetation followed by filtration by the vegetation elements. For particles smaller than 10^{-3} μm and larger than 10 μm, deposition is controlled by the rate at which particles are delivered to the canopy. For particles between these values, dry deposition is controlled by relatively inefficient filtration within the canopy.

In this study, throughfall samplers were placed beneath six types of forest canopy in the summer of 1977 both north and south of the Laurentian Divide (see section II-1.). The objective of the study was to investigate the deposition of trace elements to soil and subsequent accumulation as a result of canopy scavenging and washoff by rain. Since the actual time of deposition was not closely monitored, the loading values were calculated as follows:

$$\underset{(\mathrm{Kg.ha^{-1}.yr^{-1}})}{\mathrm{Loading}} = \mathrm{Conc.}\ (\mathrm{mg}/\ell) \times \frac{0.7\mathrm{m}}{\mathrm{yr}} \times \frac{10^{-6}\mathrm{Kg}}{\mathrm{mg}} \times \frac{10^{3}\ell}{\mathrm{m}^{3}} \times \frac{10^{4}\mathrm{m}^{2}}{\mathrm{ha}}$$

The historical annual mean precipitation in the region was assumed to be 0.7 meters.

Table 11 lists the concentrations and loading of SO_4, TOC, Zn, Cu, Ni, Fe, Pb and Cd in throughfall deposition. The loading rates expressed in units of $\mathrm{Kg.ha^{-1}.yr^{-1}}$ were calcualted from the regional mean concentration since so few data points were available. Comparison of the throughfall and bulk loading rates to the region shows that there exists no significant difference between the two values with the exception of TOC. In this case, organic carbon from the biological processes of vegetation growth may account for the discrepancy. The loading rate calculated for Fe did not include data from the Red Pine stand located adjacent to a taconite iron mine and processing facility. The Fe loading rate for this site was found to be $\sim$ 1.8 $\mathrm{Kg.ha^{-1}.yr^{-1}}$ as compared to $\sim$ .28 $\mathrm{Kg.ha^{-1}.yr^{-1}}$ derived from bulk deposition. Dry deposition measurements based on atmospheric Fe concentrations and deposition velocity to be presented later agree with the higher loading rate.

The acidity of throughfall deposition as indicated by pH measurements was not significantly different from mean pH values of bulk deposition. The values ranged from pH 4.4-6.8 for throughfall deposition as compared to a mean pH of 4.4-4.9 for bulk deposition.

Table 11

Canopy Throughfall Deposition - Concentrations and Loading

Cover Type	SO_4	TOC	Zn	Cu	Ni	Fe	Pb	Cd
				mg/ℓ				
				Concentration				
Aspen (mature)	6.0	61	.012	.002	ND	ND	.003	.00007
Aspen (sapling)	2.1	15	.004	.0004	ND	.02	.002	.00008
Aspen (sapling)	3.4	18	.005	.0003	ND	ND	.004	.00007
Red Pine	3.5	24	.008	.003	.001	.227	.004	.0001
	2.0	11	.004	.002	.002	.107	.003	.00008
	2.2	23	.017	.005	.003	.423	.004	.0002
Jack Pine	2.2	15	.007	.0007	.002	.035	.004	.00009
	2.5	14	.007	.0008	.001	.050	.003	.00007
	1.4	17	.005	.0009	<.001	.047	.003	.0002
Birch/Fir	4.3	24	.009	.0005	---	.030	.004	.00007
Black Spruce	2.5	13	.005	.0009	.001	.070	.004	.00006
	2.9	9	.011	.002	.002	.067	.003	.0003
$\bar{x}$	3.3	23	.008	.001	<.003	.041	.003	.0001
σ	1.4	17	.003	.001	.002	.021	.001	.00004
				Loading (Kg/ha/yr)				
$\bar{x}$	23	161	.056	.007	<.021	.29[a]	.021	.0007
Bulk Loading	16	27	.041	.008	<.010	.28	.050	.003

[a] Does not include Fe data from the Red Pine stand (Erie).

III.-3. Wet-Only Precipitation

Wet-only precipitation was collected at the Spruce Road site (7003) from 29 May-25 October, 1978 with an automatic collector designed to exclude dust and dryfall. Although designed for unattended, continuous operation, mechanical problems limited the quantity of data available. In addition, precipitation volume actually collected was not closely monitored, prohibiting calculation of atmospheric loading rates derived from mass measurements. Thus, geometric mean concentrations of trace elements based on all samples collected were calculated and converted to loading rates based on a mean precipitation input of 0.70 m/yr in the study region.

Table 12 lists the concentrations of trace elements in wet-only precipitation for N.E. Minnesota compared to typical ranges of element concentrations in urban and remote regions (see Tables, C,D).

Copper and Ni geometric mean concentrations in rainfall in N.E. Minnesota were found to be 3.4 and < 2 μg/ℓ, respectively. These values are typical of those reported for remote areas and substantially less than those observed in urban regions. Copper and Ni in rain have soil and industrial processes as their major sources. Since little anthropogenic activity other than coal-fired power plants is presently in the study region, natural sources were implicated for Cu and Ni.

The concentrations of Fe and Mn were well within the range expected for rainfall occurring in remote regions. Iron derived from the extensive iron mining operations in the region do not increase Fe concentrations in wet-only precipitation beyond that expected for rural areas. Aluminum in wet-only precipitation exhibited concentrations (135 μg/ℓ) greater than those expected for either remote or urban areas. Naturally-derived Al in rain is largely accounted for by Al-silicate minerals injected into the air by resuspension. The concentrations of other

Table 12

CONCENTRATION OF TRACE ELEMENTS IN WET-ONLY PRECIPITATION

Element	Urban[a]	Remote[a]	N.E. Minnesota[b]
	µg/ℓ		
Al	10-100	1-20	135
Fe	20-1000	5-200	39
Mn	0.5-50	0.5-10	3.9
Cu	0.5-30	1-20	3.4
Ni	0.5-60	0.3-10	<2
Pb	10-300	1-20	10
Zn	10-200	1-30	7.6
Ca	20-5000	20-1000	<800
Mg	20-2000	20-1000	<500
Na	10-1000	10-300	<700
K	10-1000	10-600	<200
P	10-100	7-100	4
TOC	1000-20,000	0.5	1800
Cl	1000-10,000	< 3000	< 500
SO_4	1000-30,000	1000-10,000	3100

[a] Typical ranges of element concentrations in rainfall (see Table C-1).

[b] Geometric mean concentration of trace elements in wet-only precipitation collected at Spruce Road (7003) from 29 May-250 October, 1978; n = 30-40 depending on element.

chemical clements were equal to or less than those expected for remote, mid-continental areas.

Wet deposition to N.E. Minnesota for a variety of trace elements is given in Table 13, and compared to a recent study of wet deposition in England (Cawse, 1974). Wet deposition refers to the process of in-cloud or below-cloud scavanging (removal) of atmospheric particles or gases, with subsequent deposition to a surface. In many areas of the mid-U.S.A., wet deposition accounts for ∿ 50% of the total atmospheric deposition on an annual basis (Gatz, 1975; Andren and Lindberg, 1977).

Anomalously large loadings of Al in wet deposition were noted as compared to England, and may either be an analytical artifact or due to Al-silicate removal from the atmosphere. Trace element deposition was significantly less than that reported by Cawse (1974).

The measurement of H^+ input to N.E. Minnesota was based on event, wet-only precipitation samples collected in clean polyethylene buckets in or near Ely, Minnesota in the summer of 1977 (Figure 4). The central value obtained for event rainfall was pH 4.7, as compared to mean values in bulk deposition of pH 4.4-4.9. The fact that wet and bulk precipitation had similar pH values indicates that the acid neutralization potential of particulates in bulk deposition was minimal. Hydrogen-ion loading calculated using a $[H^+] = 2 \times 10^{-5}$ equivalents/ℓ and an annual precipitation amount of 0.70 m was 140 equivalents per hectare.year. This compares to remote background loadings in the Northwest Territories (Canada) of 29. equ.ha^{-1}.yr^{-1} (Kramer, 1975) and a range of 92-460 equ.ha^{-1}.yr^{-1} in the northeastern U.S.A., Norway and Sweden (Kramer, 1977).

Table 13

WET DEPOSITION OF TRACE ELEMENTS TO NORTHEASTERN MINNESOTA[2]

	Loading Rates	
Element	N.E. Minnesota	England[b]
	$Kg.ha^{-1}.yr$	
Al	0.95	0.5
Fe	0.27	1.2
Mn	0.03	0.06
Cu	0.02	0.4
Ni	< 0.01	0.55
Pb	0.07	0.62
Zn	0.05	0.84
Ca	< 5.6	< 8.0
Mg	< 3.5	4.5
Na	< 5.1	76
K	< 1.2	< 3.6
P	0.03	--
TOC	13	--
Cl	< 3.5	--
SO_4	22	< 77
H^+[c]	140 equiv.	--

[a] Based on wet-only precipitation and 0.70 m/yr precipitation

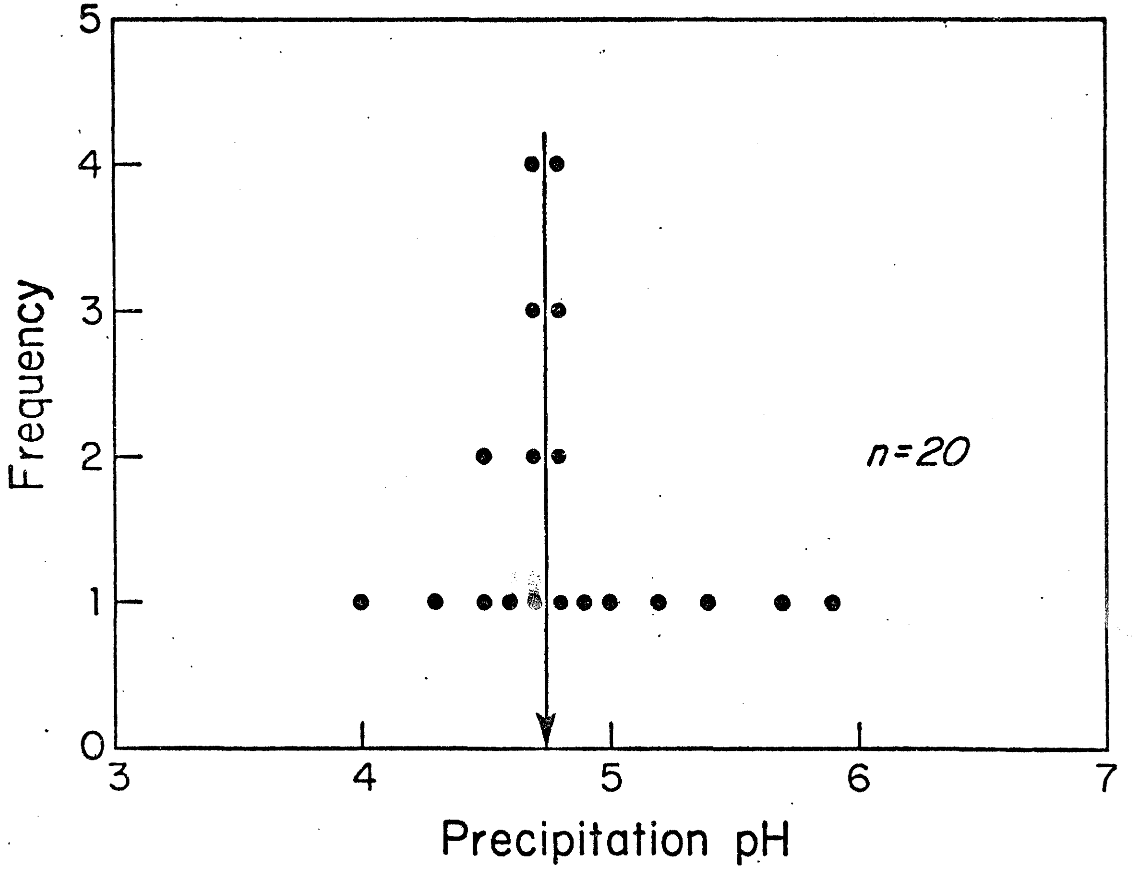
[b] Cawse (1974) for Trebanos in 1972.

[c] Based on a median regional pH of 4.7.

Figure 4

Distribution of Precipitation pH Values in

Event, Wet-Only Samples - 1977


Frequency
0
1
2
3
4
5
3
4
5
6
7
Precipitation pH
n=20

III-4. Atmospheric Particulates

III-4-1. Concentrations

Elemental concentrations found in air particulates in N.E. Minnesota are given in summary form in Tables 14 and 15. The summary statistics of elemental concentrations in air particulates found at each of eleven sites in N.E. Minnesota are given in Tables 16-26. The study period for collection of air particulates was from December, 1977 through October, 1978. Sites were sampled for 24 hours every sixth day.

The region-wide summary data (Tables 14 and 15) give maximum and minimum values, arithmetic means and standard deviations for two data combinations: 1) not-detectable data omitted in calculation of statistical summaries, and 2) not-detectable data included as analytical zero concentration. The true regional or site-specific mean can be assumed to lie between these values.

The sites were divided conveniently into urban/industrial and non-urban sampling points and are classified below:

Urban/Industrial	Non-Urban
Erie (7008)	Fernberg (7001)
Hoyt Lakes (7010)	Isabella (7004)
Babbett (7013)	Bear Head (7005)
Scanlan (7412)	Bunka (7006)
Duluth (7527)	Toimi &7007)
	Whiteface (7011)

The urban and non-urban sites can be further characterized by examining differences in mean concentrations. Sulfur, Pb and Fe were chosen to differentiate between site type, and regional means are given below:

(ng/m^3)

	S	Pb	Fe	
non-urban	670±104	21±6	613±432	n=6
urban	713±295	122±89	1842±1389	n=5

TABLE 14

STATISTICAL SUMMARY OF ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES IN NORTHEASTERN MINNESOTA[a]

ng/m^3

	Al	Si	P	S	Cl	K	Ca
Max	3048	8884	249	5623	360	1262	5017
Min	4	3	1	ND	4	1	3
Aug	299	911	51	692	83	163	321
Sig	413	1336	38	641	75	183	522

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	453	22	40	156	12865	1852	43
Min	1	4	1	ND	5	ND	ND
Avg	56	11	10	19	1050	23	8
Sig	66	5	6	23	1851	106	8

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	27	109	252	8	11	2	51
Min	ND	ND	ND	ND	ND	ND	ND
Aug	4	12	15	5	2	2	7
Sig	5	17	26	2	2	1	7

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	5	10	26	132	8	185	132
Min	ND	ND	ND	ND	ND	ND	ND
Avg	1	2	5	9	4	34	7
Sig	1	1	5	25	2	20	22

	Hg	Pb
Max	11	734
Min	ND	1
Avg	3	59
Sig	3	92

[a] Not-detectable data omitted

TABLE 15

STATISTICAL SUMMARY OF ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES IN NORTHEASTERN MINNESOTA[a]

ng/m^3

	Al	Si	P	S	Cl	K	Ca
Max	3048	8884	249	5623	360	1262	5017
Min	ND	ND	ND	ND	ND	ND	ND
Aug	240	908	49	692	34	163	320
Sig	389	1335	40	641	63	183	522

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	453	22	40	156	12865	1852	43
Min	ND	ND	ND	ND	ND	ND	ND
Aug	29	0.5	3.7	15	1047	22	2
Sig	55	2	6	22	1849	105	5

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	27	109	252	8	11	2	51
Min	ND	ND	ND	ND	ND	ND	ND
Aug	2	6	15	1	0.3	0.04	4
Sig		13	26	2	0.9	0.3	6

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	5	10	26	132	8	185	132
Min	ND	ND	ND	ND	ND	ND	ND
Aug	0.3	0.7	2	0.8	0.6	28	0.7
Sig	0.6	1	4	8	2	22	7

	Hg	Pb
Max	11	734
Min	ND	ND
Aug	0.2	58
Sig	1	91

[a] Not-detectable data included as analytical zero

TABLE 16

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT FERNBERG-7001

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	595.0	78.0	2383.0	1976.0	134.0	344.0	980.0
Min	ND	ND	27.0	101.0	ND	13.0	14.0
Avg	100.3	32.6	455.2	729.1	18.7	110.4	201.2
Sig	151.1	23.6	591.9	559.6	36.2	86.4	240.7

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	72.0	22.0	39.0	34.0	2448.0	1852.0	6.0
Min	ND	ND	ND	ND	15.0	ND	ND
Avg	15.5	0.8	11.2	5.7	376.0	75.8	0.6
Sig	22.2	3.9	6.9	9.0	564.0	332.2	1.6

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	27.0	54.0	20.0	6.0	11.0	2.0	16.0
Min	ND	ND	1.0	ND	ND	ND	ND
Avg	1.2	4.8	4.5	1.7	0.4	0.2	2.4
Sig	4.8	9.8	3.4	2.5	1.9	0.7	3.4

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	1.0	2.0	4.0	59.0	7.0	40.0	132.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.2	0.1	0.3	2.0	2.2	14.9	4.0
Sig	0.4	0.4	1.1	10.3	2.6	14.7	22.9

	Hg	Pb
Max	ND	111.0
Min	ND	ND
Avg		18.5
Sig		25.3

TABLE 17

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT ISABELLA-7004

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	697.0	111.0	2585.0	2069.0	163.0	435.0	788.0
Min	ND	ND	3.0	19.0	ND	ND	3.0
Avg	142.5	29.5	446.1	675.6	24.6	106.2	167.4
Sig	160.	27.0	610.7	606.7	45.0	99.3	205.9

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	84.0	ND	11.0	41.0	1451.0	84.0	8.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	13.1		0.9	7.5	274.5	16.1	0.4
Sig	21.3		2.9	9.3	356.6	16.6	1.8

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	4.0	6.0	20.0	6.0	1.0	2.0	13.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.6	0.8	4.6	0.2	0.0	0.1	2.0
Sig	1.2	1.7	3.9	1.0	0.2	0.7	3.0

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	2.0	5.0	4.0	ND	49.0	ND
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.2	0.7	0.6	0.1		7.7	
Sig	0.6	0.7	1.4	0.8		13.1	

	Hg	Pb
Max	ND	119.0
Min	ND	ND
Avg		18.9
Sig		21.5

TABLE 18

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT BEAR HEAD-7005

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	1494.0	125.0	5412.0	2107.0	153.0	704.0	1346.0
Min	ND	3.0	ND	26.0	ND	6.0	9.0
Avg	263.3	45.8	930.9	721.5	16.2	162.7	296.5
Sig	373.4	29.1	1364.7	603.4	40.6	158.6	355.4

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	185.0	10.0	16.0	82.0	3962.0	55.0	11.0
Min	ND	ND	ND	ND	5.0	ND	ND
Avg	29.2	1.5	6.0	15.3	747.2	12.4	1.3
Sig	46.6	3.4	5.3	18.1	962.5	11.7	3.1

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	5.0	8.0	18.0	8.0	2.0	ND	20.0
Min	ND	ND	1.0	ND	ND	ND	ND
Avg	0.9	1.9	4.7	1.8	0.2		5.1
Sig	1.5	2.8	3.6	2.7	0.5		6.0

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	4.0	17.0	ND	ND	71.0	4.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.1	1.7	2.1			23.1	0.3
Sig	0.4	1.1	4.2			17.4	1.0

	Hg	Pb
Max	3.0	125.0
Min	ND	ND
Avg	0.4	21.3
Sig	1.0	24.6

TABLE 19

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT DUNKA ROAD-7006

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	3048.0	166.0	8488.0	1997.0	133.	948.0	1607.0
Min	4.0	ND	13.0	39.0	ND	3.0	7.0
Avg	495.7	60.7	1472.5	671.7	21.3	193.1	351.7
Sig	726.6	41.2	2139.6	524.5	34.8	234.9	430.

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	267.0	17.0	18.0	116.0	6477.0	212.0	27.0
Min	ND	ND	ND	ND	22.0	ND	ND
Avg	41.103	1.0	6.3	24.3	1432.4	16.1	2.9
Sig	78.4	3.5	5.7	30.2	1703.0	34.4	6.9

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	26.0	49.0	19.0	7.0	2.0	2.0	20.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	3.6	5.9	4.8	1.1	0.2	0.1	4.4
Sig	5.8	10.9	3.7	2.1	0.6	0.5	4.5

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	6.0	26.0	132.0	7.0	87.0	8.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.2	1.0	4.7	4.2	2.1	38.8	0.4
Sig	0.5	1.6	6.4	21.1	2.5	22.7	1.5

	Hg	Pb
Max	3.0	112.0
Min	ND	ND
Avg	0.1	21.0
Sig	0.5	22.1

TABLE 20

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT TOIMI-7007

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	665.0	97:	2688.0	1603.0	126.0	417.0	922.0
Min	ND	ND	6.0	23.0	ND	4.0	ND
Avg	111.6	31.2	533.4	466.6	23.7	105.0	181.5
Sig	179.4	28.2	731.0	481.3	40.3	107.1	244.8

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	72.0	ND	1.0	44.0	1463.0	72.0	5.0
Min	ND	ND	ND	ND	6.0	1.0	ND
Avg	15.5	ND	0.1	10.3	413.0	9.5	0.3
Sig	22.2	ND	0.3	11.4	442.2	14.3	1.0

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	ND	34.0	9.0	6.0	ND	ND	10.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	ND	3.3	3.0	1.2	ND	ND	2.6
Sig	ND	7.4	2.7	2.1	ND	ND	3.1

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	3.0	5.0	ND	5.0	51.0	6.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.6	0.3	0.3	ND	0.5	23.4	0.5
Sig	0.7	0.8	1.2	ND	1.5	14.4	1.2

	Hg	Pb
Max	3.0	48.0
Min	ND	ND
Avg	0.1	13.3
Sig	0.6	13.7

TABLE 21

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT ERIE-7008

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	577.0	107.0	3143.0	1684.0	192.0	358.0	358.0
Min	ND	ND	10.0	51.0	ND	3.0	3.0
Avg	74.7	23.9	532.4	355.3	73.4	76.6	76.6
Sig	162.6	26.8	818.9	462.1	66.5	94.8	94.8

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	85.0	ND	6.0	87.0	10,771.	30.0	22.0
Min	ND	ND	ND	ND	10.0	1.0	ND
Avg	9.6		0.7	17.8	1280.0	9.2	2.1
Sig	23.3		1.9	21.0	2506.	6.9	5.6

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	5.0	9.0	36.0	6.0	ND	ND	51.0
n	ND	ND	1.0	ND	ND	ND	ND
Avg	0.3	1.4	7.7	1.5			4.1
Sig	1.2	2.6	8.1	2.3			11.6

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	3.0	5.0	ND	4.0	45.0	5.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.4	0.4	0.6		0.2	19.0	0.3
Sig	0.6	0.9	1.4		0.9	16.1	1.2

	Hg	Pb
Max	3.0	121.0
Min	ND	4.0
Avg	0.3	33.5
Sig	0.9	32.7

TABLE 22

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT HOYT LAKES-7010

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	915.0	115.0	3776.0	2019.0	122.0	549.0	930.0
Min	ND	ND	22.0	ND	ND	5.0	11.0
Avg	156.9	31.7	611.4	626.4	14.3	117.4	214.5
Sig	196.7	29.0	784.5	568.5	27.0	110.1	240.7

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	124.0	ND	21.0	54.0	6073.0	50.0	12.0
Min	ND	ND	ND	ND	38.0	ND	ND
Avg	14.7		3.9	10.7	990.6	11.5	1.6
Sig	6.5		5.4	11.9	1215.5	12.5	3.3

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	3.0	9.0	37.0	8.0	3.0	ND	44.0
Min	ND	ND	ND	ND	ND	ND	ND
g	0.5	2.8	8.0	4.3	1.1		7.6
Sig	1.0	2.7	8.1	2.8	1.1		9.6

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	5.0	2.0	8.0	3.0	1.0	185.0	5.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.4	0.2	1.9	0.5	0.0	46.0	0.6
Sig	0.9	0.6	2.5	1.1	0.2	29.9	1.5

	Hg	Pb
Max	3.0	120.0
Min	ND	1.0
Avg	0.1	30.6
Sig	0.5	27.6

TABLE 23

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT WHITEFACE-7011

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	574.0	101.0	2282.0	2103.0	139.0	344	810.0
Min	ND	ND	34.0	100.0	ND	40.	24.0
Avg	127.9	49.9	504.0	750.9	18.00	127.2	212.5
Sig	134.7	23.5	529.0	572.3	35.2	76.6	227.3

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	71.0	ND	8.0	34.0	1410.0	68.0	8.0
Min	ND	ND	ND	ND	21.0	ND	ND
Avg	8.7		0.9	7.4	432.1	11.7	0.6
Sig	18.4		2.5	8.7	363.6	13.9	1.9

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	3.0	12.0	21.0	5.0	1.0	ND	20.0
Min	ND	ND	2.0	ND	ND	ND	ND
g	0.5	1.4	7.3	0.3	0.1		2.7
Sig	0.9	2.6	4.1	1.1	0.3		4.4

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	3.0	2.0	7.0	ND	6.0	50.0	5.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.7	0.3	0.8		0.4	31.8	0.4
Sig	0.8	0.7	1.7		1.5	12.8	1.3

	Hg	Pb
Max	4.0	132.0
Min	ND	8.0
Avg	0.2	30.3
Sig	0.9	25.6

TABLE 24

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT BABBITT-7013

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	1559.0	133.0	6261.0	2189.0	120.0	630.0	1312.0
Min	ND	ND	81.0	70.0	ND	32.0	12.0
Avg	314.7	50.4	1349.5	695.9	22.3	186.2	350.1
Sig	362.5	31.3	1357.3	601.5	37.8	145.5	323.4

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	207.0	ND	9.0	132.0	9462.0	59.0	21.0
Min	ND	ND	ND	4.0	49.0	ND	ND
Avg	40.5		1.2	24.3	1483.6	16.5	1.7
Sig	48.4		2.8	25.8	2041.5	12.2	5.2

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	11.0	9.0	80.0	ND	2.0	ND	32.0
n	ND	ND	2.0	ND	ND	ND	ND
Avg	1.8	1.3	32.1		0.1		5.2
Sig	2.7	2.4	19.8		0.4		7.9

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	5.0	19.0	10.0	ND	55.0	5.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.5	0.6	4.9	0.3		29.4	0.2
Sig	0.6	1.2	4.1	1.8		14.3	0.9

	Hg	Pb
Max	ND	322.0
Min	ND	6.0
Avg		136.1
Sig		80.4

TABLE 25

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT SCANLON-7412

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	750.0	249.0	3182.0	5623.0	340.	1190.0	1065.0
Min	50.0	29.0	285.0	245.0	ND	71.0	99.0
Avg	334.9	90.8	1347.4	1173.9	57.9	357.3	430.7
Sig	205.7	57.5	797.1	1188.2	95.1	251.2	222.4

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	126.0	16.0	7.0	62.0	1998.0	108.0	ND
Min	ND	ND	ND	ND	188.0	6.0	ND
Avg	53.7	0.7	0.3	15.8	934.2	37.3	
Sig	39.9	3.3	1.5	14.5	540.	26.3	

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	13.0	35.0	85.0	6.0	2.0	ND	12.0
Min	ND	ND	20.0	ND	ND	ND	ND
Avg	3.2	15.1	41.1	0.3	0.2		2.3
Sig	3.1	9.3	17.4	1.3	0.6		3.7

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	3.0	7.0	3.0	7.0	70.0	8.0
Min	ND	ND	ND	ND	ND	ND	ND
Avg	0.1	0.6	3.5	0.1	0.5	39.7	0.4
Sig	0.5	1.0	2.3	0.6	1.6	14.8	1.7

	Hg	Pb
Max	ND	327.0
Min	ND	8.0
Avg		177.1
Sig		78.2

TABLE 26

ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATES AT DULUTH WEST-7527

ng/m^3

	Al	P	Si	S	Cl	K	Ca
Max	2355.0	243.0	8884.0	2335.0	360.0	1262.0	5017.0
Min	8.0	2.0	48.0	57.0	17.0	9.0	26.0
Avg	534.5	67.9	2181.9	712.1	163.9	334.9	1290.6
Sig	651.2	68.6	2478.5	617.7	108.6	351.5	1489.9

	Ti	V	Cr	Mn	Fe	Zn	Co
Max	453.0	13.0	40.0	156.0	12,865.0	129.0	43.0
Min	1.0	ND	ND	1.0	48.0	1.0	ND
Avg	107.8	1.2	6.2	39.2	4256.8	36.6	10.1
Sig	127.9	3.7	10.5	42.3	4407.5	35.0	11.8

	Ni	Cu	Br	Sn	Ga	Ge	As
Max	21.0	109.0	252.0	ND	4.0	ND	16.0
Min	ND	1.0	7.0	ND	ND	ND	ND
g	5.9	38.0	70.2		0.5		4.0
Sig	6.1	31.3	66.7		1.1		5.0

	Se	Rb	Sr	Cd	Sb	Ba	W
Max	2.0	10.0	23.0	ND	8.0	84.0	9.0
Min	ND	ND	ND	ND	ND	2.0	ND
Avg	0.4	1.6	6.6		0.5	29.0	0.9
Sig	0.8	2.8	6.9		1.8	25.4	2.1

	Hg	Pb
Max	11.0	734.0
Min	ND	19.0
Avg	1.3	234.3
Sig	3.0	205.6

These three elements can derive from both natural (soil) and anthropogenic sources (mining, fossil fuel combustion, vehicular traffic) and therefore a comparison of air particulate concentrations may be meaningful. Urban sites exceed non-urban sites in concentration by 580% and 300%, for Pb and Fe, respectively. The Fe concentration was skewed to a higher value by the > 4000 ng/m^3 Fe concentration average observed in Duluth, Minnesota. However, the Pb and Fe values for the non-urban sites were significantly less than for the urban sites. It is likely that the enhanced Fe content of air particulates in N.E. Minnesota was derived largely from taconite mining, processing and related activities. The two primary sources of Pb to the region are transport from distant urban/industrial areas and the local combustion of leaded gasoline. For this reason, ∿ 100 ng/m^3 or ∿ 80% of the total lead at urban sites was locally derived.

The mean S content of air particulates at the urban and non-urban sites was not significantly different. This behavior can be attributed to the regional transport and dispersion of sub-micron sized particles which contain most of the S. Because SO_2 concentrations were low in the study region, the majority of the S was likely in the SO_4 form. The source of S to the area is not defined, but transport into the region from distant sources is not unlikely.

A general examination of elemental concentrations in air particulates for the region permits elements to be broadly classified into four main groups:

1. high, with levels generally > 1000 ng/m^3 air - Fe
2. medium, with levels usually between 100-1000 ng/m^3 - Si, Al, K, S
3. low, with levels usually between 10-100 ng/m^3 air
   Ti, Mn, P, Ba, Zn, Cl, Pb, Br

4. very low, with levels usually < 10 ng/m^3 air;

Sr, Rb, Ga, Ni, Ge, V, Cr, Co, Cu, Sn, W, As, Sb, Hg, Cd, Se

The above classification is based, in general, on observations by Cawse (1974) for trace elements in air particulates at seven sites in England. Major differences occur for Fe, which is high in N.E. Minnesota, presumably due to Fe mining, and Cl which was of higher concentration in England, presumably due to a sea salt ocmponent.

TABLE 27

ELEMENTAL CONCENTRATIONS IN AIR
PARTICULATES FOR NORTHEASTERN MINNESOTA COMPARED TO REMOTE AND URBAN AREAS

Element	Urban	Remote	N.E. Minnesota Fernberg	N.E. Minnesota Region
	ng/m^3			
Al	190-4,000	2-450	100	240-299
Si	670-60,000	130-7500	455	910
K	200-5,000	10-300	110	163
Ti	18-500	1-50	16	29-56
Sr	—	—	.3	2-5
Rb	—	—	.1	.7-2
Mn	10-200	0.2-20	6	15-19
Ga	—	—	.4	.3-2
Fe	250-10,000	4-800	376	1048
Ni	2-200	0.4-10	1	2-4
Ge	—	—	.2	.04-2
V	20-600	0.5-20	.8	.5-11
P	50-200	5-100	33	50
Cr	2-100	0.1-15	11	4-10
Ba	—	—	15	30
Co	0.2-20	0.1-14	.6	2-8
Cu	10-1,000	0.4-100	5	6-12
Zn	30-3,000	0.03-150	76	22
Cl	70-7063	9-2,000	19	34-83
Sn	—	—	2	1-5
W	—	—	4	.7-7
As	1-40	0.3-5	2	4-7
Ca	150-20,000	10-2,500	201	320
S	2,000-10,000	800-13,000	729	692
Sb	—	—	2	.6-4
Pb	20-3,000	0.3-200	19	58
Br	6-700	.5-8	5	15
Hg	.2-11	.06-.4	<.2	.2-3
Cd	.3-100	0.01-4	2	.8-9
Se	—	—	.2	.3-1

Elemental concentrations in air particulates at the remote Fernberg Road site (7001) and the regional means are compared to typical ranges of concentrations observed at urban and remote areas around the world (see Tables A-F). In general, elemental concentrations in air particulates at Fernberg Road and the region were typical of remote, mid-continental areas. However, the following elements were classified as occurring at concentrations lower than expected at the remote site: Si, Ni, Cu, Co, V, Cl and S. Elements occurring at higher concentrations than expected were Fe and Cr. In the low concentration category, Cu, Ni, Co, V and S are associated usually with anthropogenic activities (base metal smelting, fossil-fuel combustion, etc.) while Si and Cl are of natural origin - soil and sea-spray, respectively. Vanadium has been used as a tracer of fuel oil combustion, but appears not to be significant at the remote site. Copper and Ni concentrations were low demonstrating the lack of man's influence on these two elements in the region.

The enhanced concentration of Fe at the remote, background site and the regional mean may demonstrate the influence of taconite iron mining processing on the air quality of the region. Preliminary evaluation of wind-rose data indicates that when winds were from the northwest (prevailing), very low concentrations were observed; southwesterly winds, however, resulted in much higher air particulate metal concentrations (D. Thingvold, personal communication). The relatively higher values observed for Cr cannot be explained at present; possible explanations include natural Cr enhancement in soil, local unrecognized source, or long distance transport into the region.

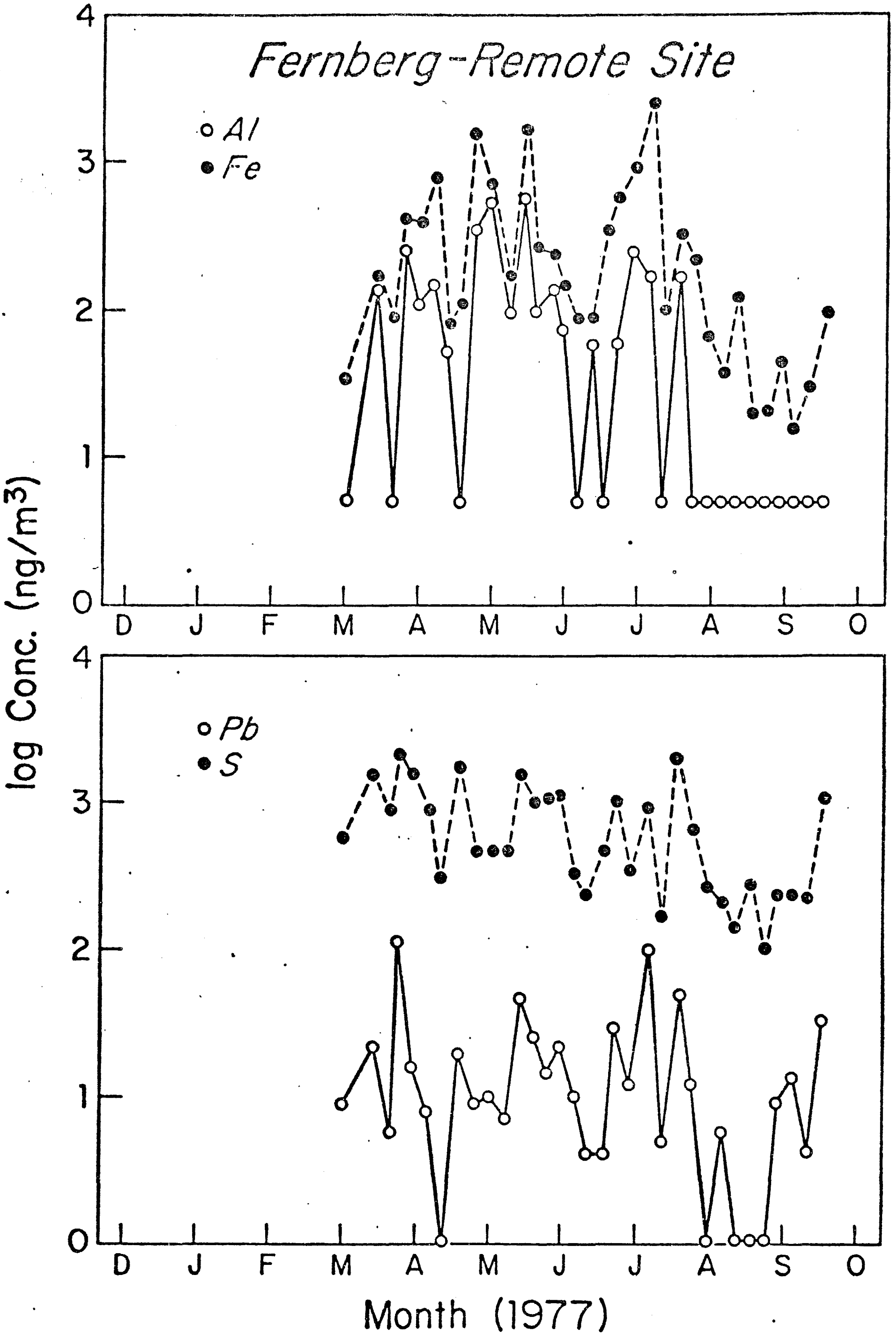
III-4-2. Seasonal Variations

Seasonal trends in the concentrations of Al, Fe, Pb and S in air particulates at Fernberg Road, Toimi and Erie are shown in Figures 5-7. The patterns observed at these three stations are, in general, typical of those

Figure 5

Seasonal Variations in Atmospheric Particulate

Concentrations (Al, Fe, Pb, S) - Fernberg Road



Fernberg-Remote Site
○ Al
● Fe
○ Pb
● S
log Conc. (ng/m³)
0
1
2
3
4
D
J
F
M
A
M
J
J
A
S
O
Month (1977)

Figure 6

Seasonal Variations in Atmospheric Particulate

Concentrations (Al, Fe, Pb, S) - Toimi

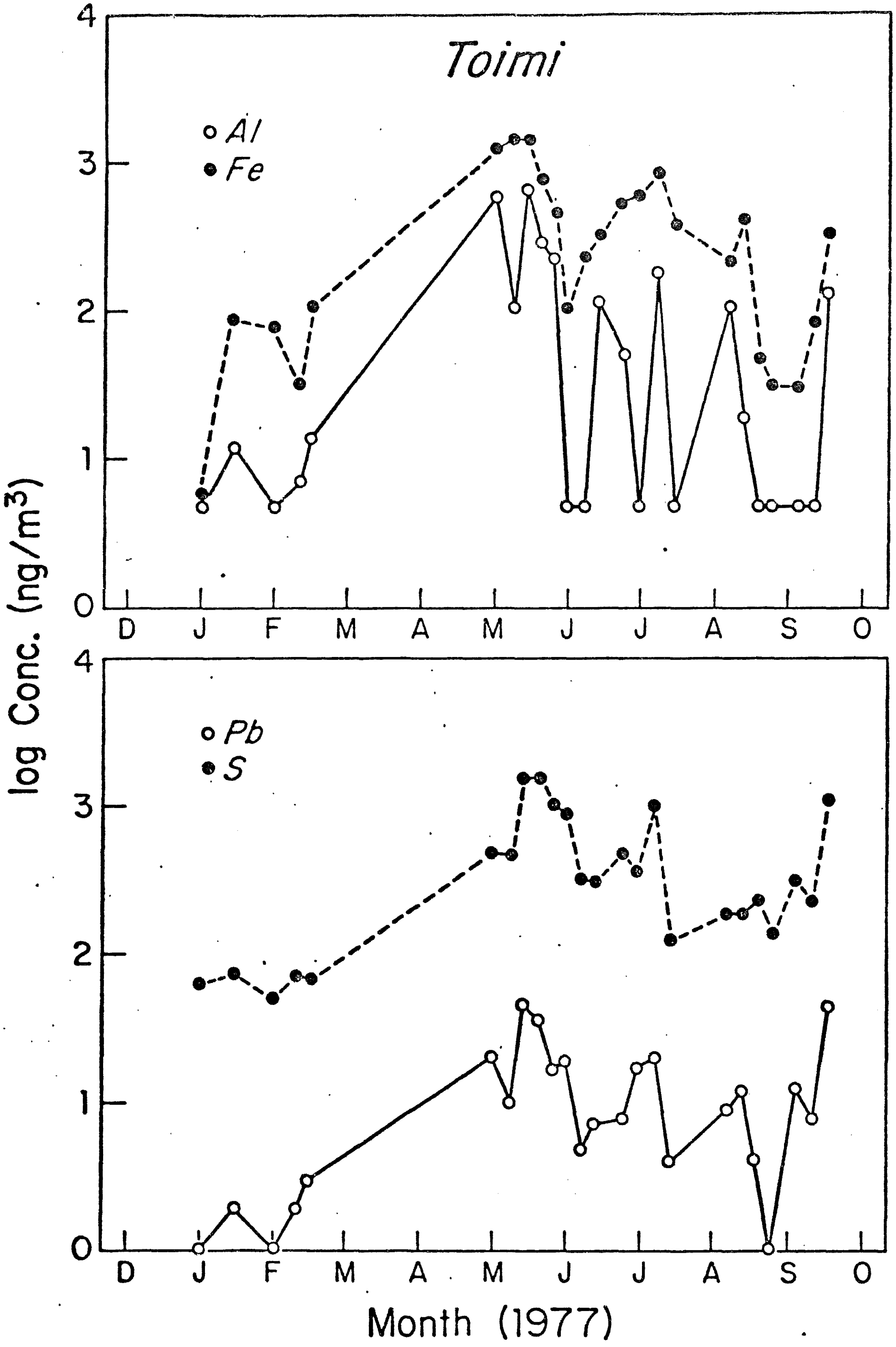
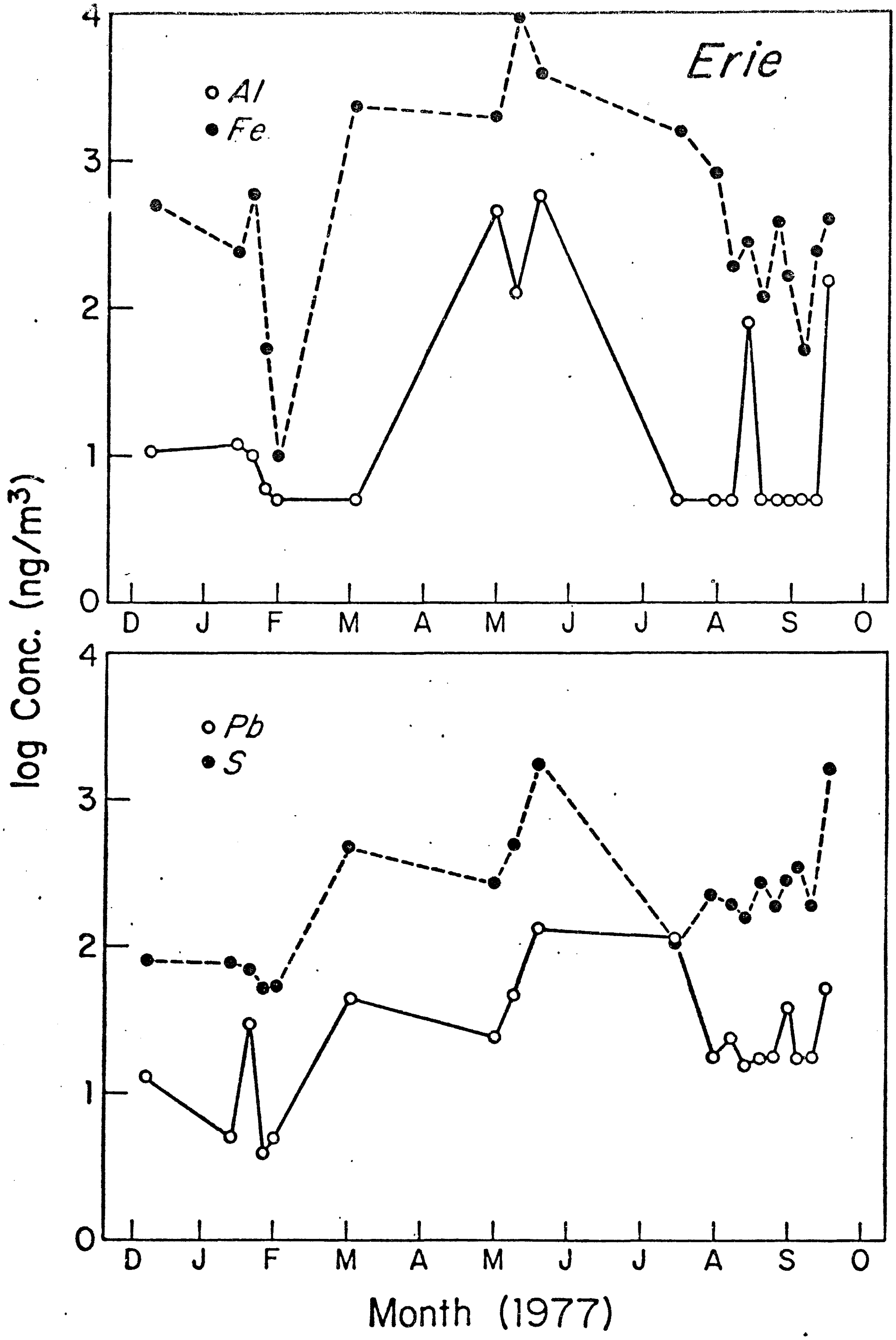

Toimi
○ Al
● Fe
○ Pb
● S
log Conc. (ng/m³)
0
1
2
3
4
D
J
F
M
A
M
J
J
A
S
O
Month (1977)

Figure 7

Seasonal Variations in Atmospheric Particulate

Concentrations (Al, Fe, Pb, S) - Erie



Erie
Al
Fe
Pb
S
0
1
2
3
4
D
J
F
M
A
M
J
J
A
S
O
log Conc. (ng/m^3)
Month (1977)

observed at all regional, non-urban sites. The four elements chosen for depiction of seasonal trends were selected because they represent coarse-size (Al, Fe) and fine-size air particles (Whitby, 1977).

The concentrations of Al and Fe peaked usually in the months of late spring and summer and occurred at lower values in winter. This observation is complicated by the fact air monitoring was not initiated at the Fernberg Road site until March, 1977, and that the taconite iron industry was shut down after late July, 1977. The effect of the mine shutdown can can best be seen in the Fe and Al concentrations at Erie (Figure 7). In this case, Fe and Al concentrations decrease by 1-2 orders of magnitude following mine shutdown. The trend is also observable at Fernberg Road (Figure 5) and to a lesser extent at Toimi (Figure 6) which appeared to be isolated from mining effects. Since less than one year of elemental data is available presently, it is uncertain whether the decrease in Fe and Al concentrations in air particulates was due to mine shutdown or a result of normal seasonal and/or meteorological phenomena.

The seasonal trends in Pb and S content of air particulates exhibited two apparently different patterns. At Toimi and Erie, S and Pb content generally increased from winter to fall, although significant variability was evident. However, Pb and S at Fernberg exhibited a trend slightly decreasing over the study period. In addition, Pb and S decreased noticeably at the remote Fernberg site following iron mining shutdown, although sample-to-sample variation limits definitive explanations.

The primary source of Pb in air particulates is leaded gasoline whereas S may be derived from fossil-fuel combustion, soil re-suspension and wet-land injection into the atmosphere. The different source functions associated with Pb and S suggest that they need not be related. However, the seasonal variations in Pb and S concentrations were nearly superimposable, suggesting that they had a common local source and/or were transported by regional air masses. The latter explanation appears more plausible since local sources are few and the matching occurred at sites throughout the study area.

Cawse (1974) and Peirsen et al. (1974) found that air concentrations increased during autumn-winter over spring-summer, and suggested that the increase could be explained by reduced atmospheric dispersion under conditions of persistent low inversion layers and the combustion of heating fuels. However, the remote, mid-continental area of N.E. Minnesota which lacks significant local sources (with the exception of Fe) was probably dominated by snow cover during winter which inhibited dust re-suspension, and forest coverage.

III-4-3. Dry deposition

Chamberlain (1953) introduced an expression for particle deposition rates as:

$$D(\mu g.m^{-2}.S^{-1}) = V_g(m.s^{-1})\ C\ (\mu g.m^{-3})$$

where D = dry deposition rate

V_g = deposition velocity

C = air concentration

The value of V_g is critical to the calculation of D, the deposition rate, and is dependent on micrometeorological conditions, surface roughness and particle size. Recently, Cawse (1974) and Peirsen et al. (1973) have measured individual element V_g for several stations in Great Britain. In these studies, the deposition surface was a Whatman 41 filter paper which may not resemble, in behavior, a forest canopy, soil or water-surface. Davidson (1977) has recently developed a model for dry deposition of Cu, Pb and Zn to a grass surface as a function of particle size. Sehmel and Sutter (1974) have measured V_g as a function of particle size over a water surface in wind tunnel experiments. In this report, Cawse's (1974) data on V_g were used to calculate deposition to N.E. Minnesota. Table 28 lists the V_g used for each element and the corresponding measured mass median particle diameter.

Dry deposition rates calculated for Fernberg, Toimi, Isabella and Dunka, as well as a regional dry deposition rate for 18 elements, are given in Table 29 . The regional value for elemental dry deposition is based on the arithmetic mean of the four sites listed above. The dry deposition rates should be considered as minimum values since V_g to a forest canopy may be greater than for a filter paper. In general, the dry deposition rates are typical of remote, mid-continental areas.

TABLE 28

Dry Deposition Velocities and Mass Median Diameters of Atmospheric Elements - Great Britain and N.E. Minnesota

Element	Chilton[a] Vg cm/sec	Chilton[a] mmd µm	Trebanos[a] Vg cm/sec	Trebanos[a] mmd µm	N.E. Minnesota mmd µm
Al	1.3	4.4	--	--	4.5-4.9
Cl	1.0	0.7	--	--	
V	0.3	0.6	0.5	0.6	
Cr	0.5	1.0	0.2	1.5	
Mn	0.6	1.3	1.1	1.5	5.0-5.2
Fe	2.5	1.1	2.1	3.5	4.8-6.5
Co	0.6	1.0	2.0	3.5	
Zn	0.6	0.9	0.2	0.9	
As	0.2	0.7	0.4	0.6	
Se	< 0.09	0.6	0.3	0.7	
Br	0.4	0.5	--	--	
Sb	0.1	0.7	0.5	0.7	
Pb	0.3	0.6	0.4	0.7	0.9-1.1
SO_4	∿0.3	0.7	--	--	
Cu	∿0.8	--	2.0	1.5	
Ni	1.4	--	1.4	0.7	
Cd	∿0.4	--	--	--	

[a] Cawse, P. A., A Survey of Atmospheric Trace Elements in the United Kingdom, AERE Rept. No. R 7669, AERE Harwell, Oxfordshire, England, 1974, 95 p. (Chilton, rural; Trebanos, industrial)

TABLE 29

Concentrations and Estimated Dry Deposition Rates of Atmospheric Particulate Elements[a]

ELEMENT	DUNKA		ISABELLA		TOIMI		FERNBERG		N.E. MINNESOTA
	C	D	C	D	C	D	C	D	D
Al	496	2.0	143	.59	112	.50	100	.46	.89±.74
S	672	.64	676	.64	467	.44	729	.69	.60±.11
Cl	21	.066	25	.079	24	.076	19	.060	.07±.01
V	1	.0009	ND	---	ND	--	0.8	.008	.0009±.0001
Cr	6	.009	1	.002	0.1	.0002	11	.020	.008±.009
Mn	24	.045	8	.015	10	.019	6	.011	0.23±.015
Fe	1432	11.3	275	2.2	413	3.3	376	3.0	4.9 ±.4.3
Zn	16	.03	16	.030	10	.019	76	.14	0.55±.057
Co	3	.0057	0.4	.0007	0.3	.0006	0.6	.0011	.0020±.0025
Ni	4	.018	0.6	.0027	ND	--	1	.0044	.008±.008
Cu	6	.015	0.8	.002	3	.0076	5	.013	.009±.006
Br	5	.0063	5	.0063	3	.0038	5	.0063	.0057±.0013
As	4	.0025	2	.0013	3	.0019	2	.0013	.0018±.0006
Se	0.2	$5.7x10^{-5}$	0.2	$5.7x10^{-5}$	0.6	.0002	0.2	$5.7x10^{-5}$	$8.5x10^{-5} \pm 5.7x10^{-5}$
Cd	4	.005	0.1	.0001	ND	--	2	.0025	.0025±.0025
Sb	2	.0006	ND	--	0.5	.0002	2	.0006	.0005±.0002
Hg	0.1	$2.8x10^{-5}$	ND	___	0.1	$2.9x10^{-5}$	ND	--	$2.9x10^{-5} \pm 7x10^{-7}$
Pb	21	.020	19	.018	13	0.12	19	.018	.017±.003

[a] Dry deposition rates are calculated based on the deposition velocities in Table and the relationship
D = VgxC where D = deposition, Vg = deposition velocity (m/sec)
C = concentration (ng/m^3); Deposition rates are given in units of Kg/ha/yr.

III-5. Size Distribution of Selected Metals in Air Particulates

III-5-1. Concentrations

Size-differentiated air particulates were collected at Kawishiwi (KL7003) and Hoyt Lakes (HL7010) from September, 1976 through December, 1977 using Delron cascade impactors (Model DCI-6). Details of the experimental procedure, results and interpretation can be found in Eisenreich *et al*. (1978).

A comparison of size fractionated aerosol samples analyzed for trace metals at KL and HL and averaged over the study period is shown in Figure 8. The data is plotted as log [metal] versus impaction stage, with stage B representing the back-up filter (smallest particle size), and stage 1, the largest particle size. The results of means for all size fractionated aerosols are given in Tables 30 and 31. Iron, Al, Mn and Ca were nearly always dominated by large particle sizes while Pb occurred primarily in small particle sizes. In general, Fe and Mn concentrations tended to increase in the < 0.5 μm size fraction suggesting a bimodal distribution for these elements, and the presence of more than one source. This pattern was identical at KL and HL, differing only in that metal concentrations were (2-3)x higher at HL than at KL.

An extensive sampling effort was implemented from the 21-27 May, 1977 at KL to obtain size distributions and concentrations of elements which occurred usually at low levels. Figure 9 shows the size-distribution patterns for Ca, Al, Fe, Zn, Mn, Pb and Cd and Table 32 presents the actual data. As expected, Ca, Al, Mn and Fe were dominated by large particle sizes (mmd > 4 μm) and Zn, Cd and Pb were dominated by small particle sizes (∿ mmd < 2 μm).

Average mass median diameters (mmd) were calculated for Fe, Al, Ca,

Figure 8

Size Distributions of Fe, Al, Ca, Mn and Pb

in N.E. Minnesota Aerosol

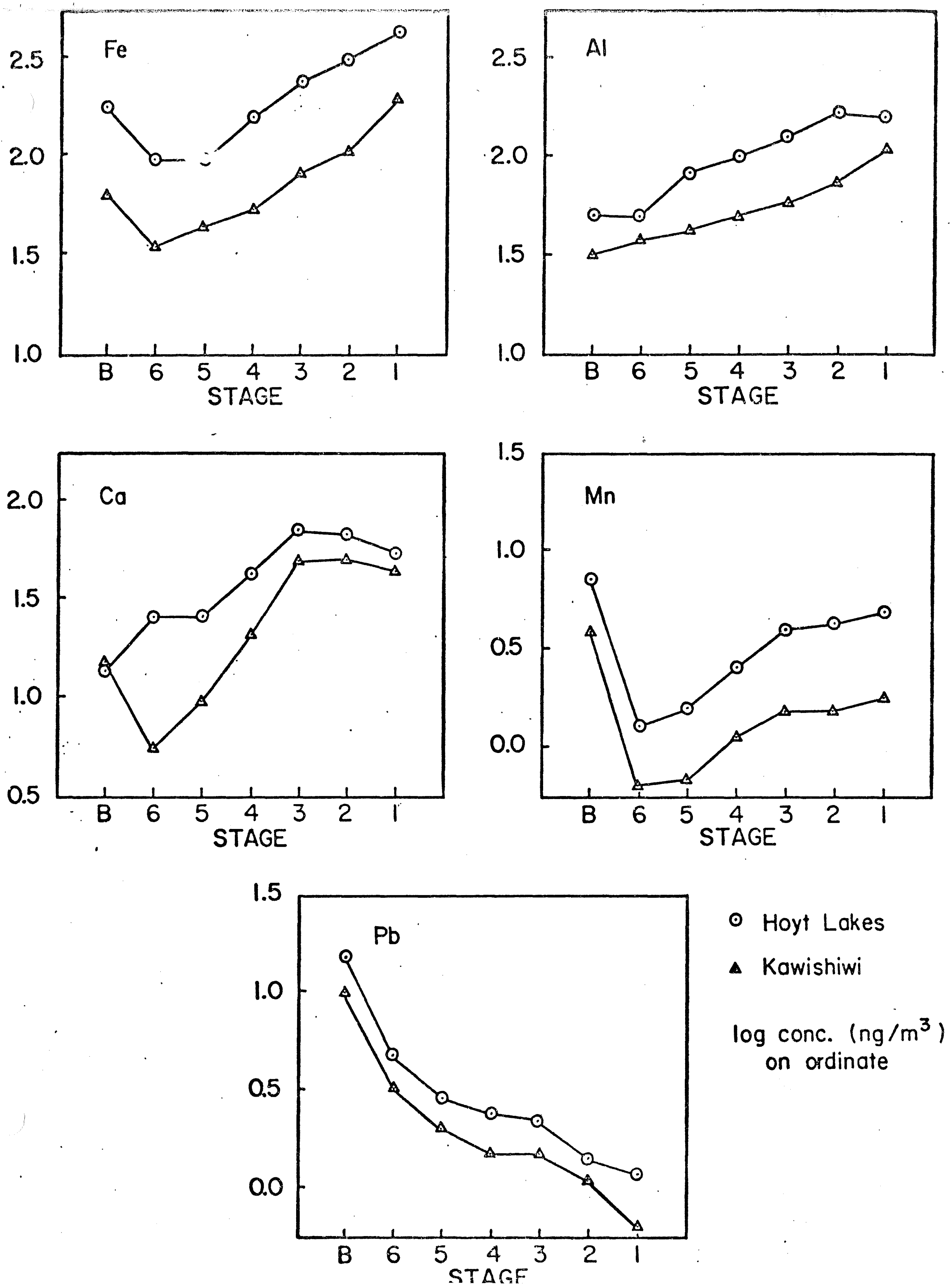

Fe
2.5
2.0
1.5
1.0
B 6 5 4 3 2 1
STAGE
Al
2.5
2.0
1.5
1.0
B 6 5 4 3 2 1
STAGE
Ca
2.0
1.5
1.0
0.5
B 6 5 4 3 2 1
STAGE
Mn
1.5
1.0
0.5
0.0
B 6 5 4 3 2 1
STAGE
Pb
1.5
1.0
0.5
0.0
B 6 5 4 3 2 1
STAGE
○ Hoyt Lakes
▲ Kawishiwi
log conc. (ng/m³) on ordinate

TABLE 30

MEAN ATMOSPHERIC METAL CONCENTRATIONS IN DIFFERENT SIZE FRACTIONS AT KAWISHIWI LABORATORY (ng/m^3)

Size Range (μm)	Fe	Al	Ca	Mn	Pb	Cu	Ni
>16	198	116	46	1.8	0.60	<1.3	<1.1
	(258)	(90)	(35)	(0.97)	(0.61)	(2.5)	(0.49)
8-16	107	74	50	1.5	1.1	<4.5	<0.93
	(153)	(56)	(36)	(0.93)	(1.5)	(6.4)	(0.30)
4- 8	83	59	49	1.5	1.5	<0.79	<0.93
	(121)	(61)	(40)	(0.92)	(1.3)	(0.95)	(0.30)
2- 4	54	50	21	1.1	1.5	<0.53	<1.0
	(57)	(37)	(20)	(0.44)	(1.0)	(0.49)	(0.24)
1- 2	44	47	9.5	0.67	2.1	<1.1	<1.2
	(46)	(28)	(8.9)	(0.38)	(1.6)	(2.1)	(0.90)
.5- 1	34	39	5.5	0.66	3.2	<1.3	<1.1
	(51)	(26)	(6.2)	(0.36)	(2.6)	(2.9)	(0.58)
<.5	61	60	15	3.8	10	ND	<8.4
	(80)	(59)	(11)	(9.0)	(14)		(6.2)

Numbers in parentheses represent one standard deviation from the mean.

TABLE 31

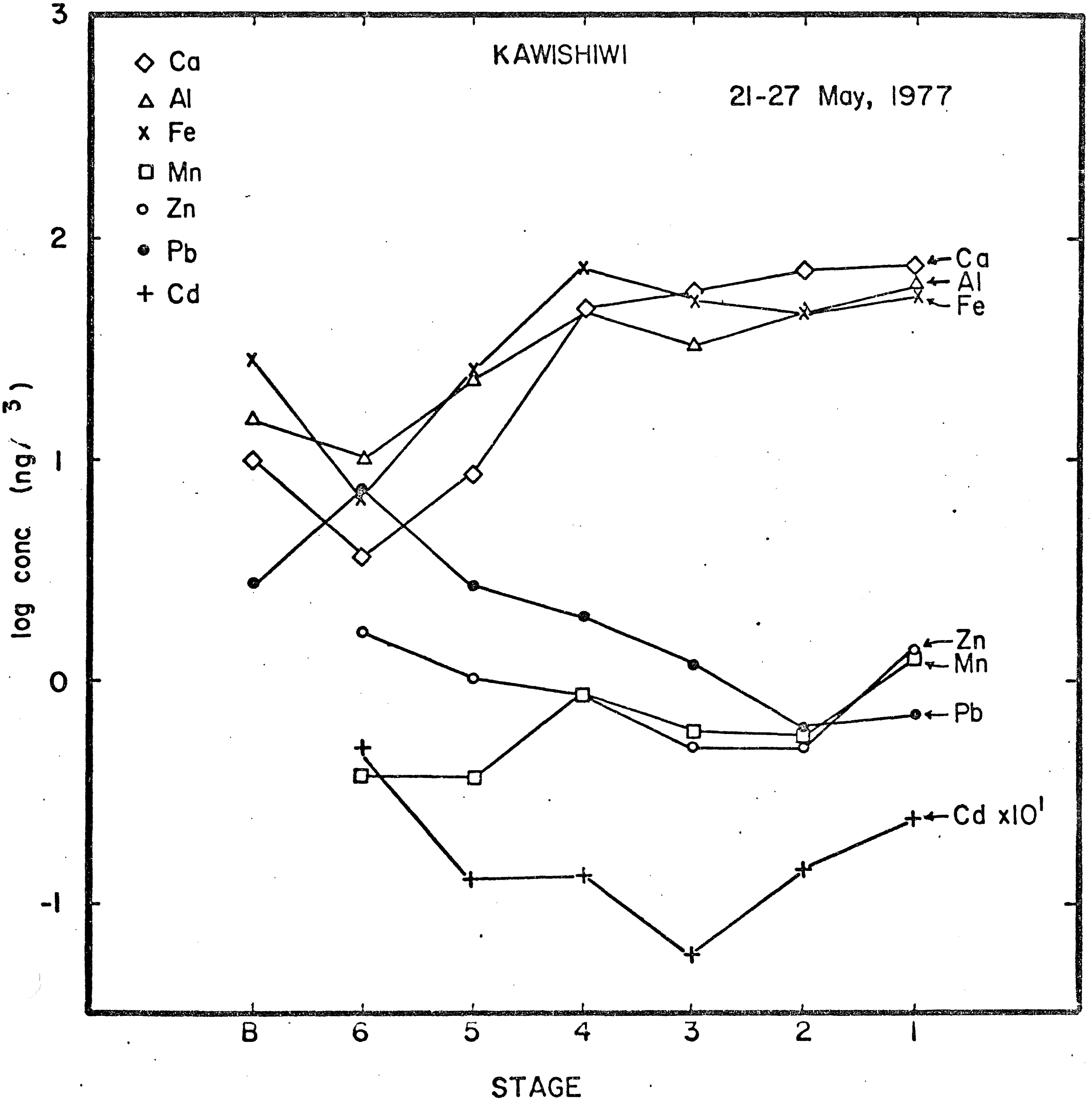
MEAN ATMOSPHERIC METAL CONCENTRATIONS IN DIFFERENT SIZE FRACTIONS AT HOYT LAKES (ng/m^3)

Size Range (μm)	Fe	Al	Ca	Mn	Pb	Cu	Ni
>16	443 (591)	162 (249)	53 (39)	4.8 (6.8)	1.2 (0.93)	<1.4 (1.5)	<2.2 (2.3)
8-16	304 (345)	168 (207)	69 (80)	4.2 (7.1)	1.4 (1.0)	<2.0 (3.0)	<2.0 (2.3)
4- 8	236 (267)	128 (142)	71 (74)	3.9 (4.9)	2.3 (1.6)	<1.0 (1.1)	<1.5 (0.96)
2- 4	158 (192)	104 (115)	43 (39)	2.6 (3.4)	2.4 (1.8)	<1.0 (1.6)	<1.4 (0.78)
1- 2	90 (115)	82 (85)	26 (39)	1.6 (1.5)	2.9 (1.9)	<2.7 (4.9)	<1.4 (0.78)
.5- 1	98 (157)	52 (43)	26 (24)	1.3 (1.0)	4.8 (3.6)	<1.9 (2.2)	<1.4 (0.78)
<.5	184 (258)	54 (65)	14 (6.5)	7.2 (9.2)	15 (15)	<0.60 ND	<14 (18)

Figure 9

Size Distribution of Ca, Al, Fe, Zn, Mn, Pb and Cd

at Kawishiwi, 21-27 May, 1977



KAWISHIWI
21-27 May, 1977
◇ Ca
△ Al
x Fe
□ Mn
○ Zn
● Pb
+ Cd
Ca
Al
Fe
Zn
Mn
Pb
Cd x10^1
3
2
1
0
-1
log conc (ng/ 3)
B
6
5
4
3
2
1
STAGE

Mn and Pb (Table 33) and ranged from 7.8 μm for Ca, 6.9 μm for Fe, 5.2 μm for Mn, and 4.9 μm for Al to 1.1 μm for Pb at KL. The calculated mmd's were 0.2 to 2.6 μm smaller at HL than at KL, but were generally larger than those observed in closer proximity to pollution sources.

Iron enrichment factors (EF's) (see III) based on crustal Al were calculated for all sampling dates at HL and KL and plotted versus stage number in Figure 10. EF's near unity represent non-enriched elements and EF's greater than ∿ 10 correspond to enriched elements versus crustal Al. Prior to late July, 1977, all aerosol samples collected exhibited Fe EF's greater than or equal to unity at both sites. Aerosols sampled subsequent to late July, 1977, EF's were less than or equal to unity. This trend is noted in Figure 10 where EF's for Fe were nearly all below the crustal reference line. The dramatic reversal of the EF trend for Fe as a function of particle size coincided with a shutdown of taconite mining activities in NE Minnesota because of a strike. Whether the change in Fe EF was a result of actual mining activities or a decrease in vehicle traffic on dirt roads cannot be surmised from this data. However, resuspended particles resulting from vehicle movement on dusty roads or blowing wind may be the major source of air particulates in the region (K. Whitby, 1978, personal communication).

Figure 10

Crustal Enrichment Factor for Fe as a Function

of Particle Size and Time

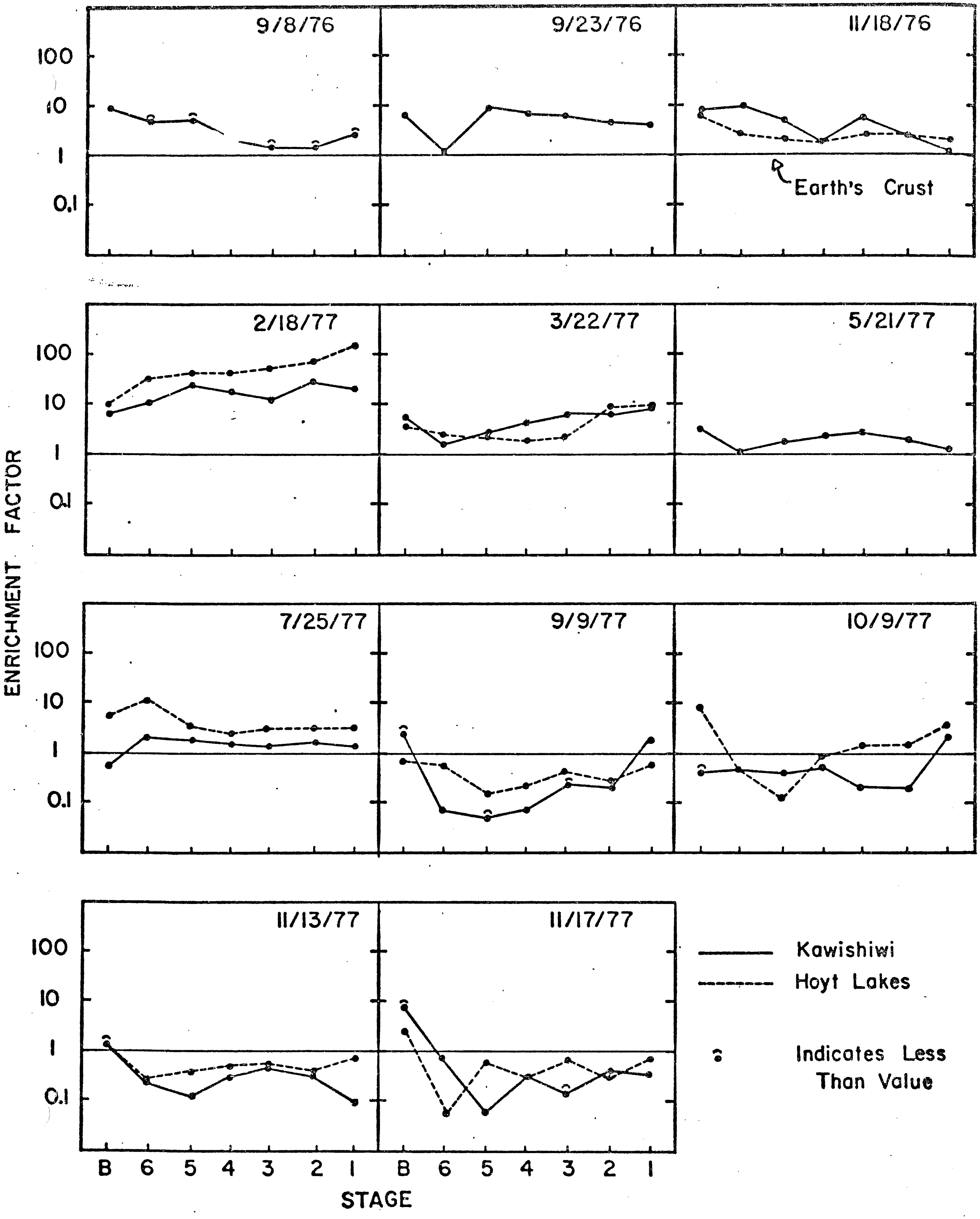

9/8/76
9/23/76
11/18/76
Earth's Crust
2/18/77
3/22/77
5/21/77
7/25/77
9/9/77
10/9/77
11/13/77
11/17/77
100
10
1
0.1
ENRICHMENT FACTOR
B
6
5
4
3
2
1
STAGE
Kawishiwi
Hoyt Lakes
Indicates Less Than Value

TABLE 33

MASS MEDIAN DIAMETERS (μm) OF PARTICULATE METAL IN NE MINNESOTA

Metal		Kawishiwi Lab.	Hoyt Lakes	University of Minnesota
Fe	Mean	6.9	7.3	5.2
	Max.	>16	10.3	
	Min.	∿.25	3.8	
	Std. Dev.	5.8	2.7	
Al	Mean	4.9	4.5	5.3
	Max.	9.8	7.8	
	Min.	0.69	3.5	
	Std. Dev.	3.0	1.5	
Ca	Mean	7.8	5.2	6.9
	Max.	14.9	7.7	
	Min.	5.5	2.7	
	Std. Dev.	3.7	1.9	
Mn	Mean	5.2	5.0	0.47
	Max.	17.2	8.1	
	Min.	0.08	0.08	
	Std. Dev.	5.1	3.3	
Pb	Mean	1.1	0.91	0.38
	Max.	3.0	2.6	
	Min.	0.04	0.18	
	Std. Dev.	1.1	0.88	

III-6. Comparison of Atmospheric Deposition Estimates to N.E. Minnesota

The atmospheric deposition of trace elements to N.E. Minnesota as determined from bulk, throughfall, wet and dry inputs is shown in Table 34. In general, there is reasonable agreement between bulk deposition and wet and dry deposition estimates given the relative uncertainty in the collection or calculation technique, except for Al and Fe. Bulk deposition of Al represented ∿ 30% of the wet and dry estimates considered separately. Bulk deposition of Fe agreed well with the throughfall and wet deposition rates considered separately but was much less than the estimated dry input. Eisenreich et al. (1978) estimated dry deposition of Fe to N.E. Minnesota based on particle size and concentration measurements and found that the dry input was ∿ 1-3 $Kg.ha^{-1}.yr^{-1}$. Given the lack of agreement amongst different loading estimates, Al and Fe atmospheric deposition rates was ∿ 0.3-1.3 and 0.3-3 $Kg.ha^{-1}.yr^{-1}$, respectively.

Elements associated with small particle sizes are removed from the atmosphere by rainfall scavanging more efficiently than by sedimentation or impaction (Cawse, 1974; Andren and Lindberg, 1977). In N.E. Minnesota Pb and SO_4 were likely associated with fine particles and deposition was dominated by wet inputs. In general, atmospheric deposition of all elements to N.E. Minnesota was typical of a remote, mid-continental area which received occasional inputs via long-range transport from urban/industrial centers.

III-7. Elemental Enrichment Factors

Atmospheric aerosols collected near the earth's surface in remote continental areas may be expected to have the earth's crust as their major natural source. By comparing the composition of the earth's crust, information as to the contribution of the crust to the total composition of the aerosol can be

TABLE 34

COMPARISON OF DEPOSITION ESTIMATES TO NE MINNESOTA

Element	Bulk	Throughfall	Wet	Dry
		$\text{Kg.ha}^{-1}.\text{yr}^{-1}$		
Al	.26	—	.95	.89
Fe	.28	.29	.27	4.9
Mn	—	—	.03	.23
Cu	.008	.007	.02	.009
Ni	< .010	< .021	<.01	.008
Pb	.050	.021	.07	.017
Zn	.041	.056	.05	.55
Ca	< 5.3	—	< 5.6	—
Mg	< 2.4	—	< 3.5	—
Na	< 3.3	—	< 5.1	—
K	< 2.5	—	< 1.2	—
P	.18	—	.03	—
TOC	27	160	13	—
Cl	8.2	—	< 3.5	.07
SO_4	16	23	22	1.8
H^+(ueq)	∿400		140	
V	—	—	—	.0009
Cr	—	—	—	.008
Co	—	—	—	.002
Br	—	—	—	.006
As	.006	—	—	.002
Se	—	—	—	8.5×10^{-5}
Cd	.003	.0007	—	.003
Sb	—	—	—	.0005
Hg		—	—	2.9×10^{-5}

obtained. In the same manner, the relative contribution of anthropogenic sources to the metal composition of the aerosol may be estimated. The comparison is obtained conveniently by calculation of elemental enrichment factors for various elements in aerosols as compared to crust material. The general formula for the calculation of enrichment factor is (Rahn, 1976):

$$EF(x)_{\text{aerosol-source}} = \frac{(x/Ref)\ \text{aerosol}}{(x/Ref)\ \text{source}}$$

where $EF(x)_{\text{aerosol-source}}$ is the enrichment factor of element (x) in the aerosol relative to a source reference element, and x/Ref is the ratio of the concentration of element (x) to a reference element in the aerosol or source material. Elements commonly used as reference elements in crustal matter are Al, Ti, Si, Fe, Ce and Sc. Elements having enrichment factors close to unity are in crustal proportions to crustal reference elements, and may be assumed to have the crust as a major source. Such elements are referred to as non-enriched, while those elements having EF's significantly greater than unity may be assumed to have a major source other than the earth's crust. In effect, elements with large EF's are thought to be derived from anthropogenic activities (Rahn, 1976; Zoller et al., 1974).

Aluminum was chosen as the crust reference element in this study for several reasons (Rahn, 1976):

1. Al is a major component of crustal material;
2. Al is a minor component of pollution aerosols;
3. Al can be detected easily by routine analytical instrumentation;
4. Al is free generally of contamination in sampling. Iron is also a popular crustal reference element, but is a major component of pollution aerosols. Ideally, a crustal reference element should have negligible pollution sources and be unreactive in the atmosphere. In addition, Fe would be

of little value as a crustal reference in NE Minnesota where taconite iron mining is prevalent. Thus aerosol-crust enrichment factors used here were calculated by the formula:

$$EF(x) = \frac{(x/Al)\ \text{aerosol}}{(x/Al)\ \text{crust}}$$

Crustal abundances were chosen over soil composition because rocks have been more extensively analyzed than soils and soil composition may vary significantly even over a small geographical area. Crustal abundances for most elements have been compiled, and Mason's (1966) data were chosen for calculation of (x/Al) ratios.

The use of elemental enrichment factors have several limitations which must be appreciated before interpretation is made. For example, EF's near unity for an element means only that the element occurs in crustal proportions to Al; this does not necessarily mean that it is derived from a crustal or natural source. In polluted areas, anthropogenic sources may emit crustal material (fly ash, road dust), but may have EF's near unity. Atmospheric concentrations may be a better indication in this case.

High enrichment factors in polluted areas are atributed almost exclusively to anthropogenic sources. However, high EF's in remote areas may be due to natural soils enriched in a specific element, action of unrecognized natural sources (forest fires, vegetation) and transport of pollutants from urban areas. Probably the most significant limitation is that the precursor of the crustal material is not yet known. For this reason, EF's between 1-10 may simply be artifacts of using the wrong reference element.

Mean regional concentrations and enrichment factors for NE Minnesota are presented in Table 35 , with the elements listed in order of increasing enrichment factor. The data indicates that the first 8 or 9 elements were

TABLE 35

Concentration Range and Mean Enrichment Factors For
Atmospheric Trace Elements in Northeastern Minnesota

	Mean Concentration[a]	Mean Enrichment Factor[b]
	---ng/m^3---	
Al	240-299	1.0
Si	908-911	0.9-1.0
K	163	2
Ti	29-56	2-4
Sr	2-5	2-4
Rb	0.7-2	3-6
Mn	15-19	5
Ga	0.3-2	7-36
Fe	1047-1050	7-6
Ni	2-4	9-15
Ge	.04-2	9-363
V	0.5-11	14-22
P	49-51	16-13
Cr	4-10	14-27
Ba	28-34	22
Co	2-8	27-87
Cu	6-12	35-59
Zn	22-23	106-89
Cl	34-83	88-173
Sn	1-5	169-680
W	0.7-7	158-1269
As	4-7	754-1059
S	692	901-723
Sb	0.6-4	1016-5438
Pb	58-59	1510-1233
Br	15	2033-1631
Hg	0.2-3	849-10200
Cd	0.8-9	1333-12040
Se	0.3-1	2033-5438

[a] Range of mean concentrations including and excluding non-detectable values

[b] Calculated on the basis of Al crustal abundance (Mason, 1966)

non-enriched in aerosol versus crustal Al and are likely associated with a source (S) derived from crustal material. The non-enriched elements (EF 1-10) include Al, Si, K, Ti, Sr, Rb, Mn, Ga and Fe. The inclusion of Fe in the non-enriched category, although being somewhat arbitrary, is important relative to its source. The concentrations of aerosol Fe in NE Minnesota were significantly elevated compared to remote, forested areas, and are due certainly to iron mining. However, the EF (Fe) was not extremely high, indicating that elemental ratios in iron oxide (taconite) deposits and associated overburden and tailings do not differ greatly from crustal proportions.

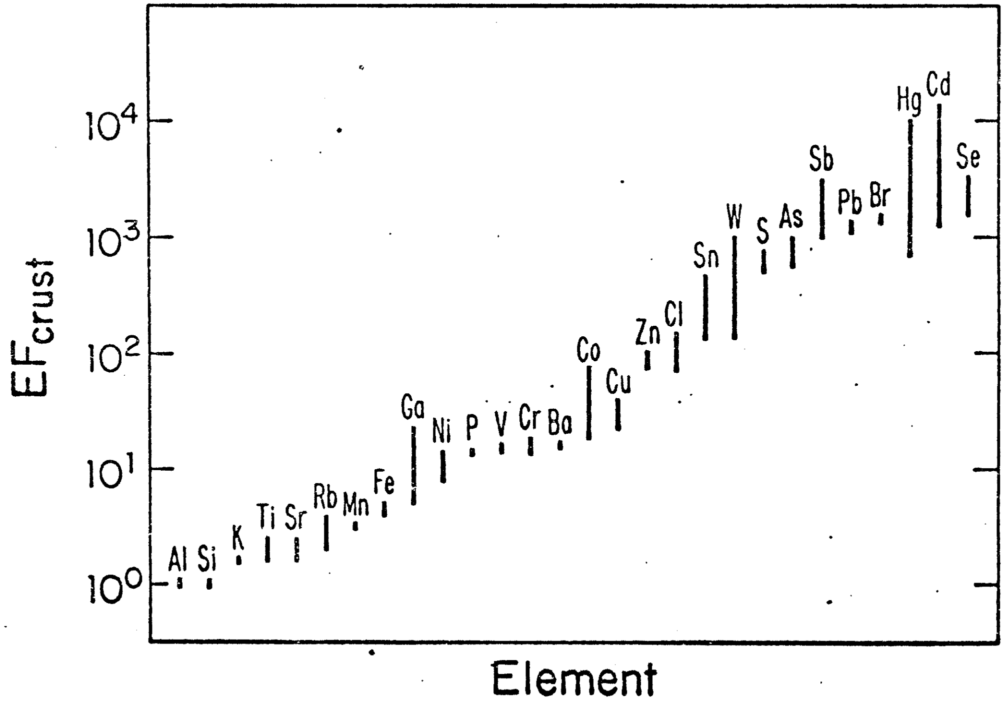
The second group of elements which were moderately enriched (EF 10-100) include Ni, Ge, V, P, Cr, Ba, Co and Cu. In some instances (e.g. P, Ba, Co), elements in this grouping may have soil or crustal material as their source but have higher EF's due to local variations in crustal abundance. The combination of local variances from crustal abundances with low level anthropogenic sources may contribute to EF's for some elements to reach 10-100.

The third group of elements having EF's exceeding 100 are so enriched that crustal or soil material are unlikely sources. This group includes Zn, Cl, Sn, W, As, S, Sb, Pb, Br, Hg, Cd and Se. Although the concentrations of these elements were not different than could be expected from remote regions, their sources are likely anthropogenic.

The EF's for 28 aerosol elements from NE Minnesota are presented in Figure 11. The presentation of data in this form is important since it can be related directly to aerosol data taken at the South Pole (Zoller, et al., 1974) and North Atlantic (Duce et al., 1975). With the exception of V, the elemental enrichment factor diagrams constructed for South Pole and North Atlantic aerosol are superimposable on Figure 11, representing NE Minnesota aerosol. This remarkable phenomenon suggests that enrichment of most elements

Figure 11

The Enrichment Factor (Crust) Values for Atmospheric Particulate Elements in N.E. Minnesota - 1977



10^4
10^3
10^2
10^1
10^0
EF_{crust}
Element
Al
Si
K
Ti
Sr
Rb
Mn
Fe
Ga
Ni
P
V
Cr
Ba
Co
Cu
Zn
Cl
Sn
W
S
As
Sb
Pb
Br
Hg
Cd
Se

in aerosol may be more a function of elemental chemistry than source. The highly enriched elements were also those with the highest boiling points. Zoller et al.,(19[illegible]) suggested that high-temperature processes such as volcanic outgassing or fossil-fuel combustion could be responsible for enrichment of these metals observed in Antarctica. The similarity of North Atlantic and South Pole enrichment factors led Duce et al. (1975) to suggest that noncrustal anthropogenic pollution transported long distances may not be the cause of the high EF's observed at the two locations. Duce et al. (1975) conclude that a vapor phase, either from a high or low temperature source, plays an important role in the atmospheric chemistry of these elements. Possible sources of elements enriched naturally include volcanism, biological mobilization, and chemical fractionation at the air-sea and air-crust interface. In NE Minnesota where anthropogenic sources are few yet in closer proximity than those noted above, high EF's may result from both anthropogenic and natural sources. Lead may be the exception in that Pb is primarily derived from gasoline combustion. The Br/Pb ratio found for the region was 0.27 and typical of that expected from aerosol derived from gasoline combustion. It can be said that Pb and Br are derived primarily from the use of automobiles in the region.

Vanadium was enriched to a lesser extent in NE Minnesota than at the South Pole (Zoller et al., 1974) and approximately the same as the North Atlantic (Due et al., 1975). This behavior suggests that aerosol V is likely derived from pollutional sources such as fuel oil combustion.

III-8. Atmospheric Deposition "Crease"

An overriding conclusion reiterated at several points in the preceding report is that the quality of precipitation (wet + dry) falling on N.E. Minnesota is typical of remote, mid-continental areas. With the exception of Fe, the trace element concentrations in rain and suspended particulates were low. However, N.E. Minnesota appears to exist in an atmospheric deposition "crease", i.e., deposition in surrounding areas is greater than that observed in N.E. Minnesota. To the north, Ontario Hydro (1977) has found that bulk deposition exceeded that for N.E. Minnesota. To the east, a similar situation has been reported by Kramer (1974), IJC (1977) and Langevin _et al_. (1978) for deposition to Lake Superior. Krupa (1977) has also found that precipitation to the south was greater than that for N.E. Minnesota. Deposition of anthropogenic trace elements in the plains of North Dakota and western Minnesota was of the same order of magnitude, whereas soil inputs were much greater. The presence of an atmospheric deposition "crease" or low in N.E. Minnesota is derived probably from dominant air mass circulation. The prevailing winds in N.E. Minnesota are from the northwest with a southeast summer component. Thus, for much of the year, N.E. Minnesota has few upwind pollution sources. However, intense low pressure centers located south of Minnesota-Wisconsin may transport pollutant-laden air masses in a northwesterly direction from the industrialized Ohio Valley and eastern Michigan with subsequent deposition to Lake Superior and near shore land masses in the form of rain or dryfall. The remote character of the Superior National Forest and BWCA, the relatively high cliffs on the north shore and Lake Superior wind patterns may inhibit transport of pollutants inland. B. Watson (personal communication, 1977) has concluded that such circulation patterns may occur six to twelve times per year, occurrences which may dominate atmospheric deposition to Lake Superior.

The effect of Sudbury and neighboring smelting facilities on air quality in N.E. Minnesota is likely small since prevailing winds blow in a different direction from the source and the distance from the source is relatively great. The effect of St. Louis and Minneapolis-St. Paul on the air quality of the region is unknown although summer air circulation patterns favor transport occasionally to N.E. Minnesota.

In summary, the study region and much of N.E. Minnesota experiences excellent air quality, with atmospheric deposition of all elements, with the exception of Fe, typical of remote, mid-continental areas. The relatively low elemental deposition rates may be related to the prevailing air mass circulation patterns in the area and the absence of significant upwind sources.

IV. References

Chamberlain, A. C., Transport of Lycopodium spores and other small particles to rougn surfaces, Proc. Roy. Soc. A, 296, 45 (1966).

Chow, T. J., Environmental pollution from industrial lead, Internat. Biogeochem. and Hydrogeochemistry Symp., Tokyo (1970).

Chamberlain, A. C., "Pollution in plant canopies," in Heat and Mass Transfer in the Biosphere, D. A. de Vries and N. H. Afgan (eds.), Hemisphere Publ. Co., Washington, D.C., p. 561 (1975).

Davidson, C. I., Deposition of trace metal-containing aerosols on smooth, flat surfaces and on wild oat grass (Avena fatua), Ph.D. thesis, Cal. Inst. of Techn., 1977.

Davies, C. N., "Deposition from moving aerosols," in Aerosol Science, C. N. Davies (ed.), Academic Press, London, p. 393 (1966).

Duce, R. A., Hoffman, G. L. and Zoller, W. H., Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural Science, 187, 59-61 (1975).

Eisenreich, S. J., Atmospheric input of trace metals to Lake Michigan, presented 21st Conf. on Great Lakes Research, May, 1978.

Eisenreich, S. J., Langevin, A. S., and Thornton, J. D., Metal composition and size distribution of atmospheric particulate matter in remote northeastern Minnesota. Prepared for Minn. Env. Qual. Council, 1978.

Gregory, P. H., Microbiology of the Atmosphere, Leonard Hill Books, Ltd., London, p. 58 (1961).

Hidy, G. M., "Removal processes of gaseous and particulate pollutants," in Chemistry of the Lower Atmosphere, S. I. Rasool (ed.), Plenum Press, New York, p. 121 (1972).

Hidy, G. M. and Heisler, S. L., "Transport and deposition of flowing aerosols," in Recent Developments in Applied Aerosol Technology, D. Shaw (ed.), John Wiley and Sons, New York (1977).

Kramer, J. R., "Acid Precipitation" in Sulfur, J. Nriagu (ed.), John Wiley and Sons (1977).

Langevin, S., Eisenreich, S. J. and Johnson, T. C., Trace elements in precipitation, air particulates and surface films on Lake Superior, in prep.

Peirson, D. H., Cawse, P. A. Salman, L. and Cambray, R. S., Trace elements in the atmospheric environment. Nature, London, 241, 252-256 (1973).

Sehmel, G. A., Particle eddy diffusiorties and deposition velocities for isothermal flow and smooth surfaces, J. Aerosol Sci., 4, 125 (1973).

Sehmel, G. A., Sutter, S. L., and Dana, M. T., Dry deposition processes, Battele NW Laboratory Report 1751, Part 1, p. 43 (1973).

Slinn, W. G. N., "Dry deposition and resuspension of aerosol particles - a new look at some old problems," in Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), ERDA, NTIS CONF-740921, p. 1 (1976).

Zoller, W. H., Gladney, E. S. and Duce, R. A., Atmospheric concentrations and sources of trace metals at the South Pole, Science, 183, 198-200 (1974).

TABLE A-1.

NUTRIENT CONCENTRATIONS IN AIR PARTICULATES-URBAN

(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
Buffalo	Pillay & Thomas (1971)					610	130	
Chicago	Brar et.al. (1970)					2100	120	
Indiana	Dams et.al. (1971)					-	94	
Indiana	Dams et.al. (1971)					-	45	
Paris	Belot et.al. (1971)					7063	433	
Boston	Zoller & Gordon (1970)					500	150	
Norway	Rahn (1976)				670	18	6.1	
Belgium	Janssens & Dams (1972)					3860	164	
Chicago	Nifong & Winchester(1970)					3070	110	
Belgium-Ind.	Heindrykx & Dams (1973)					4320	120	
Belgium-Res.	Heindrykx & Dams (1973)					2970	150	
Belgium	Rahn (1973)					2840	66	

TABLE A-1, Contd.

(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
Chicago	Murphy (1974)	60		15480			421	
London	Lee et.al. (1974)		3500-NO_3 1900-NH_4					28700
Harlow	Lee et.al. (1974)		2300-NO_3 500-NH_4					7800
Kew	Lee et.al. (1974)		2300-NO_3 500-NH_4					8700
Salford	Lee et.al. (1974)		2000-NO_3 1200-NH_4					16900
Kinder	Lee et.al. (1974)		1600-NO_3 500-NH_4					11800
Eskdalemuir	Lee et.al. (1974)		600-NO_3 200-NH_4					5400
Pasedena	Hammerle & Pierson(1975)						718	
Cambridge,Mass.	Moyers et.al. (1972)						395	
San Francisco	John et.al. (1973)					2930	220	
Chicago	Dams et.al. (1973)						67	
Indiana	Harrison & Winchester(1971)						26-300	

TABLE A-1, Contd.
(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
Belgium	Demuynck(1973) in Rahn(1976)					1440	19.5	
Cincinnati	Henry & Blosser (1971)	50	3000	30000	6000	300	50	12000
Denver	Henry & Blosser (1971)	100	2000	40000	20000	500	50	6000
St. Louis	Henry & Blosser (1971)	200	3000	40000	60000	500	50	15000
Washington	Henry & Blosser (1971)	100	2000	30000	10000	400	50	18000
Chicago	Henry & Blosser (1971)	60	8000	100000	10000	5000	50	21000
Philadelphia	Henry & Blosser (1971)	50	5000	30000	10000	100	40	9000
New York	Persiani (1971)				2020	640	560	
Surrey	Hasan & Spyrou (1972)					5300	180	
Japan-Res.	Mamuro et.al. (1971)					1550	52.3	
Japan-Ind.	Mamuro et.al. (1971)					4360	74.6	
Germany	Bogen(1973)					153	30.5	
Tucson	Moyers et.al. (1973)				16600			

TABLE A-1, Contd.
(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
New York	Morrow & Brief (1971)				4840			
Japan	Sugimae and Hosegawa(1973a)				27184			
St. Louis	Tanner et.al. (1975)				17350	402	78.5	16430
Norway	Rahn & Larssen (1973)in Rohn(1976)					86	6.78	
Norway	Rahn & Larssen (1973)in Rohn(1976)					138	8.4	
Denmark	Rahn & Larssen (1973)in Rohn(1976)					885	17.1	
Pasedena	Miller et.al. (1972)					70	600	
England	Cawse (1974)					2513	221	
England	Cawse (1974)					3065	85	
England	Cambray et.al. (1975)					3065	85	
Holland	Cambray et.al. (1975)					3190	74	
Bute	Cambray et.al. (1975)					2940	40	
Columbia,MO.	Gray et.al. (1972)					643	55	
Oak Ridge,Tenn.	Andren (1974)					345	23	

TABLE A-2

NUTRIENT CONCENTRATIONS IN AIR PARTICULATES-REMOTE

(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
Switzerland	Rahn (1972)				350	9.0	2.0	
Canada	Rahn (1971)					9	0.54	
Canada	Rahn (1971)					12	2.5	
Canada	Rahn & Winchester in Rahn (1976)					16	4.4	
Ivory Coast	Crozat et.al. (1973)					75	1.02	
Ivory Coast	Crozat et.al. (1973)					468	1.46	
Ivory Coast	Crozat et.al. (1973)					1976	0.51	
Germany	Potzl (1970)				320			
Central Europe	Reiter et.al. (1976)		924-NO_3 1295-NH_4		311	112		3147
South Pole	Duce et.al. (1973)					70	7.9	

TABLE A-3

NUTRIENT CONCENTRATIONS IN AIR PARTICULATES-OCEANS AND LAKES

(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
England	Cawse (1974)					1593		
Shetland Islands	Cawse (1974)					2970	17	
Norway	Rahn (1976)				138	294	4.7	
Norway	Rahn (1976)					4.2	0.89	
England	Cawse (1974)					2452	79	
Wales	Cawse (1974)					1532	27	
England	Cawse (1974)					2544	78	
South Pole	Zoller et.al. (1974)						0.63	
Pembroke	Keane & Fisher (1968)					2300	13	
Ivory Coast	Crozat et.al. (1973)					6530	1.61	
Southern Calif.	Hidy et.al. (1974)		889	904	1377	2202	62.3	4902
Shetland	Cambray et.al. (1975)					3310	23.3	

TABLE A-3, Contd.
(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	SO_4
North Sea	Cambray et.al. (1975)					6990	89	
Southern Lake Huron	Delumyea & Petel (1977)	7.6-105						
Hanaii	Jernigan et.al. (1971)						1.6	

OTHER

TABLE A-4

NUTRIENT CONCENTRATIONS IN AIR PARTICULATES-SELECTED AREAS

(ng/m^3)

Location	Reference	P	N	C	Si	Cl	Br	O_4
Michigan	Rahn (1971)					46	94	
Belgium	Heindrycks & Dams (1974)					4870	195	
Scotland	Dale & McDonald (1973)						75	
Sudan	Penkett (1975) in Rahn (1976)					615	10.7	
Holland	Evendijk (1974)				5200	1390	130	2400
Holland	Evendijk (1974)				7300	1030	150	13800
Holland	Evendijk (1974)				5600	1500	160	11100
England	Hamilton (1974)	140			800	2800	180	7440
Oregon	Shum & Loveland (1974)					240	29	
Maryland	Gladney (1974)						46	38100
Maine	Boyce et.al.(1975)		1200-NO_3					24900

TABLE B-1

METAL CONCENTRATIONS IN AIR PARTICULATES-URBAN

(ng/m^3)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Buffalo	Pillay&Thomas (1971)	1150		2200				800	60	220
Belgium	Rahn et.al. (1972)	665		1550	1130	2870	107	21.3		92
Chicago	Brar et.al. (1970)	310		1400				22	17	430
Indiana	Dams et.al. (1971)	285	1350	1850	1250	3950	190	9.3	54	180
Indiana	Dams et.al. (1971)	275	900	2000	1100	2150	170	6.4	11	100
Paris	Belot et.al. (1971)	1823		902				42.7	15.1	82.5
San Francisco	John et.al. (1973)	3520		863	870			5.4	8.2	17
Boston	Zoller & Gordon(1970)	800		700		2000		600		20
Norway	Rahn (1976)	175	41.5	325	230	150	18	12.5	1.95	17
Belgium	Janssens & Dams(1972)	1360		1561				52	14.4	87
Chicago	Nifong & Winchester(1970)	1070	10900	3230	2050	21700		25	69	1500
Belgium	Rahn (1976)	5340		1670	1660			49	58	874

URBAN

TABLE B-1, Contd.
(ng/m^3)

Table Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Belgium-Indust.	Heindryckx & Dams(1973)	1930		1590	1640	4670	160	58	15	570
Belgium-Resident	Heindryckx & Dams(1973)	1445		1140	1110	2320	63	48	10	142
USSR	Egorov et.al. (1970)			7.9						1.7
USSR	Egorov et.al. (1970)			130						14
USSR	Egorov et.al. (1970)			86						12
Belgium	Demuynck(1973) in Rahn (1976)	1060	149	74	179	240	<5	5.1	0.78	11.4
Cincinnati	Henry & Blosser(1971)	1000	2000	3000	1000	6000	200	10	30	300
Denver	Henry & Blosser(1971)	3000	1000	7000	1000	4000	400	20	10	70
St. Louis	Henry & Blosser(1971)	3000	2000	3000	5000	20000	300	20	20	50
Washington	Henry & Blosser(1971)	1000	2000	3000	1000	3000	400	100	20	50
Chicago	Henry & Blosser(1971)	2000	5000	4000	2000	10000	400	50	30	100
Philadelphia	Henry & Blosser(1971)	1000	5000	3000	300	8000	400	200	40	200
New York	Persiani (1971)			860				56		30
Surrey	Hasan & Spyrou(1972)	2500		4000				4210		33

TABLE B-1, Contd.
(ng/m^3)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Chicago	Lee et.al. (1972)			813				60		30
Cincinnati	Lee et.al. (1972)			1170						170
Denver	Lee et.al. (1972)			620						20
Philadelphia	Lee et.al. (1972)			540				140		50
St. Louis	Lee et.al. (1972)			810						30
Washington	Lee et.al. (1972)			490				90		20
Japan-Resident	Mamuro et.al. (1971)	1670		4660	1520			82.3	25.7	273
Japan-Indus.	Mamuro et.al. (1971)	2270		4660	2130			173	80.7	653
Germany	Bogen (1973)	224		1850					4.6	23.6
Tucson	Moyers et.al. (1973)	1300	1200	6600	2500	5700	450		4.0	42
New York	Morrow&Brief (1971)	1080	490	2040		1170		170		
Japan	Sugimae (1974)			2240				22	5.7	112
Japan	Sugimae & Hasegawa(1973a)		1244	7466		6554		200		746
St. Louis	Tanner et.al. (1975)	705	1118	3745	768	5575	362	9.75	10.5	90.5

URBAN

TABLE B-1, Contd.

($ng.m^3$)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Norway	Rahn&Larssen (1973)in Rahn (1976)	181		189	140	223		1.89	0.96	8.52
Norway	Rahn&Larssen (1973)in Rahn (1976)	346	77	190	216	174	10	4.78	1.11	11.4
Denmark	Rahn&Larssen (1973)in Rahn (1976)	907	136	521	340	474	35	11.0	23.2	464
Pasedena	Rahn&Larssen (1973)in Rahn (1976)	1000	1100	800	320	990		10		30
England	Cawse (1974)	1103		288.1				14.1	6.9	26
England	Cawse (1974)	1128		760.1				25	23	70
England	Cambray et.al. (1975)	1287		294				12.3	4.2	26
Holland	Cambray et.al. (1975)	1840		190				11.0	3.8	17.8
Bute	Cambray et.al. (1975)	1716		159				10.8	3.4	11.8
Columbia,MO.	Gray et.al. (1972)	326	61	1447	3967	850	145	3.7	3.0	32
Los Angeles	Hoffmann(1972) in Rahn(1976)	1700	490	3800		1000		12.5	6.3	53
Honolulu	Hoffmann(1972) in Rahn(1976)	2700	370	730		420		3.4	1.6	14

URBAN

TABLE B-1, Contd.

(ng/m^3)

Table Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
New York	Kneip et.al. (1974)			984				101	11	39
Chicago	Murphy (1974)	456		1978		1686		43		142
Chicago	Gatz (1975)			1500			200	80	20	100
Britian	Stocks et.al. (1961)								2-22	12-130
Pasedena	Hammerle & Pierson(1975)					239	33.2	8.6		9.3
Japan	Sugimae (1975)							120	38	280
Indiana	Harrison et.al. (1971)	160-500	530-2700	1400-3100	730-1800	1400-7000	120-280	4-18	6-113	63-390
Cambridge,Mass.	Moyers et.al. (1972)							494		
Oak Ridge,Tenn.	Andren (1974)	201		823	223	472	66	3.6	1.7	14

TABLE B-1, Contd.
(ng/m^3)

Table Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Buffalo	Pillay&Thomas (1971)	3350			70					4200
Belgium	Rahn et.al. (1972)	2760	2.77		213	2820	26.1	118	1.49	
Chicago	Brar et.al. (1970)	2400	2.8		590				9.6	
Indiana	Dams et.al. (1971)	6500	1.5	-	380	510	4.2		2.5	
Indiana	Dams et.al. (1971)	2500	0.9	-	120	175	4.3		1.9	
Paris	Belot et.al. (1971)	3500	6.79			1635			11.2	
San Francisco	John et.al. (1973)	1670	1.0		50	100				
Boston	Zoller&Gordon (1970)	1000	0.2		50	100				
Norway	Rahn (1976)	250	0.14	4.25	5.80	37.5	5.45	0.54		23.3
Belgium	Janssens & Dams (1972)	2100			70	715	35		0.70	920
Chicago	Nifong & Winchester(1970)	15500	2.3		136	3120	23			
Belgium	Rahn (1976)	26900	3.8		63	250	41		0.50	
Belgium-Indus.	Heindrykx & Dams (1973)	3040	2.0	32		440	17		0.92	
Belgium-Res.	Heindrykx & Dams (1973)	1500	1.5	32		400	14		0.52	

URBAN

TABLE B-1, Contd.
(ng/m^3)

Table

Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
USSR	Egorov et.al. (1970)	21		2.4	2.9			5.30		1.26
USSR	Egorov et.al. (1970)	160		15	14			2.34		8.25
USSR	Egorov et.al. (1970)	390		5.9				0.55		15.45
Belgium	Demuynck(1973) in Rahn (1976)	93	0.26	<6	5.3	43	43	1.3		
Cincinnati	Henry & Blosser (1971)	5000	3	20	500	2000	2	2		3000
Denver	Henry & Blosser (1971)	5000	5	20	500	200	5	1	2	3000
St. Louis	Henry & Blosser (1971)	5000	3	20	2000	2000	10	5		3000
Washington	Henry & Blosser (1971)	4000	5	50	800	400	2	0.3		4000
Chicago	Henry & Blosser (1971)	5000	10	40	400	500	2	3	1	5000
Philadelphia	Henry & Blosser (1971)	4000	20	1000	200	500	5	1	2	2000
Chicago	Lee et.al. (1972)	1100		60	100	500				3200
Cincinnati	Lee et.al. (1972)	1800		60	200	1700				1800
Denver	Lee et.al. (1972)	800		60	400	100				1800
Philadelphia	Lee et.al. (1972)	700		60	100	400				1600

URBAN

TABLE B-1, Contd.

(ng/m^3)

Table Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
St. Louis	Lee et.al. (1972)	1100		60	100	300				1800
Washington	Lee et.al. (1972)	600		60	200	300				1300
Japan-Resident	Mamuro et.al. (1971)	3930	1.77							
Japan-Indust.	Mamuro et.al. (1971)	10530	5.47							
Germany	Bogen (1973)	1041	2.2					26.8	0.17	
Tucson	Moyers et.al. (1973)	2800	1.3	6.2	400	110		3.4		400
New York	Morrow & Brief (1971)	2980		180	290					1370
Japan	Sugimae (1974)	1118		11		570		112		112
Japan	Sugimae & Hasegawa(1973a)	8254			762	1612				1004
St. Louis	Tanner et.al. (1975)	2730	1.072	8.5	78.8	242	4.3		0.212	400
Norway	Rahn & Larssen (1973)in Rahn (1976)	82.1	0.0976		5.7	21.2	0.66			
Norway	Rahn & Larssen (1973) in Rahn (1976)	172	0.44		5.7	44				
Norway	Rahn & Larssen (1973)in Rahn (1976)	464	0.26		7.9	72.5	4.3			

URBAN

TABLE B-1, Contd.
(ng/m^3)

Table Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Pasedena	Rahn & Larssen (1973)in Rahn (1976)	3200			30	180				3300
England	Cawse (1974)	411	0.46	6.5		169	6.3			156
England	Cawse (1974)	1134	0.96	12.9		405	26			411
England	Cambray et.al. (1975)	390	0.38	6.6		129	6.4			159
Holland	Cambray et.al. (1975)	355	0.28	8.9		92	4.5			118
Bute	Cambray et.al. (1975)	270	0.33	5.8		129	2.27			87
Columbia,MO.	Cambray et.al. (1972)	898	0.83			54.7	2.4		0.36	
Los Angeles	Hoffman (1972) in Rahn (1976)	1500	1.7	9.6		620				1500
Honolulu	Hoffman (1972) in Rahn (1976)	520	1.1	3.7		130				180
New York	Kneip et.al. (1974)	1438			66.7	44		5.67		1285
Chicago	Gatz (1975)	3500		40	140	300	20	10		1200
Chicago & NW Indiana	Harrison & Winchester(1971)				1000			19		1900
Pasedena	Hammerle & Pierson (1975)	268			10.8			75.7		2140

URBAN

TABLE B-1, Contd.

(ng/m^3)

Table

Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Cambridge,Mass.	Moyers et.al. (1972)									1911
Britain	Stocks et.al. (1961)		1-43	2-205	44-252	130-490	31-130			260-1430
Rome	Colacino & Lavagnini(1974)									4181
Japan	Sugimae (1975)	10600	1.2	97	170	820		28		830
New York	Colucci & Begeman (1971)									8300
Illinois	Hudson et.al. (1975)									200
Indiana	Harrison et.al. (1971)	1400-13000	0.47-3.0		25-4000	100-1600	2-12		.8-5	
Oak Ridge,Tenn.	Andren (1974)	313	0.34		8.2	23.4	1.35	4.1	0.13	90

TABLE B-2

METAL CONCENTRATIONS IN AIR PARTICULATES-REMOTE

(ng/m^3)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Switzerland	Rahn (1972)	22	22	140	53	93	8.6	0.56	0.86	4.5
Canada	Rahn (1971)	18		66	54	40	5	0.21	0.59	1.5
Canada	Rahn (1971)	40	56	147	109	140	8.5	0.37	0.7	5.6
Canada	Rahn (1976)	62	85	290	16	260	14	1.3	1.4	10
Ivory Coast	Crozat et.al. (1973)	145		175		230			7.92	3.81
Ivory Coast	Crozat et.al. (1973)	28		335		910				5.45
Ivory Coast	Crozat et.al. (1973)	71		1140		1050			6.5	15.1
Germany	Potzl (1970)			134.9						
Central Europe	Reiter et.al. (1976)	68		118	57	407				

TABLE B-3

METAL CONCENTRATIONS IN AIR PARTICULATES-OCEANS AND LAKES

(ng/m^3)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
England	Cawse (1974)	840		147.7				7.05	2.39	12.8
Shetland Islands	Cawse (1974)	1840		52.1				2.08	1.11	2.8
Norway	Rahn (1976)	439	71	43.3	48.3	46.3	3.13	1.70	0.618	2.53
Norway	Rahn (1976)	54	13	6.7	17	12	0.36	0.126	0.11	0.34
England	Cawse (1974)	932		324.9				17.2	5.09	24.52
England	Cawse (1974)	1110		318.8				16	13.9	20.2
Wales	Cawse (1974)	913		150.2				5.33	3.25	11.52
Hawaii	Hoffmann et.al. (1969)	4700		18				0.20		
Hawaii	Hoffmann et.al. (1972)	3500		6.7				0.16		0.2
USSR	Egorov et.al. (1970)			1.7					0.34	0.25
USSR	Egorov et.al. (1970)			8.3						1.1
Indian O-North	Egrov et.al. (1970)			120						7.9
Indian O-South	Egorov et.al. (1970)			12						0.24

TABLE B-3, Contd.
(ng/m^3)

Table Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
South Pole	Zoller et.al. (1974)	7.2	1.0	0.57	0.3	0.5		0.0015	0.0053	0.0103
Pembroke	Keane & Fisher(1968)	1350		50				6		13
Ivory Coast	Crozat et.al. (1973)	525		285		2620			8.44	4.42
Gulf of Guinea	Crozat et.al. (1973)			117		1889			0.981	
Atlantic O.	Duce (1973) in Rahn (1976)	7100	5800	64000		10800			65	647
Atlantic O.	Duce (1973) in Rahn (1976)	6200	820	180		27				2.1
Atlantic O.	Duce (1973) in Rahn (1976)	1800	235	13.5		76				0.195
Atlantic O.	Duce (1973) in Rahn (1976)	765	100	27		47				0.51
Atlantic O.	Duce (1973) in Rahn (1976)	933	131	17.7	33.3	40.3				0.52
Bermuda	Duce (1975) in Rahn (1976)	2176	296	459	187.4	229			0.519	3.01
New York Bight	Duce et.al. (1975)	945		208						
Southern Calif.	Hidy et.al. (1973)	922		746	326	478	40		6.13	14.5
Shetland	Cambray et.al. (1975)	2084		53.9				2.15	1.29	3.9

TABLE B-3, Contd.
(ng/m^3)

Table

Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
N. Sea	Cambray et.al. (1975)	4050		159				11.9	4.5	21.5
N. Atlantic	Dudey et.al. (1969)			811					0.388	
Atlantic O.	Duce (1975) in Rahn (1976)								70-1100	50-5400

TABLE B-2, Contd.
(ng/m^3)

Table

Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
witzerland	Rahn (1972)	90	0.091	-	1.7	21	0.40	0.37	0.023	24
anada	Rahn (1971)	71	0.042	-	0.9	3.8	0.31		-	
anada	Rahn (1971)	200	0.072	-	2.4	9	0.30		-	
anada	Rahn (1976)	290	0.14	-	4.4	15	0.45		-	
vory Coast	Crozat et.al. (1973)	245	0.194						0.425	
vory Coast	Crozat et.al. (1973)	705	0.114						0.164	
vory Coast	Crozat et.al. (1973)	935	0.55						0.62	
ermany	Potzl (1970)	94.7								
entral Europe	Reiter et.al. (1976)	95.1								33
alifornia	Chow et.al. (1972)									0.80

TABLE B-3, Contd.
(ng/m^3)

Table

Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
England	Cawse (1974)	215	0.172	4.90	74		3.25			78
Shetland Islands	Cawse (1974)	54.6	0.059	3.37		31	1.35			27.59
Norway	Rahn (1976)	51		1.31	2.3	8.93	1.86	0.124		5.5
Norway	Rahn (1976)	17	0.013		0.43	0.98	0.17	0.0059		1.1
England	Cawse (1974)	374	0.49	7.05	10.1	175	5.88			181
Wales	Cawse (1974)	184	0.245	4.3	8.3	90.7	2.5			64
England	Cawse (1974)	533	12.0	89	37	236	8.8			227
Hawaii	Hoffman et.al. (1972)	12			2					3
USSR	Egorov et.al. (1970)	4.3		0.38	0.61			0.28		0.23
USSR	Egorov et.al. (1970)	24		1.3	2.9			0.39		0.87
Indian O-North	Egorov et.al. (1970)	180		2.9	12			1.96		4.45
Indian O-South	Egorov et.al. (1970)	7		0.35	2.1			0.14		1.01
South Pole	Zoller et.al. (1974)	0.84	0.00084		0.036	0.030				0.2

TABLE B-3, Contd.
(ng/m^3)

Table

Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Ivory Coast	Crozat et.al. (1973)	770	0.201						.428	
Gulf of Guinea	Crozat et.al. (1973)	123	0.144						0.208	
Atlantic O.	Duce (1973) in Rahn (1976)	39000	14							10
Atlantic O.	Duce (1973) in Rahn (1976)	110								0.6
Atlantic O.	Duce (1973) in Rahn (1976)	10.5								0.3
Atlantic O.	Dvce (1973) in Rahn (1976)	30								0.3
Atlantic O.	Duce (1973) in Rahn (1976)	11.3								0.43
Bermuda	Dvce (1975) in Rahn (1976)	275			2.44	6.02		0.382		6.76
New York Bight	Duce et.al. (1975)	188				46.9		1.02		134
outhern Calif.	Hidy et.al. (1974)	529			131	79				179
hetland	Cambray et.al. (1975)	86	0.26	3.56		31	1.47			38
orth Sea	Cambray et.al. (1975)	330	0.36	10.0		153	5.1			147
. Atlantic	Dudey et.al. (1969)	499	0.167		319	8.50		4.20	0.0624	
tlantic O.	Dvce (1975) in Rahn(1976)	3.4-220			.12-10	.3-27		.003-.62		.10-64

OTHER

TABLE B-4

METAL CONCENTRATIONS IN AIR PARTICULATES-SELECTED AREAS

Table Location	Ref.	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
Michigan	Rahn (1971)	120	160	580	340	650	35	3.6	3.8	41
Belgium	Heindrycks & Dams (1974)	1160	1000	2860	1680	4260	213	75	30	212
USSR	Egorov et.al. (1970)			86						21
Scotland	Dale and McDonald(1973)	350		460					17.5	29
Sudan	Penkett (1975) in Rahn (1976)	338.5		1663		1.37		5.83	5.34	19.5
Holland	Evendijk (1974)	1810		1710	990			37	18	106
Holland	Evendijk(1974)	2240		2260	1220			61	71	135
Holland	Evendijk(1974)	2230		1480	850			48	20	83
England	Hamilton (1974)	428	290	370	980	330	31.9	32.1	4.9	14.3
Oregon	Shum & Loveland (1974)	340		450	85		69	2.8	6	2.7
Maryland	Gladney (1974)	440	170	910		143	59	35	2.8	13.5
NW Indiana	Gatz (1975)			2000			200	80	40	300
Chadron, Nebraska	Struempler(1975)			535						5.7
Britain	Stocks et.al. (1961)								1-3	5-13

OTHER

TABLE B-4, Contd.
(ng/m^3)

Table Location	Ref.	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Michigan	Rahn (1971)	950	0.34	-	15	130	4.6		0.61	
Belgium	Heindryckx & Dams(1974)	3710	3.94	24	110	96	48		1.9	
USSR	Egorov et.al. (1970)	410		7.2	13			4.23		15.81
Scotland	Dale & McDonald(1973)	5900	0.9			300				
Tasmania	Stebbins (1975) in Rahn (1976)				5.2	21				34
Sudan	Penkett (1975) in Rahn (1976)	1968	0.65		27	22.95			<0.2	
Holland	Evendijk (1974)	1800	5.7	1.4	260	410	6.8	7.7	0.44	
Holland	Evendijk (1974)	3000	7.8	0.4	700	650	13.8	5.9	0.59	
Holland	Evendijk (1974)	2100	4.7	0.2	200	420	6.3	2.7	0.28	
England	Hamilton(1974)	400	1.1	8.6	26.4	200	6.6	0.4	1.0	260
Oregon	Shum & Loveland (1974)	160								
Maryland	Gladney (1974)	640	0.41	24	11.5	68	3.8			315
NW Indiana	Gatz (1975)	6000		60	200	400	5	20		1500
Chadron, Neb.	Struempler(1975)		3.3		5.3	16		0.57		45
Britain	Stocks et.al. (1961)		0.3-0.9	1-75	7.-38	48-205	5-27			80-470

URBAN

TABLE C-1

NUTRIENT CONCENTRATIONS IN PRECIPITATION-URBAN (mg/1)

Location	Reference	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Yonkers, NY	Jacobson et.al. (1975)	Rain		0.80-NO_3 1.16-NH_4					4.8
Central, NY	Likens (1972)	Rain	6.3-PO_4	1.1-NO_3					
Sweden	Dickson (1975)	Rain	.065-PO_4	0.873-NO_3 1.2-NH_3					
New York	Likens (1972)	Bulk	0.015-PO_4	.250-NO_3 .240-NH_3					
Chicago	Murphy (1974)	Rain Snow	.034(TP) .034(TP)						
Gainsville,Fl.	Brezonik et.al. (1975)	Rain	.052(TP) .010(Ortho)	.14 - NH_3 .06 - NO_3					
Heidelberg,Ger.	Bogen (1974)	Rain					1.54	7.2	

TABLE C-2

NUTRIENT CONCENTRATIONS IN PRECIPITATION-REMOTE (mg/l)

Location	Reference	Ppt Type	P	N	C	Si	Cl	Br	SO_4
NWT	Kramer(1973a)	Rain	.0005-PO_4	.001-NO_3 1-NH_3					
Antarctica	Gjessing & Gjessing(1973)	Ground Snow	.006-PO_4	.002-NO_3					1.6
Norway	Scholdager (1973)	Rain & Snow							.1-12
Norway	Bjor et.al. (1974)	Rain							.05-56
Sierra,Nevada	Feth et.al. (1964)	Snow	.030-Ortho	.180-NH_3 .070-NO_3					
Nova Scotia	Herman & Gorham(1957)	Snow		.130-NH_3 .070-NO_3					
Northern Europe	Oden in Feth et.al.(1964)	Snow		.180-NO_3					
Minn. Prairie	Gorham (1975)	Snow	.069-(TP)						
Minn. Forest	Gorham (1975)	Snow	.016-(TP)						
N.Dakota Wetlands	Adomaitis et.al. (1967)	Snow	.106-(TP)	1.70-NO_3					
N. Minn. Forest	Comerford & White (1976)	Rain	.036-(TP)	.788-TKN					
N. Carolina & Tenn.Forest	Swenk & Henderson(1976)	Bulk	.007-PO_4	0.12-NO_3 0.02-NH_4			0.35		
NE Minnesota	Wright (1976)	Rain	.021-(TP)						

TABLE C-3

NUTRIENT CONCENTRATIONS IN PRECIPITATION-OCEANS AND LAKES (mg/l)

Location	Reference	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Manitoba	Murphy (1974)	Rain	.054-PO_4						
Sweden	Hornstrom et.al. (1973)	Rain							7-7.3
Sweden	Andersson(1972)	Bulk							3.3-6.
Lake Michigan	Murphy & Doskey (1976)	Rain	.023-(TP) .011-DRP .014-TRP						
N.Central Florida Lake	Brezonik et.al. (1969)	Rain	.015-0 .033-(TP)	.31-Ton .21-NH_3 .21-NO_3					
NW Ontario (10 lake surfaces)	Barico & Armstrong(1971)	Snow	.035-0 .006-(TP)	.039-NH_3 .206-NO_3					
L. Ontario	Shiomi & Kuntz (1973)	Bulk	.058-(TP) .024-0	1.53-NO_3 0.62-NH_3			1.60		10.01
S. Lake Huron	Delumyea & Petel (1977)	Rain	.001-.037						
L. Michigan-N.	Eisenreich et.al.(1977)	Bulk	0.05		3.8 TOC	0.146-SiO_2	2.5		
L. Michigan-S.	Eisenreich et.al.(1977)	Bulk	0.064		6.2 TOC	0.356-SiO_2	2.9		

OTHER

TABLE C-4

NUTRIENT CONCENTRATIONS IN PRECIPITATION-SELECTED AREAS (mg/l)

Location	Reference	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Norway	Semb (1975)	Rain		.80-NO_3 1.16-NH_4					8.0
Central Texas	Cooper et.al. (1975)								
Iowa	Tabatabai & Laflen (1975)	Rain		0.6-NO_3 .63-NH_4					.89
Maine	Boyce et.al. (1975)	Snow & Rain		1.3-NO_3					
Tennessee	Shriner(1975)			.26-NO_3 .13-NH_4			.47		2.9
Sweden,Nationwide	Malmer (1974)	Rain		.028-NO_3 .056-NH_3					1.5-2.7
N. Ontario	Kramer (1975)	Bulk	.564-T .27-0	.093-NO_3 .365-NH_3					.5
NWT	Whelpdale & Summers (1975)	Rain & Snow							.1-8
NWT	Kramer (1973a)	Rain							<.5
N.E. U.S.	Pearson & Fisher (1971)	Bulk							2-38
N.E. U.S.	Likens (1975)	Bulk							3.2-5.0
Sweden	Malmer (1974)	Bulk							1.5-27

OTHER

TABLE C-4, Contd.
(mg/l)

Location	Reference	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Canada-West Coast	Whelpdale & Summers (1975)	Bulk							0.1-13
Canada-West Central	Whelpdale & Summers (1975)	Bulk							0.1-11
Canada-E. Central	Whelpdale & Summers (1975)	Bulk							<.3-80
Canada-East Coast	Whelpdale & Summers (1975)	Bulk							.9-3.2
Sudbury, Ont.	Kramer (1975)	Rain							<.5-9.4
N.E. U.S.	Pearson & Fisher (1971)	Bulk	.04-PO_4	.34-NO_3 .25-N					4.3
Newfoundland	Gorham (1961)	Rain							2.2
Wisconsin	Gorham (1961)	Rain							2.9
Ojebyn,N.Sweden	Gorham (1961)	Rain							2.5
Ultuna,Central Sweden	Gorham (1961)	Rain							2.6
Georgetown, British Guiana	Gorham (1961)	Rain							1.3
C. Alberta,Can.	Summers & Hitchen (1973)	Rain							2.7
Norway	Dovland et.al.(1976)	Rain							1-4
Worldwide	Junge & Werby (1958)	-							2.2

TABLE D-1

METAL CONCENTRATIONS IN PRECIPITATION-URBAN, REMOTE, OCEANS AND LAKES (μg/l)

Table

Location	Ref.	Ppt Type	Na	Mg	Al	K	Ca	Ti	V	Cr	Mu
URBAN											
NYC	Volchok et.al. (1973)	Rain								5-60	ND-50
Tennessee	Andren et.al. (1975)	Bulk									12
Central,NY	Likens (1972)	Rain	48	19.2	36	12	148				5
Oak Ridge.Tenn.	Elwood & Henderson (1975)	Rain		90		140	690				
		Bulk		240		390	1300				
Heidelberg,Ger.	Bogen (1974)	Rain	757			800				3.6	25.4
Walker Branch Watershed,Tenn.	Andren & Lindberg (1977)	Rain								1.87	14.8
REMOTE											
New Hampshire	Likens et.al. (1967)	Bulk	120	40		70	160				
N. Minn.Forest	Comerford & White (1976)	Rain		229		539	1667				
N. Carolina & Tenn.Forest	Swank & Henderson(1976)	Bulk	170	50		80	230				
Nebraska	Struempler(1976)	Rain & Snow			350						5.20
NE Minn.	Wright (1976)	Rain	100	70		110	420				
N.Hampshire Forest	Likens et.al. (1967)	Rain	155	90		200	280				

TABLE D-1, Contd.
(μg/l)

Table Location	Ref.	Ppt Type	Na	Mg	Al	K	Ca	Ti	V	Cr	Mu
LAKES & OCEANS											
Sweden	Dickson (1975)	Rain								<5	5
		Bulk									5-180
Sweden	Soderland (1975)	Rain								.2	11
L. Ontario	Shiomi & Kuntz(1973)	Bulk	2690	820		560	5040				
L. Michigan-N	Eisenreich et.al.	Bulk	0.59	0.67							
L. Michigan-S	(1977)	Bulk	0.64	0.78							
OTHER											
Nationwide, U.S.	Lazrus et.al. (1970)	Bulk									12
N. Ontario	Kramer(1975)	Bulk									5
Norway	Semb (1975)	Rain					500				
Central Texas	Cooper et.al. (1975)	Rain				54	42				
Maine	Boyce et.al. (1975)	Snow & Rain	543				434				
Minnesota	Krupa et.al. (1975)	Rain	120	53		100	390			<20	<10
Tennessee	Shriner(1975)	Rain	260	140		320	930				
N.E. U.S.	Pearson & Fisher (1971)	Bulk		110		160	600				

URBAN

TABLE D-1, Contd.
(μg/l)

Table Location	Ref.	Ppt Type	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
URBAN											
Heidelberg,Ger.	Bogen (1974)	Rain	1746	1.8						1.3	
Walker Branch Watershed,Tenn.	Andren & Lindberg (1976)	Rain			5.7	14.5	34.9			0.15	15.6
Tennessee	Andren et.al. (1975)	Bulk			3-9	4-24	18-60		4-22	.08-.50	5-29
Central, NY	Likens (1972)	Rain	40								
REMOTE											
New Hampshire	Schlesinger et.al.1974	Bulk							0.6	0.06	13.4
Nebraska	Struempler (1976)	Rain & Snow				4.4	10		0.31		4.8
Antarctica	Gjessing & Gjessing (1973)	Ground Snow	25			16	27		1.4		1.6
OCEANS & LAKES											
Lake Ontario	Shiomi & Kuntz (1973)	Bulk	34		4	6	80		1		20
Sweden	Dickson (1975)	Bulk	30-220		48	.5-30	20 -300		.2-7		14-70
		Rain	216		48	9	311		7		64
Sweden	Soderland (1975)	Rain			5	7	60		.3	.2	10
Sweden	Andersson (1972)	Bulk	30-220		48	.5-30	20 -300		.2-.7		14-70

TABLE D-1, Contd.
(μg/l)

Table Location	Ref.	Ppt Type	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
OTHER											
Northwest Terr.	Kramer (1975)	Bulk	31		0.3	1	52		.15		1
Delaware	Biggs et.al. (1973)	Rain				.3-60			.4-80	<.1-3.6	.6-60
Nationwide U.S.	Lazrus et.al. (1970)	Bulk			4	21	110				34
Canada	Zitko & Carson (1971)	Rain	45			6.4	36		.6	.11	2.8
N. Ontario	Kramer (1975)	Bulk	50-1760		<.1-63	3-150	30-6800		.2-42		4-69
Central Texas	Cooper (1975)	Rain	83			2	3	4			4
Minnesota	Krupa (1975)	Rain	<10			<10	15		<2		<20

TABLE E-1

ATMOSPHERIC LOADING RATES OF METALS-URBAN, REMOTE, OCEANS AND LAKES, SELECTED AREAS

Table			kg/ha/yr								
Location	Ref.	Ppt Type	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
N.E. U.S.	Pearson Fisher 1971	Bulk		1.30		1.79	6.78				
Maine	Boyce et al 1975	Snow Rain	0.65								
Michigan	Richardson Merva 1975	Bulk	6.3	1.70		2.80	9.0				
New York State	Richardson Merva 1975	Bulk	1.0	1.0		2.3	4.0				
Central Germany	Mayer et al 1975	Bulk	8.2	3.70	1.30	6.0	20.0				
Norway	Abrahamsen 1975	Rain	6.0	0.70		0.60	0.90			0.40	1.17
Switzerland	Imboden et al 1975	Bulk								0.02	.20
U.S.A.	Lazru et al 1970	Rain									.09
Tennessee	Andren et al 1975	Rain								.04	0.26

TABLE E-1, (Contd.)

Table				kg/ha/yr							
Location	Ref.	Ppt Type	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
URBAN											
New York City	Volchok et al 1973	Bulk								.110- .303	.194
Connecticut	Morgan et al 1942	Rain	1.20	7.0		12.0	28.0				
Walker, Tenn.	Andren & Lindberg 1977	Rain								.036	.253
N.Minn.Forest	Commerford & White 1976	Rain		1.25		2.57					
N. Caroline	Swank & Henderson 1976	Bulk	3.52	1.11		1.62					
REMOTE											
N. Carolina	Swank & Henderson 1976	Dry	.610	0.20		0.51					
Nebraska	Struempler 1976	Rain Snow			1.40						
N.E. Minnesota	Wright 1976	Rain	.624	.425- .465		.740	2.75				

TABLE E-1, (Contd.)

Table			kg/ha/yr								
Location	Ref.	Ppt Type	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn
L. Superior	Vol. I ULRG p.46	Bulk	1.81	0.67		1.57	3.98				
L. Huron	Vol. I ULRG p.47	Bulk	6.15	11.25		4.39	38.35				
L. Huron	Vol. I ULRG p.48	Bulk	7.02	1.12		5.02	45.14				
Georgian Bay	Vol. I ULRG p.49	Bulk	1.56	.78		1.04	5.21				
N. Channel	Vol. I ULRG p.50	Bulk	1.59	.79		1.06	5.31				
L. Superior	Vol. III ULRG	Bulk	1.83	.68		1.59	4.03				
U.Great Lakes	Vol. III ULRG	Bulk	2.16	1.80		.90	8.53				
L. Ontario	Shiomi & Kuntz 1973	Bulk	12.73	4.09		3.11	2.61				
Norway Coast	Abrahamsen 1975	Rain		1.00		1.20	1.00				
N.L. Michigan	Eisenreich et al	Bulk	1.82	3.24		1.06	10.80				
S.L. Michigan	Eisenreich et al	Bulk	3.76	4.52		2.26	24.84				

URBAN

TABLE E-1, (Contd.)

Table					kg/ha/yr						
Location	Ref.	Ppt Type	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
New York City	Volchok et al 1973	Rain			1.72	.27-.69	4.40				1.06-1.49
New York City	Volchok 1973	Rain				1.35	5.48		.04		1.97-4.75
REMOTE											
New Hampshire	Schlesinger et al 1974	Bulk							.009	.001	.196
Walker,Tenn.	Andren & Lindberg 1977	Rain			.091	.232	.499			.003	.246
Nebraska	Struempler 1976	Rain Snow				.018	.04		.001		.019

TABLE E-1, (Contd.)

Table				kg/ha/yr							
Location	Ref.	Ppt Type	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
L. Superior	ULRG 1976	Bulk	1.170		.015	.044			.006		.078
L. Huron	ULRG 1976	Bulk	.630		.029	.104			.011		.107
L. Huron	ULRG 1976	Bulk	.368		.014	.57			.009		.077
Georgion Bay	ULRG 1976	Bulk	1.253		.068	.219			.011		.167
N. Channel	ULRG 1976	Bulk	1.275		.068	.223			.010		.170
L. Superior	ULRG 1976	Bulk	1.183		.015	.045			.007		.079
U.Great Lakes	ULRG 1976	Bulk	.832		.037	.064			.006		.122
L. Ontario	Shipmi Kuntz 1973	Bulk	.205		.020	.040	.505		.008		.130

OTHER

TABLE E-1, (Contd.)

Table			kg/ha/yr								
Location	Ref.	Ppt Type	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Michigan	Richardson Merva 1975	Bulk	.300								
Central Germany	Maypr et al 1975	Bulk	1.000								
Canada	Hutchinson & White 1975	Bulk	6.100	.065	2.100	2.900	.637				.585
Canada, St. Andrews	Zitko & Carson 1971	Rain	.048			.069	.365		.006	.001	.029
NWT Canada	Kramer 1975	Rain	.318		.003	.010	.548		.002		.01
N.W. England	Andren et al 1975	Rain			.088	.332	1.226		.255	.003	.197
Switzerland	Imboden et al 1975	Bulk	2.00			.402	2.701		.006		1.716
U.S.A.	Lazrus et al 1970	Rain	.080		.033	1.86	.767				.270
Delaware	Biggs et al 1973	Rain				.037			.084	.001	.062
Tennessee	Andren et al 1975	Rain			.091	.234	.511		.157	.003	.248

TABLE F-1

ATMOSPHERIC LOADING RATES OF NUTRIENTS-URBAN, REMOTE, OCEANS AND LAKES, SELECTED AREAS

Table Location	Ref.	Ppt Type	P	kg/ha/yr N	C	Si	Cl	Br	SO_4
Akron, Ohio	Junge 1956	Rain		9.40 NO_3 2.62 NH_4					
Urbana, Ill.	Junge 1956	Rain		2.27 NO_3 0.65 NH_4					
Indianapolis,In.	Junge 1956	Rain		4.63 NO_3 2.08 NH_4					
Columbia, Mo.	Junge 1956	Rain		8.70 NO_3 3.48 NH_4					
Duluth, Mn.	Putnam Olson 1960	Rain		1.76 NO_3 5.00 NH_4					
Wisconsin	Shah 1962	Rain		12.0 TOT					
Hamilton, Ont.	Matheson 1951	Snow Rain		1.78 NO_3 3.20 NH_4					
Ottawa, Can.	Shutt 1925	Rain		1.97 NO_3 4.45 NH_4					
California	Junge 1956	Rain		1.60 NO_3 1.0 NH_4					
Ely, Nevada	Junge 1956	Rain		.69 NO_3 1.0 NH_4					
Amarillo, Tex.	Junge 1956	Rain		1.98 NO_3 1.17 NH_4					
Glasgow, Mt.	Junge 1956	Rain		3.0 NO_3 2.21 NH_4					
Washington,D.C.	Junge 1956	Rain		5.07 NO_3 0.65 NH_4					

URBAN

TABLE F-1, (Contd.)

Table			kg/ha/yr						
Location	Ref.	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Albany, N.Y.	Junge 1956	Rain		8.35 NO_3 1.48 NH_4					
Geneva, N.Y.	Collison Mensching 1932	Rain		10.0 TOT					
Geneva, N.Y.	Collison Mensching 1932	Rain		6.70 NO_3 6.70 NH_4					
Ithaca, N.Y.	Wilson 1921	Rain		1.13 NO_3					
Ithaca, N.Y.	Leland 1952			1.40 NO_3 4.50 NH_4					
Ithaca, N.Y.	Buckman Brady 1961	Rain		8.0 NO_3 4.1 NH_4					
Connecticut	Voigt 1959	Rain	.10 TOT	.50-TOT					
Connecticut	Jacobsen et al 1948	Rain		4.5-TOT					
New Brunswick,NJ	Prince et al 1941	Rain		5.60 NO_3 5.60 NH_4					
North Carolina	Junge 1956	Rain		8.0 NO_3 1.30 NH_4					
Tallahassee,Fla.	Junge 1956	Rain		2.30 NO_3 .75 NH_4					
Roanoke, Va.	Junge 1956	Rain		8.90 NO_3 2.36 NH_4					
Chicago, Ill.	Murphy Cesaretti1974	Rain	.250TOT						
Europe	Benaire 1975	Bulk							2.80
Yonkers,N.Y.	Jacobsen et al 1975	Rain		3.78 NO_3					

URBAN

TABLE F-1, (Contd.)

Table				kg/ha/yr					
Location	Ref.	Ppt Type	P	N	C	Si	Cl	Br	SO_4
Iowa	Tabatabui Laflen 1975	Rain Snow		$6.0\ NO_3$ $6.0\ NH_4$			1.0		4.12
Connecticut	Morgan et al 1942	Rain		3.0-TOT					17.0
Green Bay,Wis.	Sridharan 1972	Rain	.08-TOT				22.0		31.0
Madison,Wis.	Kluesenen 1972	Rain Snow	.180 Sng .230-TOT						
Melbourne,Aust.	Attwill 1966	Bulk	.30-TOT						
Norway	Abrahamsen et al 1975	Rain	$.110\text{-}PO_4$	$4.02\ NO_3$ $3.29\ NH_4$					

REMOTE

TABLE F-1, (Contd.)

Table				kg/ha/yr					
Location	Ref.	Ppt Type	P	N	C	Si	Cl	Br	SO_4
N.E., U.S.	Pearson Fisher 1971	Bulk	.474-PO_4	3.84 NO_3 3.82 N					
N. Minn.	Commerford White 1976	Rain	.258 TP	4.38 (TKO)					
N. Carolina & Tenn.	Swank Henderson1975	Bulk	.190 PO_4	2.88 NO_3 .520 NH_4					
N. Minn Lakes	Wright 1976	Rain	JP .137-.144						
N.W. Ontario	Barcia & Armstrong 1971	Snow Rain	.270 (TP)						3.65
NWT Canada	Kramer 1973b	Bulk Rain							3.65
NWT Canada	Kramer 1973a	Bulk Rain							25.-51.
Norway	Scholdger	Rain							18.-40.
Sweden	Hornstrom et al 1973	Rain							7.3-40.0
Great Lakes,Can.	Shiomi Kuntz 1973	Bulk							51.0
N. Ontario	Kramer 1975	Bulk							1.8-62.0
Canada	Nyborg Crepin 1975	Rain							1.20
Wisconsin	Shah 1962	Rain		9.0-(T)					14.0

REMOTE

TABLE F-1, (Contd.)

Table			kg/ha/yr						
Location	Ref.	Ppt Type	P	N	C	Si	Cl	Br	SO_4
U.S.A.	Wolaver & Lreth 1972	Bulk							26.0
Thunder Bay,Ont.	Aeres 1975								32.0
Grand Marais,Mn.	Aeres 1975								32.0
Two Harbors,Mn.	Aeres 1975								

TABLE F-1, (Contd.)

Table Location	Ref.	Ppt Type	kg/ha/yr P	N	C	Si	Cl	Br	SO_4
New Jersey	Malo Purvis 1964	Rain		3.32 NH_4 9.20 TOT					
S.E. N.Virginia	Gambell Fisher 1964	Rain		2.20 NO_3 13.0 NH_4					
S.E. N.Virginia	Gambell Fisher 1964	Rain		1.26 NO_3					
N. Virginia	Gambell Fisher 1964	Rain		5.0 NO_3					
E. Virginia	Junge 1956	Rain		3.18 NO_3 1.17 NH_4					
Norway	Abrahamsen et al 1975	Rain	.020 PO_4	1.60 NO_3	9.00				4.90
New York State	Richardson Merva 1975	Bulk	TOT .60 PO_4	3.30 NH_4 4.40 NO_3			10.0		50.0
Michigan	Richardson Merva 1975	Bulk	.60(TPO_4)	3.50 NO_3 2.0 NH_4		5.8	9.41		18.0
Maine	Boyce et al 1975	Rain Snow		1.76 NO_3					1.30
Oklahoma	Finnel & Houghton1931	Rain		.806 NO_3					
New Zealand	Miller et al 1961	Bulk	.80 (T)						
England	Carlisle et al 1966	Bulk	.85 (T)						
England	Allen et al 1968	Bulk	.20 (T)						
Ghana	Ingham 1973	Bulk	3.0 (T)						
Italy	Imporato 1964	Bulk	2.0 (T)						

OTHER

TABLE F-1, (Contd.)

Table			kg/ha/yr						
Location	Ref.	Ppt Type	P	N	C	Si	Cl	Br	SO_4
France	Farrugle 1960	Bulk	.40 (T)						
Scandinavian	Tamn 1953	Rain	1.0 (T)						

TABLE F-1, (Contd.)

Table Location	Ref.	Ppt Type	kg/ha/yr P	N	C	Si	Cl	Br	SO_4
Lake Michigan	Murphy 1974	Rain	.767 TOT .274 ORTHO						
Lake Ontario	Shiomi & Kuntz 1973	Rain	1.28 TOT .58 ORTHO	20.40 NO_3 11.71 NH_4					
Lake Superior	R I J C 1976	Bulk	.096	6.73 TOT			6.64		26.53
Lake Huron	R I J C 1976	Bulk	.085	7.1 TOT			6.70		31.50
Lake Huron	R I J C 1976	Bulk	.075	5.70 TOT			5.51		
Georgian Bay	R I J C 1976	Bulk	.088	9.40 TOT			8.34		
N. Channel	R I J C III 1976	Bulk	.092	9.61 TOT			8.51		
Lake Superior	R I J C III 1976	Bulk	.098	6.83 TOT			6.71		
Lake Huron	GLWQB 1976	Bulk	.18						
Lake Superior	GLWQB 1976	Bulk	.13						
Lake Michigan	GLWQB 1976	Bulk	.29						
Lake Erie	GLWQB 1976	Bulk	.43						
St. Lawrence	GLWQB 1976	Bulk	.30						
Lake Ontario	GLWQB 1976	Bulk	.27						

TABLE F-1, (Contd.)

Table Location	Ref.	Ppt Type	kg/ha/yr P	N	C	Si	Cl	Br	SO_4
Norway, Coast	Abrahamsen et al 1975	Rain							
Lake Michigan	Murphy Doskey 1976	Rain	.172 (TP)						
Lake Michigan	Murphy Doskey 1976	Rain	.086 (ORP)						
Lake Michigan	Murphy Doskey 1976	Rain	.103 (TRP)						
S.L. Huron	Delumyer & Petel 1977	Rain	.04 (TAP)						
S.L. Huron	Delumyer & Petel 1977	Dry	.062 (TAP)						
S.L. Huron	Delumyer & Petel 1977	Bulk	.237 (TAP)						
N.L. Michigan	Eisenreich et al	Bulk	.221 (TP)		16.68(T)	.673 (R)	11.64		14.64
S.L. Michigan	Eisenreich et al	Bulk	.364 (TP)		36.0 (T)	2.04 (R)	16.8		32.04

1. Abbott, D. C., Cain, J. and Barrentine, B., Organochlorine Pestidices in the Atmosphere, Nature, 211, 259(1966).
2. Abrahamsen, G., Horntvedt, R. and Tveite, B., Impacts of Acid Precipitation on Coniferous, Proceedings of the International Symposium on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.
3. Abrahamsen, G., *et al*., Impacts of Acid Precipitation on Coniferous Forest Ecosystems, Res. Rep. 2-75, Project, Acid Precipitation-Effects on Forest and Fish, NSF Project, NISK, 1432 AASLH, Norway, 1975.
4. Allen, S. E., Carlisle, A., White, E. J. and Evans, C. C., The Plant Nutrient Content of Rainwater, J. Ecol., (Brit.), 56, 497-504 (1968).
5. Anderson, B., Food Selectivity of Perch (Perca Fluviatilisl.) In: *Acidified Lakes on the West Coast of Sweden*, Sotvattens Laboratoriet, Drottningholm, Sweden, Report 17, 1972, Text in Swedish, 1972.
6. Andren, A. W., In: *Ecology and Analysis of Trace Contaminants*, W. Fulkerson, W. D. Schultz and R. I. Van Hook, eds., Oak Ridge National Laboratory Report ORNL-NSF-EACT-11.
7. Andren, A. W., *et al*., Atmospheric Input and Geochemical Cycling of Selected Trace Elements in Walker Branch Watershed, Environmental Sci. Div. Public. No. 728, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830, 1975.
8. Andren, A. W. and Lindberg, S. E., Atmospheric Input and Origin of Selected Elements in Walker Branch Watershed, Oak Ridge, Tennessee, Water, Air, and Soil Pollution, 8, 199-215 (1977).
9. Arthur, R. D., Cain, J. D. and Berrentine, B. F., Atmospheric Levels of Pesticides in the Mississippi Delta, Bull. Environ. Cont. & Tox., 15 (2), 129-133 (1976).

10. Atmospheric Loading of the Upper Great Lakes, Canada Centre for Inland Waters, Vol. 3, December 1975, Appendix 9, 197 .

11. Attwill, P. M., The Chemical Composition of Rainwater in Relation to the Cycling of Nutrients in Natural (Mature) Eucalyptus, Plant and Soil, 24, 390-406 (1966).

12. Barica, J. and Armstrong, F. A. J., Contribution of Snow to the Nutrient Budget of Some Small Northwest Ontario Lakes, Limnol. and Oceanog., 16, 891-899 (1971).

13. Belot, Y., Diop, B. and Marini, T., Composition Minerale de la Matiere Particulaire en Suspension dans l'Air dans des Zones Urbaines. Presented at Commission des Commuautes Europeenes Symposium International "La Radioecologie Appliquee a la Protection de l'Homme et de son Environment, Rome, Sept., 1971.

14. Benarie, M., Transport of Pollutants Considered from the Point of View of a Short and Medium Range Material Balance, Proceedings of the International Symposium on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

15. Bidleman, T. F., Rice, C. P., and Olney, C. E., High Molecular Weight Hydrocarbons in the Air and Sea: Rates and Mechanisms of Air/Sea Transfer, Chapt. 13, In: Marine Pollutant Transfer, eds., H. L. Windom and R. A. Duce, Lexington Books, 1977.

16. Bidleman, T. F. and Olney, C. E., Long Range Transport of Toxaphene Insecticides in the Atmosphere of the Western North Atlantic, Nature, 257 (5526), 475-477 (1975).

17. Bidleman, T. F. and Olney, C. E., Chlorinated Hydrocarbons in the Saragsso Sea Atmosphere and Surface Water, Science, 183, 516-518 (1974).

18. Biggs, R. B., et al., Trace Metals in Several Delaware Watersheds, Univ. of Delaware Water Resources Center, Newark, Delaware, 1973.

19. Bjor, E., et al., Distribution and Chemical Enrichment of Precipitation in a Southern Norway Forest Stand, Acid Precip. Effects on Forest and Fish, Res. Rep. No. 1-74, SNSF-Project, NISK, 1432, Norway, 1974.

20. Bogen, J., Trace Elements in Atmospheric Aerosol in the Heidelberg Area, Measured by Instrumental Neutron Activation Analysis, Atm. Envir., 7, 117-1125 (1973).

21. Bogen, J., Trace Elements in Precipitation and Cloud Water in the Area of Heidelberg, Measured by Instrumental Neutron Activation Analysis, Atm. Envir., 8, 835-844 (1974).

22. Boyce, S. D., Butcher, S. S. and Smith, J., The Effects of a Local Source on the Composition of Precipitation in South-Central Maine, Proceedings of the Int. Symp. of Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

23. Brar, S. S., Nelson, D. M., Kline, J. R., Gustafson, P. F., Kanabrocki, E. L., Moore, C. E. and Hattori, D. M., Instrumental Analysis for Trace Elements Present in Chicago Area Surface Air, J. Geophys. Res., 75, 2939-2945 (1970).

24. Brezonik, P. L., Proc. First Specialty Symposium on Atmospheric Contribution to the Chemistry of Lake Waters, 166-186 (1975).

25. Buckman, H. O. and Brady, N. C., The Nature and Properties of Soils, The MacMillan Co., New York, 6th ed., 567 p, 1961.

26. Burghardt, E. and Jeltes, R., Gas Chromatographic Determination of Aromatic Hydrocarbons in Air Using a Semi-Automatic Preconcentration Method, Atm. Envir., 9, 935-940 (1975).

27. Cambray, R. S., Jefferies, D. F. and Topping, G., An Estimate of the Input of Atmospheric Trace Elements into the North Sea and the Clyde Sea (1972-3), ARE Harwell Report R 7733, H. M. Stationery Office, London, 26 p., 1975.

28. Campbell, J. M. and Clemmesen, J., Dan. Med. Bull., 3, 205 (1956).

29. Carlisle, A. A., Brown, H. F. and White, E. F., The Organic and Nutrient Elements in the Precipitation Beneath Sessile Oak Canopy, J. Ecol., 54, 87-98 (1966).

30. Cautrelk, W. and Van Cauwenberghe, K., Determination of Organic Compounds in Airborne Particulate Matter by Gas Chromatography-Mass Spectrometry, Atm. Envir., 10, 447-457 (1976).

31. Cawse, P. A., A Survey of Atmospheric Trace Elements in the U.K. (1972-73), AERE Harwell Report R 7669, H. M. Stationery Office, London, 84 pp., 1974.

32. Chow, T. J., et al., Lead Aerosol Baseline Concentration at White Mountain and Laguna Mountain, California, Science, 178, 401 (1972).

33. Ciaccio, L. L., Rubino, R. and Flores, J., Composition of Organic Constituents in Breathable Airborne Particulate Matter Near a Highway, Envir. Sci. & Technol., 8 (10), 935-940 (1974).

34. Cleary, G. J. and Sullivan, J. L., Med. J. Aust. 1, 758-763 (1965).

35. Colacino, M. and Lavagnini, A., Particulate Lead Pollution in Rome's Atmosphere, J. Water, Air, and Soil Pollut., 3, 209-216 (1974).

36. Collison, R. C. and Mensching, J. E., Lysimeter Investigation II: Composition of Rain Water at Geneva, New York for a Ten-Year Period, p. 3-19, In: Bulletin 193, New York State Agr. Expt. Station, Ithaca, N. Y., 1932.

37. Colucci, J. M. and Begeman, C. R., Carcinogenic Air Pollutants in Relation to Automotive Traffic in New York, Environ. Sci. & Technol., 5 (2), 145-150 (1971).

38. Comerford, N. B. and White, E. H., Nutrient Input by Precipitation in Northern Minnesota Forest Ecosystem, J. of the Minnesota Academy of Science 42, 22-24 (1976).

39. Cooper, H. B., Demo, J. M. and Lopez, J. A., Chemical Composition of Acid Precipitation in Central Texas, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

40. Crozat, G., Domergue, J. L., Bogui, V. and Fontan, J., Etude de l'Aerosol Atmospherique en Cote d'Ivoire et dans le Golfe de Guinee, Atm. Envir., 7, 1103-11 (1973).

41. Cukor, P., Ciaccio, L. L., Lanning, E, W., Rubino, R. L., and J. Smith, Some Chemical and Physical Characteristics of Organic Fractions in Airborne Particulate Matter, Envir. Sci. & Technol., 6 (7), 633-640 (1972).

42. D'Ambrosio, A., Pavelka, F., Centro Provincial Perllo Studia Sugli Inquinamenti Atmosferci, 1958.

43. Dale, I. M. and McDonald, C., Neutron Activation Analysis of Air Pollutants, Prof. Soc. Analyt. Chem., 10, 204-205 (1973).

44. Dams, R., Robbins, J. A., Rahn, K. A. and Winchester, J. W., Quantitative Relationships Among Trace Elements Over Industrialized N.W. Indiana, In: Nuclear Techniques in Environmental Pollution, International Atomic Energy Agency, Vienna, p. 139-157 (1971).

45. Davidson, C. I., Deposition of Trace Metal-Containing Aerosols on Smooth, Flat Surfaces and on Wild Oat Grass (Avena fatua), Ph.D. Thesis, Cal. Tech., 160 p., 1977.

46. Delumyea, R. G. and Petal, R. L., Atmospheric Input of Phosphorus to Southern Lake Huron, April-October, 1975 EPA-600/3-77-038, 54 p., 1977.

47. De Maio, L. and Corn, M. J.,

48. Dickson, W., The Acidification of Swedish Lakes, Institute Freshwater Research, Drottningholm, Sweden, Report 54, p. 8-20, 1975.

49. Dong, M., Locke, D. C. and Ferrand, E., High Pressure Liquid Chromatographic Method for Routine Analysis of Major Parent Polycyclic Aromatic Hydrocarbons in Suspended Particulate Matter, Anal. Chem., <u>48</u>, 368-372 (1976).

50. Duce, R. A., Zoller, W. H. and Moyers, J. L., Particulate and Gaseous Halogens in the Antartic Atmosphere, J. Geophysical Res., <u>78</u> (33) 7802-7810 (1973).

51. Duce, R. A., Hoffman, G. L. and Zoller, W. H., Atmospheric Trace Metals at Remote Northern and Southern Hemispheric Sites: Pollution or Natural? Science, <u>187</u>, 59-61 (1975).

52. Dudey, N. D., Ross, L. E. and Noshkin, V. E., Application of Activation Analysis and Ge(Li) Detection Techniques for the Determination of Stable Elements in Marine Aerosols. In: <u>Modern Trends in Activation Analysis</u>, J. R. DeVoe, P. D. LeFleur, eds., Nat. Bureau of Std., Special Pub. 312, Vol. I, p. 55-61, 1969.

53. Egorov, V. V., Zhigalovskaya, T. N. and Malakhov, S. G., Microelement Content of Surface Air Above the Continent and the Ocean, J. Geophys. Res., <u>75</u>, 3650 (1970).

53a. Eisenreich, S. J., Emmling, P. J. and Beeton, A. M., Atmospheric Loading of Phosphorus and Other Chemicals to Lake Michigan, J. Great Lakes Res., (1977).

54. Elwood, J. W. and Henderson, G. S., Hydrologic and Chemical Budgets at Oak Ridge, Tennessee, Pub. No. 682, Environmental Science Div., Oak Ridge National Laboratory, p. 31-51, 1975.

55. Evendijk, J., Ondergock naar Sporenelementen in Atmospherisch Stof te Rotterdam (I), Extern, 3, 555-573 (1974).

56. Farrugia, (Unknown, See Vollenweider, p. 112), 1960.

57. Feth, J. H., Rojers, S. M. and Roberson, C. E., Chemical Composition of Snow in the Northern Sierra Nevada and Other Areas, U.S. Geol. Surv. Water Supply Pap. 1535-J, 39 p., 1964.

58. Finnell, H. H. and Houghton, H. M., Soil Nitrogen Income from Rainwater, Bull. 23, Pan. Agr. Expt. Sta. (Oklahoma), 1931.

59. Fox, M. and Staley, S., Determination of Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter by High Pressure Liquid Chromatography Coupled with Fluorescence Techniques, Anal. Chem. 48 (7), 992-998 (1976).

60. Freeman, J. F., Nitrogen in the Rainwater of Different Parts of Kentucky, J. Amer. Soc. Agron., 16, 356-358 (1924).

61. Frink, C. R., Voigt, G. K. and Musser, M., Potential Effects of Acid Precipitation on Soils in the Humid Temperature Zone, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

62. Galloway, J. N., Likens, G. E. and Edgerton, E. S., Hydrogen Ion Speciation in the Acid Precipitation of the Northeastern United States, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

63. Gambell, A. W. and Fisher, D. W., Occurrence of Sulfate and Nitrate in Rainfall, J. Geophys. Res., 69, 4203-4210 (1964).

64. Gatz, D. F., Pollutant Aerosol Deposition into Southern Lake MIchigan, Water, Air, and Soil Pollution, 5, 239-251 (1975).

65. Gjessing, Y. T. and Gjessing, E. T., Chemical Composition of an Antartic Snow Profile, Vatten, 3 (1973).

66. Gladney, E. S., Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, 1974.

67. Gordon, R. J. and Bryan, R. J., Patterns in Airborne Polynuclear Hydrocarbon Concentrations at Four Los Angeles Sites, Environ. Sci. & Technol., 7, (11), 1050-1053 (1973).

68. Gordon, R. J., Distribution of Airborne Polycyclic Aromatic Hydrocarbons Throughout Los Angeles, Environ. Sci. & Technol., 10 (4), 370-373 (1976).

69. Gorham, E., Acid Precipitation and Its Influence Upon Aquatic Ecosystems - an Overview. Proc. of the Int. Symp. of Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

70. Gray, D., Kay, D. M., Eichor, J. and Vogt, J. R., Determination of the Trace Element Levels in Atmospheric Pollutants by Instrumental Neutron Activation Analysis, IEEE Trans. Nucl. Sci. NS19, 194, 1972.

71. Great Lakes Water Quality, Fifth Annual Report Appendix B, to the Implementation Committee Great Lakes Water Quality Board, June, 1977, p. 90.

72. Hammerle, R. H. and Pierson, W. R., Sources and Elemental Composition of Aerosol in Pasadena, California, by Energy-Dispersive X-Ray Fluoresence, Environ. Sci. & Technol., 9 (12), 1058-1068 (1975).

73. Harrison, P. R., Rahn, K. A., Dams, R., Robbins, J. A., Winchester, J. W., Brar, S. S. and Nelson, D. M., Areawide Trace Metal Concentrations Measured by Multielement Neutron Activation Analysis, J. Air Pollut. Contr. Assoc., 21 (9), 563-570 (1971).

74. Harrison, P. R. and Winchester, J. W., Area-Wide Distribution of Lead, Copper and Cadmium in Air Particulates from Chicago and Northwest Indiana,

75. Harvey, G. R. and Steinhauer, W. G., Atmospheric Transport of Polychlorobiphenyls to the North Atlantic, Atm. Environ., 8, 777-782 (1974).

76. Hasan, O. and Spyrou, N. M., Air-Pollution Study of Guildford, Surrey, Using Neutron Activation Analysis, In: Nuclear Activation Techniques in the Life Sciences, International Atomic Energy Agency, Vienna, p. 263-276, 1972.

77. Hauser, T. R. and Pattison, J. N., Analysis of Aliphatic Fraction of Air Particulate Matter, Environ. Sci. & Technol., 6 (6), 549-555 (1972).

78. Heindryckx, R. and Dams, R., Elemental Aerosol Concentrations of an Industrial Area, Tijdschrift van het BECEWA, 26, 61-66 (1973).

79. Heindryckx, R. and Dams, R., Continental, Marine, and Anthropogenic Contributions to the Inorganic Composition of the Aerosol of an Industrial Zone, J. Radioanal. Chem., 19, 339-349 (1974).

80. Henry, W. M. and Blosser, E. R., Identification and Estimation of Ions, Molecules, and Compounds in Particulate Matter Collected from Ambient Air, Battelle Columbus Laboratories Technical Report CPA-70-159, Columbus, Ohio, 1971.

81. Herman, F. A. and Gorham, E., Total Mineral Material, Acidity, Sulphur and Nitrogen in Rain and Snow at Kentfield Novia Scotia, Tellus, 9, 180-183 (1957).

82. Hettche, H. O., Inte. J. Air Water Pollution, 8, 185-191 (1964).

83. Hidym G. M., Mueller, P. K., Wang, H. H., Karney, J., Twiss, S., Imada, M. and Alcocer, A., Observations of Aerosols Over Southern California Coastal Waters, J. Appl. Meteor., 13, 96-107 (1974).

84. Hoffman, G. L., Duce, R. A. and Zoller, W. H., Vanadium, Copper and Aluminum in the Lower Atmosphere Between California and Hawaii, Environ. Sci. & Technol., 3, 1207-1210 (1969).

85. Hoffman, G. L., Duce, R. A. and Hoffman, E. J., Trace Metals in the Hawaiian Marine Atmosphere, J. Geophys. Res., 77, 5322-5329 (1972).

86. Hornstrom, E., et al., Effects of the Acidification on Lakes in the Swedish West Coast Region, Phytoplankton, Diatoms, Chemistry, Zoo-planctonStaters, Naturvardsverk, Publikationer, 1973-1977, Sweden, 1973.

87. Hudson, J. L., Stukel, J. J., and Solomon, R. L., Measurement of the Ambient Lead Concentration in the Vicinity of Urbana-Champaign, Illinois, Atm. Environ., 9, 1000-1006 (1975).

88. Hutchinson, T. C. and Whitby, L. M., The Effects of Acid Rainfall and Heavy Metal Particulates on a Boreal Forest Ecosystem Near the Sudbury Smelting Region of Canada, Proc. of the Int. Symp. of Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

89. Imporato, G., Ammonia, Nitrate, Nitrite, Phosphate and Sulphate Contents of Rainfall, Ann. Fac. Agr. Portici, 29, 369-378 (1964).

90. Imboden, D. M., et al., Atmospheric Loadings of Metals in Switzerland, EAWAG News, 4, 5 (1975).

91. Ingham, G., The Fertility of the Air, South Africa J. Sci., 39, 35-43 (1943).

92. Jacobson, H. G. M., Swanson, C. L. M. and Smith, E., Effects of Various Fertilizer Cations and Anions on Soil Reaction Leaching Nitrification of Urea and Related Characteristics in an Uncropped Soil, Soil Sci., 65, 437-460 (1948).

93. Jacobson, J., Hellar, L. I. and Van Leuken, P., Acidic Precipitation at a Site Within the Northeastern Conurbation, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

94. Janssens, M. J. and Dams, R., Analyse en Interpretatie van de Anorganische Samenstelling der Aerosolen in Mechelen, Rep. Inst. Nucl. Sciences, Univ. of Ghent, Belgium, 75 p., 1972.

95. Jernigan, E. L., Ray B. J. and Duce, R. A., Lead and Bromine in Atmospheric Particulate Matter on Oahu, Hawaii, Atm. Environ., 5, 881-886 (1971).

96. John, W., Kaifer, R., Rahn, K. and Wesolowski, J. J., Trace Element Concentration in Aerosols from the San Francisco Bay Area, Atm. Envir., 7, 107-118 (1973).

97. Junge, C. E., Recent Investigations in Air Chemistry, Tellus, 8, 127-139 (1956).

98. Keane, J. R. and Fisher, E. M. R., Analysis of Trace Elements in Air-Borne Particulates, by Neutrol Activation and Gamma-Ray Spectrometry, Atm. Envir., 2, 601-612 (1968).

99. Kertesy, Saringer, M. and Morlin, Z., On the Occurrence of Polycyclic Aromatic Hydrocarbons in the Urban Area of Budapest, Atm. Envir., 9, 830-834 (1975).

100. Kluesener, J. W., Nutrient Transport and Transformation in Lake Wingram, Wisconsin, Ph.D. Thesis, Water Chemistry Dept. Univ. Wisconsin, Madison, 1972.

101. Kneip, T. J., Eisenbud, M., Kleinman, M. T., Bernstein, D. M., Lippman, M. and Riddick, R., Trace Metals in Urban Aerosols, Second Annual Progress Report to the American Petroleum Institute and the Edison Electric Institute, 1974.

102. Kramer, J., Fate of Atmospheric SO_2 (and Related Substances) Scavenged by Precipitation, Dept. of Geology, McMaster Univ., Hamilton, Ont. MS, 1973.

103. Kramer, J., Emission Test Values at the Copper Cliff Stack, International Nickel Company, from Ministry of Environment Report MS, 1973.

104. Kramer, J., Fate of Atmospheric Sulfur Dioxide and Related Substances as Indicated by Chemistry of Precipitation, Report Dept. of Geol., McMaster Univ., Hamilton, Ont., 1975.

105. Krups, S., Coscio, M. R. and Wood, F. A., Evidence for Multiple Hydrogen-Ion Donor Systems in Rain, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

106. Lazrus, A., et al., Lead and Other Metal Ions in U.S. Precipitation, Environ. Sci. & Technol., 4, 55 (1970).

107. Lee, R. E., Goranson, S. S., Enrione, R. E. and Morgan, G. B., National Air Surveillance Cascade Impactor Network, II. Size Distribution Measurements of Trace Metal Components, Environ. Sci. & Technol., 6, 1025-1030 (1972).

108. Lee, R. E., Cadwell, J., Akland, G. G. and Fankhauser, R., The Distribution and Transport of Airborne Particulate Matter and Inorganic Components in Great Britain, Atm., Envir., 8, 1095-1109 (1974).

109. Leland, E. W., Nitrogen and Sulfur in the Precipitation at Ithaca, Agron., J. 44, 172-175 (1952).

110. Likens, G. E., Borman, F. H., Johnson, N. M. and Pierce, R. S., The Calcium, Magnesium, Potassium, and Sodium Budgets for a Small Forest Ecosystem, Ecology, 5 (48), 772-785 (1967.

111. Likens, G. E., The Chemistry of Precipitation in the Central Finger Lakes Region, Technical Report 50, Cornell Univ. Water Resources and Marine Sciences Center, Ithaca, N.Y. 1972.

112. Lunde, G. and Bjorseth, A., Polycyclic Aromatic Hydrocarbons in Long Range Transport Aerosols, Nature, 268 (5620) 518-519 (1977).

113. Malmer, N., On the Effects on Water, Soil, and Vegetation of an Increasing Atmospheric Supply of Sulphur, National Swedish Environment Protection Board, SNV PM 402E, Solna, Sweden, 1974.

114. Malo, B. A. and Purvis, E. R., Soil Adsorption of Atmospheric Ammonia, Soil Science, 97, 243-247 (1964).

115. Mamuro, T., Matsuda, Y., Mizohata, A. and Matsunami, T., Activation Analysis of Airborne Dust, In: Annual Report of the Radiation Center of Osaka Prefecture, 12, 1-9, 1971.

116. Matheson, D. H., Inorganic Nitrogen in Precipitation and Atmospheric Sediments, Canadian J. Technol., 29, 406-412 (1951).

117. Mayer, R. and Ulrich, B., Acidity of Precipitation as Influenced by the Filtering of Atmospheric Sulfur and Nitrogen Compounds-Its Role in the Element Balance and Effect on Soil, Proceeding of the Int. Symp. on Acid Precipitation and the Forest Ecosystem(1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

118. McClure, V. E. and Lagrange, J., Deposition of Heavy Chloriante Hydrocarbons from the Atmosphere, Bull. Envir. Cont. & Tox., 17 (2), 219-224 (1977).

119. Miller, M. S., Friedlander, S. K. and Hidy, G. M., A Chemical Balance for the Pasadena Aerosol, J. Coll. Interface Sci., 39, 165-176 (1972).

120. Mohan, A. M. and Vohra, K. G., The Concentrations of Benzo (a) Pyrene in Bombay, Atm. Envir., 9, 430-408 (1975).

121. Morgan, M. F., Jacosen, H. G. M. and Street, O. E., The Neutralization of Acid-Forming Nitrogenous Fertilizers in Relation to Nitrogen Availability and Soil Bases, Soil Sci., 54, 127-148 (1942).

122. Morrow, N. L. and Brief, R. S., Elemental Composition of Suspended Particulate Matter in Metropolitan New York, Environ. Sci. & Technol., 5, 786-789 (1971).

123. Moyers, J. L. *et al*., Trace Metal Concentrations in the Tucson Area Atmosphere, In: *Final Report to the Arizona Mining Association*, Atmospheric Analysis Laboratory, Dept. of Chemistry, University of Arizona, Tucson, p. 219-245, 1973.

124. Moyers, J. L., Zoller, W. H., Duce, R. A. and Hoffman, G. L., Gaseous Bromine and Particulate Lead, Vandium, and Bromine in a Polluted Atmosphere, Environ. Sci. & Technol., 6 (1), 68-71 (1972).

125. Murphy, T. and Cesarotti, D. J., Phosphorus Inputs from the Atmosphere M.S., Presented at 37th Ann. Mtg. Am. Soc. Limnol. and Oceanogr., Seattle, Washington, June 27, 1974.

126. Murphy, T., Sources of Phosphorus Inputs from the Atmosphere and Their Significance to Oligotrophic Lakes, VILU-WRC-74-0092, Research Report No. 92, 1974, 45 p.

127. Murphy, T. and Doskey, P. V., Inputs of Phosphorus from Precipitation to Lake Michigan, J. Great Lakes Res., 2 (1), 60-70 (1976).

128. Murphy, T. and Rzeszutko, C. R., Polychloriante Biphenyls in Precipitation in the Lake Michigan Basin, EPA Report, Grant #803195, US EPA, Duluth, Minnesota 55804, 1976.

129. Nifong, G. D. and Winchester, J. W., Particle Size Distributions of Trace Elements in Pollution Aerosols, University of Michigan Technical Report ORA 08903-8-T, Ann Arbor, 1970.

130. Nyborg, N. and Crepin, J., Effect of Sulfur Dioxide on Precipitation and on the Sulphur Content and Acidity of Soils in Alberta, Canada, Proc. of the Int. Symp. of Acid Precipitation and the Forest Ecosystem (1st) Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

131. Peakall, D. B., DDT in Rainfall in New York Following Application in the Pacific Northwest, Atm. Envir. <u>10</u>, 899-900 (1976).

132. Pearson, F. J. and Fisher, D. W., Chemical Composition of Atmospheric Precipitation in the Northeastern United States, Geological Survey Water Supply Paper 1535 p., 1971.

133. Penkett, S. A., The Chemical Composition of the Sudan Aerosol, AERE Harwell, personal communication, 1975.

134. Persiani, C., The Detection of Selected Air Pollutants Using a Laboratory Neutron Generator, Amer. Ind. Hyg. J., <u>32</u>, 573-578 (1971).

135. Pillay, K. K. S. and Thomas, C. C., Determination of Trace Element Levels in Atmospheric Pollutants by Neutron Activation Analysis, J. Radioanal. Chem., <u>7</u>, 107-108 (1971).

136. Potzl, K., Inorganic Chemical Analysis of Non-polluted Aerosols, Sampled at 1800 Meters Altitude, J. Geophys. Res., <u>75</u>, 2347-2352 (1970).

137. Prince, A. L., Toth, S. J., Blair, A. W. and Bear, F. E., Forty-Year Study of Nitrogen Fertilizers, Soil Science, <u>52</u>, 247-261 (1941).

138. Putnam, H. D. and Olson, T. A., An Investigation of Nutrients in Western Lake Superior, Sch. of Public Health, Univ. Minnesota, 1960.

139. Rahn, K. A., Sources of Trace Elements in Aerosols - An Approach to Clean Air, Ph.D. Thesis, Univ. of Michigan, Ann Arbor, Xerox University Microfilms (order no. 72-4956), 325 p.

140. Rahn, K. A., Study of the Atmospheric Aerosol on the Jungfraujoch - Progress Report, December 1972, Institut voor Nucleaire Wetenschappen, Rijksuniversiteit, Ghent, Belgium, 17 p., 1972.

141. Raymond, A. and G. Guiochon, G., Gas Chromatographic Analysis of C_8-C_{18} Hydrocarbons in Paris Air, Environ. Sci. & Technol., 8 (2), 143-149 (1974).

142. Reiter, R., Sladkovic, R. and Potzl, K., Chemical Components of Aerosol Particles in the Lower Troposphere Above Central Europe Measured Under Pure Air Conditions, Atm. Envir., 10, 841-853 (1976).

143. Richardson, C. J. and Nerva, G. E., The Chemical Composition of Atmospheric Precipitation from Selected Stations in Michigan, Proc. of the Int. Symp. of Acid Precipitation and the Forect Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

144. Risebrough, R., Huggett, R. J., Griffin, J. J. and Goldberg, E. D., Pesticides: Transatlantic Movement in the Northeast Trades, Science, 159, 1233-1235 (1968).

145. Sawicki, E., Hauser, T. R., Elbert, W. C. and Meeker, F. T., J. Amer. Ind. Hyg. Assoc. J., 23, 137-144 (1962).

146. Schlesinger, W. H., Reiners, W. A. and Knopman, D. S., Heavy Metal Concentrations and Deposition in Bulk Precipitation in Montane Ecosysteme of New Hampshire, USA, Environ. Pollut., 6, 39-47 (1974).

147. Scholdager, J., Sulphur Pollutants in Air and Precipitation at Norwegian Background Stations, Daily Measurements, Nov.'71 to June '72, Teknisk Notat, NR 52-73, Norwegian Institute for Air Res., 2007, Kjellar, Norway, 1973.

148. Schuetzle, D., Cronn, D. and Crittenden, A. L., Molecular Composition of Secondary Aerosol and Its Possible Origin, Environ., Sci. & Technol., 9 (9), 838-845 (1975).

149. Schutzle, D., Crittenden, A. L., and Charlson, R. J., Application of Computer Controlled High Resolution Mass Spectrometry to the Analysis of Air Pollutants, J. Air Pollut., Contr. Assoc. 23 (8), 704-709 (1973).

150. Semb, A., Measurement of Acid Precipitation in Norway, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecocystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

151. Shah, K. M., Sulfur and Nitrogen Brought Down in Precipitation in Wisconsin, M.S. Thesis, Soils Dept., Univ. Wisconsin, Madison.

152. Shaw, J. H., et al., Nitrous Oxide in the Earth's Atmosphere, Phys. Rev., 74, 978-979 (1948).

153. Shiomi, M. T. and Kuntz, K. W., Great Lakes Precipitation Chemistry Part I, Lake Ontario Basin, Proc. 16th Conf., Great Lakes Res., p. 581-602, 1973.

154. Shriner, D. S., Effects of Simulated Rain Acidified with Sulfuric Acid on Host-Parasite Interactions, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PB-258645.

155. Shum, Y. S. and Loveland, W. D., Atmospheric Trace Element Concentrations Associated with Agricultural Field Burning in the Williamette Valley of Oregon, Atm. Envir., 8, 6450655 (1974).

156. Shutt, F. T., Report of the Dominion Chemist for Year Ending March 31, 1925 (17 year series), p. 68-74, Dept. of Agric. Dom., Can., 1925.

157. Simmonds, P. G., Kerrin, S. L., Lovelock, J. E. and Shair, F. H., Distribution of Atmospheric Halocarbons in the Air Over the Los Angeles Basin, Atm. Envir., 8, 209-216 (1974).

158. Sodergren, A., Chlorinated Hydrocarbon Residues in Airborne Fallout, Nature, 236, 395-397 (1972).

159. Soderlund, R., Some Preliminary Views of the Atmospheric Transport of Matter to the Baltic Sea, Report AC-31, MISU-IMI, Arrhenius Laboratory, Fack, S-104 05 Stockholm, Sweden, 1975.

160. Spencer, W. F., Movement of DDT and Its Derivatives Into the Atmosphere, Residue Reviews, 59, 91-119 (1975).

161. Sridharan, N., Aqueous Environmental Chemistry of Phosphorus in Lower Green Bay, Wisconsin, Ph.D. Thesis, Water Chem. Dept., Univ. Wisconsin, Madison, 1972.

162. Stanley, C. W., Barney, J. E., Helton, M. R. and Yobs, A. R., Measurement of Atmospheric Levels of Pesticides, Environ. Sci. & Technol., 5, 430-435 (1971).

163. Stocks, P., Commins, B. T. and Aubrey, K. V., A Study of Polcyclic Hydrocarbons and Trace Elements in Smoke in Merseyside and Other Northern Localities, Intem. J. Air Water Pollut., 4, 141 (1961).

164. Struempler, A. W., Trace Element Composition in Atmospheric Particulates During 1973 and the Summer of 1974 at Chadron, Neb., Environ. Sci. & Technol., 9 (13), 1164-1168 (1975).

165. Sugimae, A. and Hasegawa, T., Emission Spectrographic Determination of Trace Metals in Airborne Particulates Collected on a Membrane Filter, Japan Analyst, 22, 3-9 (1973).

166. Sugimae, A., Sensitive Emission Spectrometric Method for the Analysis of Airborne Particulate Matter, Anal. Chem., 47 (11), 1840-1843 (1975).

167. Swank, W. T. and Henderson, G. S., Atmospheric Input of Some Cations and Anions. Forest Ecosystems in North Carolina and Tennessee, Water Resources Res., 12 (3), 541-546 (1976).

168. Tamm, C. O., Growth Yields and Nutrition in Carpets of a Forest Moss, Medd Stat. Skogdforskn. Inst. 43, 1-140 (1953).

169. Tanner, T. M., Young, J. A. and Cooper, J. A., Multielement Analysis of St. Louis Aerosols by Nondestructive Techniques, Chemosphere, 5, 211-220 (1974).

170. Tarrant, K. R. and Tatton, J. G., Organochlorine Pesticides in Rainwater in the British Isles, Nature, 219, 725-728 (1968).

171. Tabatabai, M. A. and Laflen, J. M., Nutrient Content of Precipitation Over Iowa, Proc. of the Int. Symp. on Acid Precipitation and the Forest Ecosystem (1st), Held at Columbus, Ohio, May 12-15, 1975, U.S. Dept. of Commerce NTIS, PT-258645.

172. The Waters of Lake Huron and Lake Superior Vol. I Summary and Recommendations, Rept. to Int. Joint Commission by the Upper Lakes Reference Group, Windsor, Ontario, 1976, p. 46.

173. ibid., p. 47.

174. ibid., p. 48.

175. ibid., p. 49.

176. ibid., p. 50.

177. The Waters of Lake Huron and Lake Superior, Vol. III Part A, Lake Superior Rept. to the Int. Joint Commission by the Upper Lakes Ref. Group, p. 87, 1976.

178. Voigt, G. C., Distribution of Rainfall Under Forest Stands, Forest Service, 1959.

179. Volchok, H. L., _et al_., Atmospheric Trace Metal Studies, Chemical Analysis of the Environment, Ahuja, S. (ed.) Plenum Press, New York, 1973.

180. Waller, R. E., Cummins, B. T. and Lawther, P. J., Brit. J. Ind. Med., _22_, 128-138 (1965).

181. Weibel, S. R., Weidner, R., Choen, J. and Christianson, A. G., J. Am. Water Works Assoc., _58_ (8), 1075-1080 (1966).

182. Whelpdale, D. M. and Summers, P. W., Acid Precipitation in Canada, Rep. ARQT-5-75, Atmospheric Dispersion Div. Atmos. Environ. Serv. Downsview, Ont. 143H5t4, 1975.

183. Wright, R. F., The Impact of Forest Fire on the Nutrient Influxes to Small Lakes in Northeastern Minnesota, Ecology, _57_, 649-663 (1976).

184. Wilson, B. D., Nitrogen in the Rain Water at Ithaca, New York, Soil Science, _11_, 101-110 (1921).

185. Yobs, A. R., Hanan, J. A. and Stevensen, B. L., Levels of Selected Pesticides in Ambient Air of the U.S.,Symp. on Pesticides in Air, 163rd ACS Meeting, Boston, Ma., April 11, 1972.

186. Zitko, V. and Carson, A. V., Heavy Metals in the Precipitation in the Vicinity of St. Andrews, N.B.FI Sheries Research Board of Canada, Manuscript Report Series No. 1129, Biological Station, St. Andrews, N.B., 1971.

187. Zoller, W. H. and Gordon, G. E., Instrumental Neutron Activation Analysis of Atmospheric Pollutants Utilizing Ge(Li) ray detectors, Anal. Chem., 42, 257-265 (1970).

188. Zoller, W. H., Gladney, E. S. and Duce, R. A., Atmospheric Concentrations and Sources of Trace Metals at the South Pole, Science, 183, 198-200 (1974).