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Great Lakes National
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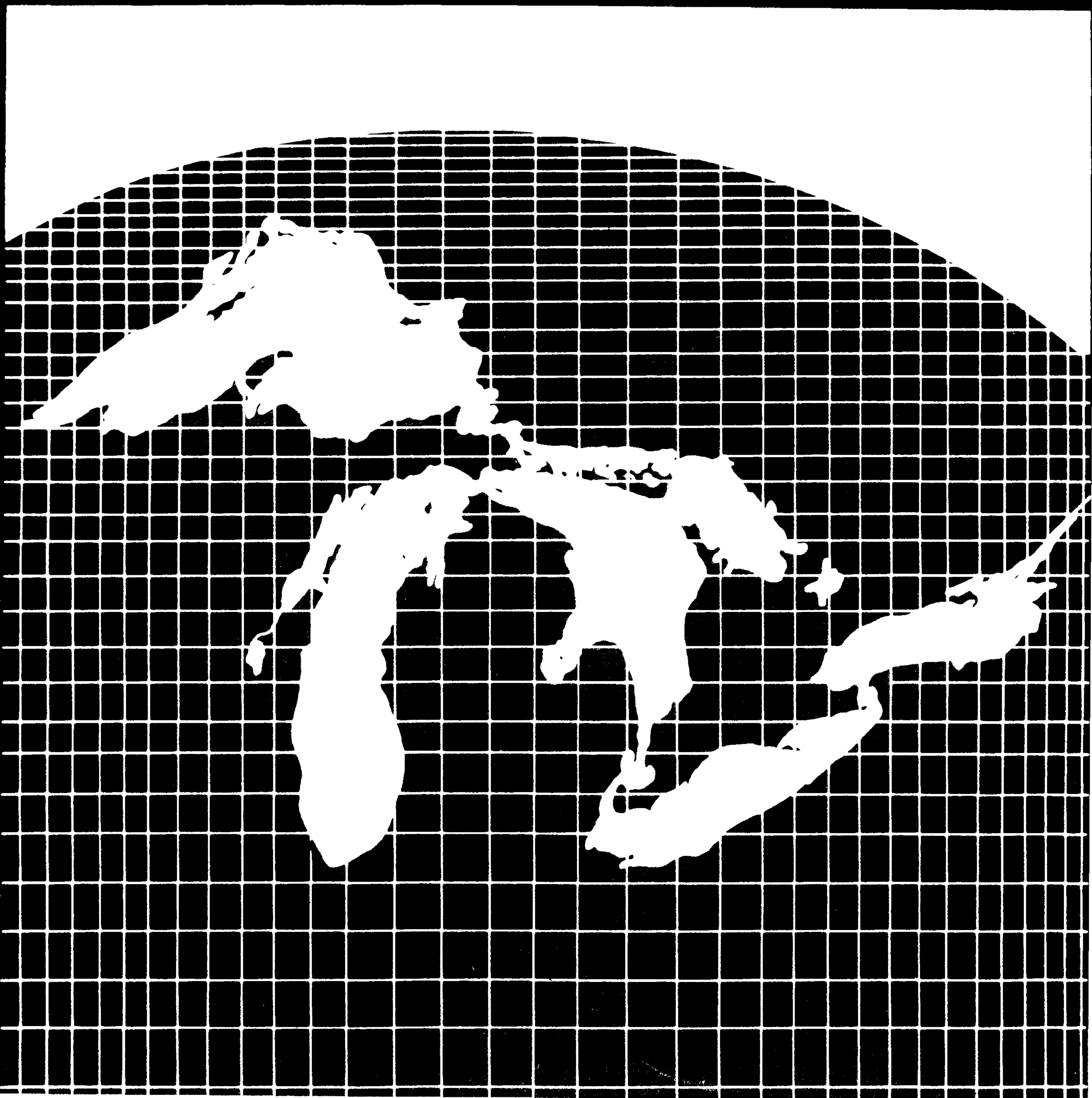
Great Lakes Atmospheric Deposition (GLAD) Network, 1982 and 1983



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Great Lakes Atmospheric Deposition (GLAD) Network, 1982 and 1983: Data Analysis and Interpretation

by

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GREAT LAKES ATMOSPHERIC DEPOSITION (GLAD) NETWORK, 1982 AND 1983: DATA ANALYSIS AND INTERPRETATION

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1. INTRODUCTION

1.1. Background

Under the Great Lakes Water Quality Agreement of 1972, the United States and Canada were provided a framework for the surveillance, monitoring, research, protection, and reclamation of the physical and chemical quality of the Great Lakes system. Within this framework, the monitoring of atmospheric deposition in the U.S. is coordinated by the Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency (U.S. EPA, 1985). Research in the 1970's had shown that atmospheric deposition was an important source of certain organic and inorganic chemicals to lake watersheds. A network of stations to measure and characterize this deposition was established in 1976. In 1981 the GLNPO upgraded this earlier measurement network by establishing the Great Lakes Atmospheric Deposition (GLAD) network. Its purpose was to determine atmospheric loadings of metals, nutrients, and major inorganic species to the Great Lakes and to evaluate annual trends in the chemical loadings of these species to the Lakes. During 1981 and early 1982, 36 monitoring stations were installed along the U.S. shores of the 5 Lakes. The GLAD network was designed to collect wet-only deposition samples at these near-shore locations.

1.2. Purpose

The purpose of this study was to analyze and interpret atmospheric wet deposition data collected by the GLAD network, including:

1) an assessment of data quality,
2) a comparison of specific pairs of GLAD and National Atmospheric Deposition Program (NADP) sites,
3) estimation of atmospheric loadings of selected elements to the five Great Lakes, and
4) an analysis of the potential change in loading estimates caused by closing certain GLAD sampling sites.

1.3. Scope

This report describes and interprets data collected in the GLAD network during 1982 and 1983. At some sites, data from one of the two years were ignored if that year's data failed to meet the screening criteria described later in this report. The sampling sites in the GLAD network that provided data analyzed in this report are listed in Table 1, which gives information about site name and code, location, elevation, and start date. GLAD site QG, the Copper Harbor site, Keweenaw Co., Michigan, did not meet selection criteria for either year, and does not appear in Table 1.

Site information is given in Table 2 for a comparison subnetwork of National Atmospheric Deposition Program (NADP) precipitation sampling sites in the Great Lakes area. Figure 1 shows the locations of sampling sites in both networks. The 16 GLAD sites closed in January 1986 are shown as solid circles in Figure 1.

2. METHODS

2.1. Sampling and Analysis

Collection and analysis of samples and data reporting for the GLAD network were the responsibility of the Great Lakes National Program Office. Details of these respective procedures have been described in GLNPO documents (GLNPO, 1985; GLNPO, undated), but for completeness brief descriptions are provided here.

The purpose of the GLAD network is to provide measurements of wet-only atmospheric deposition that may be used to estimate chemical loadings to the Great Lakes. To do this, some GLAD sites were sited in lakefront cities so as to measure deposition from industrial, transportation, and residential sources in and near urban areas. Other samplers were placed in lakeshore sites in rural areas to measure deposition of area-wide sources. In addition, one site was located in central Minnesota, about 200 km west of Lake Superior, to measure regionally representative deposition from sources largely upwind of the Great Lakes. This site satisfied the same siting criteria as NADP sites.

Precipitation samples were collected in AeroChem Metrics samplers, which were designed to collect wet-only samples by uncovering a plastic bucket only during precipitation. These buckets were lined with polyethylene bags. Field observers were instructed to inspect the sampler every Tuesday at about 9 A.M. local time. When a bag contained 500 mL or more of liquid precipitation (or at least 1.25 in. of snow), a sample was collected and another bucket and liner installed. Samples not meeting this minimum volume were left in the field for one or more additional weeks, until sufficient sample had accumulated. Beginning in 1984, rain gauges were installed at GLAD sites, so that an independent measurement of the precipitation amount was available. Rain gauge measurements could be used to assess the catch efficiency of the wet-only collectors and to calculate chemical loadings by forming the product of precipitation amount and chemical concentration. Prior to the installation of

Table 1. GLAD Network Sites.[a]

Site Name	Site Code	County/State	Latitude	Longitude	Elevation MSL(m)	Start Date
		Lake Superior				
Ontonagon	QF	Ontonagon, MI	46 49 11	089 38 18	194	07/07/81
Grand Marais	QJ	Alger, MI	46 39 54	085 58 16	194	07/14/81
Hovland	QA[b]	Cook, MN	47 50 50	089 57 50	224	07/21/81
Gooseberry Falls	QB[c]	Lake, MN	47 08 17	091 28 16	210	09/22/81
Duluth	QD	St. Louis, MN	46 46 07	092 05 15	186	07/21/81
Gull Lake	RQ	Crow Wing, MN	46 24 40	094 21 09	376	01/19/82
Cornucopia	QE[b]	Bayfield, WI	46 51 44	091 08 13	195	02/17/81
		Lake Michigan (North)				
Escanaba	QL	Delta, MI	45 44 44	087 03 02	181	06/09/81
Empire	QV	Leelanau, MI	44 51 14	086 02 05	229	06/30/81
Beaver Island	QW[b]	Charlevoix, MI	45 43 40	085 32 25	195	09/22/81
Green Bay	QM[b]	Brown, WI	44 31 50	087 54 44	201	03/31/81
Manitowoc	QN	Manitowoc, WI	44 03 56	087 39 23	182	04/07/81
		Lake Michigan (South)				
South Water Plant	QR	Cook, IL	41 45 23	087 32 39	181	06/02/81
Jardine Plant	QQ	Cook, IL	41 53 41	087 36 20	180	06/02/81
Evanston	QP	Cook, IL	42 03 33	087 40 22	180	07/07/81
Benton Harbor	QT	Berrien, MI	42 07 26	086 28 30	183	02/03/81
Muskegon	QU[b]	Muskegon, MI	43 08 52	086 16 04	186	03/24/81
Milwaukee	QO	Milwaukee, WI	43 04 31	087 53 02	205	03/17/81
		Lake Huron				
Bay City	AQ	Bay, MI	43 39 44	083 54 39	179	03/24/81
Port Austin	BQ	Huron, MI	44 02 50	082 59 47	180	04/07/81
Mount Clemens	DQ[c]	Macomb, MI	42 34 00	082 50 22	177	05/11/82
Port Sanilac	CQ	Sanilac, MI	43 25 36	082 32 32	187	03/17/81
Tawas Point	QZ	Iosco, MI	44 15 42	083 26 30	180	05/05/81
		Lake Erie				
Dunkirk	KQ	Chautauqua, NY	42 30 13	079 19 26	182	01/19/82
Grand Island	LQ[b]	Erie, NY	43 03 26	078 58 09	173	01/26/82
Toledo	FQ	Lucas, OH	41 41 18	083 24 39	176	01/27/81
Put-In-Bay	GQ[b]	Ottawa, OH	41 39 29	082 49 40	180	02/17/81
Lorain	HQ[b]	Lorain, OH	41 28 20	082 08 36	186	02/17/81
Fairport Harbor	IQ	Lake, OH	41 45 17	081 16 22	187	01/27/81
Ashtabula	JQ	Ashtabula, OH	41 54 30	080 46 30	179	02/02/82
Erie	SQ	Erie, PA	42 07 42	080 06 03	192	01/25/82
		Lake Ontario				
Olcott	MQ[b]	Niagara, NY	43 20 27	078 41 35	88	01/19/82
Rochester	NQ	Monroe, NY	43 13 48	077 34 45	81	02/02/82
Cape Vincent	PQ	Jefferson, NY	44 07 30	076 20 30	79	01/26/82
Fair Haven	TQ[c]	Cayuga, NY	43 19 08	076 42 11	74	01/09/82

[a] Except as noted, these sites all have valid wet-only data for at least 3/4 of the precipitation and 3/4 of the 1/82 through 12/83 summary period.

[b] Valid data for 1982 only.

[c] Valid data for 1983 only.

Table 2. NADP Network Sites in the Great Lakes Region.[a]

Site Name	Site Code	County/State	Latitude	Longitude	Elev. MSL (m)	Start Date
Bondville	IL11	Champaign, IL	40 03 12	88 22 19	212	02/27/79
Shabbona	IL18	DeKalb, IL	41 50 29	88 51 04	265	05/26/81
Argonne	IL19	DuPage, IL	41 42 04	87 59 43	229	03/11/80
Salem	IL47	Marion, IL	38 38 36	88 58 01	173	04/15/80
Indiana Dunes National Lakeshore	IN34	Porter, IN	41 37 57	87 05 16	208	07/15/80
Purdue University Agricultural Farm	IN41[b]	Tippecanoe, IN	40 28 17	86 59 18	215	07/13/82
Douglas Lake-Univ. of Michigan Biol. Sta.	MI09	Cheboygan, MI	45 33 40	84 40 42	233	07/03/79
Kellogg Biol. Sta.	MI26	Kalamazoo, MI	42 24 37	85 23 34	288	06/26/79
Wellston	MI53[b]	Wexford, MI	44 13 28	85 49 07	292	10/10/78
Chassell	MI99[b]	Houghton, MI	47 06 17	88 33 05	277	02/15/83
Marcell Exper. Forest	MN16	Itasca, MN	47 31 52	93 28 07	431	07/06/78
Fernberg	MN18	Lake, MN	47 56 45	91 29 43	524	11/18/80
Ashland Wildlife Area	MO03	Boone, MO	38 45 13	92 11 55	239	10/20/81
Washington Crossing	NJ99	Mercer, NJ	40 18 54	74 51 17	72	08/04/81
Aurora Research Farm	NY08	Cayuga, NY	42 44 02	76 39 35	249	04/17/79
Chautauqua	NY10	Chautauqua, NY	42 17 58	79 23 47	488	06/10/80
Huntington Wildlife	NY20	Essex, NY	43 58 20	74 13 19	494	10/31/78
Bennett Bridge	NY52[b]	Oswego, NY	43 31 34	75 56 50	245	06/10/80
Jasper	NY65	Steuben, NY	42 06 22	77 32 08	634	02/19/80
Delaware	OH17	Delaware, OH	40 21 19	83 03 58	285	10/03/78
Caldwell	OH49	Noble, OH	39 47 34	81 31 52	276	09/26/78
Wooster	OH71	Wayne, OH	40 46 48	81 55 31	315	09/26/78
Kane Exper. Forest	PA29	Elk, PA	41 35 52	78 46 04	618	07/18/78
Leading Ridge	PA42	Huntingdon, PA	40 39 32	77 56 10	282	04/25/79
Lake Dubay	WI28[b]	Portage, WI	44 39 53	89 39 08	338	06/29/82
Trout Lake	WI36	Vilas, WI	46 03 09	89 39 11	501	01/22/80
Spooner	WI37	Washburn, WI	45 49 21	91 52 30	331	06/03/80
Parsons	WV18	Tucker, WV	39 05 23	79 39 44	305	07/05/78
Mount Forest[c]	CAN2[b,c]	Wellington, ONT	43 59 29	80 44 46	410	05/05/81

[a] Except as noted, these sites all have valid wet-only data for at least 3/4 of the precipitation and 3/4 of the 1/82 through 12/83 summary period.

[b] Valid data for 1983 only.

[c] This site is located in lower Ontario Province, and it was operated for the purpose of intercomparing Canadian and U.S. Data

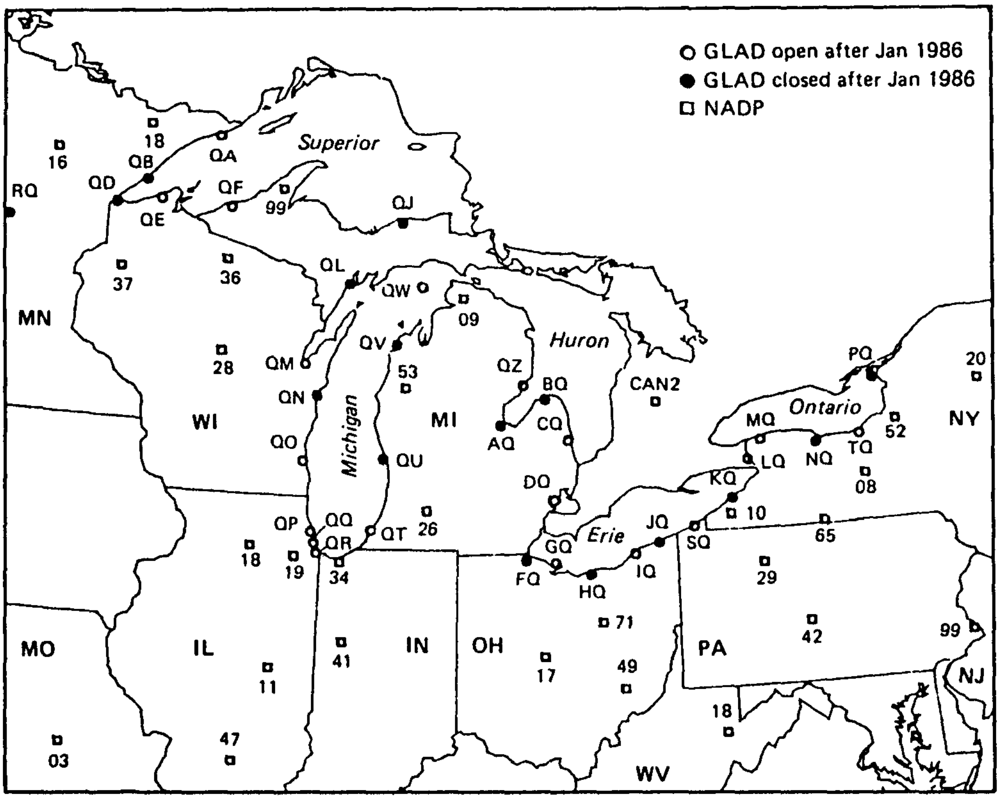

Figure 1. Network map for GLAD and NADP sampling sites. (GLAD site QG, in Keweenaw Co., MI, did not meet selection criteria, and does not appear on this map.)

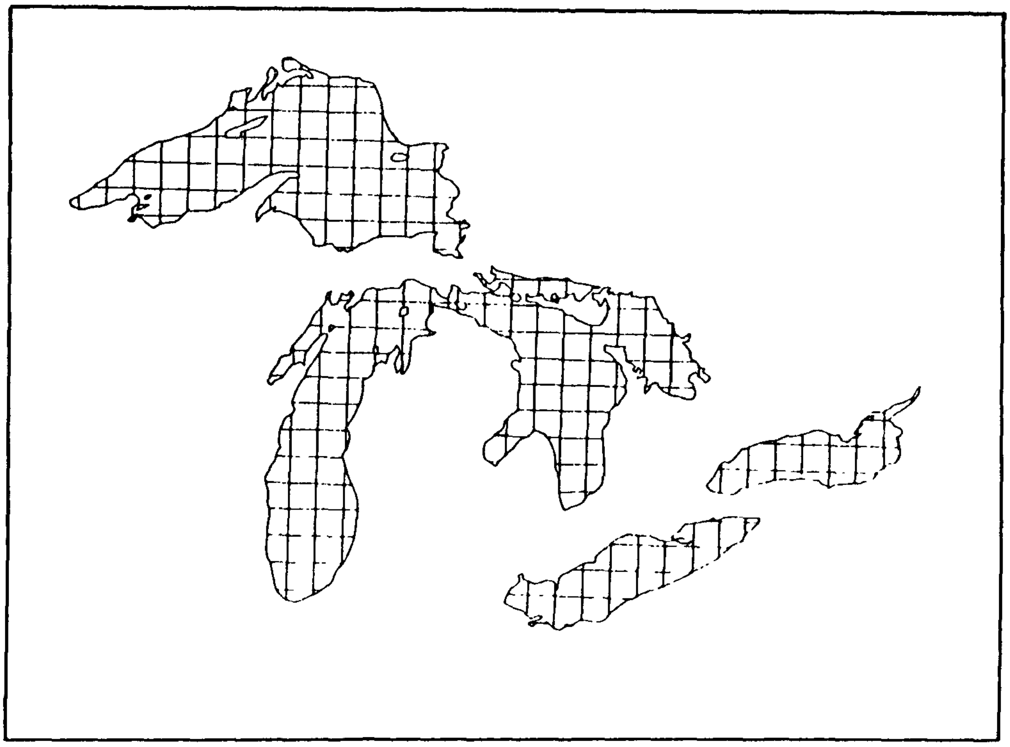

Figure 2. Grid used for over-lake deposition flux calculations.

the gauges, the only on-site measurement of precipitation amount was the collected volume from the AeroChem Metrics samples.

After collection, a 20-40 mL aliquot of sample was decanted from the bag for field pH and conductance measurements. Next, a half liter polyethylene bottle was filled and shipped to the EPA analytical laboratory. Upon arrival at the laboratory, samples were stored at 4°C prior to preparation for analysis. Samples were split and preservatives were added to the splits, as appropriate to the analysis (e.g., nitric acid was added to the split intended for metals analyses).

Ca, Mg, and Na ions were measured using the inductively-coupled argon plasma (ICAP) method. Flame atomic absorption spectrophotometry (AAS) was used for K analyses, and flameless AAS for Pb and Cd analyses. Automated wet chemical methods (Technicon) were used to determine NH_4, NO_3+NO_2, SO_4, and Cl.

2.2. Data Screening Criteria

As indicated in footnotes of Tables 1 and 2, the criteria for including data from a GLAD or NADP sampling site in this study were that the site have valid data for at least 75% of the two-year period and valid data representing at least 75% of the two-year precipitation total. Since GLAD sites did not have rain gauge measurements during 1982 and 1983, it was necessary to convert sample volumes to precipitation amounts in order to calculate the two-year precipitation totals. (See Appendix A for a list of criteria for selecting valid samples.) If a sampling site did not meet the 2-year criteria, it was reevaluated for inclusion of one year's data only, using a one-year precipitation total calculated from sample volumes.

Whereas internal NADP data screening criteria assure that only samples with analyses for all ions measured are included in the data available to the public, no similar requirement was placed on the GLAD data. Thus, samples appear in the GLAD data for which one or more analyses may be missing. This means that the checks for data completeness (75% of the time and 75% of the precipitation during the two-year period) had to be applied ion by ion for the GLAD data, instead of sample by sample, as for the NADP data. This resulted in a varying number of valid sites from which to draw maps of concentration distributions for the various ions. Sites excluded from the spatial analyses of concentrations for the various ions are listed in Table 3.

Table 3. GLAD Sites Excluded from Spatial Analyses of Concentration because of Data Completeness Criteria.

Ion	Sites excluded
Cl	AQ, BQ, CQ, KQ, LQ, MQ, PQ, QA, QD, QF, QJ, QL, QM, QP, QT, QU, QV, QW, QZ, RQ
Ca	MQ, QU, QW
Mg	QD, QU, QW
K	QB, QD, QE, QU, QW
Na	QU, QW
NH_4	DQ, QM
SO_4	QA, QL, QQ, RQ
Pb	GQ, HQ, LQ, MQ, QA, QB, QD, QE, QG, QM, QU, QW
Cd	GQ, HQ, LQ, MQ, QA, QE, QG, QM, QU, QW

2.3. Data Quality Checks

Several checks of internal self-consistency of the sample analytical results are possible. These include 1) ion balance calculations, 2) comparisons of measured and calculated conductance, and 3) comparisons of measured pH and conductance. Further details of each of these data quality check procedures are given in the following paragraphs.

Based on the concept that the net charge of all ions in an aqueous solution should be zero, a comparison of the total measured anion and cation equivalents is useful in establishing the possibility of either 1) the lack of analysis of one or more important ions, or 2) inaccurate analyses. In other words, if all ions in solution have been measured, and measured accurately, the difference between the sums of anion and cation equivalents should be zero. We express any differences as the ion percent difference (IPD), defined as follows:

$$\text{IPD} = 100 \times \frac{\text{Sum A equiv} - \text{Sum C equiv}}{\text{Sum A equiv} + \text{Sum C equiv}},$$

where (Sum A equiv) is the sum of the chemical equivalent concentrations of the measured anions plus the concentration of bicarbonate, HCO_3^-, calculated from the measured pH. (See Stensland and Bowersox (1984) for details of the exact method used to calculate HCO_3^-.) Also, (Sum C equiv) is the sum of the chemical equivalent concentrations of the measured cations, including H^+ from the measured pH. The performance of the GLAD precipitation sampling and analysis program was examined by comparing plots of the frequency distribution of the IPD for the GLAD and NADP data (see Section 3.1).

A further check on the completeness and accuracy of precipitation composition analysis can be made by comparing measured conductance against conductance calculated by summing the contributions from the individual measured ions. Again, if all ions present were measured, and measured accurately, the conductance percent difference (CPD), defined as:

$$\text{CPD} = 100 \times \frac{\text{Calc Cond} - \text{Meas Cond}}{\text{Meas Cond}}$$

would equal zero. (See Lockard (1987) for the formula used to calculate conductance.) Also in this case, we evaluated the GLAD network data from a plot of the frequency distribution of its CPD in comparison with that of the NADP network (see Section 3.1).

As examination of the GLAD data set progressed, the possibility of biased pH measurements arose. This suggested a test of the consistency of the measured pH and conductance measurements. The test consisted of a plot of measured pH vs measured conductance in view of the relationship between the two. Specifically, for a given measured pH, the measured conductance must be at least that of the corresponding $H+$ concentration. The GLAD data set was evaluated from such a plot, noting the frequency with which samples occurred in the "forbidden zone" of the plot, where measured pH and conductance values were inconsistent with each other. The results were compared to a similar plot for the NADP data.

A slight variation of the previous test was also carried out using calculated pH instead of measured pH, in a test of the hypothesis that there was pH bias in the data.

2.4. Calculation of Integrated Ion Concentrations

Some measure of the overall concentration of each ion at each sampling site is necessary both for showing spatial patterns on maps and for use in estimating long-term (annual or longer) wet deposition fluxes. For this work we used sample volume-weighted mean concentrations. These concentrations were computed for each site using the combined 2-yr data set wherever possible, or for individual years, when data for only one year were available. This method was chosen as the best for providing overall spatial patterns of the concentrations. It did not allow for comparison of yearly patterns. In any case, such a comparison was not feasible, since the screening process produced a different set of valid sites for any ion in each year. To reduce the set of sites to only the ones that were valid in both years would have resulted in too little data for a representative comparison of the year to year differences.

2.5. Metal Concentrations

Data for the toxic metals Hg, Cd, and Pb were examined in some detail to ascertain whether they were suitable for determining precipitation-only fluxes to the lakes. Separate summaries of our findings appear in Table 4 for 1982 and 1983. In 1982, about 40-50% of the samples were analyzed for Hg and Cd, and only about 8% were analyzed for Pb. Many of the samples analyzed had concentrations less than detection limits, as indicated in the table. Close examination of the data revealed that most of the 1982 Cd and Pb measurements were made using the ICAP method, for which detection limits were higher than for the furnace AA method. This appears to account for the high fraction of less-than-detection- limit values for 1982. With such few data available, it was not possible to provide reliable flux estimates for 1982.

The situation was much improved in 1983, when virtually all the Cd and Pb analyses were done using the furnace AA method (see Table 4). Thus, fluxes of Cd and Pb to the Great Lakes were computed for 1983.

2.6. Paired Site Comparisons

Measured ion concentrations at paired GLAD and NADP sites were compared in two ways. First, box diagrams of percentile distributions (Cleveland, 1985) were prepared for four species common to both the GLAD and NADP networks: sulfate, nitrate, ammonium, and calcium. When plotted side by side, these provide a convenient visual comparison between sites. Second, the measured concentrations at the respective sites were subjected to the nonparametric Wilcoxon rank sum test (SAS Institute, Inc., 1982) to estimate the probability that they came from the same population.

2.7. Deposition Calculations

Our objective was to estimate climate-averaged loadings of atmospheric pollutants to the five Great Lakes from precipitation alone. This was a two-step process. First, deposition fluxes were computed as the product of ion concentrations and precipitation amounts (depth). Then, to get annual loadings, the calculated fluxes were integrated over the lake areas.

Ideally, the fluxes would be measured over a suitably long period. Unfortunately, the GLAD data set is not among the very few with such a record of measurements. Further, rain gauge measurements were not available at the GLAD sites for 1982 or 1983. Since year to year fluctuations in mean precipitation are likely to be greater than those in volume-weighted mean concentration, we chose to compute deposition fluxes as the product of the available short-term mean concentrations and long-term (30-yr) mean precipitation values. The 30-yr precipitation record available from the National Weather Service (NWS) has the added advantage that the spatial density of samplers is much greater than that of the combined GLAD and NADP networks. Fluxes computed in this way should be better approximations of the climate-averaged loadings than those measured for one or two years, although not as good as those measured over, perhaps, a 20-yr period.

Table 4. Summary of GLAD Toxic Metal Measurements

(a) 1982

	Hg	Cd	Pb
Total samples	975	975	975
Total measurements	482 49.4% of 975	403 41.3% of 975	81 8.3% of 975
Measurements above analytical detection limit	37 7.7% of 482	45 11.2% of 403	48 59.3% of 81
Typical detection limit	0.1 ug/L	Highly variable	2.0 ug/L
Sites with >3 values above detection limit	Hovland, MN Fairport Harbor, OH Lorain, OH	Erie, PA Grand Marais, MI Manitowoc, WI	Grand Island, NY
Method	Cold vapor AA	ICAP, Furnace AA	ICAP, Furnace AA

(b) 1983

	Hg	Cd	Pb
Total samples	966	966	966
Total measurements	506 (52.4% of 966)	834 (86.3% of 966)	822 (85.1% of 966)
Measurements above analytical detection limit	352 (69.6% Of 506)	689 (82.6% of 834)	807 (98.2% of 822)
Typical detection limit	0.1 ug/L	0.10 ug/L	0.6 ug/L
Method	Cold vapor AA	Furnace AA	Furnace AA

Computations were carried out at the vertices of each grid box in Figure 2. Spatial distributions of annual wet deposition fluxes were computer-plotted from these gridded values. Annual wet loadings to the lakes were estimated from the values computed for each grid box having some portion of its area over one of the lakes. A mean value for each of these boxes was computed as the arithmetic mean of the values at the vertices. Where only a portion of the box was over water, the grid-box deposition was decreased by multiplying by the water-area/total-area ratio, so as to include only the over-water portion of the deposition.

The accuracy of the areal integration is shown in Table 5 by a comparison of lake areas computed by integrating whole and partial grid boxes over the lakes with literature values of lake area. The differences from literature values assume that the literature values are accurate to four significant figures and are expressed as percents of the literature values. The differences are quite small, probably within measurement accuracy. Nevertheless, computed fluxes were increased by the ratio of the literature area to the grid-box area for the respective lakes.

Table 5. Comparison of Grid-Box Integrated Lake Areas with Literature Values.

	Grid-box integrated area (sq km)	Literature[a] area (sq km)	Difference (percent)
Superior	80,200	82,410	-2.7
Michigan	56,840	58,020	-2.0
Huron	58,170	59,600	-2.4
Erie	25,350	25,740	-1.5
Ontario	19,070	19,530	-2.3

[a] Todd (1970).

Values of precipitation at the grid vertices were estimated using an objective analysis procedure developed by Achtemeier (1987) and Achtemeier, *et al.* (1977), based on earlier work by Barnes (1964, 1973). These estimates are based on measured values at the 5 nearest sampling sites, weighted using a negative exponential function of distance from the grid point. Each grid point value is based on measured, not interpolated, values; thus grid values over the lakes were based on on-shore measurements. A map of the precipitation measurement network is shown in Figure 3. The data used in this analysis were obtained from the NOAA National Climatic Center (NCC), Asheville NC. They are 30-yr (1951-80) precipitation normals, which are computed as the arithmetic mean of 30 annual precipitation amounts. Station histories, documented at NCC, were used to screen all precipitation data from 1) the NWS cooperative station network, and 2) the NWS first order station network. This screening was conducted by the NCC staff. The data used in our analysis were screened to assure that instrument exposure and station location were "homogeneous" for the 30-yr period. Where it was determined that there were inhomogeneities, the records at the two locations or for the two gauge exposures were compared to

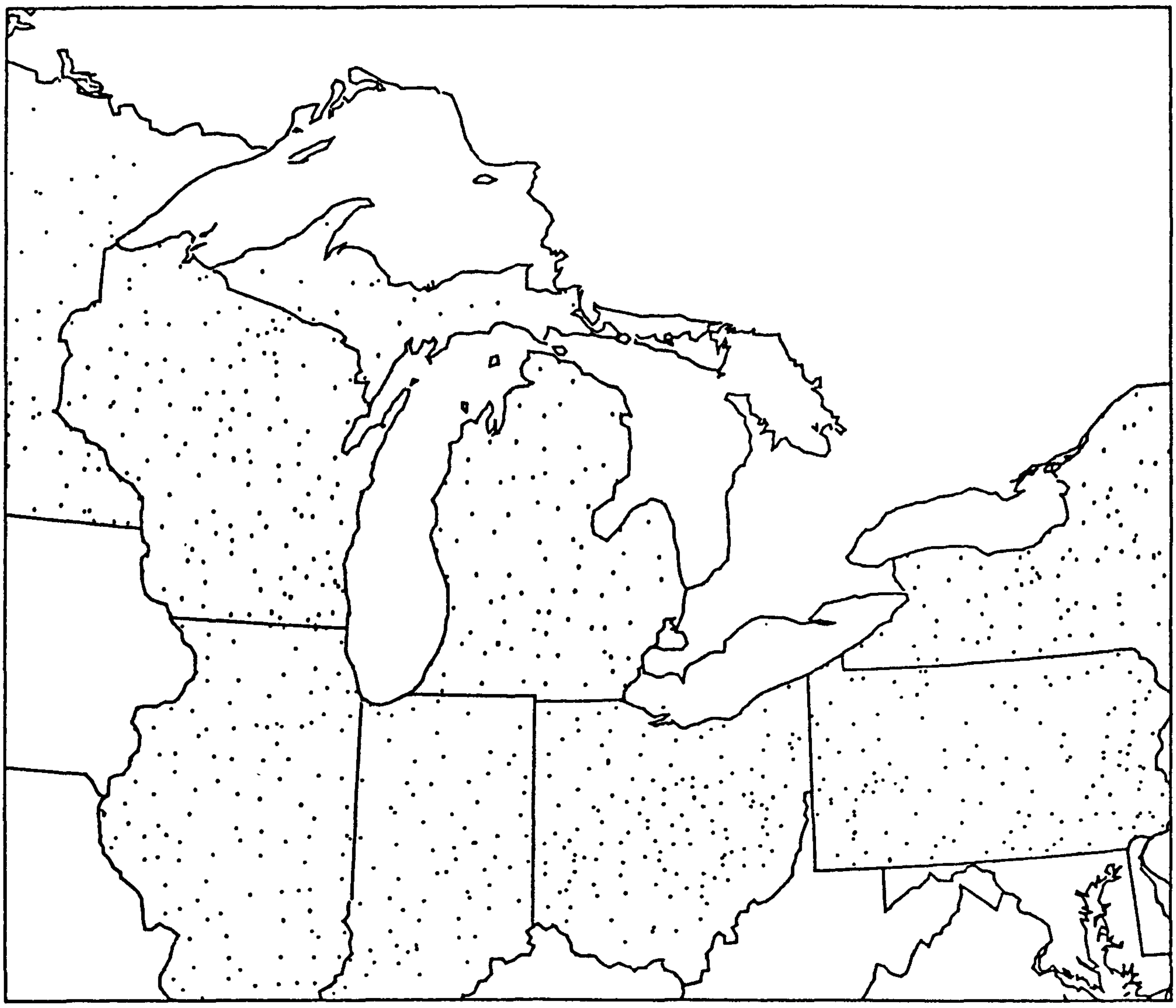

Figure 3. National Weather Service observer network used for 30-yr mean annual precipitation distribution.

nearby homogeneous data to ascertain that the records were unaffected by the change of location or exposure. A brief description of this approach is available (National Climatic Center, 1982).

Ion concentrations at the grid points were estimated similarly, also using the nearest 5 measurements. The map of sampling sites is shown in Figure 1. Separate concentration and associated deposition estimates were made for 1) the NADP sites only, 2) the combined GLAD and NADP networks, and 3) the full combined network less certain GLAD sites or combinations of GLAD sites. These results were compared to show the effect on deposition of 1) adding the full GLAD network to the NADP network, 2) removing GLAD sampling sites closed in January 1986 from the full set of GLAD and NADP sites, and 3) various options for closing GLAD sites in addition to the 16 closed in January 1986.

3. RESULTS AND DISCUSSION

3.1. Data Quality Checks

Results of the internal data consistency checks described earlier are presented here, beginning with the ion balance test.

Frequency distributions of IPD for both the GLAD and NADP networks appear in Figure 4, and the results of certain statistical tests on the data are given in Table 6. The 798 GLAD samples have a relatively broad distribution and a median IPD of -20.6% (mean = -21.3%), which is significantly different from zero. The negative value indicates either an excess of cations or a deficit of anions. The 2168 NADP samples have a relatively narrow distribution and a median IPD of 2.59% (mean = 2.66%), which is much closer to, but still significantly different from, zero and indicates a slight excess of anions or deficit of cations. The sign of this difference is consistent with the absence of trace metal measurements of NADP samples.

Frequency distributions of CPD for both networks appear in Figure 5, and associated statistics in Table 7. The GLAD samples again have a relatively broad distribution and a median CPD of 47.9% (mean = 70.0%), which is significantly greater than zero. Combined with the ion balance results, this indicates a broad tendency for excess cations in the GLAD data. The NADP samples exhibit a narrow, highly peaked distribution with a median CPD of -8.73% (mean = -9.34%), which is also significantly different from zero, and, as before, is consistent with the absence of measurements of trace components.

Comparisons of the IPD and CPD distributions of the GLAD and NADP data show large differences that were not expected. Both data sets were derived from the same geographic area, thus one would expect the measured chemical composition of precipitation from the two networks to be similar. Some GLAD sites were in urban and industrial regions, which could lead to significant inputs of substances that were not measured routinely. This could explain the greater variability (larger spread) of the IPD and CPD distributions of the GLAD data. Another source of the variability could result from measurement problems and this was explored next.

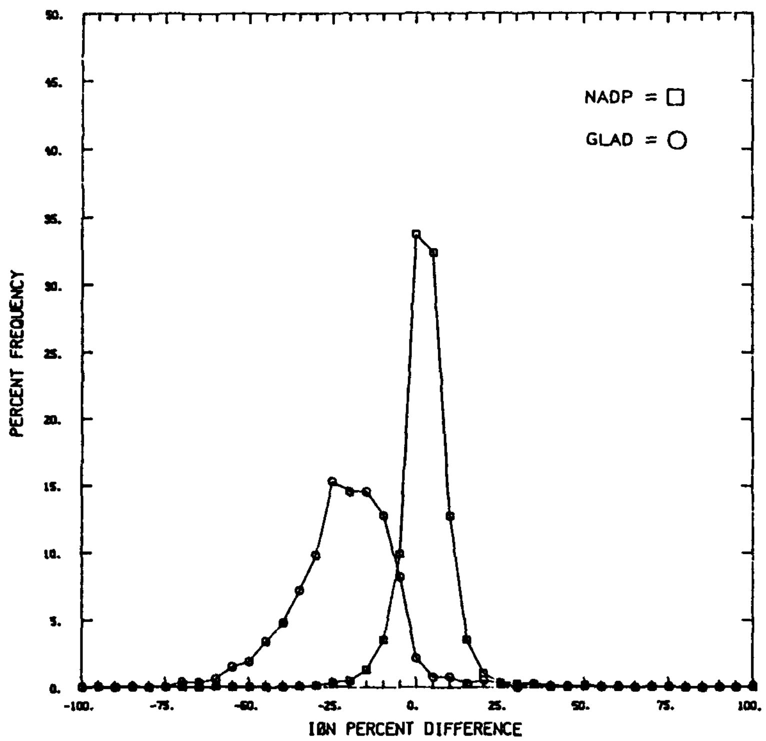

Figure 4. Frequency distributions of ion percent difference (IPD) for GLAD and NADP networks, 1982-1983.

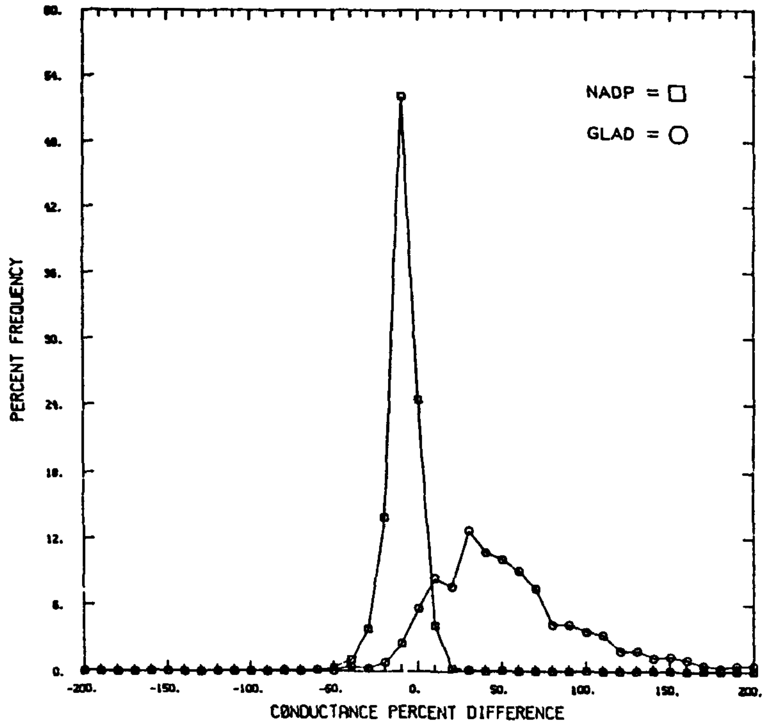

Figure 5. Frequency distributions of conductance percent difference (CPD) for GLAD and NADP networks, 1982-1983.

Table 6. Summary of Ion Percent Difference Results for GLAD and NADP Sites (1982-1983). (Also see Figure 4.)

	GLAD	NADP
N	798	2168
Median	-20.6	2.59
Mean	-21.3	2.66
Std dev	15.7	7.22

Tests:

1) GLAD median $\neq 0$ ($P = 0.0001$, sign rank test).
2) NADP/NTN median $\neq 0$ ($P = 0.0001$, sign rank test).
3) Reject H_0 ($P = 0.0001$, Wilcoxon 2-sample test) that GLAD = NADP.
4) Reject H_0 ($P = 0.0001$, Brown-Mood test) that GLAD median = NADP median.

Table 7. Summary of Conductance Comparison Results for GLAD and NADP Sites (1982-1983). (Also see Figure 5.)

	GLAD	NADP
N	795	2168
Median	47.9	-8.73
Mean	70.0	-9.34
Std dev	161	9.38

Tests:

1) GLAD median $\neq 0$ ($P = 0.0001$, sign rank test).
2) NADP/NTN median $\neq 0$ ($P = 0.0001$, sign rank test).
3) Reject H_0 ($P = 0.0001$, Wilcoxon 2-sample test) that GLAD = NADP.
4) Reject H_0 ($P = 0.0001$, Brown-Mood test) that GLAD median = NADP median.

Since H^+ is the major contributor to the conductance of precipitation samples, we chose to investigate the possibility that a negative pH bias (erroneously high H^+ concentrations) was a cause of the cation excess indicated by the combined results of the ion balance calculations and the comparison of calculated and measured conductances. The plots of measured pH versus measured conductance described in Section 2.2. should confirm or refute the suggestion of a pH bias in the GLAD measurements.

Figure 6(a) shows results for the two-year GLAD data set. A considerable number of the data points are in the "forbidden" zone below the sloping line showing conductance of H^+ only, as a function of measured pH. In comparison, the NADP data in Figure 6(b) behave as expected, with no measurements in the forbidden zone. The results in Figure 6, by themselves, indicate that either the pH or the conductance measurements are biased low, but we already know from the results in Figures 4 and 5 that we have an excess of cations, which is consistent only with a pH bias. This is further confirmed in Figure 7(a), where the pH calculated from the other ion measurements shows a much closer correspondence to the ideal that no points should occur in the forbidden zone beneath the sloping line.

Strictly speaking, however, the prohibition against points below the line is not absolute when all the other ions in solution are considered. In very acidic samples, small imprecisions in the pH and conductance measurements can produce points below the line. Note that a few points occur below the line for both GLAD data in Figure 7(a) and NADP data in Figure 7(b).

By comparison with results for comparable NADP samples, the distributions of ion balance and conductance differences for the GLAD network clearly show an anomalous cation excess. The occurrence of many points in the "forbidden zone" in a plot of measured pH versus measured conductance for the GLAD data shows that the cation anomaly was caused by biased pH measurements. This was further confirmed when the anomaly largely disappeared in a comparable plot of calculated pH vs measured conductance for the same samples.

Because of the strong evidence of a pH bias in the GLAD data, no further use was made of the GLAD pH data.

3.2. Concentration Spatial Distributions

3.2.1. Effect of Adding GLAD Sites to the NADP Data Set

An important potential benefit of the GLAD network is the additional spatial resolution in the Great Lakes region that it might provide to national atmospheric deposition networks. We present here a series of figures comparing objectively-analyzed spatial distributions of concentration. The objective analysis scheme described in section 2.7 was used to develop these figures. In each figure, the top (a) panel shows the concentration pattern resulting from regional NADP data alone, and the bottom (b) panel shows the patterns obtained when the GLAD data were added to the data set.

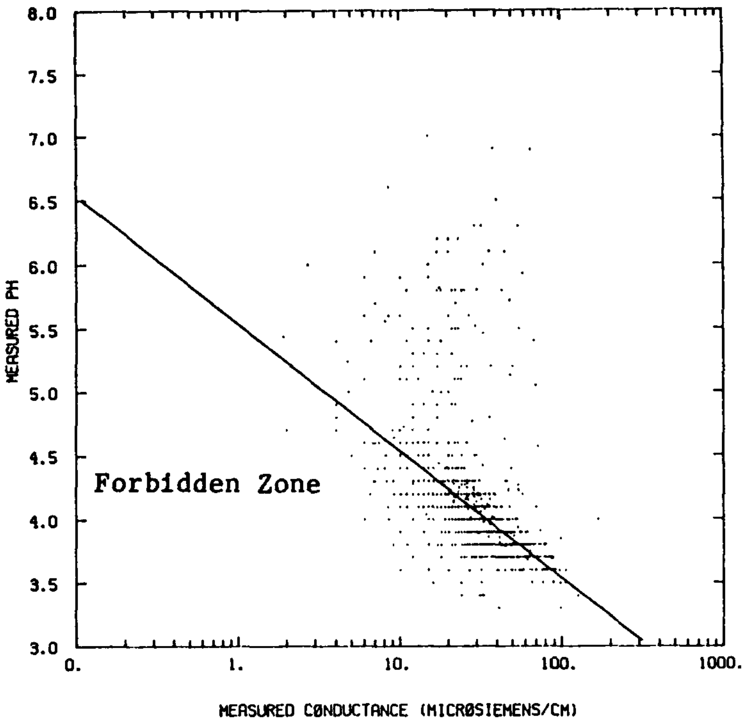

Figure 6(a). Scatterplot of measured pH and conductance for the GLAD network, 1982-1983. There is a "forbidden zone" beneath the sloping line, which corresponds to the conductance due only to the measured H^+ ion in solution.

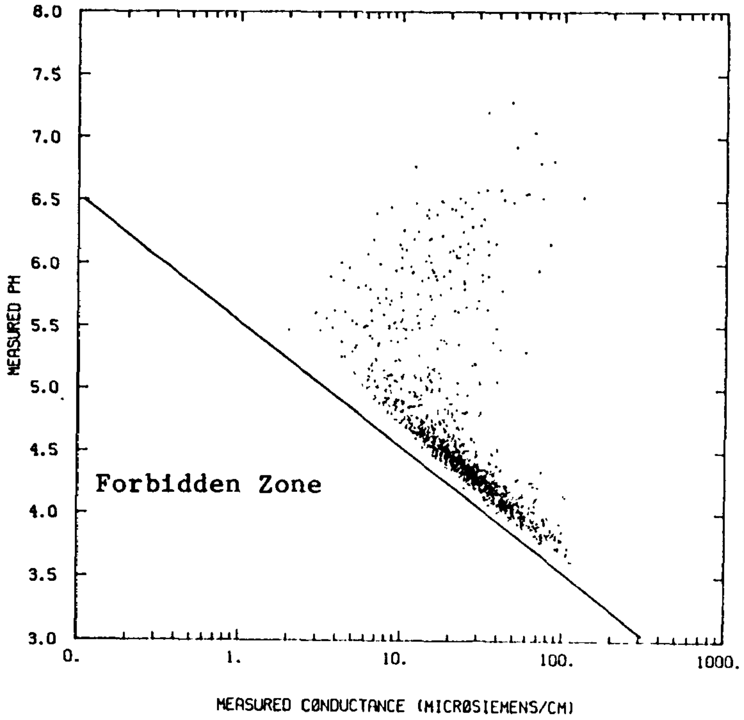

Figure 6(b). Scatterplot of meaured pH and conductance for the NADP/NTN network, 1982-1983. The sloping line defines a "forbidden zone," as described above.

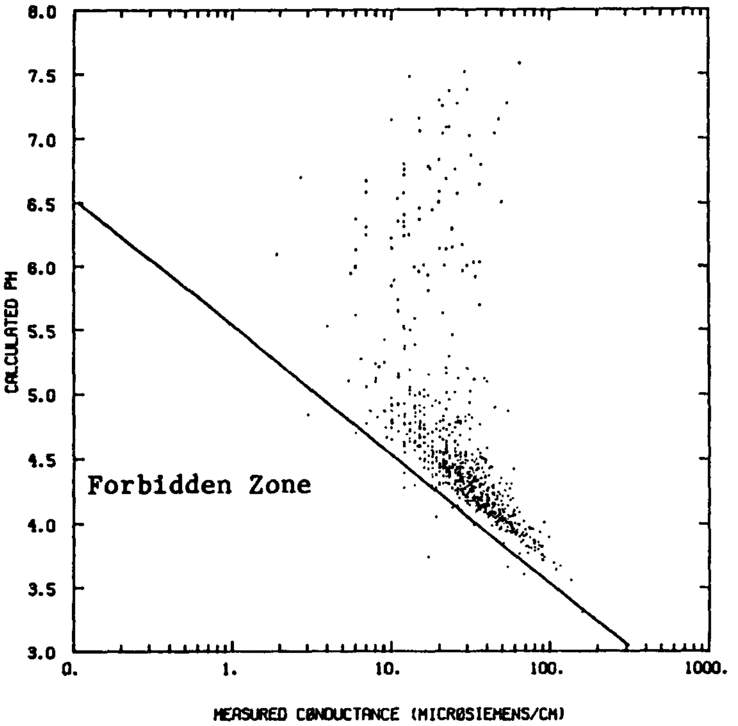

Figure 7(a). Scatterplot of calculated pH vs measured conductance for the GLAD network, 1982-1983. The sloping line defines a "forbidden zone," as described in Figure 6(a).

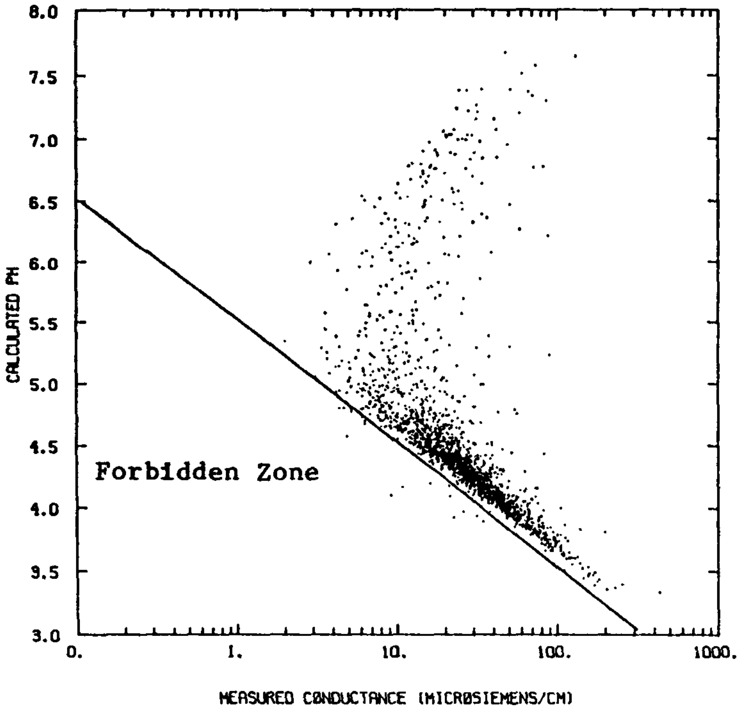

Figure 7(b). Scatterplot of calculated pH vs measured conductance for the NADP/NTN network, 1982-1983. The sloping line defines a "forbidden zone," as described in Figure 6(a).

Figure 8 compares the respective concentration patterns for SO_4. The broad patterns are quite similar, as one would expect. However, the GLAD data provide additional detail in the pattern near and over the Great Lakes. Relatively minor differences appear over Lakes Superior, Michigan, and Huron, but considerable detail is added over Lakes Erie and Ontario. Concentrations at most GLAD sites along the lower Lakes are 1.5 to 2 times higher than at NADP sites in this area. To the extent that the sampling locations were representative of their locales, and to the extent that there were no other sampling, analytical, or data handling biases, the GLAD data add information useful for computing lake loadings. However, there are large uncertainties in the sizes and shapes of the areas represented by urban samplers. Further research is needed to quantify the effect of these uncertainties on computed lake loadings.

Figure 9 compares patterns with and without GLAD data for Ca. Judging from the magnitudes of the additional urban peaks provided by the GLAD data, their utility is even more striking than in the SO_4 case. This is to be expected, since many of the GLAD sites were in or near urban areas having sources of Ca, such as unpaved roads and parking lots, construction, and demolition. Since aerosols carrying Ca are emitted at ground level and since they are emitted as large particles, they tend to be transported over shorter distances than SO_4, prior to being deposited in precipitation. Ca concentrations along the lower Lakes are 2 to 3 times higher than at NADP sites in this area.

Figure 10 compares patterns with and without GLAD data for NO_3. Again, the GLAD data add resolution. In this case the additional features in the concentration pattern from the combined networks are somewhat broader in spatial scale than we saw with Ca. This is consistent with the somewhat more distributed nature of automotive exhaust, the major NO_x source, as compared with the more localized Ca sources. Though NO_3 concentrations at most GLAD sites were higher than at nearest NADP sites, values were less than twice as high. This feature is also consistent with the suggestion that the gaseous NO_x is more widely dispersed before it is deposited by precipitation.

Figure 11 compares patterns for NH_4. Again, some increased detail is seen near the lakes, but not the extreme local concentrations of Ca.

In general, the differences between the combined NADP-GLAD and NADP-alone patterns were greater over Lakes Erie and Ontario than over the other Lakes. Ion concentrations at (urban) GLAD sites along these lower Lakes were unquestionably greater than those at NADP sites in the same geographic area. At GLAD sites along the other Lakes, Chicago stands out as a major deposition area. For NO_3, concentrations were anomalously high in the eastern Wisconsin area.

In summary, there was an apparent influence from local (urban) sources on GLAD data (if there were no important sampling biases). This urban effect results in ion concentrations that were higher than at the regionally more representative NADP sites. The spatial extent of this local influence has a large uncertainty. More research is needed to improve the quantification of this effect. This urban effect is most apparent at GLAD sites along Lakes Erie

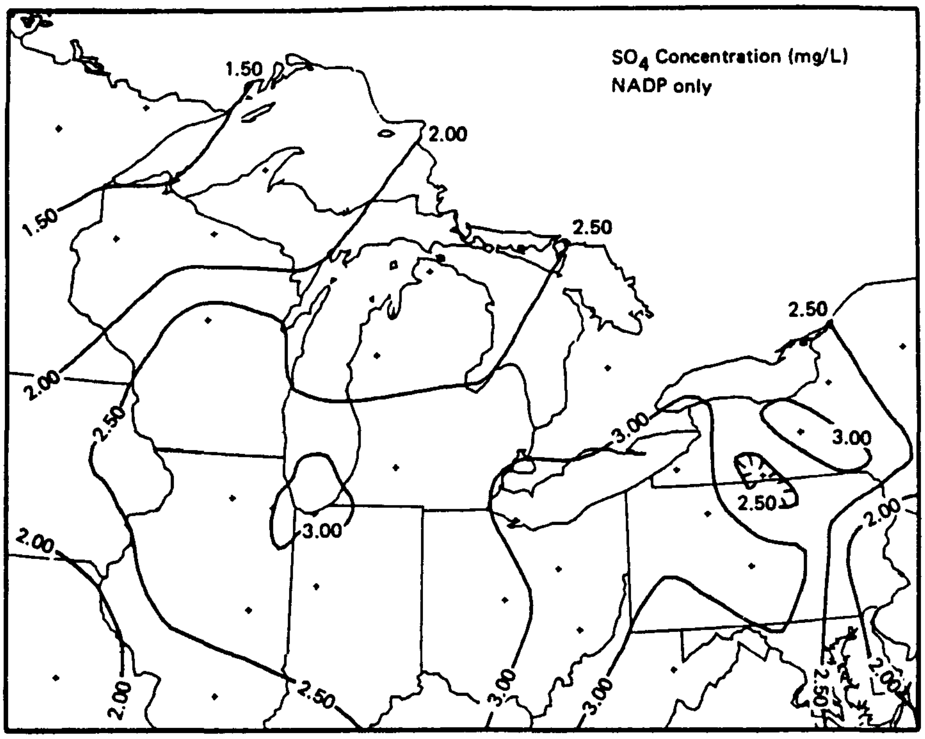

Figure 8(a). Spatial distribution of volume-weighted SO_4 concentrations in the Great Lakes region, using NADP data for 1982-83.

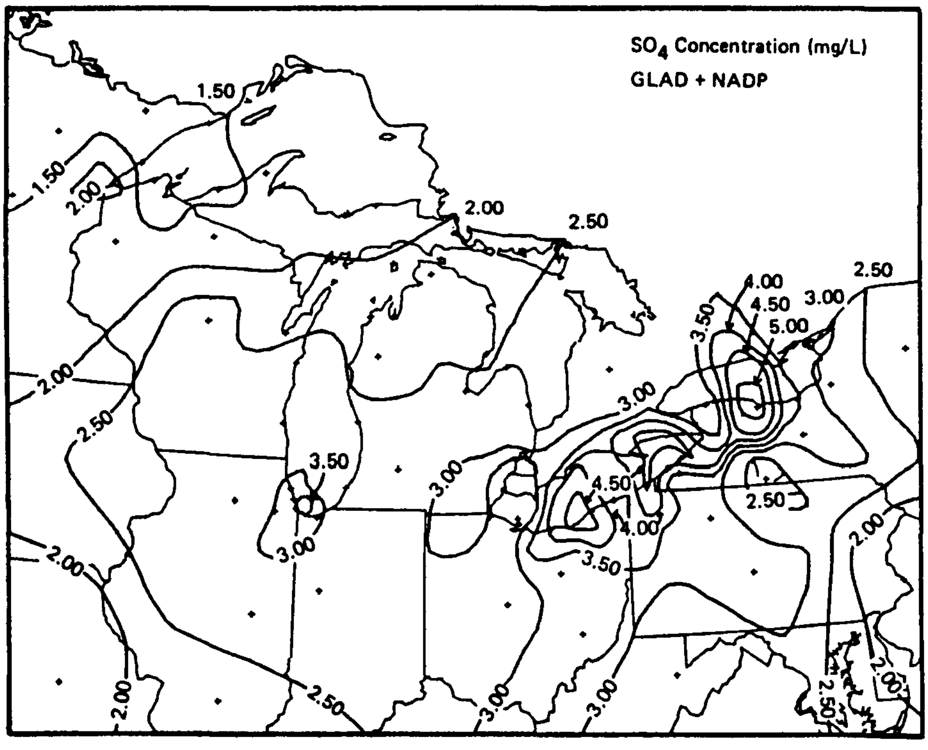

Figure 8(b). Same as (a), but using the combined GLAD/NADP data set.

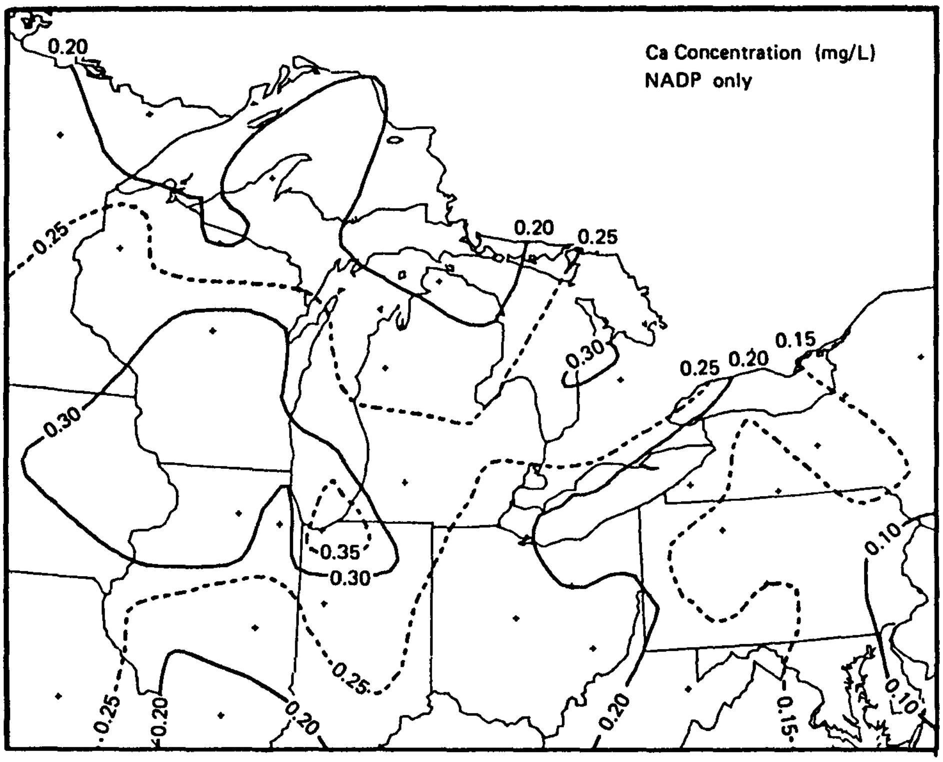

Figure 9(a). Spatial distribution of volume-weighted Ca concentrations in the Great Lakes region, using NADP data for 1982-83.

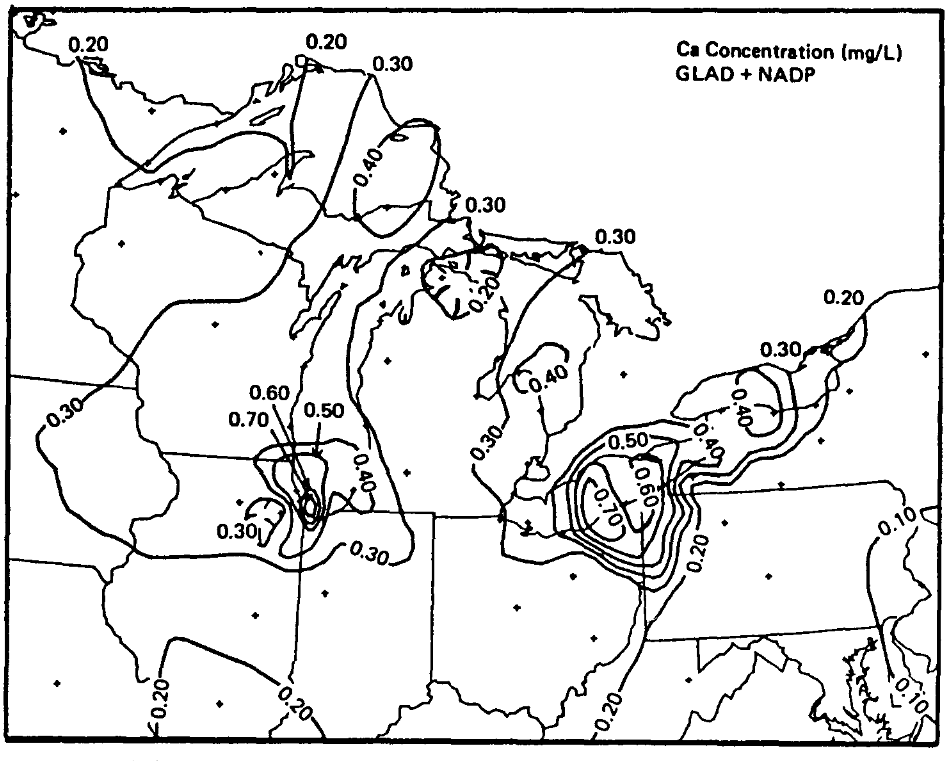

Figure 9(b). Same as (a), but using the combined GLAD/NADP data set.

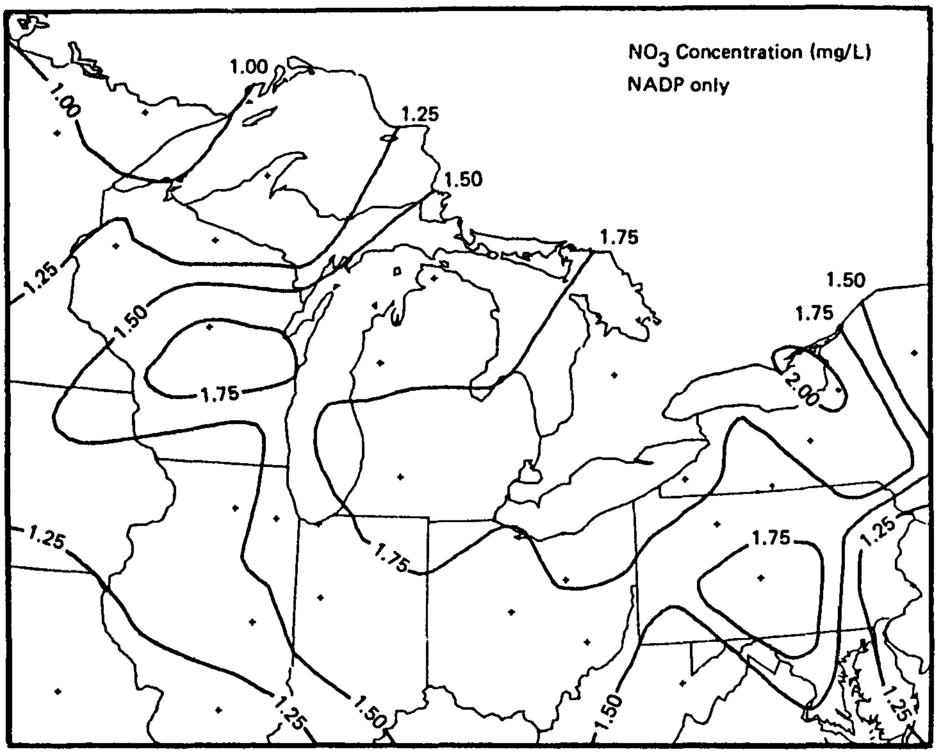

Figure 10(a). Spatial distribution of volume-weighted NO_3 concentrations in the Great Lakes region, using NADP data for 1982-83.

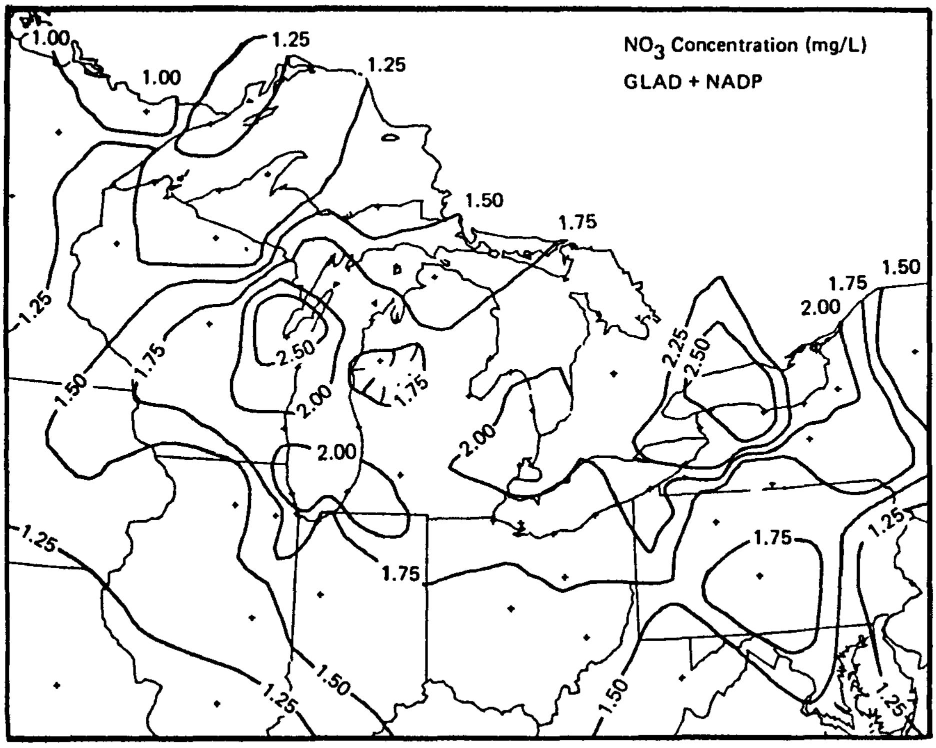

Figure 10(b). Same as (a), but using the combined GLAD/NADP data set.

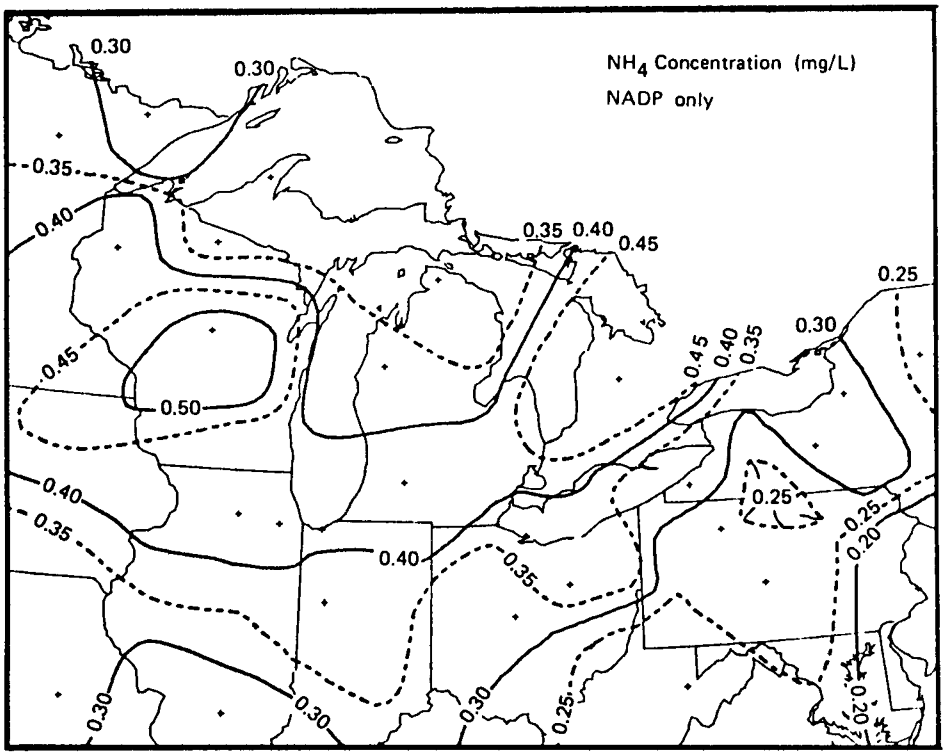

Figure 11(a). Spatial distribution of volume-weighted NH_4 concentrations in the Great Lakes region, using NADP data for 1982-83.

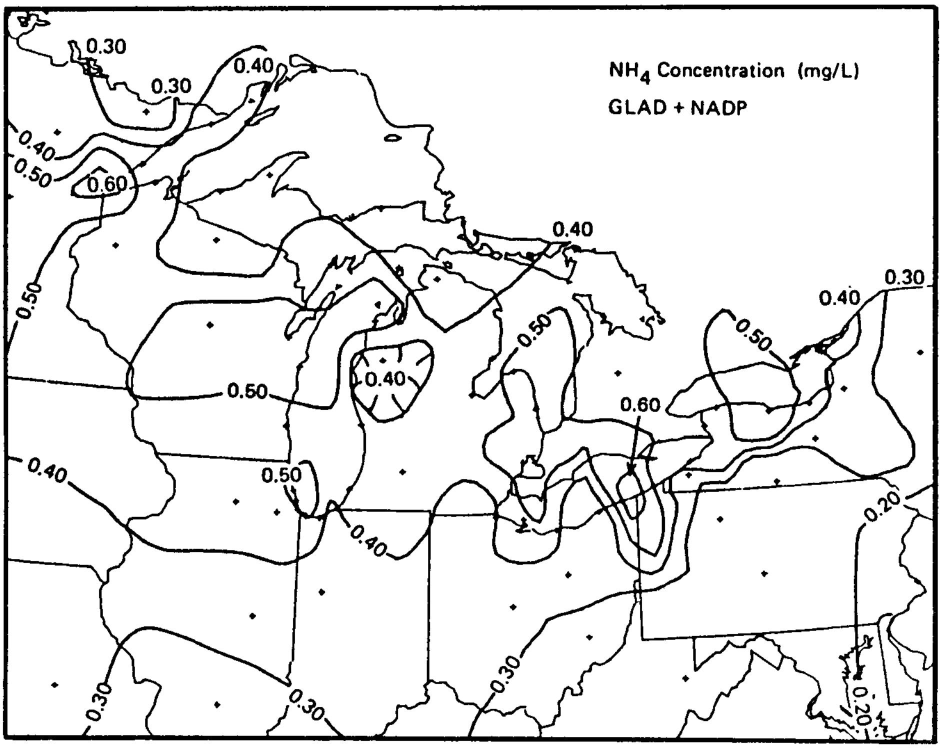

Figure 11(b). Same as (a), but using the combined GLAD/NADP data set.

and Ontario. Many of the sites along Lakes Superior, Huron, and northern Lake Michigan were rural and did not exhibit this urban effect.

3.2.2. Additional Ions, Combined Data Set

Beside SO_4, Ca, NO_3, and NH_4, for which we examined the effect of adding the GLAD sites to the regional NADP network, the spatial patterns of volume-weighted concentrations of four additional ions are shown, using the combined data set from both networks.

Figure 12 shows the spatial pattern of Na concentrations in the combined data set. Aside from the sea-salt influence seen in the SE corner of the map near the Atlantic coast, the major concentration peaks occur in urban or other lakeshore areas. A very similar pattern occurred for Cl (Figure 13). The same general patterns also occurred for Mg (Figure 14) and K (Figure 15).

3.2.3. Paired Site Comparisons: GLAD vs NADP

A map showing the 12 pairs of sites for which a comparison was requested by GLNPO is given in Figure 16. Comparisons were made for SO_4, Ca, NO_3, and NH_4 in the form of box diagrams of concentration percentile distributions. These comparisons were made partly as an indirect check on the accuracy of ion concentration measurements, and partly for the purpose of suggesting where GLAD measurements might be providing little additional information in addition to that already available from the NADP network.

Table 8 lists the pairs of sites at which ion concentrations were compared and provides a key to the numbers by which the sites are labeled on the abscissas of Figures 17-20.

At each site in Figures 17-20, concentration percentiles are represented by a box diagram (Cleveland, 1985) in which the diamond symbol in the middle of the "box" represents the 50th percentile, and the top (a triangle) and bottom (a plus sign) of the box are at the 75th and 25th percentiles, respectively. The upper (an x) and lower (a square) extremes, connected by single lines, represent the 90th and 10th percentiles, respectively. The site pairs are ordered from left to right in the figure approximately in order from NW to SE across the Great Lakes basin. Asterisks on site pairs indicate that the distributions of ion concentrations were significantly different at the 1% level. Parentheses on site pairs denote differences significant at the 5% level.

Figure 17 shows paired site comparisons for SO_4. Note that generally lower concentrations prevail in the NW portion of the basin (left side of the figure), and higher concentrations occur in the SE (right side of the figure).

Detailed comparisons of individual site pairs require consideration of possible local sources, differences in siting criteria (e.g., GLAD allows rooftop sampling; NADP does not), distance between sites, and other issues. However, we can gain a general impression of how the two networks compare in

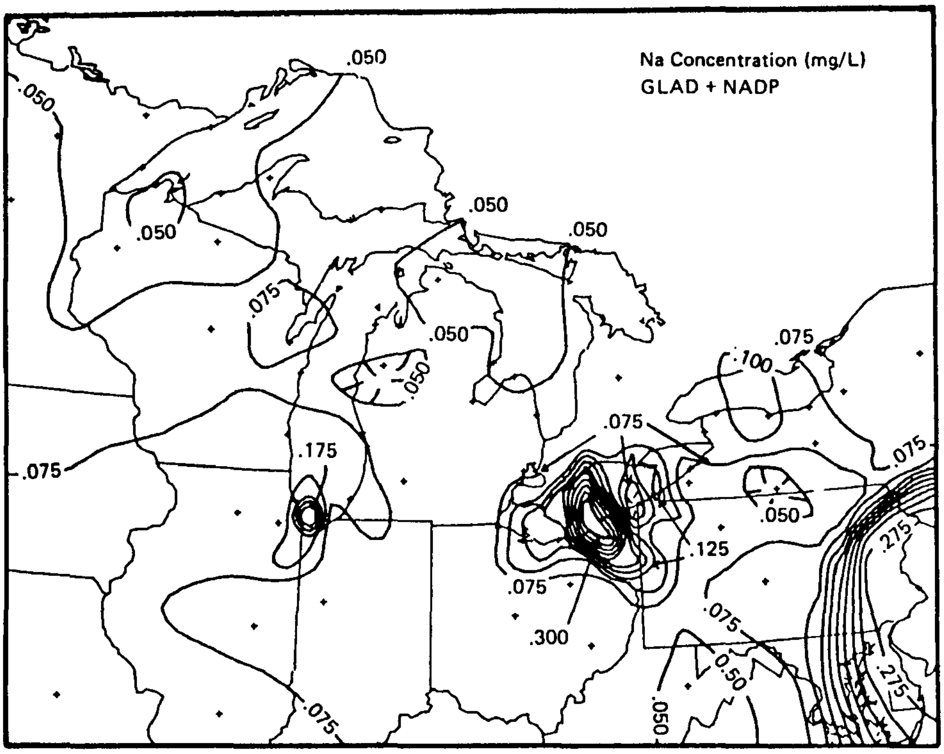

Figure 12. Spatial distribution of volume-weighted Na concentrations in the Great Lakes region, GLAD/NADP data, 1982-83.

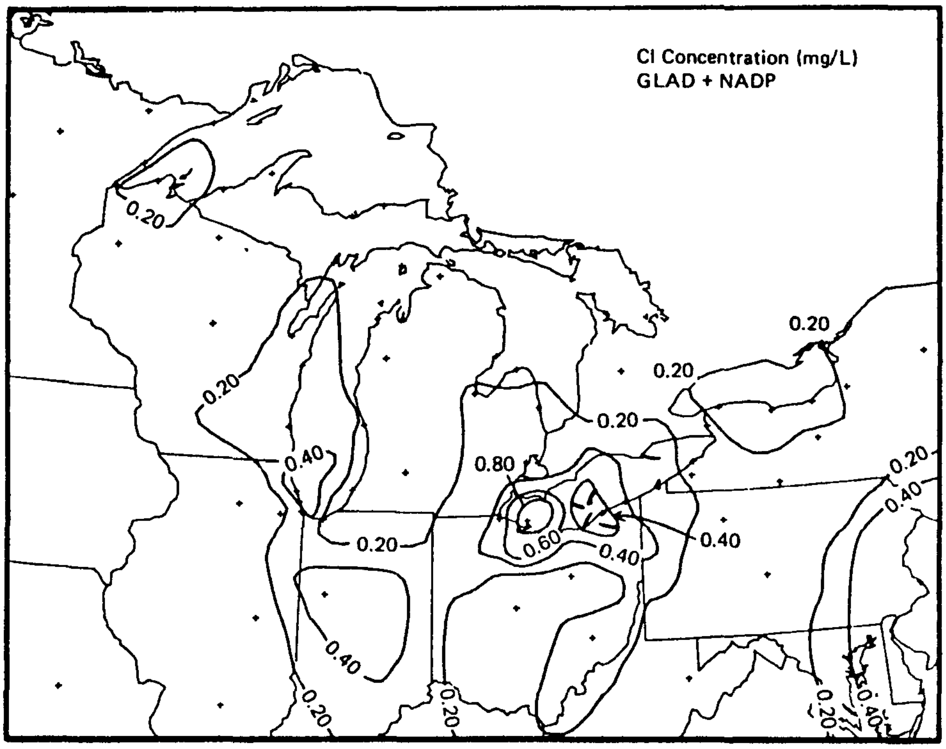

Figure 13. Spatial distribution of volume-weighted Cl concentrations in the Great Lakes region, GLAD/NADP data, 1982-83.

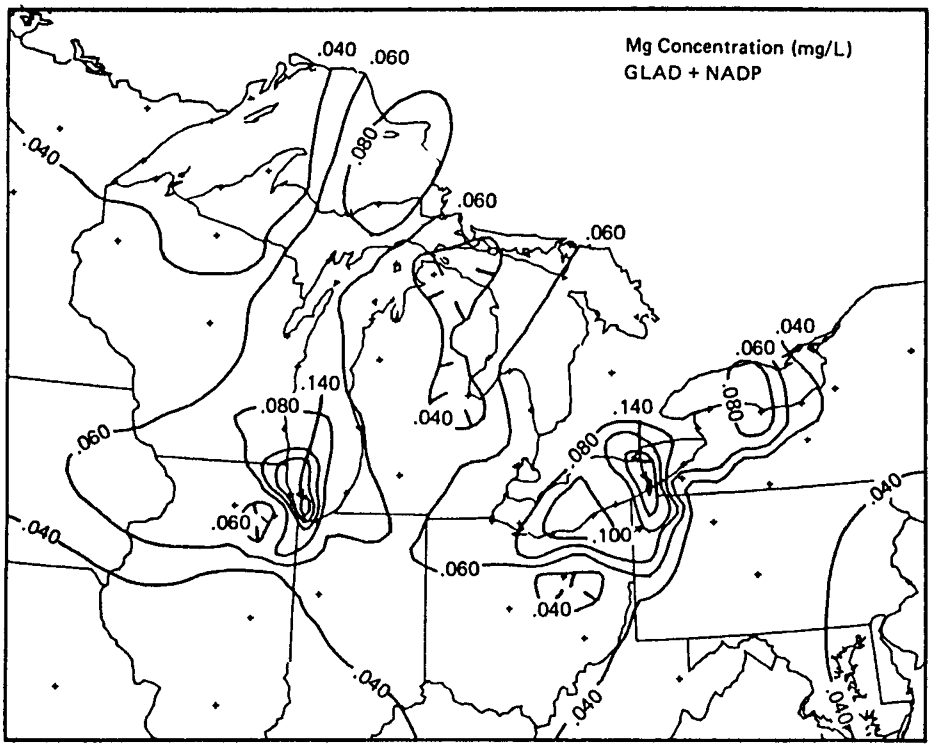

Figure 14. Spatial distribution of volume-weighted Mg concentrations in the Great Lakes region, GLAD/NADP data, 1982-83.

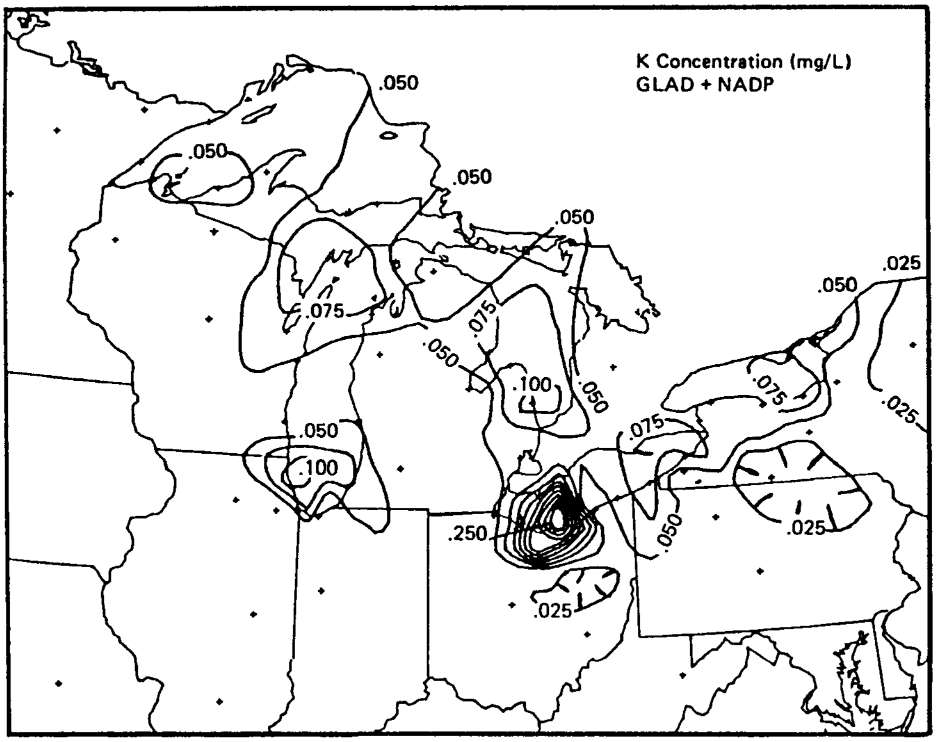

Figure 15. Spatial distribution of volume-weighted K concentrations in the Great Lakes region, GLAD/NADP data, 1982-83.

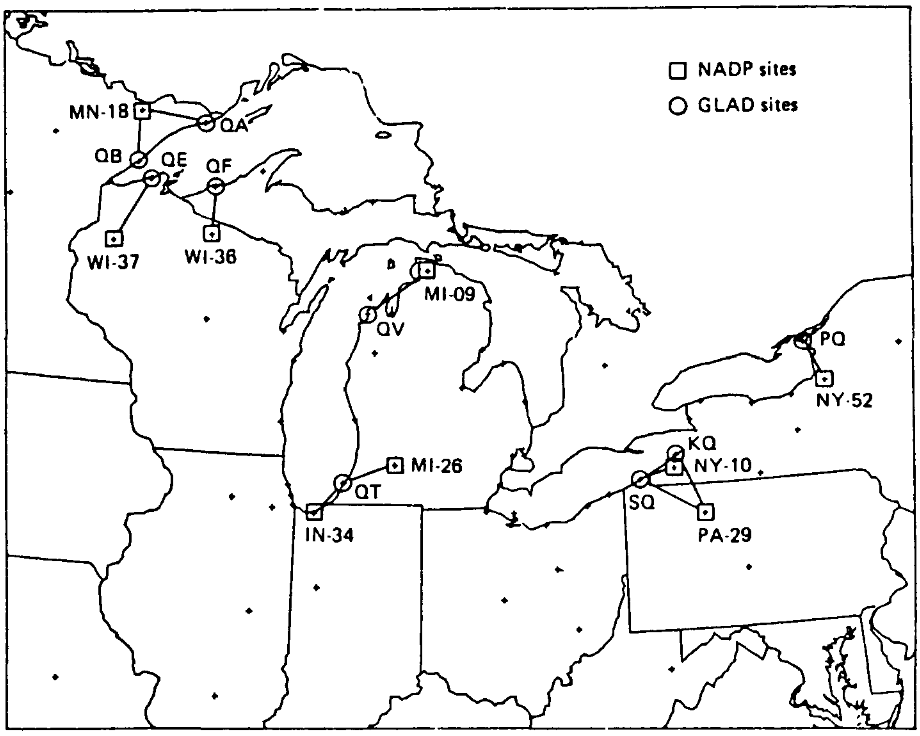

Figure 16. Map showing locations of GLAD--NADP site pairs for which ion concentrations were compared.

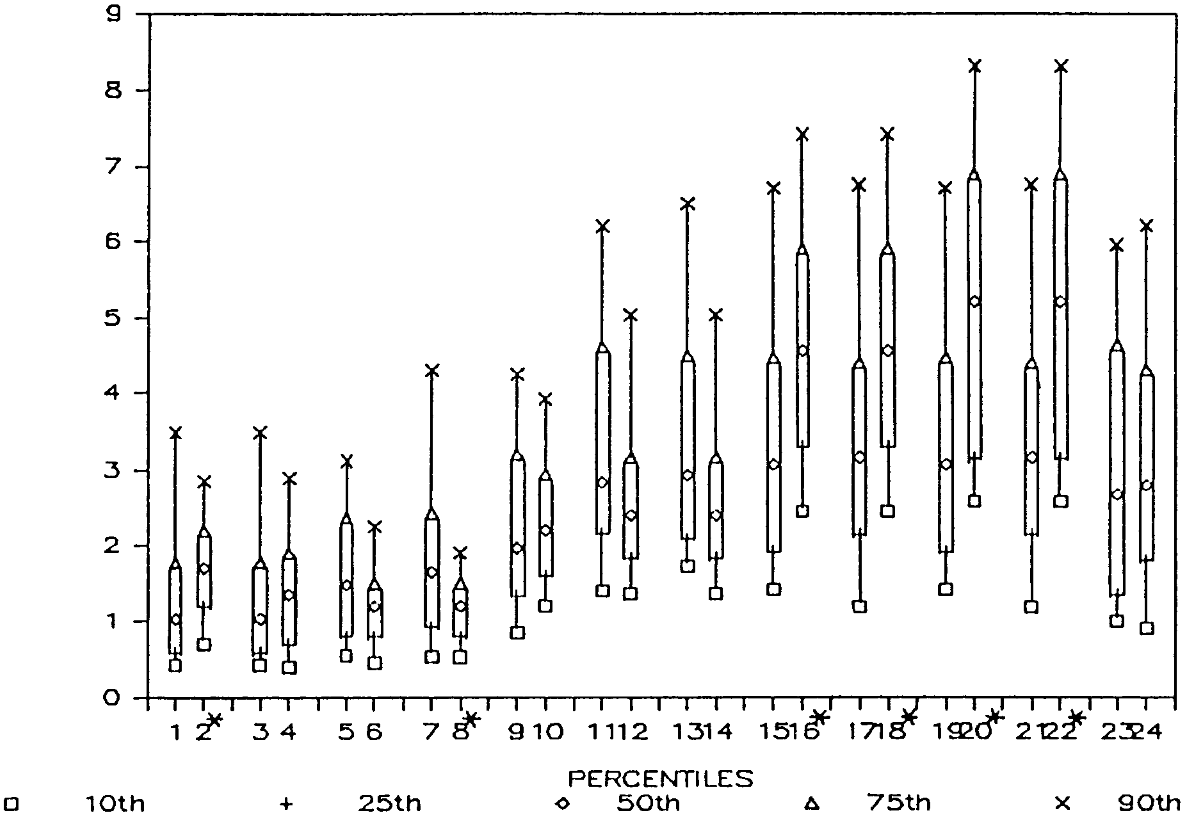

Figure 17. Paired site comparisons of SO_4 concentration percentiles, using box diagrams. Asterisks signify that distributions were different at the 1% level, based on the Wilcoxon rank sum test.

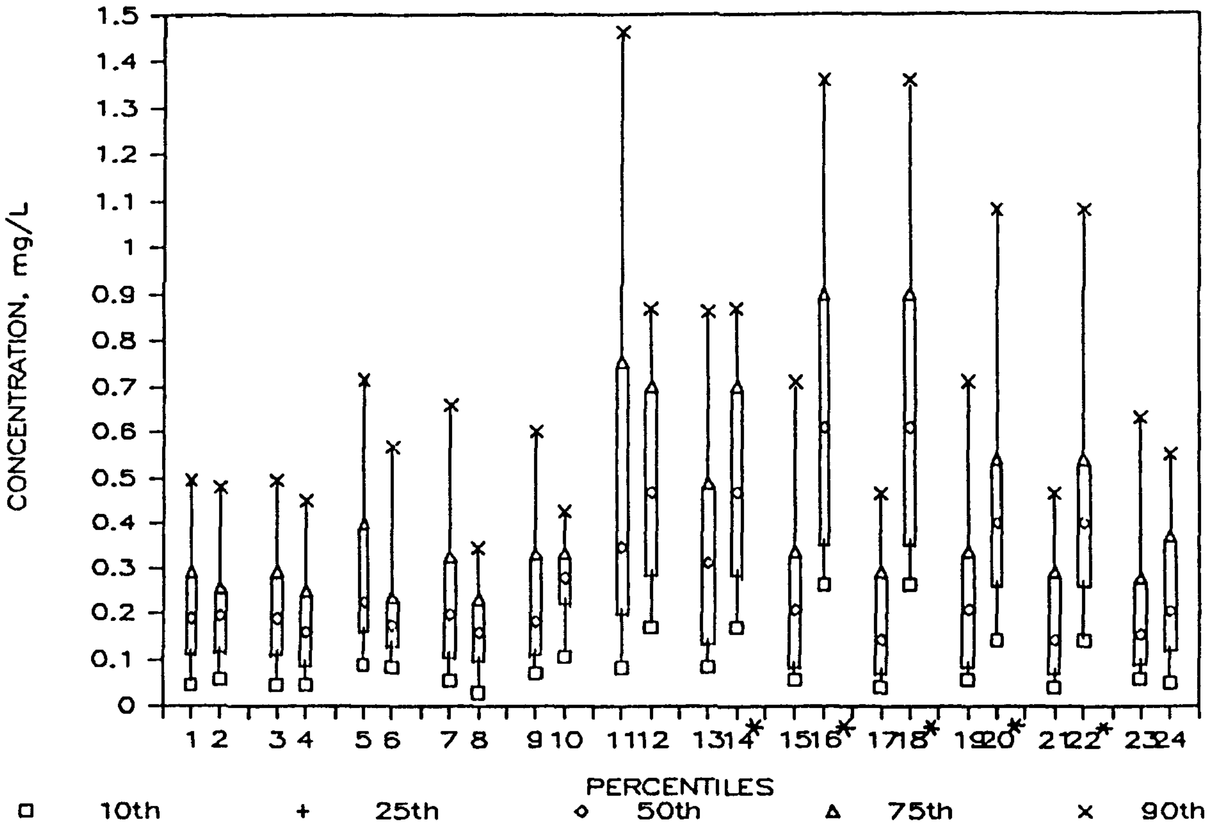

Figure 18. Paired site comparisons of Ca concentration percentiles, using box diagrams. Asterisks signify that distributions were different at the 1% level, using the Wilcoxon rank sum test.

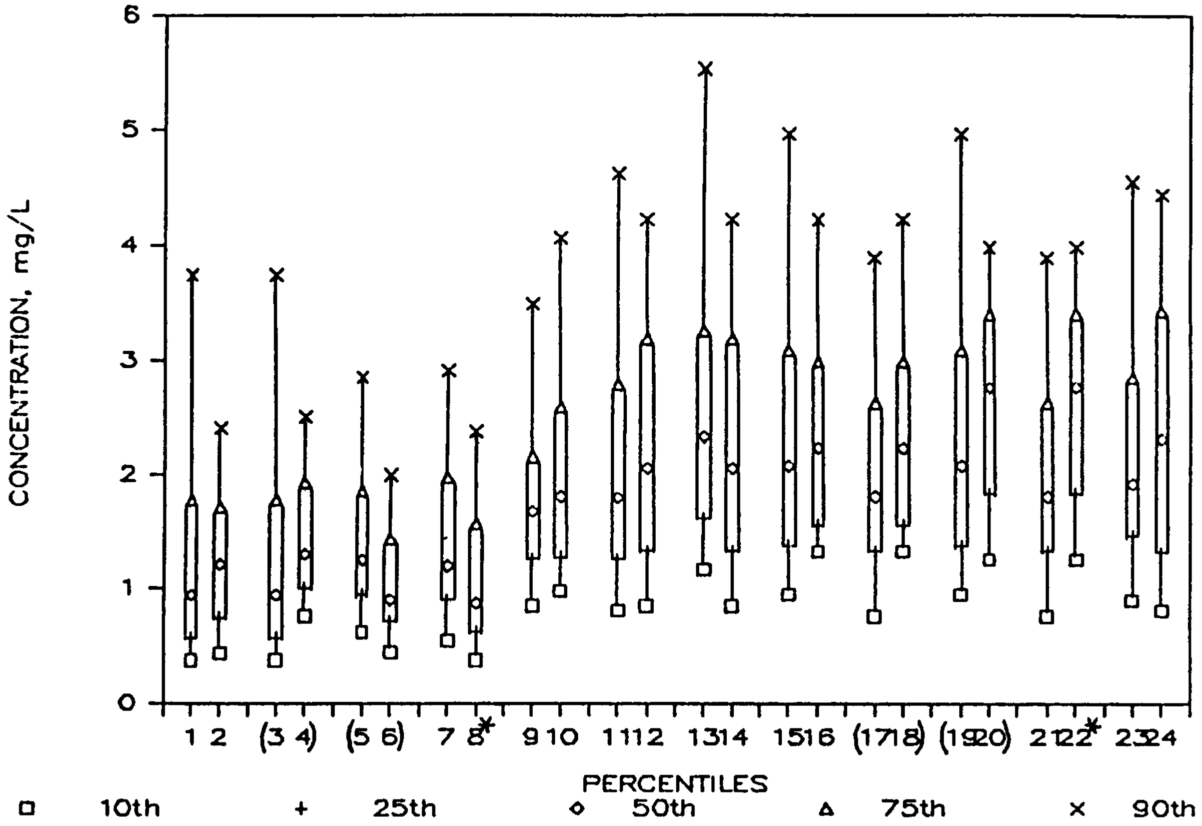

Figure 19. Paired site comparisons of NO_3 concentration percentiles, using box diagrams. Asterisks signify that distributions were different at the 1% level, using the Wilcoxon rank sum test. Parentheses indicate differences significant at the 5% level.

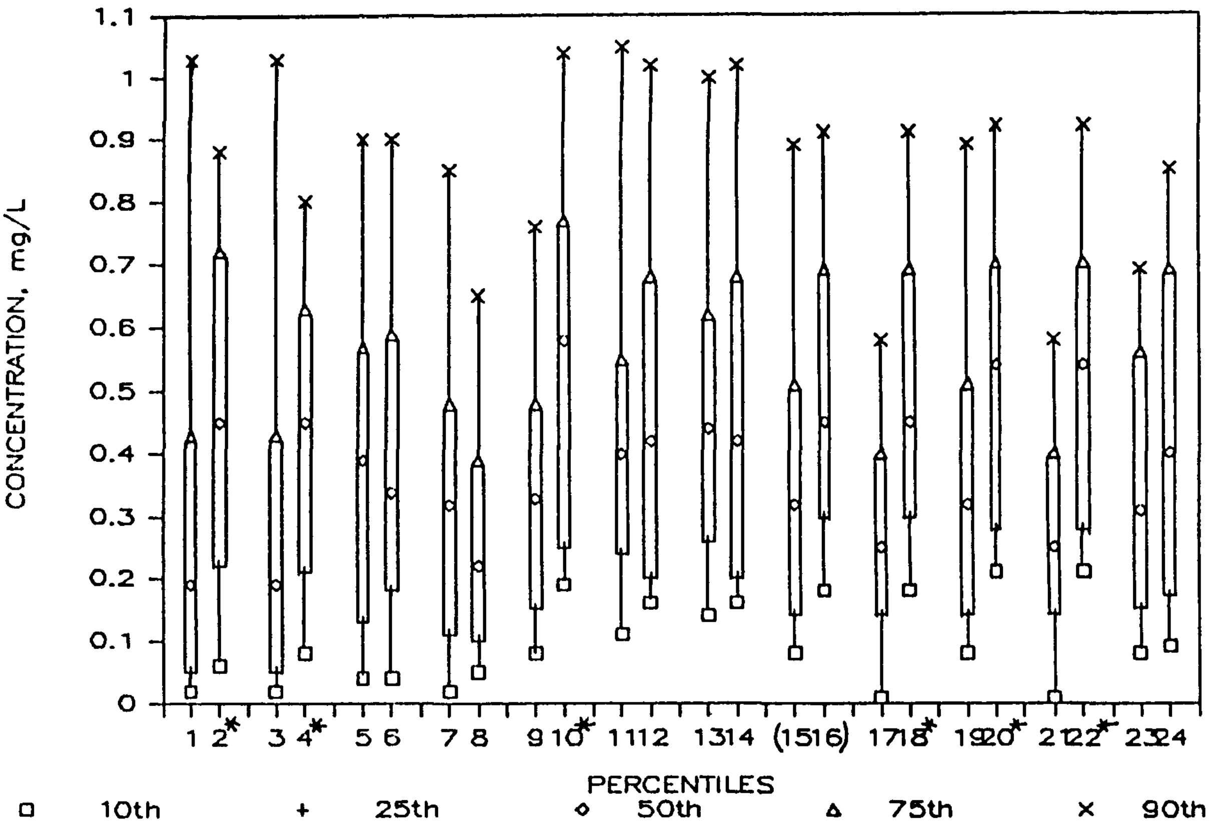

Figure 20. Paired site comparisons of NH_4 concentration percentiles, using box diagrams. Asterisks signify that distributions were different at the 1% level, using the Wilcoxon rank sum test. Parentheses indicate differences significant at the 5% level.

Table 8. Key to GLAD/NADP Paired Site Comparisons in Figures 17-20.

					Are concentration distributions different at the 1% level?			
No. on graph	Site code[a]	Site type[b]	Separation distance (km)	Site name	SO_4	Ca	NO_3	NH_4
1	MN-18	remote		Fernberg				
2	QA	rural	115	Hovland	Y	N	N	Y
3	MN-18	remote		Fernberg				
4	QB	rural	90	Gooseberry Falls	N	N	(N)[c]	Y
5	WI-37	rural		Spooner				
6	QE	rural	134	Cornucopia	N	N	(N)	N
7	WI-36	rural		Trout Lake				
8	QF	remote	85	Ontonagan	Y	N	Y	N
9	MI-09	rural		Douglas Lake				
10	QV	rural	133	Empire	N	N	N	Y
11	IN-34	suburban		Indiana Dunes				
12	QT	urban	74	Benton Harbor	N	N	N	N
13	MI-26	suburban		Kellogg Biol Sta				
14	QT	urban	89	Benton Harbor	N	Y	N	N
15	NY-10	rural		Chautauqua				
16	SQ	urb100	61	Erie	Y	Y	N	(N)
17	PA-29	rural		Kane Exp Forest				
18	SQ	urb100	138	Erie	Y	Y	(N)	Y
19	NY-10	rural		Chautauqua				
20	KQ	suburban	22	Dunkirk	Y	Y	(N)	Y
21	PA-29	rural		Kane Exp Forest				
22	KQ	suburban	115	Dunkirk	Y	Y	Y	Y
23	NY-52	rural		Bennett Bridge				
24	PQ	rural	74	Cape Vincent	N	N	N	N
				Y's:	6	5	2	6
				N's:	6	7	10	6
				Y's with GLAD higher:	5	5	1	6

[a] In each pair, the NADP site is odd-numbered and the GLAD site is even.

[b] Definitions of site types are: remote — no towns within 15 km; rural — no towns of population 10,000 within 15 km; suburb (suburban) — towns of population 10,000 to 100,000 within 15 km; urban — site in a town of population 10,000 to 100,000; urb100 — site in a city of population over 100,000.

[c] Parentheses signify that differences were not significant at the 1% level, but were significant at the 5% level.

terms of the concentrations of dissolved constituents. We do this by noting the number of pairs, compared to the total, for which the GLAD sites had the higher 50th percentile values.

A more quantitative comparison of the ion concentration measurements at paired GLAD and NADP sites was made using the nonparametric Wilcoxon rank sum method to test for differences in the overall concentration distributions between sites. Table 8 shows the results of testing for the significance (1% and 5% levels) of differences between concentration distributions for SO_4, Ca, NO_3, and NH_4 at each pair of sites.

For SO_4, the GLAD site had the higher 50th percentile value in eight of the twelve pairs. The difference in distributions was significant at the 1% level for five of these pairs, of which four involved either the Erie (SQ) or Dunkirk (KQ) GLAD sites. Both the SQ and KQ sites had a much different physical setting than the NADP sites with which they were compared. SQ was in Erie, Pennsylvania, a city of over 200,000 people, and KQ was near Dunkirk, New York, a town of over 10,000 people. NADP sites NY-10 and PA-29 both have a rural setting. Thus, SO_4 differences at these pairs are not surprising, given the likely presence of SO_x sources near the GLAD sites.

For one pair of sites, the NADP site had a 50th percentile value greater than that of its GLAD counterpart, significant at the 1% level. For this pair the situation was reversed; the GLAD site, QF, was a "remote" site with no towns within 15 km, whereas the NADP site, WI-36, at Trout Lake, is in a rural area with pulp and paper industry about 50 km SSE and occasional forest cutting in the area. Differences in sulfate concentrations are consistent with the regional decrease in concentrations from S to N across northern Wisconsin. Local sources from the few small towns in the vicinity are unlikely to be the cause of the difference. There were no additional pairs where differences, in either direction, were significant at the 5% level.

These results show some tendency for the GLAD sites to have higher SO_4 concentrations, but of course do not distinguish between true spatial differences and possible analytical bias. Analytical bias can only be determined from duplicate sampling and/or laboratory comparisons, and such activities were not carried out for the GLAD network.

Figure 18 shows paired site comparisons for Ca. For the GLAD sites, there appear to be higher concentrations at all percentiles in the SE portion of the region, compared to the NW, but this does not appear to hold for the NADP sites. As a result, the differences between the GLAD and NADP sites are larger in magnitude in the SE than elsewhere. For Ca, the 50th percentile values were higher at the GLAD site in nine of the twelve pairs, and higher at the NADP site in three pairs. Where the GLAD site had the higher 50th percentile concentration, the differences in distribution were significant (1%) in five pairs, four of which again involved the urban or suburban sites at Erie and Dunkirk, respectively. The fifth pair involved the "urban" GLAD site QT, at Benton Harbor, Michigan, and the "suburban" NADP site at Kellogg Biological Station, MI-26. Results from all five of these pairs are consistent with the stronger influence of local traffic, construction, and other activities on Ca concentrations at the more urban GLAD sites than at the regional NADP sites.

There were no additional pairs where the GLAD distribution was significantly greater at the 5% level, and no pairs where the NADP distribution was significantly greater at either the 1% or 5% level.

Figure 19 shows paired site comparisons for NO_3. As in the case of SO_4, there is a trend from lower concentrations at all percentiles in the NW to higher concentrations in the SE, and this occurred for both networks. For NO_3, the 50th percentile values were higher at the GLAD site in nine of the twelve pairs. In only one (Dunkirk) of these nine cases was the difference in distributions significant at the 1% level, but in three other cases (two involving Erie or Dunkirk) the differences were significant at the 5% level. An urban influence, similar in direction, but smaller in magnitude than for Ca and SO_4, is the explanation for these differences. Apparently the NO_x sources are not as localized as those of large-particle Ca and point-source SO_x. There was also one case where the NADP distribution exceeded GLAD at the 1% level, and another where the difference (in the same direction) was significant at the 5% level.

Figure 20 gives the paired site data for NH_4. The evidence for overall spatial trends is weak or lacking. The variability in the measurements, as indicated by the ratio between the 90th and 10th percentile values, is the highest of the four ions examined, and occurs over the whole region in both networks. Also in this case, 50th percentile values are typically higher at the GLAD sites, occurring that way in nine of the twelve pairs. Of these nine pairs, six (three of these involving Erie or Dunkirk) were significant at the 1% level, and one more (Erie) at the 5% level. The NADP distributions were never significantly greater than those of their GLAD counterparts at either 1% or 5%.

To summarize the site comparisons for SO_4, Ca, NO_3, and NH_4, we note that the GLAD sites often had concentrations significantly higher than the paired NADP sites. The GLAD concentration distributions exceeded those of their NADP counterparts at the 1% level much more than expected by chance for SO_4, Ca, and NH_4, and somewhat more than expected by chance for NO_3. However, most of these significant differences involved either the Erie or Dunkirk sites. These differences could reflect true spatial gradients, or could alternatively be related to differences in siting criteria (many GLAD sites are on roofs in urban areas, while NADP sites are on the ground in regionally representative locations) or local sources. It will take a careful intercomparison study with co-located samplers to quantify the importance of these factors.

3.3. Precipitation Amount

Precipitation amount is the other factor, besides concentration, that goes into the calculation of deposition, and the year-to-year variability of its mean value is generally much greater than that of ion concentrations in precipitation. To show ion fluxes to the lakes that represent long-term means, we calculated deposition as the product of 2-yr volume-weighted mean concentrations and 30-yr mean precipitation.

Figure 21 shows the distribution of the 30-yr mean annual precipitation over the lakes. Precipitation amounts generally range from about 90 cm in the southern portions of the region to about 75 cm in the northern portions. As was the case for concentrations, there were no routine over-water measurements of precipitation from which to calculate ion deposition fluxes. Instead, overland measurements from around the Lakes were used. These data were analyzed using the same procedure applied to the ion concentrations. Isopleths were drawn from the resulting grid point data set. Studies by Changnon (1972), Wilson (1977), and Bolsenga (1979) have shown that precipitation data from onshore gauges near the shore is a good estimate of what fell over the Lakes, because the excess precipitation that falls over the Lakes in the winter is about counter-balanced by the deficit over the Lakes in the summer. On an annual basis, the lake-land differences are less than measurement errors.

Table 9 summarizes the annual precipitation fluxes to the individual lakes, showing 30-yr means for the 1951-80 period, and comparative 30-yr means and standard deviations, as well as maximum and minimum annual values from an independent estimate based on the 1954-83 period. Except for Lake Huron, where there is about a 10% difference, the agreement between estimates based on slightly different but largely overlapping 30-yr periods is very close, providing further evidence that the areal integration method is a reasonable one. We have examined the data for an explanation of the 10% difference for Lake Huron. The difference was not caused by unusual values during the non-overlapping years of the two data sets. It appears to be related to differences in the measurement networks (only the 1954-83 data set includes Canadian data), and the respective methods used for areal integration.

3.4. Deposition

3.4.1. Spatial Patterns

Spatial patterns of annual wet-only deposition fluxes are given in Figures 22-31 for ten ions measured in precipitation. Except for the Cd and Pb results (Figures 30 and 31), the computed deposition patterns are based on a combined data set from the NADP and GLAD networks, using data for 1982 and 1983. The NADP does not analyze for metals, so the Cd and Pb results were computed from GLAD data for 1983. This was the only year of the two examined that had adequate metals data. As explained in detail in Section 2.6, the depositions were computed from 2-yr (or 1-yr, as available) volume-weighted mean concentrations and 30-yr mean precipitation values.

Figure 22 shows the spatial pattern of SO_4 wet deposition over the Great Lakes. Annual fluxes ranged from about 10 kg/ha in the NW portion of the basin to about 45 kg/ha in the SE. Maximum values occurred at GLAD sites in urban and/or industrial areas such as the south end of Lake Michigan and the south shore of Lake Erie. A similar overall pattern was observed for the wet deposition of Ca (Figure 23). Minimum annual fluxes of about 2 kg/ha occurred in western sections of Lake Superior and northern sections of Lakes Michigan and Huron. Maximum values of 6 kg/ha or more occurred near Chicago in southern Lake Michigan and over the southern shore of Lake Erie. The spatial patterns of deposition fluxes of SO_4 and Ca resemble their concentration patterns.

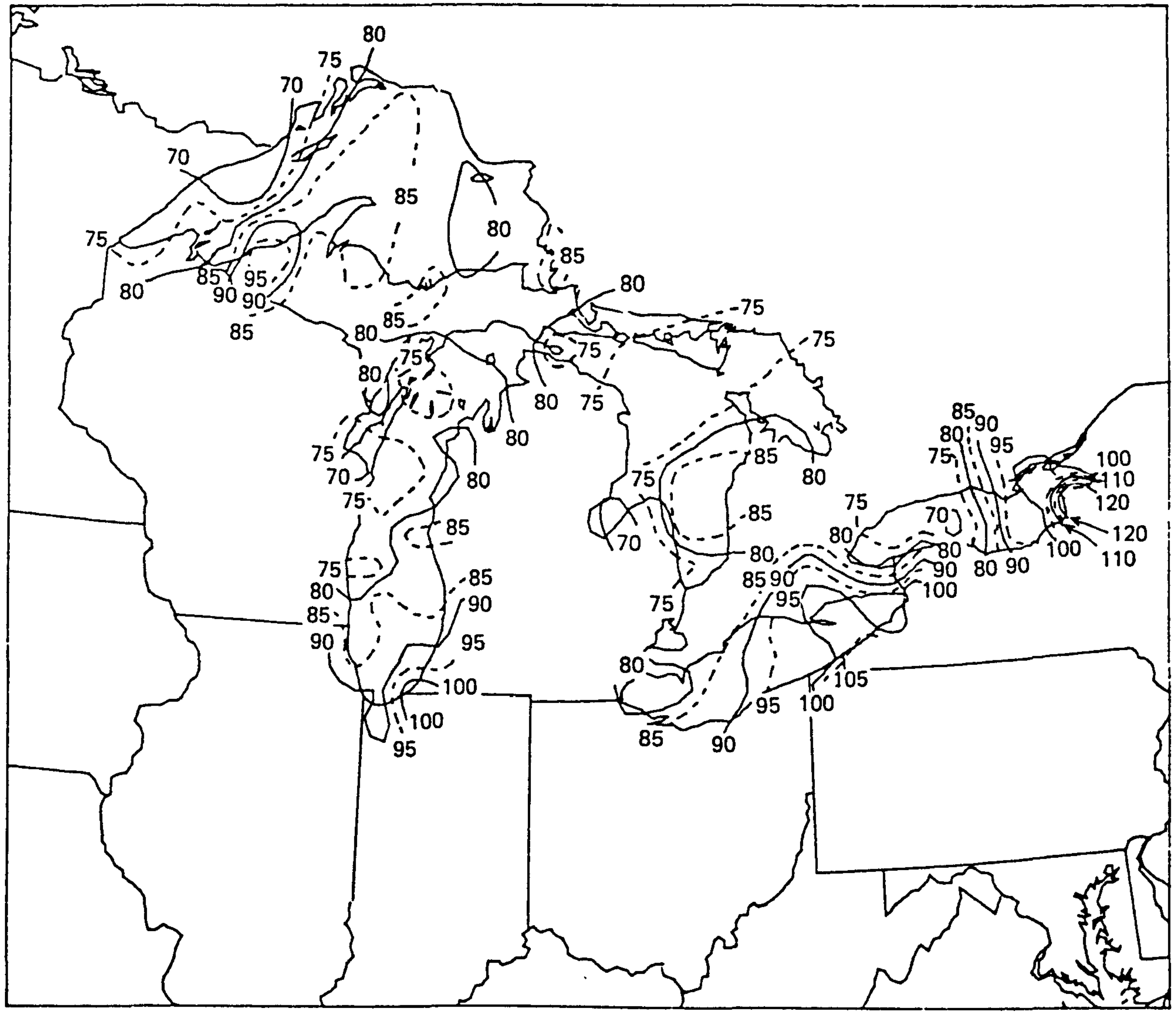

Figure 21. Distribution of 30-yr mean annual precipitation (centimeters) over the Great Lakes. Data source: National Climatic Center, Asheville, NC.

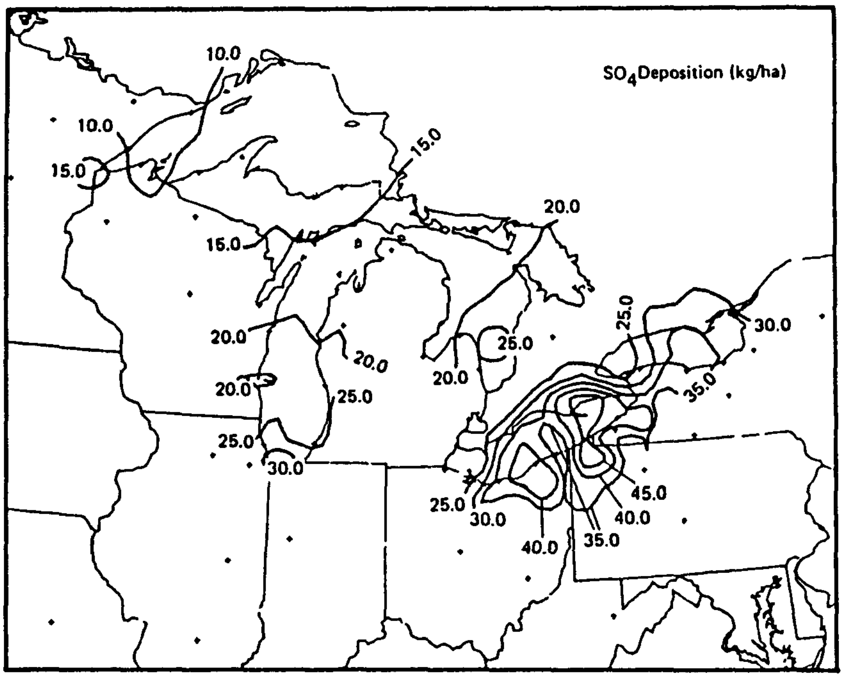

Figure 22. Spatial distribution of annual deposition fluxes of SO4 over the Great Lakes, using GLAD-NADP data, 1982-83.

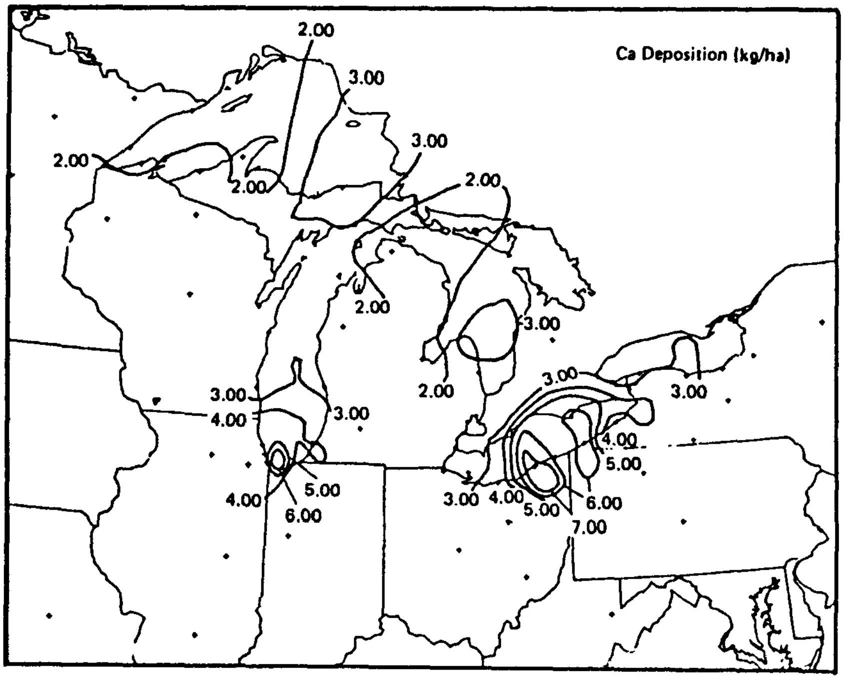

Figure 23. Spatial distribution of annual deposition fluxes of Ca over the Great Lakes, using GLAD-NADP data, 1982-83.

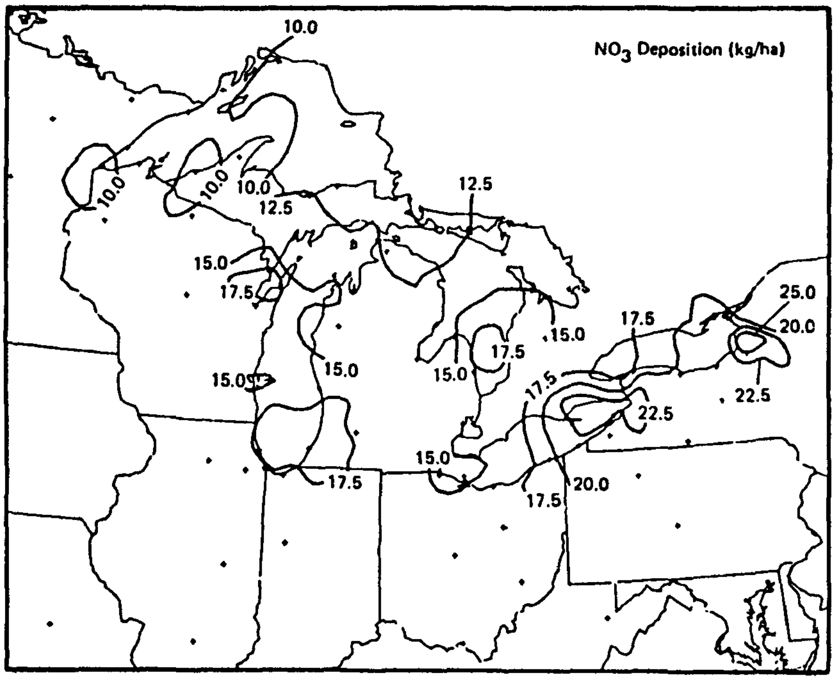

Figure 24. Spatial distribution of annual deposition fluxes of NO_3 over the Great Lakes, using GLAD-NADP data, 1982-83.

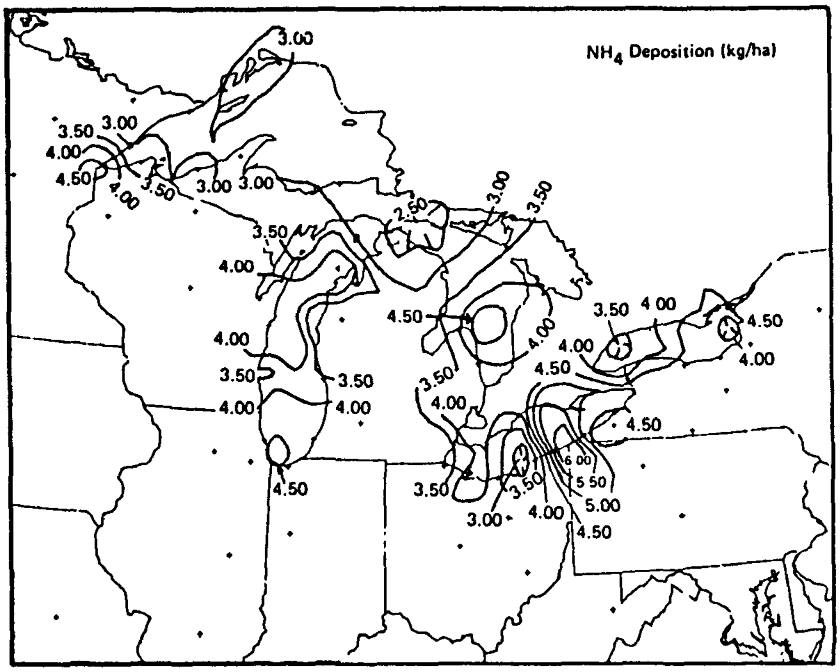

Figure 25. Spatial distribution of annual deposition fluxes of NH_4 over the Great Lakes, using GLAD-NADP data, 1982-83.

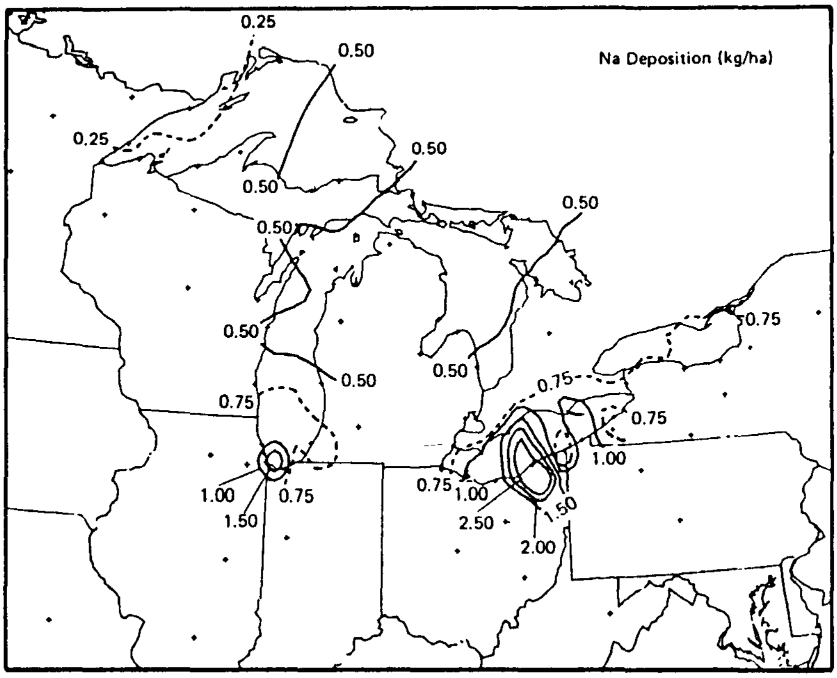

Figure 26. Spatial distribution of annual deposition fluxes of Na over the Great Lakes, using GLAD-NADP data, 1982-83.

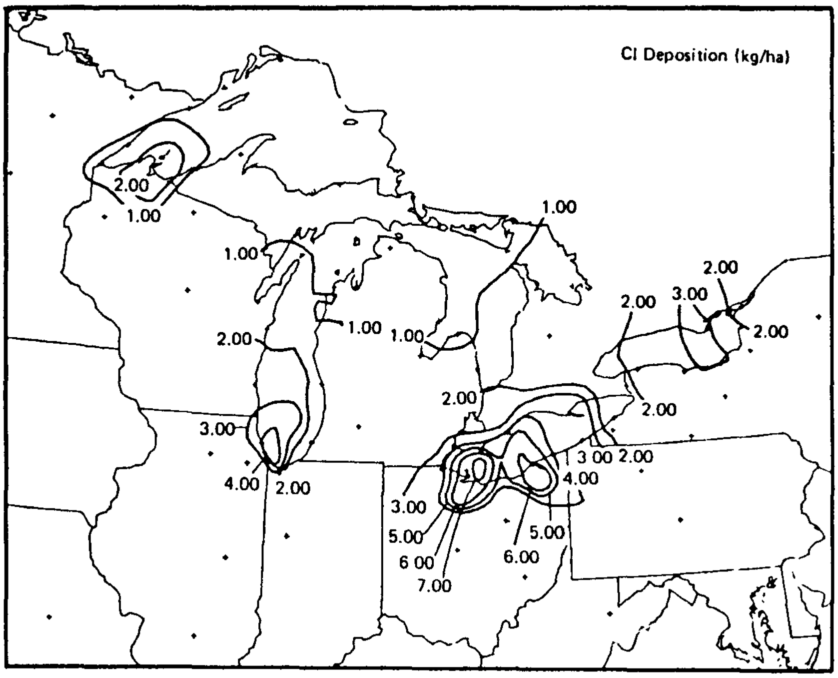

Figure 27. Spatial distribution of annual deposition fluxes of Cl over the Great Lakes, using GLAD-NADP data, 1982-83.

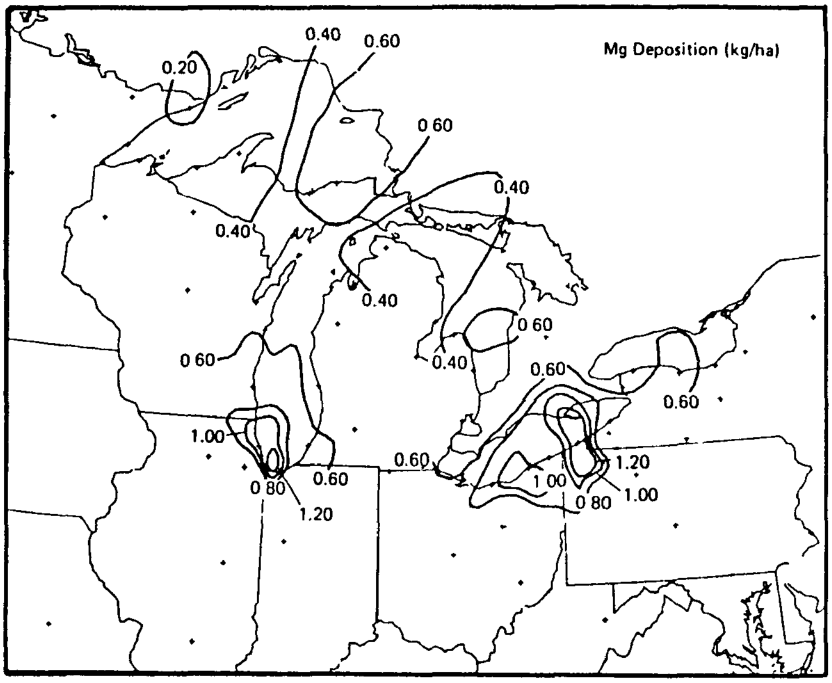

Figure 28. Spatial distribution of annual deposition fluxes of Mg over the Great Lakes, using GLAD-NADP data, 1982-83.

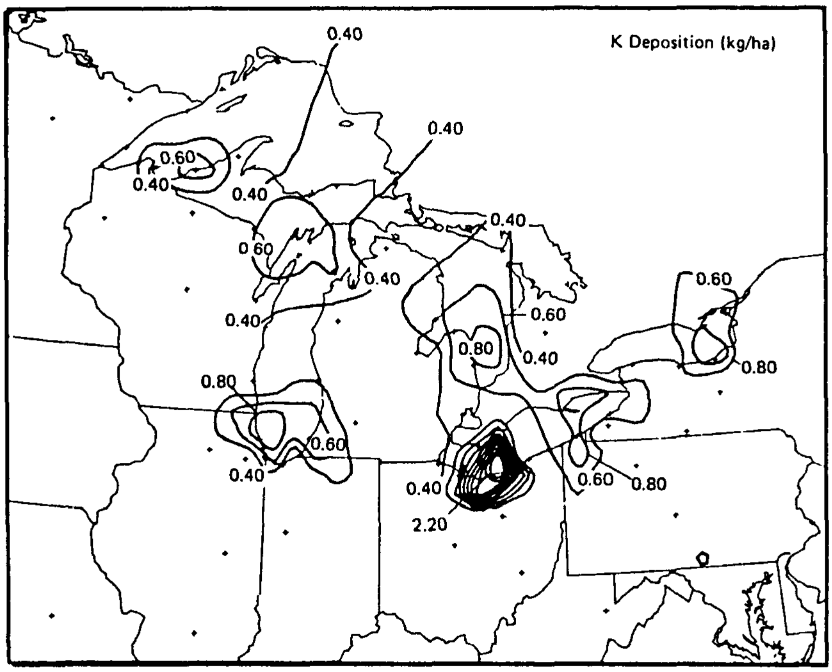

Figure 29. Spatial distribution of annual deposition fluxes of K over the Great Lakes, using GLAD-NADP data, 1982-83.

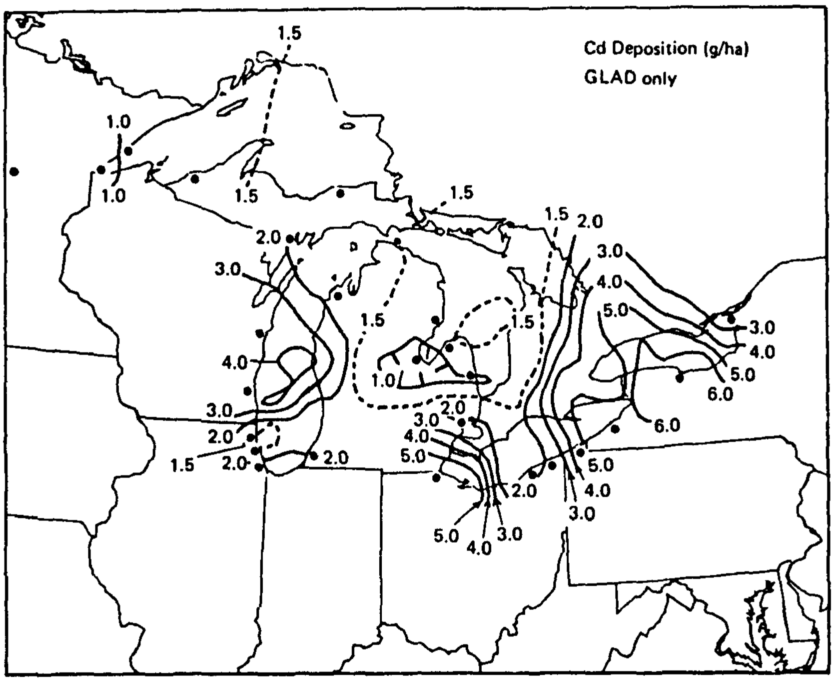

Figure 30. Spatial distribution of annual deposition fluxes of Cd over the Great Lakes, using GLAD data, 1983.

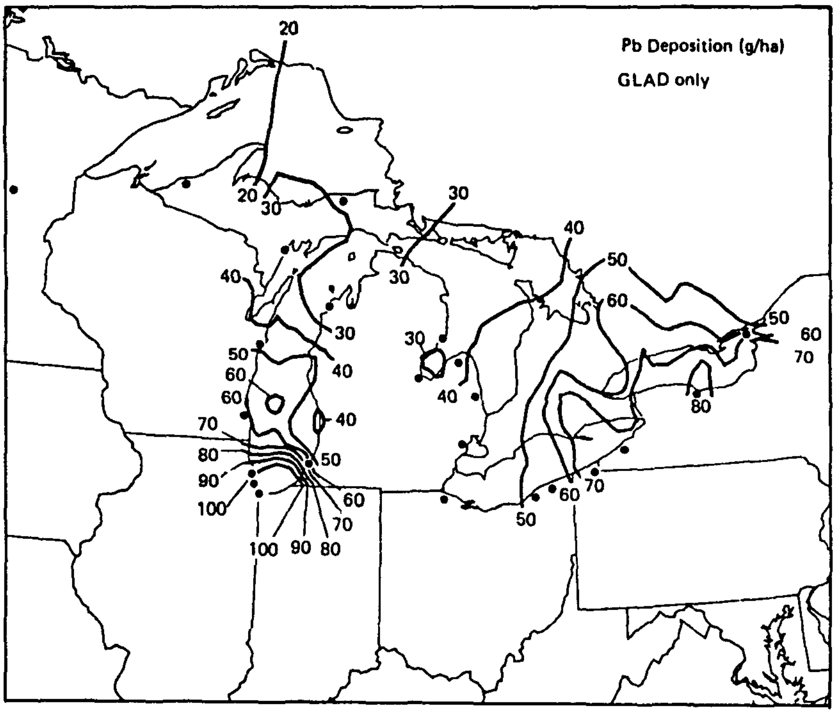

Figure 31. Spatial distribution of annual deposition fluxes of Pb over the Great Lakes, using GLAD data, 1983.

Table 9. Summary of Precipitation Fluxes to the Great Lakes, 1951-1980.

	1951-80[a] mean (cu km)	1954-83[b] mean (± S.D.) (cu km)	1954-83 minimum (cu km)	1954-83 maximum (cu km)
Superior	65.6	64.3 ± 8.0	52.3	80.5
Michigan	46.0	46.3 ± 5.4	36.4	55.7
Huron	44.7	50.1 ± 4.5	39.8	57.3
Erie	23.2	23.3 ± 2.8	15.5	29.5
Ontario	16.3	16.5 ± 1.6	13.4	20.0

[a] Data source: 1951-80 30-yr normal precipitation data, National Oceanic and Atmospheric Administration, Environmental Data and Information Service, National Climatic Center, Asheville, NC, September, 1982.

[b] Data source: National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, MI, July, 1986. (H. Hartman, personal communication.)

Figure 24 shows the spatial distribution of NO_3 wet deposition. Annual fluxes ranged from about 10 kg/ha over W Lake Superior to 20 kg/ha or more over E sections of Lakes Erie and Ontario. The overall pattern is similar to those of SO_4 and Ca, but the locations of the maxima over the lower lakes are quite different. From maximum to minimum, Ca and SO_4 fluxes vary by factors of about 3.5 and 4.5, respectively, whereas NO_3 has a smoother pattern and varies by a factor of only about 2.2. The pattern for NH_4 (Figure 25) also shows similarities and differences compared to those already presented. Maxima occurred in the Chicago area, and near Erie, Pennsylvania, as seen for ions already discussed. New areas with relatively high wet fluxes of NH_4 included the Duluth, Minnesota, area at the W tip of Lake Superior, and central portions of the W shore of Lake Michigan (Milwaukee to Green Bay). Southern Lake Huron also showed a stronger maximum than seen there for the ions presented previously. The minimum NH_4 wet fluxes occurred over N Lake Huron. Again these patterns bear a strong resemblance to the respective concentration patterns.

Wet deposition patterns for Na and Cl appear in Figures 26 and 27, respectively. Na fluxes ranged from about 0.25 to 2.5 kg/ha, a factor of 10 between the minimum and maximum. The range of the Cl fluxes was also rather large, with minimum values of less than 1 kg/ha and a maximum of about 7. The Cl pattern was similar to the Na pattern, with low values over large areas of Lakes Huron and Superior and local maxima near Chicago and Cleveland. Cl also had additional maxima over Lake Ontario and W portions of Lakes Erie and Superior.

Annual patterns of wet deposition fluxes for Mg and K are shown in Figures 28 and 29, respectively. The Mg pattern was a very close copy of the Ca pattern in Figure 23, except that the Mg fluxes were a factor of 5 lower, ranging from about 0.2 to 1.2 kg/ha. The primary maxima occurred at Chicago and over the S shore of Lake Erie. The overall pattern for K was similar, except for a strong maximum over W Lake Erie and additional maxima over the SW shore of Lake Superior, Green Bay, S Lake Huron, and E Lake Ontario.

Annual wet deposition fluxes of Cd and Pb, based only on 1983 GLAD data, are shown in Figures 30 and 31, respectively. GLAD network sites used in the analyses are shown in both figures. As for other spatial analyses, only sites meeting the screening criteria were used. This explains why the sites that appear in these two figures are not necessarily the same as in others. Minimum fluxes of both metals occurred in the N areas of the Great Lakes basin. Lowest measured annual Cd fluxes were about 1 g/ha, with maximum values in excess of 6 g/ha. Annual wet fluxes of Pb ranged from less than 20 to more than 100 g/ha. Maximum Cd fluxes occurred over the middle and the S tip of Lake Michigan, much of Lake Ontario, and both the W and E extremes of Lake Erie. Pb flux maxima occurred in the Chicago area, E Lake Erie, and much of Lake Ontario.

For most ions, minimum wet fluxes occurred over Lake Superior and the N portions of Lakes Michigan and Huron. The locations of flux maxima varied somewhat from ion to ion, but the Chicago area and various locations along the S shore of Lake Erie were often included. In general, the wet deposition patterns may be viewed as the product of the regional patterns of precipitation depth and ion concentrations in precipitation, modified locally by strong sources. Since precipitation increases somewhat from N to S, and concentrations in general also increased from N to S or NW to SE, a rather strong increase in deposition also occurred from N or NW to S or SE.

The additional spatial resolution provided by the GLAD sites makes it possible to observe deposition maxima near strong source regions. These local maxima are important in estimating lake loadings. Thus, the combined NADP and GLAD data should provide better estimates of lake loadings of the major ions than those computed from NADP data alone. Nevertheless, uncertainty still exists regarding the dimensions of the areas represented by individual sites in urban or industrial locations, as well as in extrapolating measurements made on land to off-shore locations.

The deposition patterns produced by objective analysis are determined by the number and location of the sampling sites, as well as the objective rules used for interpolation between observations. Over southern Lake Michigan, for example, the patterns were largely determined by three observations along the Chicago lakefront and one at Benton Harbor, across the lake. The analysis method ignores the fact that the lake is there, i.e., that sources are effectively absent, and that lake-related meteorological processes may affect deposition patterns over the lake.

Observations of deposition patterns east of St. Louis, based on bulk precipitation sampling (Gatz, 1980a, 1980b), showed that pollutants with urban sources were deposited in concentrations more than 5 times the regional mean within about 20 km of their suspected sources. At greater distances, deposition decreased rapidly. In contrast, Figure 31 shows a 100 g/ha isoline of Pb deposition extending more than half of the roughly 110 km distance between Chicago and Benton Harbor. The references above suggest that deposition much higher than that shown in Figure 31 may have occurred over a small area close to the Chicago shore, along with a broad area farther out in the lake where deposition was lower than shown in Figure 31. However, the magnitude of the error in the objective analysis, and even its sign, is not obvious. Similar uncertainty exists regarding deposition gradients near source areas on the other lakes. Additional research on the variation of wet deposition with distance from sources will be needed to improve methods of estimating lake loadings from land-based measurements.

3.4.2. Effects on Deposition Estimates of Closing GLAD Sites

The improved resolution provided by the GLAD network data for 1982-1985 may have diminished with the closing of 16 GLAD sites in January 1986. This section examines the effects on deposition estimates of closing these sites.

To simulate the effects of reducing the number of sites in the GLAD network, we computed deposition with and without selected sites. Differences were characterized by 1) the resulting changes in deposition flux patterns or 2) the changes in lake loadings, or both. These differences were used to estimate the effects of 1) the closing of 16 GLAD sites in January 1986, and 2) the possible closing of selected additional GLAD sites in the future.

Spatial distributions of the differences in wet deposition fluxes for 1982-1983, computed with and without the sites closed in 1986, are shown in Figures 32-35 as percentages of the values computed for the full (pre-1986) network. Differences were calculated by subtracting the grid point data field resulting from the objective analysis of the reduced network from the grid point data field from the full network, and converting these differences to percentages. For all four ions examined, both positive (higher deposition in the reduced network) and negative (lower deposition in the reduced network) changes occurred locally near the sites removed. The increases ranged as high as 35%, and the decreases as high as 45% in limited areas. Negative changes occurred where the grid point field of deposition fluxes from the combined GLAD and NADP networks was reduced locally by the removal of a data point (i.e., a site) from the objective analysis. Positive changes occurred where the grid point field was increased locally when a site was removed. The magnitude of the percent differences was largest for Ca, which is consistent with the observation that Ca had very large local maxima at urban GLAD sites.

The overall net changes in lake loadings estimates for each of the five lakes are shown in Table 10. These loading estimates resulted from integrating the over-lake deposition fluxes for each Lake. The changes were predominantly negative; that is, the loadings computed from the reduced network were smaller than those from the full network. This again is consistent with the fact that many of the GLAD sites were in urban and suburban areas, where local effects were apparent in the concentration and deposition patterns discussed earlier. For SO_4, the changes were less than ±5%, except for a -12.6% change in Lake Ontario. The same was true for NO_3, except for a -5.2% change, also in Lake Ontario. For NH_4, the changes ranged from -1.4% to -14.2%, with the largest change occurring in Lake Michigan and the next largest (-10.8%) in Lake Erie. For Ca, the changes ranged from +4.3% (Lake Erie) to -26.8% (Lake Superior), the largest change observed for any of the four ions. Changes of more than 10% (both negative) also occurred in Lakes Huron and Ontario.

Table 11 shows the simulated effects on computed lake loadings of closing additional existing sites. The table gives values of percent change in the loadings of SO_4, NO_3, NH_4, and Ca to Lakes Superior, Michigan, Erie, and Ontario, based on loadings computed with and without certain sites (or combinations of sites) in the data set. The reference data set was the combined GLAD and NADP networks in operation after January 1986.

The upper portion of Table 11 shows percent differences in loadings to Lake Superior on the assumption that the Hovland (QA), Cornucopia (QE), and Ontonagan (QF) sites were closed--either individually, or in all possible combinations of two and three sites. For SO_4, removal of sites from the data set in any possible combination resulted in <u>increases</u> in the computed loadings to Lake Superior, although the maximum increase was only 2.5% for the case where sites QE and QF were removed.

For NO_3, NH_4, and Ca, the computed changes were either increases or decreases, depending on which sites or combinations of sites were removed from the data set. For NO_3, the largest change was a decrease of 5.1%, for the case where all three sites were removed. Removal of all three sites also had the

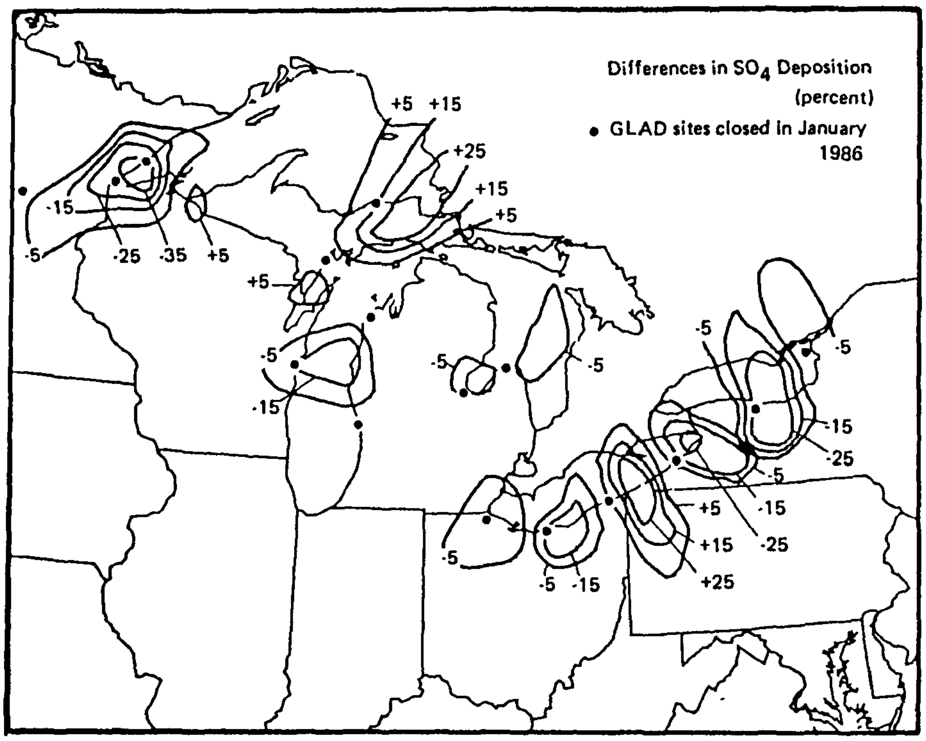

Figure 32. Spatial distribution of percent differences that result from calculation of the SO_4 deposition flux from all the sites compared to those remaining open after January 1986.

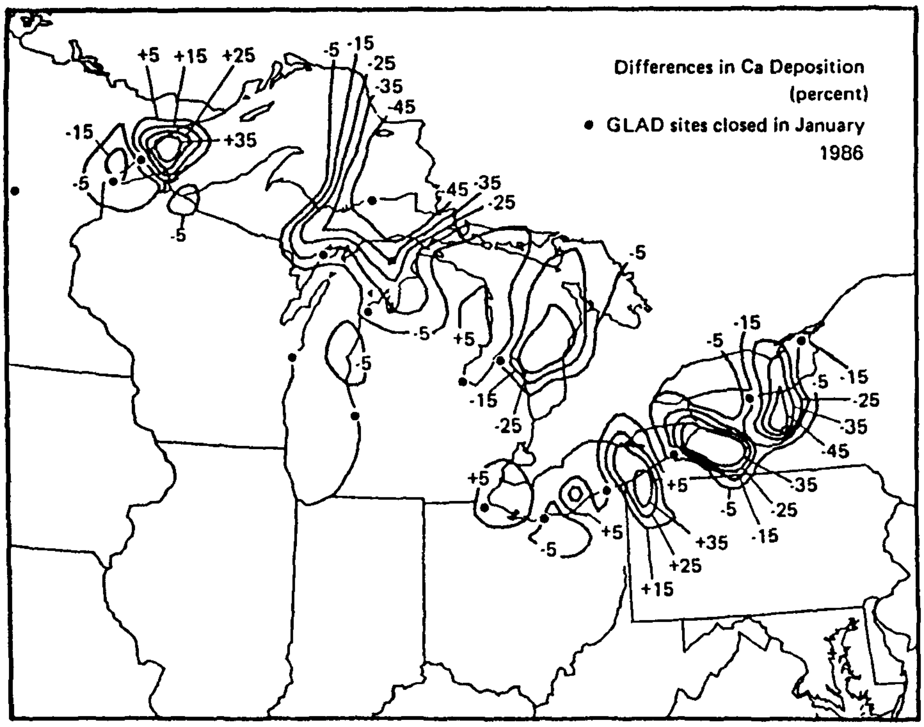

Figure 33. Spatial distribution of percent differences that result from calculation of the Ca deposition flux from all the sites compared to those remaining open after January 1986.

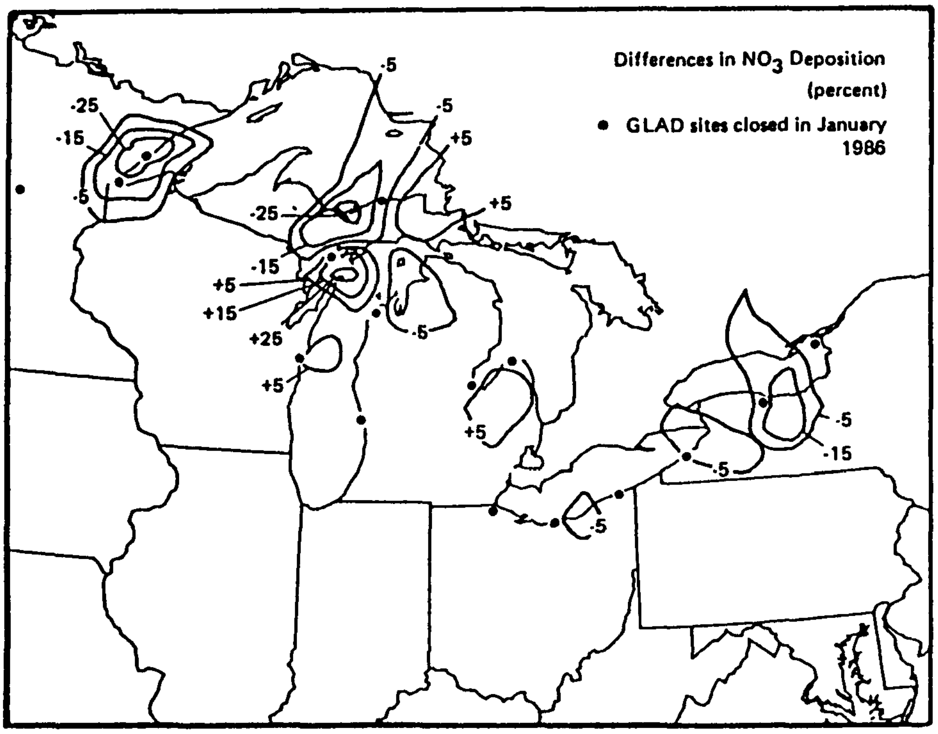

Figure 34. Spatial distribution of percent differences that result from calculation of the NO_3 deposition flux from all the sites compared to those remaining open after January 1986.

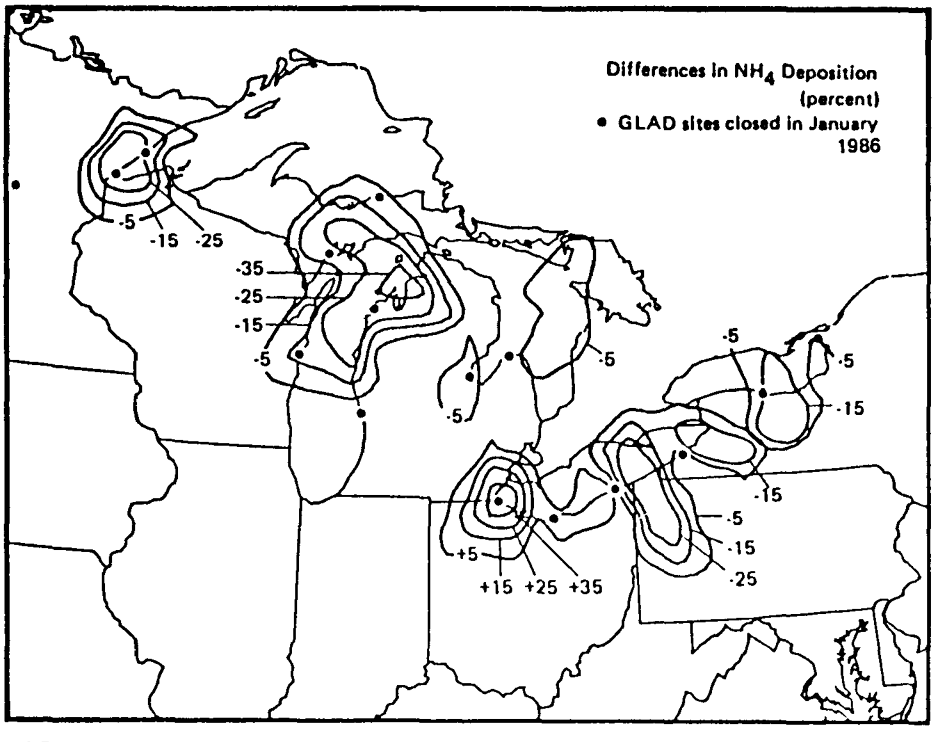

Figure 35. Spatial distribution of percent differences that result from calculation of the NH_4 deposition flux from all the sites compared to those remaining open after January 1986.

Table 10. Comparisons of Wet-Only Atmospheric Loadings (1000s of Tonnes/yr) to the Great Lakes from 1) All Valid NADP and GLAD Sites Operating in 1982-83 with 2) All Valid NADP Sites Plus the Valid GLAD Sites that Remained Open after January 1986.

Lake	Ion	NADP + GLAD (sites before 1-86)	NADP + GLAD (sites after 1-86)	Percent difference
Superior	SO_4	104	109	+4.8
	NO_3	81.2	78.6	-3.2
	NH_4	22.9	22.6	-1.4
	Ca	18.6	13.6	-26.8
Michigan	SO_4	118	115	-2.6
	NO_3	90.3	90.3	0.
	NH_4	22.1	18.9	-14.2
	Ca	16.7	15.7	-6.1
Huron	SO_4	116	114	-2.1
	NO_3	83.4	83.5	+0.1
	NH_4	20.6	19.9	-3.2
	Ca	13.8	12.1	-12.4
Erie	SO_4	90.3	88.9	-1.6
	NO_3	47.0	45.4	-3.5
	NH_4	11.1	9.93	-10.8
	Ca	12.1	12.7	+4.3
Ontario	SO_4	60.7	53.1	-12.6
	NO_3	37.3	35.3	-5.2
	NH_4	8.07	7.40	-8.4
	Ca	5.13	4.31	-16.0

Table 11. Effect of Closing Additional GLAD Sites, Compared (Percent Change) to the Network Still Open after January 1986.

Site(s) closed	SO_4	NO_3	NH_4	Ca
Lake Superior				
Hovland (QA)	0.	-3.9	-5.5	1.8
Cornucopia (QE)	0.9	-0.1	-2.0	-1.0
Ontonagan (QF)	0.8	0.6	1.3	-2.3
QA + QE	0.9	-4.3	-8.2	0.9
QA + QF	0.5	-4.1	-4.8	-1.3
QE + QF	2.5	0.8	-0.8	-4.5
QA + QE + QF	2.3	-5.1	-9.0	-4.7
Lake Michigan				
Benton Harbor (QT)	1.9	-1.5	-0.5	-0.7
Lake Erie				
Erie (SQ)	-6.2	-4.5	-7.7	-11.7
Lake Ontario				
Erie (SQ)	0.	0.1	0.2	0.5

maximum impact on computed NH_4 loadings, a decrease of 9.0%, and computed Ca loadings, a decrease of 4.7%.

Table 11 also shows the effect on computed loadings to Lake Michigan of removing the Benton Harbor (QT) site. Only minor changes occurred, ranging from a decrease of 1.5% in the NO_3 loading to an increase of 1.9% in the SO_4 loading.

The biggest effect on any lake from removing sites occurred on Lake Erie, when the Erie (SQ) site was removed. Smaller loadings were computed for all four ions without the urban Erie site in the data set. The decreases ranged from 4.5% for NO_3 to 11.7% for Ca.

The effects on Lake Ontario loadings from removing the Erie site are also shown. All changes were either zero or very small increases, the maximum change being an increase of 0.5% in the computed Ca loading. The change in the loading estimates for Lake Ontario from the closing of SQ was the result of the objective analysis procedures used to calculate deposition fluxes. The value calculated at each grid point was based on the values at the five nearest measurement sites. Calculation of one or more grid box fluxes over Lake Ontario was thus affected by measurements at the SQ site. Removal of SQ eliminated its use in the calculations and this resulted in a slight change in the loadings estimates, which were calculated by adding all the over-lake grid box fluxes.

The results in Table 11 appear to vary with the observed variability of deposition over the various lakes. Removal of a single site from Lake Erie, which shows highly variable deposition because of its highly urbanized shoreline, resulted in changes of about 5-12% in computed lake loadings. On the other hand, three sites could be removed from Lake Superior, where deposition patterns are relatively uniform, before comparable changes were seen.

3.4.3. Atmospheric Loadings to the Lakes and Comparison to Previous Estimates

3.4.3.1. Results

A summary of atmospheric wet-only deposition loadings to the Great Lakes from the combined GLAD-NADP networks is given in Table 12. Previous results based on modeling (Acres Consulting Services, Ltd., 1975, 1977) and on bulk precipitation measurements (Acres Consulting Services, Ltd., 1975, 1977; Eisenreich et al., 1977) are given in Table 12 for comparison. Also shown for comparison are non-atmospheric loadings to each lake. Most of those shown were computed from the total lake loadings of Upchurch (1976) by removing his estimated contributions from precipitation. However, additional values from other sources are also provided for some of the lakes.

For sulfate, the present (GLAD-NADP) wet-only loading estimate was about 35% of that of the Acres model, which includes both wet and dry deposition, in four of the five lakes, and about 50% of it in Lake Superior. The present wet-only loadings estimates ranged from about 50% to 90% of those based on previous bulk precipitation measurements. Thus, the present estimates of wet-only sulfate deposition were smaller than: 1) previous modeling estimates, which

Table 12. Atmospheric Loadings (1000s of Tonnes/yr) to the Lakes from GLAD-NADP Data, and Comparisons with Previous Estimates and Non-Atmospheric Loadings

Lake	Ion	NADP+GLAD (wet only)	Acres model[a] (wet + dry)	Precipitation chemistry[a] (bulk)	Estimated[b] non-atmospheric loadings
Superior	SO_4	104	210	220	
	Cl	7.5	0.19	55	98
	Ca	18.6	1.3	33	670
	Mg	3.4	0.60	5.6	
	Na	3.5	0.37	15	
	K	3.1	1.1	13	
	NO_3-N	18.4			10
	NH_4-N	17.8			
	Total	36.2			
	N		17	56	
Michigan	SO_4	118	330	135^{d}	
	Cl	10	NA^{c}	82^{d}	81
	Ca	16.7	1.8	103^{d}	1650
					294^{d}
	Mg	3.3	0.81	22^{d}	259^{d}
	Na	3.4	0.50	16^{d}	
	K	2.8	1.5	9.6^{d}	
	NO_3-N	20.4			6.6
	NH_4-N	17.2			
	Total	37.6			
	N		42	NA	
Huron	SO_4	116	380	230	
	Cl	5.6	0.20	49	170
	Ca	13.8	1.6	280	NA
	Mg	2.6	0.73	8.2	
	Na	2.4	0.47	45	
	K	2.7	1.4	32	
	NO_3-N	18.8			5.9
	NH_4-N	16.0			
	Total	34.8			
	N		31	52	

Table 12. (continued)

Lake	Ion	NADP+GLAD (wet only)	Acres model[a] (wet + dry)	Precipitation chemistry[a] (bulk)	Estimated[b] non-atmospheric loadings
Erie	SO_4	90	270	120	
	Cl	11	NA	NA	400
	Ca	12	1.2	23	2300
	Mg	2.2	0.55	6.6	
	Na	3.3	0.37	13	
	K	2.2	1.1	22	
	NO_3-N	10.6			27
	NH_4-N	8.6			
	Total	19.2			
	N		29	19	
Ontario	SO_4	61	120	88 102[f]	4500[g]
	Cl	4.9	NA	15[f]	240 4300[g]
	Ca	5.1	0.62	32 51[f]	3200 6500[g]
	Mg	1.0	0.29	4.1 8.1[f]	1450[g]
	Na	1.5	0.19	19 25[f]	2000[g]
	K	1.1	0.55	3.3 6.1[f]	210[g]
	NO_3-N	8.4			10
	NH_4-N	6.3			
	Total	14.7			
	N		14	21	

[a] Source: Acres Consulting Services, Ltd. (1975) for Lakes Superior and Huron; Acres Consulting Services, Ltd. (1977) for the other lakes, except as noted.

[b] Source: Upchurch (1976), except as noted. Does not include wet deposition or inputs from upstream Great Lakes.

[c] NA = not available.

[d] Eisenreich et al., (1977).

[e] Sum of tributary and erosion inputs from Eisenreich (1980), based on Robbins et al., (1972), Schmidt (1977), Monteith and Sonzogni (1976), and Fitchko and Hutchinson (1975).

[f] Shiomi and Kuntz, (1973).

[g] Niagara River loadings to Lake Ontario, from Shiomi and Kuntz (1973).

included both wet and dry deposition, and 2) previous bulk (open-bucket) precipitation measurements, which included wet deposition as well as dry materials deposited with generally unknown efficiencies.

Only one estimate of non-atmospheric lake loading was available for SO_4, that being for Lake Ontario. Comparison of the atmospheric and non-atmospheric loadings indicates that atmospheric deposition of SO_4, at least for Lake Ontario, was negligible compared to other sources.

For chloride, the GLAD-NADP wet-only loading estimates (Table 12) exceeded the Acres modeling estimates by factors of about 30 to 40 for Lakes Superior and Huron, the only two lakes for which Acres estimates for Cl were available. On the other hand, the wet-only loadings estimates were only about 1/8 of the bulk precipitation loadings estimates for Lakes Superior, Michigan, and Huron, and about 1/3 the reported value for Lake Ontario. This seems to indicate that the Cl loadings estimated by the Acres model were much too low, and that the bulk precipitation measurements were strongly affected by either dry deposition or perhaps contamination.

The wet-only Cl loadings represent about 2-12% of the non-atmospheric loadings of Upchurch (1976) for the various lakes. However, it should be noted that an independent estimate (Shiomi and Kuntz, 1973) of non-atmospheric Cl loading of Lake Ontario is far higher than that of Upchurch.

For calcium, the present wet-only loadings estimates were consistently higher than the model results by a factor of about 10 for all the lakes. Conversely, the present estimates ranged from 5-56% of the previous estimates based on bulk precipitation measurements. Differences between wet-only and bulk precipitation loadings were much as expected, because atmospheric Ca is primarily on large particles, for which dry deposition can account for a large fraction (probably more than half) of the total deposition. It is worth noting that dry deposition of large particles to open buckets may be a reasonable approximation of ambient dry deposition to natural surfaces, so that the bulk deposition measurements may be a reasonable estimate of combined wet and dry deposition for Ca.

The order-of-magnitude differences between the present estimates and the model suggest major deficiencies in the model results for Ca. Inadequate emissions data was a likely cause. In any case, as we shall see next, atmospheric loadings of Ca were a relatively minor source, compared to those from non-atmospheric sources.

Comparison of atmospheric and non-atmospheric inputs of Ca to the lakes shows that the atmosphere was not a major source of Ca to the lakes (unless dry deposition made a large contribution not measured in the bulk collectors used previously). The present wet-only loadings represented only 0.2% (Lake Ontario) to 2.8% (Lake Superior) of the estimated non-atmospheric inputs shown in Table 12. However, notice again the wide disparity in non-atmospheric loadings estimates by various authors for Lakes Michigan and Ontario.

For magnesium, the new wet-only loadings again exceeded those from the Acres model by factors of 3-6 for the several lakes and were exceeded by those of the previous bulk measurements by about the same range of factors. From the available estimates of the non-atmospheric Mg loadings for Lakes Michigan and Ontario, it appears that wet deposition accounted for only about 1% of the total.

For sodium, as for Cl, Ca, and Mg, the loadings from the model were much too small, and the bulk measurements must have included either a large dry deposition component or suffered from contamination, or both. There was a non-atmospheric loadings estimate only for Lake Ontario, but it indicated that wet deposition contributed very little to the total lake loadings of Na.

For potassium, the wet-only loadings again exceeded those of the Acres model, but in this case by a factor of only about 2. As before, the loadings estimates from the bulk precipitation measurements were much higher, in this case by factors of 3-10. Again, the one estimate of non-atmospheric loadings (for Lake Ontario) suggests that the wet-only contribution to total lake loadings was very small.

Comparison of nitrogen loadings estimates required summing the nitrate N (NO_3-N) and ammonium N (NH_4-N) (see Table 12) to get a total N comparable to the total N reported for the modeling and bulk precipitation measurements (Acres Consulting Services, Ltd., 1975). Model estimates and bulk measurements differed by a factor of only about 2, the present wet-only estimates falling somewhere in between. The only measure of nitrogen available from non-atmospheric sources was NO_3-N. The present estimates of wet-only input exceeded Upchurch's non-atmospheric inputs in four of the five lakes, which suggests that atmospheric sources were relatively important for nitrogen.

Atmospheric loadings of metals, particularly the potentially toxic ones such as Hg, Pb, and Cd, are of much interest. These metals were not measured by the NADP network, and, as indicated earlier, GLAD for 1982 were insufficient for loadings estimates. The same was also true for Hg in 1983. However, the measurements of Cd and Pb for 1983 were considerably improved over those for 1982, and concentrations above detection limits were reported for most samples. Thus, we have computed loadings to the five lakes for these two metals from GLAD measurements (only). The results are given in Table 13, along with previous atmospheric loadings estimates from bulk precipitation measurements and from models and a few non-atmospheric loadings estimates.

As we saw in the case of the major ions, the new loadings estimates for wet-only deposition were in most cases much lower than previous estimates of wet and dry input, based on both modeling results and bulk precipitation measurements. For Lake Superior, the wet-only loadings estimates for Pb and Cd were only a quarter to a third of the previous estimates.

For Lake Michigan, the wet-only loadings estimates for Pb were about a third to a fifth of the bulk measurements of Eisenreich (1980) and the IJC (1977) (Acres) model results. However, the new estimate slightly exceeded the early model estimates of combined wet and dry deposition of Winchester and Nifong (1971) and Gatz (1975). It also exceeded the tributary inputs calculated by Winchester and Nifong (1971), but was less than the combined tributary and shoreline erosion loadings of Eisenreich (1980). For Cd in Lake

Table 13. Loadings Estimates (Tonnes/Yr) to the Great Lakes for Cd and Pb, Based on GLAD 1983 Concentration Measurements and 30-yr Mean Precipitation, Compared with Previous Estimates from the Literature Based on Bulk Precipitation Measurements and Modeling and with Estimates of Non-Atmospheric Inputs.

	Superior		Michigan		Huron		Erie		Ontario	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
GLAD wet-only measurements (1983)										
This study	170	12	240	15	214	8.3	142	8.7	125	9.5
Bulk precipitation measurements										
IJC (1977)	650	55	NA	NA	780	79	2200	150	280	45
Eisenreich (1980)			640	11						
Shiomi and Kuntz (1973)									255	17
Model estimates (wet + dry)										
IJC (1977)	780	34	1100	48	960	39	650	25	440	18
Winchester and Nifong (1971)			220	1.2						
Gatz (1975)			200	3.2						
Non-atmospheric loading estimates										
Eisenreich (1980)			420[a]	87[a]						
Winchester and Nifong (1971)			100[b]							
Shiomi and Kuntz (1973)									700[c]	

[a] Tributaries, plus shoreline erosion.
[b] Tributary input.
[c] Niagara River input to Lake Ontario.

Michigan, the new wet-only estimate slightly exceeded that based on Eisenreich's (1980) bulk measurements, was about a third of the IJC (1977) model estimate, and greatly exceeded the two earlier model estimates. The new wet-only estimate is about 17% of Eisenreich's (1980) estimate of Cd loading from tributaries and shoreline erosion.

For Lakes Huron, Erie, and Ontario, the new wet-only estimates for Pb were only about 25-50% of most of the previous estimates, and only 5% of the 2200 metric tonnes/yr estimate for Lake Erie based on bulk precipitation measurements. The estimated wet-only loading of Pb to Lake Ontario was about 17% of the Niagara River loading. The new estimates for wet-only Cd loading of the same three lakes ranged from 5-50% of the previous estimates.

Finally, wet-only loadings estimates from this study, presented in Tables 12 and 13, are further summarized and compared in Table 14 with previous estimates of loadings from bulk sampling and modeling. Comparisons are made of the ranges of ratios of the previous estimates for the various lakes to the current wet-only estimates. For example, for Cd (Table 13) the lowest IJC model/wet ratio, about 2, occurred for Lake Ontario and the highest, about 5, for Lake Huron. Similarly, the lowest bulk/wet ratio, about 0.8, occurred for Lake Michigan, and the highest, about 17, occurred for Lake Erie.

Table 14. Comparison of current estimates of wet-only lake loadings with previous estimates based on modeling (IJC, 1977) and bulk sampling.

Species	Model/Wet	Bulk/Wet
Pb	4 - 5	2 - 15
Cd	2 - 5	0.8 - 17
Ca	0.07 - 0.1	2 - 6
Mg	0.2 - 0.3	2 - 7
K	0.3 - 0.5	3 - 10
Na	0.1 - 0.2	4 - 20
Cl	0.03	3 - 8
SO_4	1 - 3	0.7 - 2
N	0.5 - 1.5	1 - 1.5

The species measured in precipitation have been grouped according to patterns of comparison with previous results. For example, the results for Pb and Cd were similar in that in general the loadings estimated by both previous methods exceeded the currently estimated loadings by factors of two or more. The same was true for the elements grouped in the middle of Table 14 in comparison with the bulk-sample estimates, but for this group the opposite was true in comparison to the previous model estimates. For SO_4 and N, at the bottom of the table, the current loadings estimates were mostly within a factor of two of both previous estimates.

3.4.3.2. Discussion

There are at least two very striking results here: 1) for many elements the current wet-only loadings estimates were much smaller than those made earlier based on bulk sampling, and 2) these large differences were not seen for SO_4 and N. Another is that the wet-only loadings for some elements were substantially higher than the corresponding estimates from the Acres model. This very likely resulted from a model input of these elements that was inadequate or incomplete.

Several possible explanations for the differences between bulk and wet-only loadings estimates come to mind, and depending on which is true (or which combination is true), there could be important implications regarding the direction of future research and policy for the Great Lakes. It seems possible that the differences may have been caused, at least in part, by one or more of the following:

1) Analytical bias, or loss or gain of ions from container walls,
2) Differences in precipitation amount,
3) Contamination of the bulk collections by debris (bird droppings, etc.) and/or resuspended local surface dust,
4) Valid (i.e., non-contaminant) dry deposition to the bulk collectors, or
5) Reductions in pollutant emissions between observation periods.

Since several analytical laboratories analyzed samples from the bulk precipitation sampling network (IJC, 1977) and an entirely different laboratory analyzed samples from the GLAD wet-only network, one possible explanation for differences is analytical bias. Without a direct comparison of laboratory performance on standard samples or split samples, such bias is difficult to quantify. In any case, analytical bias is not likely to be large enough to explain the differences of factors of two or more observed here.

A related possible problem is the adsorption or desorption of metal ions by or from container walls. For adsorption on walls to have caused the observed differences, the losses would had to have occurred in the polyethylene bags or bottles used respectively to collect and ship the samples. However, Chan et al., (1983) have reported negligible losses of Pb and Cd to polyethylene on one-day contact, and, on 29-day contact, minimal loss of Pb and about 10% loss of Cd. Sample contamination by desorption of metal impurities from container walls is also possible, but it is quite unlikely that the massive contamination required to cause the observed differences would have gone undetected by normal laboratory quality control procedures or blank measurements. Thus, it appears unlikely that interactions between precipitation samples and container walls could have caused the observed differences.

A procedural difference in the computation of loadings from the respective bulk and wet-only measurements is another possible reason for the observed differences in lake loadings. The bulk network was in operation during 1973 and 1974 (IJC, 1977), and loadings calculations were based on measured precipitation during the period of operation. In contrast, the observed (weighted mean) wet-only concentrations were converted to lake loadings using the 30-yr mean annual precipitation for each lake, as described earlier. If actual precipitation during the bulk network operation was larger than the 30-yr means, this would cause the loadings estimated from the bulk sampling data to be higher than those from the wet-only data, even if the concentrations were identical.

To evaluate this potential effect, annual precipitation fluxes to each of the five lakes for 1973 and 1974 were computed from precipitation data supplied by H. Hartman (see footnote to Table 9). The largest departure from the 30-yr mean for any lake in either year was +6.0% for Lake Michigan in 1973. Thus, this difference in methods of estimating lake loadings cannot account for the observed large (factor of 2 and greater) differences in loadings.

Another possible explanation is that the bulk sampler collections included sizeable contributions from local surface dust. This dust would include wind-blown emissions from soils and both paved and unpaved roads. Thus, it would naturally contain most of the major cations, and at times also Na and Cl from winter road salting. In urban and industrial locations, it might also contain high concentrations of Pb, Cd, and other pollutant metals, which are known to occur in high abundance sorbed on surface dust after previous wet or dry deposition (Hopke et al., 1980; Harrison et al., 1981). On the other hand, any previously deposited soluble anions in surface dust would be leached into deeper soil layers by subsequent rainfall, so deposition of resuspended local surface dust in bulk samplers would not cause significant differences between bulk and wet-only collections for SO_4 and N. This is consistent with the observations in Table 14.

Special observations were conducted as part of the IJC bulk sampler network to determine whether the bulk samplers collected resuspended surface dust (J.R. Kramer, personal communication, 1987). The observations consisted of monthly bulk precipitation samples collected in samplers 1) on the roof of an 8 ft high field shelter, 2) on top of an adjacent 30-75 ft tower, and 3) on a buoy anchored 6 mi offshore. These observations were made in clearings at three lakeshore sites--two relatively isolated, and one in a town with a population of about 7500. One of the isolated sites was near Red Rock, Ontario, on the northern shore of Lake Superior. The other isolated site was on Duck Island, near Manitoulin Island in northern Lake Huron. The third site was at the town of Goderich, Ontario, on the eastern shore of Lake Huron. A statistical comparison of constituent concentrations measured in the various types of samplers indicated that small amounts of reentrained surface dust were entering the bulk samplers at times (J. R. Kramer, personal communication, 1987), although an independent analysis of the data (Acres Consulting Services, Ltd, 1975) pointed out that the higher loadings often measured by the samplers on towers compared to those near the ground was inconsistent with this interpretation.

The special observations of the IJC network also included simultaneous wet-only and bulk sampling at the three sites described above. Data on elemental and ionic concentrations, both total and filtered, are available (J.R. Kramer, personal communication, 1987) for both types of samplers. These data may be suitable for clarifying the role of local resuspended dust deposited in the bulk samplers.

If contributions of local surface dust to the previous bulk collections are a major cause of the observed differences between bulk and wet-only collections, some may argue that such deposits should be included when tallying atmospheric deposition inputs to the lakes. There are several reasons why such actions would be risky. It is true, of course, that some surface dust resuspended over land areas will travel over, and fall into the lakes, but the affected areas of the lakes are not known with any accuracy. The flux to the lakes will be greatest at the shoreline and decrease as some unknown function of distance away from shore. The second reason is the absence of a proven method for estimating the "locally resuspended" portion of the deposition measured in bulk samples. A third reason is the lack of a procedure to estimate deposition to a natural surface from that measured in a bulk collector.

If indeed local surface dust accounts for much of the difference between the lake loadings estimated from bulk and wet-only collections, then it is likely that the contribution of atmospheric deposition to the total input of metals like Pb and Cd has been over-estimated, although it is not possible to say how large the overestimate is.

The possibility of this explanation should be explored further through detailed examination and comparison of bulk/wet-only differences in metal deposition at urban and remote sites. These differences should be greatest at urban locations where the surface dust would be contaminated with these metals, and probably negligible at remote sites. Side-by-side comparison of the respective types of samplers should also be carried out in both urban and remote locations.

Another possible explanation is that the observed differences between the lake loadings estimated previously from bulk sampling and the current ones from wet-only sampling represent true dry deposition (i.e., other than locally resuspended surface dust) to the bulk samplers. If this is the case, then dry deposition to the lakes may be a much larger fraction of total deposition than previously thought. However, from the measurements available, it is impossible to say whether that is true, since there is no proven method for using surrogate surface dry deposition measurements to predict deposition to the surfaces of the Great Lakes.

A few independent estimates of dry deposition of Pb and Cd are available in the literature for comparison. Sievering et al. (1984) estimated a dry deposition input of 200-500 tonnes/yr of Pb to the S basin of Lake Michigan; this compares reasonably well to the difference (400 tonnes/yr) between bulk and wet-only inputs to all of Lake Michigan in Table 13. However, the comparison is much less consistent in the case of Cd. The Cd dry deposition loadings available in the literature are also for the S basin of Lake Michigan. The estimates are 1.7 tonnes/yr (Gatz, 1975) and 2.2 tonnes/yr (Tisue and Fingleton, 1984). Comparison of these estimates to the differences between loadings estimated from bulk and wet-only sampling are not possible, however, for reasons explained next.

Lake Michigan presents an anomaly with respect to the comparison of loadings estimates from wet-only and bulk precipitation measurements in that it is the only lake where the wet-only estimate actually exceeded the previous bulk-sampling estimate (15 vs 11 tonnes/yr, Table 13). It may be significant that the bulk precipitation measurements for Lake Michigan were carried out by a different group (Eisenreich, 1980) than those for the other four lakes (IJC, 1977), for which the loadings based on bulk sampling exceeded those from wet-only sampling by amounts ranging from 35-141 tonnes/yr (Table 13).

It is clear that there are only a few estimates of dry deposition of metals to the Great Lakes. It is equally clear to workers in this field that, although such measurements are badly needed to understand all the processes of atmospheric deposition to the lakes, the methods currently available are inadequate. Further research is needed to develop the needed methods.

Another possible explanation of the differences between current and previous estimates of lake loadings is that the deposition data merely reflect the reductions in emissions that have taken place during the time between the respective observations. For Pb, Eisenreich et al. (1986) reported marked decreases in concentrations and deposition in precipitation in Minnesota between 1979 and 1983, a period when the amounts of Pb used in gasoline also dropped substantially. No similar reduction in a major Cd source is known, but gradual reductions in Cd emissions may also have occurred between the mid-1970s and the early 1980s due to economic factors and the gradual implementation of improved emission control technology.

On the other hand, this explanation is not likely to apply to the alkali and alkaline earth elements Na, Mg, K, and Ca, for which previous bulk precipitation loadings also greatly exceeded recent wet-only loadings. It is possible, of course, and we suggest that it is quite likely, that emission reductions explain the most of the differences in Pb (and perhaps Cd) loadings, while the exclusion of local resuspended dust from the wet-only samples (but not the bulk samples) explains most of the observed differences for the alkali and alkaline earth elements.

Uncertainties in computed loadings near strong source areas, arising from the objective analysis method used, were discussed earlier in this report. The sign and magnitude of the possible errors cannot now be estimated. Judging from the rather limited lake areas involved, however, it appears quite unlikely that they could account for the observed many-fold differences between our wet-only loadings estimates and those based on previous bulk sampling.

4. CONCLUSIONS

The Great Lakes precipitation chemistry data analyzed in this report represent the first two full calendar years (1982 and 1983) of data from an ongoing network sampling operation. A number of important conclusions can be drawn at this point:

1. GLAD pH measurements were biased low during 1982-1983, and should not be used.

2. Constituent concentrations at GLAD sites exceeded their counterparts at the nearest NADP sites (at the 1% significance level) much more than expected by chance for SO_4, Ca, and NH_4, and somewhat more than expected by chance for NO_3. Most of these differences involved comparisons of an urban GLAD site in Erie, Pennsylvania, and a suburban GLAD site in Dunkirk, New York. These differences could reflect true spatial gradients, or be related to differences in siting criteria or local sources. In the absence of a side-by-side comparison of NADP and GLAD sites, it is not possible to quantify sampling or analytical biases between the two networks for the four ions tested, SO_4, Ca, NO_3, and NH_4.

3. GLAD data add useful spatial resolution to other available precipitation chemistry data sets. Based on valid GLAD and NADP data from 1982-83, the closing of 16 GLAD sites (actually closed in January, 1986) generally resulted in a decrease in the loadings estimates to each of the 5 Lakes for SO_4, Ca, NO_3, and NH_4. Decreases exceeded 10% for Ca (26.8%) in Lake Superior, NH_4 (14.2%) in Lake Michigan, Ca (12.4%) in Lake Huron, NH_4 (10.8%) in Lake Erie, and SO_4 (12.6%) and Ca (16.0%) in Lake Ontario. Closing of additional sites would result in further reductions in the spatial resolution of deposition and in the ability to quantify the loadings.

4. Spatial distributions of wet deposition fluxes show that annual values were 2-10 times higher in the S or SE portions of the network than in the N or NW portions. This results from both an increase in average precipitation amount and an increase in constituent concentrations from N or NW to S or SE. This is a general feature of all the deposition flux patterns, though there are important (but not consistent) exceptions at one or more sites for nearly all ions.

5. Annual precipitation-only loadings of Pb to the five Great Lakes, based on the 30-yr mean annual precipitation and 1983 GLAD concentrations, ranged from 125 to 240 tonnes. These values are about 20% of previous model loadings estimates of wet and dry deposition to the respective lakes, and 7-50% of previous estimates made from bulk precipitation sampling data.

For Cd the range of the same loadings was 8 to 15 tonnes per lake per year. This is about 20-30% of previous wet and dry loadings estimates from models and 5-120% of loadings estimates from bulk precipitation data.

For Cl and the major cations Mg, K, Na, and Ca, the precipitation-only loadings greatly exceed those from the model. They are much smaller than those based on earlier bulk sampling, but they are relatively insignificant compared to non-atmospheric loadings.

For SO_4 and N, the precipitation-only loadings were within a factor of about 2 of those from the model and from earlier bulk sampling.

6. The marked differences between current (precipitation-only) loadings estimates and earlier (bulk precipitation) estimates are not likely to be accounted for by analytical bias, interactions with container walls, or differences in precipitation amount.

The observed large differences between present and earlier loadings estimates for the cations and Cl and the small differences observed for SO_4 and N are consistent with contamination of the bulk samples by resuspended surface dust and (for Cl) episodic road salt spray. The soluble anions are not constituents of the surface dust and would not accumulate in it from previous wet or dry deposition.

The same explanation may account for some or all of the differences found for Cd, as well. For Pb, however, at least a part of the differences are likely to have been caused by recent reductions in Pb emissions from automobile exhaust, which are due to the current limitations on the Pb content of gasoline.

7. To the extent that these explanations cannot account for the observed differences, we must attribute them to dry deposition (from non-local sources) in the bulk collectors. If contaminant dry deposition were truly a minor portion of the observed differences, then dry deposition would have to be a major portion. In that case, one might begin to suspect that dry deposition to the lakes is more important, relative to wet deposition, than has been thought up to now. However, that could only be a very tentative suspicion, because we do not know how to infer dry deposition to natural surfaces from dry deposits in bucket collectors.

5. RECOMMENDATIONS FOR FURTHER RESEARCH

1. Additional GLAD data now available for 1984-1986 should be analyzed, to help to verify or refute the conclusions based on the 1982-1983 data. However, data reporting, editing, clean-up, and archiving procedures should be improved, so that users can be provided with error-free data sets.

2. The GLAD network should be continued, with as many sites as practical, to provide a spatial resolution of wet deposition consistent with that of relevant major sources of toxic contaminants. In addition, research should be conducted to improve estimates of over-water wet deposition fluxes from land-based measurements, especially near major sources of important airborne pollutants.

3. Additional research should be conducted to explain the differences between lake loadings calculated from the earlier bulk precipitation measurements and the current wet-only measurements. Analyses should be carried out on any existing, but unanalyzed, data sets from co-located bulk and wet-only collectors. Additional field comparisons of these samplers should be conducted in both urban and remote locations.

4. Where possible, Canadian data on precipitation amount and chemical composition should be combined with the GLAD data base as additional years of data are added, so that subsequent analyses and loadings calculations are based on data from both sides of all the Great Lakes.

5. Additional research is needed to provide valid methods of measuring or estimating dry deposition of both gaseous and particulate forms of toxic pollutants to the Great Lakes.

6. To verify that the differences between GLAD and NADP data are not related to sampling, analytical, or data handling procedures, or analytical biases, a co-located GLAD and NADP site should be operated for at least one year at an urban location. Differences, if any, at such a site are more likely to be manifested than in a clean rural environment.

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APPENDIX A
CRITERIA FOR SELECTION OF VALID SAMPLES

1. NADP Network (Bowersox, 1984)

a) The sample must have been a wet-only deposition sample. Samples exposed continuously during both precipitation and dry weather (i.e., bulk samples) were considered invalid.

b) Standard procedures, as specified in NADP field (NADP, 1982) and laboratory (Peden et al., 1986) manuals, must have been followed. When followed, these procedures assure that the sample will not have been exposed to uncontrolled ambient conditions in the field or laboratory and that the samples will not have come in contact with surfaces that were not cleaned according to specified procedures.

c) A complete set of ion concentration measurements must be present.

d) The sample must not have been grossly contaminated by foreign matter (e.g., leaves, seeds, bird feces, or insects).

e) There must have been a measurement of precipitation amount from the rain gauge or sample volume. (Where precipitation was not reported, sample volume converted to precipitation amount was substituted; sample volume was a required measurement.)

f) Note: any sample that was of insufficient volume to measure all of the ions and for which the total precipitation reported from the rain gauge was < 0.01 in. was considered a valid "zero" measurement by default.

With two exceptions these are the same criteria used to select "valid" samples for the annual NADP data summaries (e.g., NADP Subcommittee Number 3, 1985). The exceptions are 1) that the 6-8 day limit on the duration of the sampling period was not used to exclude samples here, and 2) that samples of insufficient volume for a complete analysis and "T" (trace) rainfall amounts were considered valid "zero" measurements here, but not in the cited data summaries. Very similar criteria are also being used by the U.S.-Canadian Unified Deposition Data Base Committee (undated) to select valid samples to verify an atmospheric deposition model that has been applied to data for eastern North America.

2. GLAD

a) Samples must have a measured sample volume.

b) All other samples in the data set provided by EPA/GLNPO were considered valid. We assumed that gaps in the computer data record represented samples that were invalidated at EPA/GLNPO or in their analytical laboratory.

Based on these lists of criteria for NADP and GLAD data, it is evident that there are differences in the degree or extent to which these two data sets could be matched in terms of their quality. The NADP data provide a more complete set of codes and information from which to apply screening criteria. Some screening is implicit in the standard operating procedures employed by the GLAD monitoring program (GLNPO, undated). To some extent these may equate to the procedures for identifying samples that fail NADP criteria (b) and (d). The most notable differences relate to NADP criteria (a) and (e), verification that the sample is precipitation-only and the presence of an independent measurement of precipitation amount. It was not until 1984/85 that rain gauges were installed at GLAD sites. In addition, there is no provision for continuously monitoring the operation of the AeroChem Metrics sampler at GLAD sites, as is the case with the open/close recorder in use at NADP sites.

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16. ABSTRACT

In 1981 the Great Lakes National Program Office(GLNPO) of the U.S. Environmental Protection Agency(U.S. EPA) established a network of Great Lakes Atmospheric Deposition(GLAD) sites to determine atmospheric loadings of metals, nutrients, and major inorganic species to the Great Lakes and to evaluate annual trends in the chemical loadings of these species to the lakes. This network was designed to collect wet-only deposition samples at near-shore locations.

This study contains an analysis and interpretation of atmospheric wet deposition data collected by the GLAD network. Included in this study are: an assessment of data quality; a comparison of specific pairs of GLAD and National Atmospheric elements to the five Great Lakes; and an analysis of the potential changes in loading estimates caused by closing certain GLAD sampling sites.

17. KEY WORDS AND DOCUMENT ANALYSIS

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