Final Report

ANALYSIS OF DRY DEPOSITION MONITORING DATA IN MINNESOTA AND SURROUNDING AREAS

SYSAPP95-94/087

January 1995

Prepared for

Ms. Evelyn Orr
Air Quality Division
Minnesota Pollution Control Agency
520 Lafayette Road
Saint Paul, MN 55155-3898

Prepared by

Till E. Stoeckenius
Stella B. Shepard
Robert K. Iwamiya

Systems Applications International
101 Lucas Valley Road
San Rafael, CA 94903

Acknowledgments

Several people contributed valuable ideas and information to this study. Evelyn Orr of the Minnesota Pollution Control Agency (MPCA) made available all of the monitoring and quality assurance data analyzed here along with relevant agency reports, provided the descriptions of monitoring networks presented in Appendix A, and also provided numerous insightful comments and suggestions which greatly improved the quality of this report; several of Ms. Orr's colleagues at the MPCA also contributed valuable comments. The IMPROVE monitoring data were provided by the National Park Service and the University of California; the Wisconsin Dry Deposition Network data were provided by the State of Wisconsin Department of Natural Resources; and the Ontario monitoring data were provided by the Ontario Ministry for Energy and the Environment.

EXECUTIVE SUMMARY

Air monitoring data of species important to dry deposition collected by the Minnesota Pollution Control Agency (MPCA) at 13 sites in Minnesota between 1984 and 1993 were analyzed along with similar data collected at sites in northeastern Minnesota, Ontario, and Wisconsin by three other organizations. The analyses were designed to yield information needed to

- evaluate the accuracy and precision of the measurements,
- identify the major features of the ambient data including means, relationships between sites and species, and sources of variability,
- compare MPCA monitoring methods and results with those of similar networks with stations in and around Minnesota, and
- guide future analyses by identifying areas for further investigation.

Weekly integrated particulate and gaseous species concentration data collected by the MPCA were analyzed in several ways. Quality assurance data collected in conjunction with the ambient monitoring program were examined to assess the accuracy and precision of the dry deposition data sampling and analysis methods. Exploratory statistical analyses identified unusual data values as well as the major features of the data including frequency distributions, seasonal and annual means, and correlations in weekly concentrations between monitored species and between sites. Trends in seasonal mean concentrations were computed and compared for selected species.

The MPCA sampling methodology was further evaluated by comparing data from sites co-located with those of other networks. Comparisons included data from the IMPROVE monitoring network operated by the National Park Service and data collected by the Ontario Ministry of Energy and the Environment. Comparisons did not include data from the Wisconsin Dry Deposition Network since no co-located monitoring took place. Data from all three monitoring networks were combined to examine the spatial variations in ambient data over the Minnesota–Wisconsin–Southern Ontario region.

Sites included in the MPCA dry deposition network are shown in Figure ES-1; site location information and the site abbreviations used throughout this report are presented in Table ES-1. The KOC and PAR sites are located within the Minneapolis–St. Paul (Twin Cities) metropolitan area, the CED site is located on the edge of this area, and all other sites are located in rural and remote parts of the state. Of the thirteen sites, four (CED, ELY, MAR, and SAN) were operational throughout most of the 1984–1993 period of network operations, the BIR site operated from 1987 to 1993, and the FIN site

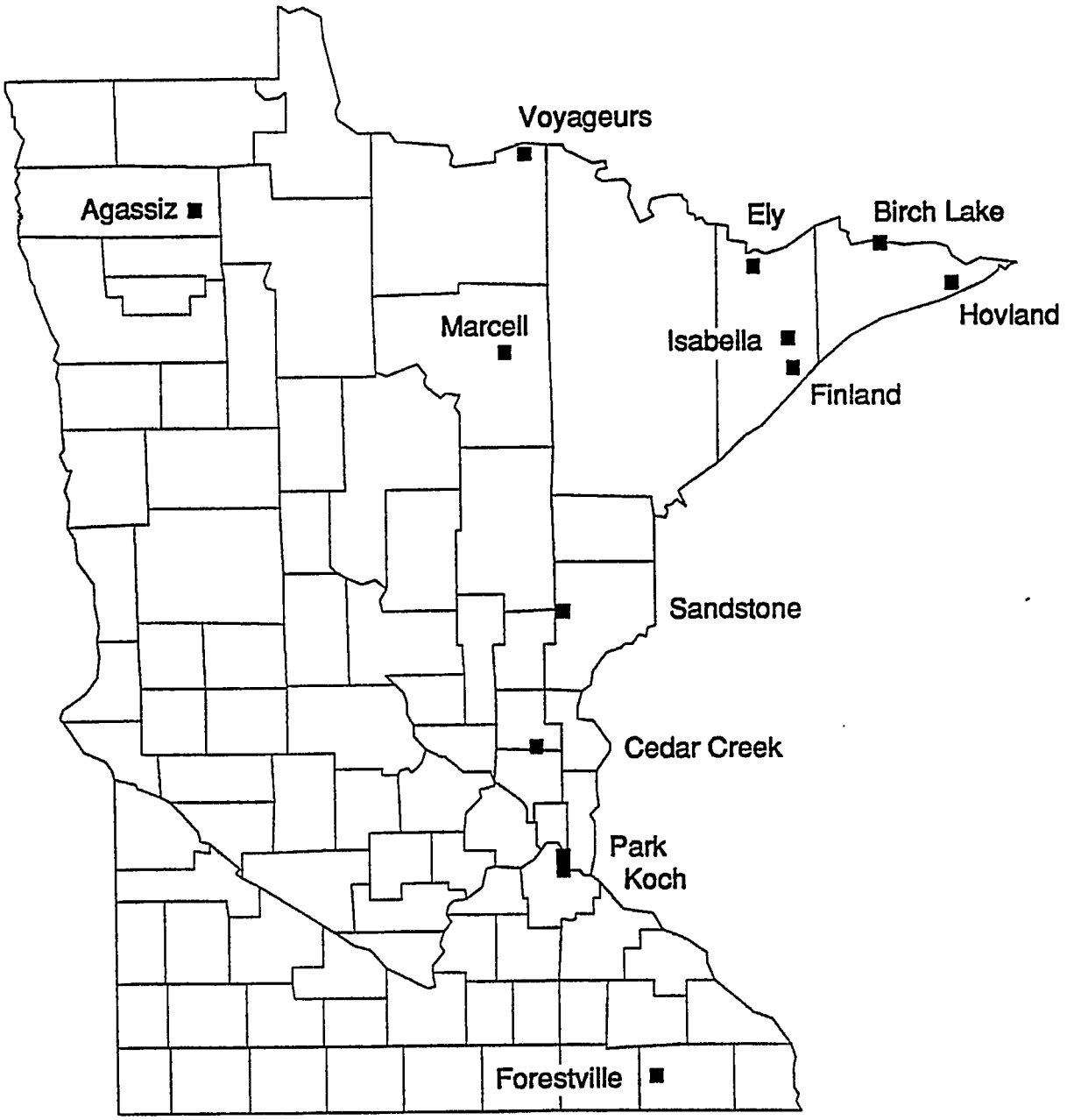

FIGURE ES-1. MPCA dry deposition monitoring sites.

TABLE ES-1. MPCA site descriptions.[1]

Site	Abbreviation	Location	Description
Agassiz	AGA	Lake Agassiz National Wildlife Refuge near Thief River Falls, MN	Remote, northwest Minnesota Vegetation: wetland vegetation, aspen/willow Minimal point and mobile sources Moderate agricultural impact
Birch Lake	BIR	Birch Lake on the Gunflint Trail near Grand Marais, MN	Remote, near Class I Wilderness area Vegetation: boreal forest, spruce/fir/aspen Minimal point and mobile sources impact No agricultural impact
Cedar Creek	CED	Cedar Creek Natural History Area near East Bethel, MN	Rural, near Minneapolis/St. Paul metro area Vegetation: red oak, old fields Significant point and mobile sources impact Significant agricultural impact
Ely	ELY	Fernberg Road near Ely, MN	Remote, near Class I Wilderness Vegetation: boreal forest, spruce/fir/aspen Minimal point and mobile sources impact No agricultural impact
Finland	FIN	Wolf Ridge Environmental Learning Center near Finland, MN	Rural, north shore Lake Superior Vegetation: red maple/northern hardwoods Moderate point and mobile sources impact No agricultural impact
Forestville	FOR	Forestville State Park near Preston, MN	Rural, southeast Minnesota Vegetation: northern hardwoods Moderate point and mobile sources impact Significant agricultural impact
Hovland	HOV	Minnesota Department of Natural Resources Forestry Station at Hovland, MN	Remote, north shore Lake Superior Vegetation: boreal forest, spruce/fir/aspen Minimal point and mobile sources impact No agricultural impact
Isabella	ISA	Isabella, MN	Remote, near Class I Wilderness area Vegetation: boreal forest, spruce/fir/aspen Minimal point and mobile sources impact No agricultural impact
Koch	KOC	Koch Refinery near Inver Grove Heights, MN	Urban, Minneapolis/St. Paul metro area Significant point and mobile sources impact Significant agricultural impact
Marcell	MAR	Marcell Experimental Forest near Grand Rapids, MN	Remote, north central Minnesota Vegetation: aspen/spruce/fir Minimal point and mobile sources impact No agricultural impact
Park	PAR	Ashland Oil Refinery near St. Paul Park, MN	Urban, Minneapolis/St. Paul metro area Significant point and mobile sources impact Significant agricultural impact
Sandstone	SAN	Grindstone Lake in Audubon Center of the Northwoods near Sandstone, MN	Rural, east central Minnesota Vegetation: northern hardwoods/white pine Moderate point and mobile sources impact Moderate agricultural impact
Voyageurs	VOY	Voyageurs National Park near International Falls, MN	Remote, near Class I Wilderness area Vegetation: aspen/spruce/fir Minimal point and mobile sources impact No agricultural impact

[1] Table prepared by MPCA Acid Deposition Program.

operated between 1989 and 1993. All other sites were only operational for relatively brief intervals.

Prior to 1 July 1987, the MPCA sampling system consisted of a three-stage stacked filter unit with a 8-μm polycarbonate coarse particle filter followed by a 1-μm teflon fine filter and a KOH-impregnated cellulose filter. Particulate matter collected on the first two particle filters was analyzed for anions (SO_4, NO_3, Cl) and cations (Ca, K, Mg, Na, NH_4) in solution and total particle mass (measurements from both filters were summed). SO_2 was determined from SO_4 absorbed on the KOH filter.[1] Beginning with samples collected on 1 July 1987 and continuing throughout the remainder of the monitoring period, the coarse particle filter was replaced with a 2-μm maximum pore size teflon filter and the middle fine particle filter was replaced with a 0.2-μm nylon filter for the collection of HNO_3 as NO_3. This filter was also analyzed for SO_4 to account for a small amount of SO_2 which did not pass through to the final KOH filter. Total SO_2 concentrations were thus defined as the sum of the concentrations determined from the nylon and KOH filters. As some SO_4 was found on KOH and nylon filters not exposed in the field, an adjustment to the SO_2 concentrations was made to account for the blank filter values. No adjustment was necessary for HNO_3 determined from the nylon filter. Finally, total adjusted SO_4 was defined as the sum of SO_4 from the KOH, nylon (with blank corrections), and particle filters and total NO_3 was defined as the sum of NO_3 determined from the nylon and particle filters. A complete list of analytes is presented in Table ES-2.

Major results and conclusions of the analyses described above are summarized in the following sections. Throughout this discussion, analyte concentrations from each filter are referred to by the acronyms defined in Table ES-2. For example, concentrations of SO_4 determined from the particle filter are referred to as PSO4.

ANALYSIS OF QUALITY ASSURANCE DATA

Quality assurance data collected by the MPCA (spiked filter analyses, duplicate samples, co-located measurements, blank filter analyses, interlaboratory comparisons, and external and internal QA audit reports) were used to assess the accuracy and precision of the sampling and analysis methodology. As no formal data quality objectives were established for this monitoring program, it is not possible to evaluate results from the QA data analysis in absolute terms. Nevertheless, reviews of MPCA site audits and examination of the above QA data indicate that the accuracy and precision of the MPCA sampling and analysis methods are reasonably good given the difficulties involved in making measurements of particulate matter and trace gases (some of which are quite volatile) in relatively clean, remote environments.

Accuracy of KOH and nylon filter SO_4 and NO_3 measurements at typical ambient concentrations observed at non-urban sites in the monitoring network was roughly ± 10 percent as determined from spiked filter analyses. Duplicate sample analyses indicated an average analytical method precision of better than 2.5 percent for these analytes. The

[1] All chemical symbols are defined in the Glossary.

TABLE ES-2. Analytes determined from MPCA monitoring data.

Filter	Analyte	Description[2]
KOH-impregnated cellulose	KSO4	SO_4 concentration from KOH-impregnated cellulose filter
	KSO2	SO_2 concentration from SO_4 measured on KOH-impregnated filter (equals 0.667 × KSO4)
Nylon	NSO4	SO_4 concentration from nylon filter
	NSO2	SO_2 concentration from SO_4 measured on nylon filter (equals 1.016 × NSO4)
KOH, nylon	TASO2	Total adjusted SO_2 (equals KSO2 + NSO2 where both KSO2 and NSO2 have been adjusted for respective blank values) (see text)
Nylon	NHNO3	HNO_3 concentration from NO_3 measured on nylon filter
Particle[1]	PSO4	SO_4 concentration from particle filter
	PNO3	NO_3 concentration from particle filter
	PCL	Cl concentration from particle filter
	PCA	Ca concentration from particle filter
	PK	K concentration from particle filter
	PMG	Mg concentration from particle filter
	PNA	Na concentration from particle filter
	PNH4	NH_4 concentration from particle filter
	PNO2	NO_2 concentration from particle filter
	PMASS	Total particle mass concentration from particle filter
KOH, nylon, particle	TASO4	Total SO_4 concentration (equals (1.499 × TASO2) + PSO4)
Nylon, particle	TNO3	Total NO_3 concentration (equals (0.984 × NHNO3) + PNO3)

[1] Represents sum of coarse and fine filters prior to 1 July 1987.
[2] See Glossary for list of chemical symbols. All concentrations are in $\mu g/m^3$ and were obtained by dividing weekly filter loadings by weekly air flow (see text).

more rigorous precision check provided by the co-located monitors revealed a total sampling and analysis system median precision of ±10–15 percent with 90 percent of observations falling within ±50 percent of each other.

Duplicate sample analyses indicated an average analytical method precision of better than 6 percent for PSO4, PNO3, and PNH4, while co-located samples showed that most measurements were within ±15 percent for PSO4 and ±40 percent for PNO3 and PNH4. A precision of ±20 percent was achieved for PMASS. EPA external audits indicated that PSO4 and PNO3 analyses were accurate to within about 4 percent and 2 percent, respectively.

QA data for the remaining particle filter analytes (PCL, PCA, PK, PMG, and PNA) indicated a level of precision that was lower overall than for the SO_4, NO_3, and NH_4 analytes. Measurements of PCL were the least precise by a wide margin, with 10 percent of co-located measurements differing by more than 100 percent and even larger

discrepancies found in the duplicate sample analyses. However, spiked filter analyses of PCL indicated that good accuracy can be achieved in the laboratory, at least at concentration levels typical of urban areas. The relatively large discrepancies frequently seen in co-located PCL measurements may be due to the presence of a small number of relatively large Cl-containing particles on one filter but not the other.

Trend analyses conducted for this study relied on the comparability of samples collected prior to March 1989 (which were analyzed by Interpoll Laboratories, Inc.) and samples collected after that date (which were analyzed by the MPCA Air Quality Laboratory). Direct comparisons of results from the two labs was not possible due to a lack of overlapping data. However, overlapping data were available for analyses of precipitation samples. An examination of these data suggested the possibility of large biases between the two laboratories for species other than SO_4 and NO_3. However, the data are insufficient to determine if these biases are characteristic of all measurements made over the monitoring period by each laboratory. Further analysis of this issue is warranted. In particular, a time series intervention analysis (Rao and Padmanabhan, 1983; Tiao et al., 1989) could be conducted to determine if a statistically significant shift in the data occurred at the time of changeover in laboratories.

Analysis of QA data from other indirect dry deposition monitoring networks was outside the scope of this study but would be useful for developing a context in which to judge the relative accuracy and precision of the MPCA network data and for identifying any areas in which improvements could be made.

EXPLORATORY STATISTICAL ANALYSES

The MPCA dry deposition data were found to have the following basic features:

- Examination of the raw data revealed at least 12 weekly concentrations that could be classified as outliers. These values are assumed to be unrepresentative of ambient conditions and were removed from the data set prior to further analysis. Some small negative concentrations, representing actual laboratory instrument responses, were also identified. These values were retained in the data to avoid biasing summary statistics. The negative values were small (in absolute terms) in comparison to median or average concentrations for all analytes except PCL. Some of the negative PCL concentrations at rural sites are larger in absolute value than those for other analytes and are large compared to the generally small median and mean PCL concentrations found at these sites. Further investigation of the negative PCL values is recommended, although their presence is not believed to have had a major effect on the analyses presented in this report.

- Annual mean concentrations computed for each analyte show a noticeable decrease in NSO4 concentrations in 1992 and 1993 that does not correspond to a similar increase or decrease in KSO4 concentrations. The cause of the smaller NSO4 values (especially in 1993) is not readily apparent, and further investigation is recommended.

- Distributions of all analytes were found to be skewed, with means greater than medians as is typical of ambient concentration data. Normal probability plots confirm that log-concentrations are normally distributed to within a good approximation. Linear correlations from these plots (which would be close to one for normally distributed data) are greater than 0.96 for all analytes.

- Seasonal summaries revealed that sulfur species (TASO4, TASO2, and PSO4) are more abundant during the winter and spring, possibly reflecting increased fossil fuel use during the cold weather months. TNO3 is less seasonally dependent, but NHNO3 is higher in the summer than in the winter, an effect that may be partially due to an actual seasonal difference in the partitioning of total nitrate into HNO_3 and particulate NO_3 and partially due to volatilization of particulate NO_3 during the summer. PMASS concentrations are highest in summer along with PCA and PMG, indicating greater amounts of soil dust during the warm season. Road salt impacts are evident in higher winter Cl concentrations at the urban sites (KOC and PAR) and near-urban site (CED).

- Site, season, and year factors each contribute a statistically significant portion of the observed variability in weekly concentrations of TASO2, NHNO3, PSO4, and PNO3. However, these three factors taken together account for less than half of the total variability.

- Significant differences in both analyte concentrations and the relationships between analytes were noted between the two urban sites (KOC and PAR) and the other sites in the network. The near-urban site (CED) exhibits characteristics between these two extremes. Concentrations of most analytes are higher at the urban sites, except those associated with soil dust. TASO2 concentrations are particularly high at PAR, indicating the influence of nearby sources. The presence of these sources also accounts for the different patterns in inter-analyte and inter-site correlations between PAR (and to a lesser extent between KOC and CED) and the more remote sites. Concentrations were found to be well correlated between remote sites for most analytes, and inter-analyte correlations suggest that these sites are responding to distant sources of SO_x and NO_x. More sophisticated approaches are recommended for further analysis of the relationships between analytes at each site and between sites for each analyte. In particular, factor analysis could be used to identify the major common factors responsible for the bulk of the observed variability in ambient concentrations.

ANALYSIS OF TRENDS

An analysis of linear trends in seasonal mean concentrations over the monitoring period revealed the following major features:

- SO_2 trends, estimated for the 1984–1993 period by assuming that the KOH filter SO_4 measurements made prior to 1987 were equivalent to the nylon plus KOH filter SO_4 measurements made after 1987, revealed decreasing concentrations in most seasons at all sites except FIN (where data are available only from 1988 on). Trends in the fall were statistically significant at all sites except at FIN and

at BIR (where data are available only from 1987 on). PSO4 trends were also negative in the fall at all sites with statistically significant values at CED, ELY, and MAR. Trends in other seasons are not significant. Trends in total SO_4 are similar to those for PSO4.

- PNO3 trends for the 1984–1993 period were generally positive with some statistically significant values at sites located closest to Minneapolis–St. Paul (CED and SAN). TNO3 trends for the 1987–1993 period were found to be generally negative in the spring and summer and positive in the fall and winter with the positive trend at SAN being the only statistically significant value.

- Trends in PCA were negative in all seasons at all remote sites (BIR, ELY, FIN, MAR) with some statistically significant values. In contrast, PCA trends were positive (although not statistically significant) at the two urban-influenced sites (CED and SAN).

- PNH4 trends were small and of mixed sign, with only one statistically significant value (a 0.047 $\mu g/m^3$ per year increase in the spring at SAN).

- PMASS concentrations decreased at all sites, with most spring and summer trends being statistically significant. These trends are consistent with the decreases in sulfates and calcium, although other species may also have contributed. PMASS concentrations decreased at CED and SAN despite the slight increases in PCA.

Additional trend analyses are recommended. In particular, it is recommended that trends in calcium/sulfate and ammonium/sulfate ratios be examined to determine the general change in acidity (Ca and Mg concentrations were found to be highly correlated at all sites). Also, application of more sophisticated trend detection techniques such as those reviewed by Cohen and Stoeckenius (1992) would help detect trends in cases of highly variable concentrations. This should be extended to examine trends over the network as a whole rather than just looking at individual sites. Finally, trends from these analyses should be compared with regional emission trends to identify potential cause-and-effect relationships. Emissions from a wide area must be considered as most of the SO_4 fine particle mass at the MPCA sites is estimated to originate from emissions occurring outside of Minnesota (MPCA, 1985).

COMPARISON WITH OTHER DRY DEPOSITION MONITORING TECHNIQUES

The MPCA sampling methodology differs in some respects from that used by other monitoring networks operating in the upper Midwest (IMPROVE, WDDN) and southern Canada (Ontario). The WDDN and Ontario networks use stacked filter samplers that operate on the same principles as those employed by the MPCA but with some minor differences in the arrangement of filters. IMPROVE samplers consist of separate filter modules for measuring non-nitrate particles, particulate nitrate, and SO_2. Comparisons of MPCA data with IMPROVE and Ontario sampler data at co-located sites were conducted to evaluate the impact of differences in sampling and analysis methods on the concentration measurements. Comparisons with Wisconsin monitoring data were not

possible since no co-located sites existed. Although the sampling methods are similar, a comparison of MPCA and Wisconsin monitoring data should be conducted to establish comparability.

Due to project resource constraints, no extensive quality assurance of the non-MPCA data was conducted, although a few obvious outliers were removed. It is believed that the data are generally of good quality, but additional data checking is recommended.

Comparisons of MPCA monitoring data with co-located IMPROVE and Ontario data were summarized in Table 6-17 (page 6-24), which includes a summary of the MPCA co-located monitor QA data to help put the inter-network comparisons in perspective. These comparisons indicate substantial variability and some potential biases between measurements made by the different networks. In the case of the IMPROVE data, these differences may be at least partially attributable to differences in sampling methods. Sampling methods at the Ontario sites, however, are very similar to those used by the MPCA and thus should be less of a factor. Of the two Ontario sites with co-located MPCA data (WLF and FRN), comparisons between WLF and the MPCA FIN site must be treated with caution as they are limited to only 10–15 samples, and these two monitors are located far enough apart to raise the concern that they are not truly equivalent. These limitations do not, however, affect comparisons between the FRN and MPCA ELY sites.

For all analytes examined, absolute percent differences between MPCA and IMPROVE and Ontario data are greater than between co-located MPCA data. These larger differences may be due to differences in either sampling or analysis methods. However, EPA audits of the MPCA analysis procedure for PSO4 and PNO3 showed agreement with other networks to within a few percent. Assuming similar results for the IMPROVE and Ontario analysis procedures, the larger inter-network differences must be due to differences in sample collection methods or other factors, at least for particulate SO_4 and NO_3. It is also possible that differences in analytical methods (e.g., ion chromatography vs. PIXE) contributed to the larger differences in some cases, especially for analytes that occur in significant non-soluble fractions.

Inter-network comparisons revealed the following major features:

- Best agreement between monitoring networks was achieved for particulate SO_4 although absolute percent differences are still three to four times greater than for the MPCA co-located site comparisons. SO_2 concentrations at the Ontario sites were slightly higher on average (0.4 $\mu g/m^3$) than corresponding MPCA measurements, although the bias was not constant over the observed range of concentrations. Comparisons with IMPROVE samplers could not be made due to a lack of data.

- Particulate NO_3 measurements at the IMPROVE and Ontario monitors were higher on average than corresponding MPCA values. These comparisons are subject to considerable scatter as indicated by regression R-square values of 0.2 for IMPROVE and 0.5 for Ontario.

- Concentrations of Ca, K, Mg, and, to a lesser extent, Na recorded at the MPCA ELY monitor were higher than those seen at the IMPROVE BOW monitor, most likely because the IMPROVE sampler is designed to collect only fine particles and these cations may frequently be associated with larger particles. Comparisons with the Ontario data for these analytes and Cl showed good agreement for Ca and a wider range of differences for Cl, K, Mg, and Na.

- Comparisons between NH_4 concentrations measured at the MPCA ELY and Ontario FRN sites showed large percentage differences, although the mean difference is small in absolute terms (0.07 $\mu g/m^3$).

SPATIAL ANALYSIS

Analysis of the spatial distributions of total sulfates and total nitrates in the Minnesota–Wisconsin–Southern Ontario region revealed similar patterns in concentrations averaged over all years and from year to year, with concentrations increasing from north to south and southeast. Minimum total sulfate concentrations occurred in extreme northeastern Minnesota and southern Ontario, with slightly higher values at the Ontario EAR and PKL sites further to the north.

Examination of spatial patterns in averages over all available data of TASO2, NHNO3, PSO4, PNO3, PCL, PCA, PNH4, and PMASS at MPCA sites revealed the following major features:

- TASO2 and, to a lesser extent, PSO4 concentrations decreased steadily to the north of Minneapolis–St. Paul (Twin Cities), although the mean TASO2 concentration at FIN was nearly twice that at BIR and ELY (all three stations were operational over roughly the same time period). PSO4 concentrations were only slightly higher at FIN. This pattern reflects the dominance of local SO_2 sources in the Twin Cities area and the possible impact of a nearby source at FIN.

- The spatial distribution of PNH4 was similar to that of PSO4, consistent with the assumption that most sulfate is in the form of ammonium sulfate.

- NHNO3 concentrations exhibited a less steep north-south gradient than TASO2 while PNO3 followed a distribution similar to that for PSO4.

- PCL concentrations were much higher at the urban sites (KOC and PAR) than at the non-urban sites, consistent with the pattern one would expect from road salt influences.

- PCA and PMASS concentrations were highest in urban areas and at sites influenced by agricultural activities, consistent with the expected distribution of soil dust loadings.

APPLICATION TO FUTURE ANALYSES

The results of this study indicate that the MPCA dry deposition monitoring network has produced high-quality data that accurately capture many significant aspects of ambient fine particle, SO_2, and HNO_3 concentrations in Minnesota. Many questions about the nature of ambient concentration levels were raised as a result of this investigation, and future analyses designed to address these questions are recommended as described above. Along with these analyses, the data can be used together with estimates of deposition velocities to calculate total dry deposition rates. Atmospheric dispersion and receptor modeling can then be applied to determine the relative contribution of emission sources to deposition and to formulate control strategies.