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Assessment of Temporal and Spatial Variability in Wet Sulfate and Nitrate Deposition

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Abstract: Precipitation chemistry measurements are collected in North America in part to monitor changes and to detect temporal trends in deposition. An analysis using seasonal wet sulfate and nitrate data over the period 1980–1984 is proposed. A principle component analysis indicates that there are no significant spatial shifts in the data. Seasonal deposition estimates for each of five regions are then determined by kriging. Temporal trends are assessed using first a run test. Subsequently, a pairwise seasonal comparison taking into account estimates of deposition uncertainties is used. The study reveals that there are significant temporal trends in sulfate and nitrate deposition in a region which includes South Eastern Ontario. The causes of the trends however, cannot be determined without the aid of a comprehensive model which takes into consideration the atmospheric processes.

Key words: Trends; wet sulfate and nitrate; principle component angle; kriging; run test.

1. Introduction

Some of the purposes for which precipitation chemistry measurements have been routinely collected in North America are: (1) to monitor changes and to detect temporal trends in deposition of pollutants related to acid deposition and (2) to aid in calibration or evaluation of performance of long range transport and deposition models. Once calibrated or evaluated, such models can be used to assess the impact of changes in emission rates and to evaluate various control strategies for reducing acidic deposition (Venkatram and Karamchandani (1986), Streets, Knudson, and Shannon (1983), National Acid Precipitation Assessment Program (NAPAP) (1987)).

Several wet deposition monitoring networks operate in the United States and Canada. These consist of: NADP/NTN (the National Atmospheric Deposition Program/ National Trends Network), MAP3S (the Multi-State Atmospheric Pollution and Power Production Study Network) and UAPSP (the Utility Acid Precipitation Study Program) in the United States, CAPMoN (the Canadian Air and Precipitation Monitoring Network) which includes sites from CANSAP (the former Canadian Networks for Sampling Acid Precipitation) as well as APN (the Air and Precipitation Monitoring Network), APIOS-C and APIOS-D (the Acidic Precipitation in Ontario Study: Cumulative and Daily Networks respectively) in Canada. These networks report their monitoring

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data to the Acidic Deposition System (ADS) in the United States (Olsen and Slavich (1986)).

NADP was established in 1978 in the United States by the Association of State Agricultural Experiment Stations. Its primary objective was to characterize spatial and temporal trends in atmospheric chemistry. In 1982, it was merged with the federally supported NTN and became the NADP/NTN. From the original sites it grew to 195 sites in 1985. Data are collected weekly under strict sampling protocols. MAP3S was created in 1976 in order to develop a data base for the evaluation of regional transport and deposition models. Samples from nine sites located in the northeastern United States are collected on a precipitation event basis. UAPSP was established in 1981 for a similar purpose as MAP3S and collects daily samples. CAPMoN, operated by the Atmospheric Environment Service, was established in 1983 through an upgrade and amalgamation of the CANSAP and APN networks. It includes 18 sites in eastern Canada. Samples are obtained on a daily basis. The objectives of CAPMoN are to measure temporal and spatial variations as well as long term trends in concentration of acidifying species in precipitation and air chemistry. From 1980 to 1983, CANSAP collected samples on a monthly composite basis. APIOS daily and cumulative networks were established in 1980 by the Province of Ontario in order to determine deposition patterns in Ontario. These networks deploy 36 sites located primarily in southern Ontario. The cumulative network has a sampling period of 28 days.

Each network has its own set of criteria for site selection as well as its own sampling and chemical analysis protocols (NAPAP (1987)). The choice of sampling time interval is closely linked with the objectives of the network: longer intervals being used in routine monitoring networks to capture long term trends in deposition, while shorter intervals (subevent to daily) in research networks are aimed at investigating short term variability. The networks maintain a high level of quality assurance and quality control from sampling in the field to laboratory analysis and final treatment of the data. These checks provide information on the accuracy and precision of the precipitation chemistry data collected. Accuracy refers to the bias between the laboratory analyses and a control and does not address the capability of a measurement to replicate the true atmospheric conditions. Precision refers to the ability to reproduce the same analytical result for consecutive analyses of the same sample. The calculation of seasonal and annual average concentration and deposition amounts from site data in the ADS data base follows a procedure recommended by the Unified Database Deposition Committee (Olsen et al. (1989)) to ensure that a standardized data set is created. The quality of the site data is judged by six quantitative measures of data completeness and site repesentativeness. The data completeness measures consist of: percent precipitation coverage length, percent total precipitation, percent valid sample length of record, percent valid samples, percent collection efficiency and percent seasalt correction. Each datum is assigned a level of quality from 1 to 4. Levels 1 and 2 data are considered to be of the highest quality and are appropriate for trend analysis and evaluation of acid deposition models. Level 3 data are of marginal quality and are considered to have rather high uncertainty. Their usage may be justified in assessing the effects of acid deposition on the environment. Level 4 data are generally not recom-

mended for use (Olsen et al. (1989); Voldner and Alvo (1989)).

In the next section, we present a brief survey of previous attempts to address temporal trends in deposition. A quantitative approach is then proposed for assessing the ability of the present networks to detect temporal trends in regional wet sulfur and nitrogen deposition for the period 1980–1984. It builds on work by Voldner et al. (1988) and Voldner and Alvo (1989).

2. Previous Approaches

Until 1986, studies of trends in acid deposition data in North America have been restricted either to individual sites or to a qualitative assessment of annual spatial patterns (NAPAP (1987)). The National Research Council (1986) reviewed the available literature up to 1986. Data obtained prior to 1970 were usually of insufficient quality or quantity to indicate long term trends in precipitation chemistry. An exception was data from the U.S. Geological Survey's (USGS) nine-site bulk sampling network in New York and Pennsylvania from 1965 to 1980 and data from the Hubbard Brook bulk sampling site in New Hampshire from 1964 to 1981. Hence, these data were analyzed by several authors (National Research Council (1986)). Hidy, Hansen, Hewy, Ganesan, and Collins (1984) reported a statistically significant decrease of about 2% per year in sulfate ion concentration at two sites in New York state, while similar results were reported for Hubbard Brook (Hales 1986) and Likens, Bermann, Pierce, Eaton, and Munn (1984)). The remaining U.S. sites showed either small decreases or no changes in sulfate concentration. Changes in the concentration of other ions at the Hubbard Brook and USGS sites were not consistent. Thus, changes in nitrate concentration were site dependent and variable. Results pertaining to the temporal variability for shorter periods around 1980, as found by the National Research Council (1986), Schertz and Hirsch (1985), Dana and Easter (1987) are reported in NAPAP (1987). Schertz and Hirsch (1985) and NAPAP (1987) used the Kendall seasonal test to determine the occurrence of a change during the period 1979–1982. In order to estimate the magnitude of the change, use was made of Sen's median slope technique. Regression models with a linear time term as well as terms for seasonal effects were used by Dana and Easter (1987). The coefficient of the linear time term provided an estimate of the rate change in the period. These studies restricted attention to a few individual sites and the results may not be applicable to larger regions.

To investigate spatial and temporal variability in concentration, Barrie and Hales (1984) and Summers, Bowersox, and Stensland (1986) visually compared hand drawn or objectively analyzed maps. Summers et al. (1986) also examined changes in regional totals computed from averaging site data within a region. Seilkop and Finkelstein (1987) analyzed annual trends in sulfate and nitrate deposition by making direct year to year comparisons on gridded data determined by an interpolation method known as kriging. Areas of $4° \times 4°$ were used in order to make area-wide comparisons. The fact that the error variance due to interpolation is reduced by considering areas makes such comparisons from year to year more sensitive than those made at individual points. It was noted that sulfate deposition decreased from 1980 to 1983 in the region with boundaries from southern Illinois to Ohio and western Pennsylvania to southern Ontario. Nitrate deposition decreased over northern Ohio, western Pennsylvania and New York. It was observed that the reasons for the

observed trends may be due in part to the reduced emissions during the period. NAPAP (1987)) and Endlich, Eynon, Fereh, and Maxwell (1986) visually compared patterns of annual average concentrations and deposition determined by kriging. For the years 1980–1984, it was found that maximal concentrations occurred in south-western Ontario and the northern Ohio River Valley states. Only within the area of highest concentrations did sulfate concentrations decrease. Year to year patterns for sulfur deposition varied more than the patterns for concentrations perhaps owing to changes in precipitation. Finally, it was noted that changes in the number of sites used in the interpolation could cause changes in the locations of the contour lines, irrespective of whether or not real changes in data occurred. This problem is especially important in regions with few monitoring sites. More recently, Ro et al. (1988) reported on wet and dry deposition of sulfur and nitrogen compounds in Ontario and observed that in all central and southern Ontario, the average wet sulfate deposition exceeded 20 kg/ha/yr. By computing area-wide arithmetic averages over monitoring site data in northern, central and southern Ontario, it was noted that year to year variations were small. Zemba, Golomb, and Fay (1988) presented 1982–1985 average spatial and seasonal wet sulfate and nitrate deposition patterns in eastern North America. Spatial patterns were depicted as contour maps determined from a mathematical algorithm which "interpolates irregularly spaced data to an internal grid". The authors identified that the "highest sulfate depositions (greater than 35 kg/ha/yr) occurred over the region which includes west Pennsylvania, the Virginias, east Michigan and southern Ontario between Lakes Huron and Erie." On the other hand, nitrate depositions were highest (greater than 20 kg/ha/yr) in the region between Lakes Michigan and Ontario. It was noted that the contour map for annual wet sulfate was orientated along a south west to north east axis. The seasonal nature of the data was "addressed" by averaging over the months from April to September during which time it is stated 65 to 70% of the total deposition is received. The choice of a long averaging period may obscure important seasonal fluctuations. The authors however, were concerned with reductions and claim that the deposition patterns resemble the emission patterns over this period. Seilkop and Finkelstein (1987) also made a similar observation for annual deposition.

Our results generally support the findings of Zemba et al. (1988), Ro et al. (1988) and Seilkop and Finkelstein (1987) but provide further information on the time of occurrence of the trend, its general location in terms of region and its magnitude.

3. The Problem of Trend Detection

There are a number of considerations on the problem of detecting trends in deposition in eastern North America. Measurements are often collected by the monitoring networks at irregularly spaced locations and at varying time intervals (daily, weekly or monthly). Variability in site data may result from microclimatic conditions or from changes in local emission sources. There may be changes in a network's protocol such as changes in instrumentation and sampling time which may affect the data. Sampling error in field collection and laboratory analyses as well as differences in protocols between networks are causes of concern. For longer sampling periods, as a result of evaporative losses, the concentration in precipitation tends to be greater leading to higher estimates of deposition, if the UDDC procedure is used. These

measurements are also more prone to contamination. Finally, there may be missing data which need to be compensated for. This compensation introduces errors which can be substantial if major events are missed (Barrie and Sirois (1986)). As seen in Section 4, differences in deposition estimated from co-located samplers may exceed the variability between years. Hence, the detection of trends from individual sites may be difficult.

The problem of trend detection in deposition data has been interpreted as the detection of changes on the deposition patterns recreated from the site data (e.g., Seilkop and Finkelstein (1987); NAPAP (1987); Voldner and Alvo (1989)). By focusing attention to the spatial patterns generated from the site data, one attempts to compensate for local variability and measurement errors which can be considerable. The use of patterns in reporting and in analyzing precipitation chemistry measurements has recently gained in popularity (Eynon and Switzer (1983); Finkelstein (1984); Voldner et al. (1988); Endlich, Eynon, Fereh and Maxwell (1986); Hsu (1986); Seilkop and Finkelstein (1987); NAPAP (1987); Voldner and Alvo (1989)). Egbert and Lettenmaier (1986) proposed an analysis which takes into account the space-time structure of deposition data. However, their approach which is based in part on kriging, requires more extensive data. In the present study, we are concerned with estimating deposition over relatively large regions in North America (NAPAP (1987)). The use of regions provides a spatial smoothing which tends to reduce the variability in pattern incurred by changes in both the quantity and the location of monitoring sites. This point has already been noted by Seilkop and Finkelstein (1987). Such regions must be chosen large enough to permit a smoothing of local variability, yet small enough not to obscure regional trends.

The regions chosen here are defined in part along geographic boundaries and in part on the basis of emission/deposition levels (Clark et al. (1989)). Although this choice is subjective and can subsequently be refined in further studies, it serves at present to illustrate our approach. As to the choice of time interval, in an effort to reduce short-term temporal variability, it was decided to restrict attention to seasonal deposition. The seasons were defined as follows: winter: December, January and February; spring: March, April and May; summer: June, July and August; fall: September, October and November.

Centroids and the principal component angle as determined from site data are used to investigate the shift in pattern from season to season or from year to year. Highly fluctuating patterns may obscure trends in deposition in a region. It should be pointed out that through pattern shifts, deposition in a region may remain constant although deposition in a sub-region may be grossly altered. Also, the occurrence of pattern shifts may lead to a comparison of a high deposition region in one season with a low deposition region in another. These situations should be avoided. The determination of centroids and the principal components angle are discussed in Section 5.

The estimates of deposition over regions are derived using kriging, an interpolation method named after the mining engineer D.H. Krige who first popularized its use. The method, briefly described in Section 6, has received considerable attention in recent years (Barnes (1980)) and it has been used in the analysis of acid precipitation data (Eynon and Switzer (1983); Le and Petkau (1988); Finkelstein (1984); Seilkop and Finkelstein (1987); Voldner and Alvo (1989)).

Further analyses are performed for each region by treating the seasonal data as a time series beginning with winter 1980. Seasonal data naturally provide a longer time series and more importantly, they provide the continuity in the distribution of deposition over the year (Voldner et al. (1988)). The effect of seasonality is reduced by subtracting the mean for each season from the seasonal values. The time ordered residuals are then tested for large scale trend using the median Run test with a 5% level of significance (Gibbons (1971), p. 62). A run is defined as a consecutive collection of residuals all either above or below the median. If the data do not exhibit a trend, then a moderate number of runs is expected. In the case of a trend however, there should be fewer runs. The Run test which proceeds under the assumption that every ordering of the data in time is equally likely, is frequently used in time series analyses to test for trends. A shortcoming of the test in our context is that it implicitly assumes that the uncertainty is the same for each seasonal estimate. Moreover, it does not permit a quantification of the observed change.

A more detailed pairwise analysis is then used to determine the magnitude of observed changes and to assess their significance. In order to assess the significance of an observed change in a region from one season to another, we compute the ratio

$$|S_1 - S_2|/\{\text{var } S_1 + \text{var } S_2\}^{1/2}$$

where S_1 and S_2 represent depositions in different seasons. The two seasons were considered to be significantly different if the ratio above exceeded 1.96. If each difference has a normal distribution, the level of significance is then .05 for each pairwise comparison. Although not considered here, an overall level of significance can be obtained from the Bonferroni inequality (Miller (1981)) in the case where several simultaneous pairwise comparisons are made. For example, if each of k pairwise comparisons is made at level α/k, then the overall level will be at least α.

4. Variability in Site Data

In order to quantify the within site variability, the standard deviations relative to the mean for both annual wet sulfate and nitrate deposition were computed at co-located or closely located sites (within

Table 1. Ratios of average standard deviation within sites to average standard deviation between years for wet sulfate

Cluster*	Annual	Winter	Spring	Summer	Fall
Fernberg, Minn.	.56	...	.24	.26	1.00
Dorset, Ont.	1.55	.77	.79	.84	.83
Kejimkujik, N.S.	.15	.55	.16	.33	.30
Pennsylvania State, PA.	.40	.88	.25	.67	.77
Bondville, Ill.	.59	...	.28	.34	.46
Walker B., Tenn.	.14	.04	.19	.27	.50
R.T.P., N.C.	.14	.09	.05	1.00	2.47
Clinton, N.C.	.44	.25	.22	.61	.85
Finley, N.C.	.16	.07	.14	.47	.30
Selma, Ark.	.13	.24	.19	.18	.08

...Value unobserved.
*Site information are available from the Unified Data Base Committee.

Table 2. Ratios of average standard deviation within sites to average standard deviation between years for nitrate

Cluster	Annual	Winter	Spring	Summer	Fall
Fernberg, Minn.	1.25	...	.29	.22	1.00
Dorset, Ont.	2.12	1.16	.86	.98	1.06
Kejimkujik, N.S.	.20	.59	.27	.23	.88
Pennsylvania State, PA.	.22	.36	.05	.28	.61
Bondville, Ill.	.94	...	.27	.28	.96
Walker B., Tenn.	.39	.52	.14	.21	.40
R.T.P., N.C.	.27	.12	.07	.50	3.29
Clinton, N.C.	.48	.33	.27	1.23	.78
Finley, N.C.	.27	.28	.19	.43	.26
Selma, Ark.	.17	.28	...	...	.24

...Value unobserved.

50 km) for the period 1980–1984. The site data obtained from the ADS data base meet the level 1 or level 2 criteria for quality. Tables 1 and 2 display the ratio of the average annual and seasonal standard deviations within sites to the average standard deviation between years for corresponding periods for sulfate and nitrate, respectively. For a given site, let d_{ij} represent the deposition at year i and collector j, where $j = 1, 2, \ldots, J_i$ and $i = 1, 2, \ldots, I$. Define $n = \sum J_i$, and let

$$r = \frac{\{\sum\sum((d_{ij} - \bar{d}_i))^2/(n - I)\}^{1/2}}{\{\sum(\bar{d}_i - \bar{d})^2/(I - 1)\}^{1/2}} \quad (4.1)$$

where $\bar{d}_i$ is the average deposition over all collectors at the monitoring site for year i and $\bar{d}$ is the average deposition over all collectors and all years at the given site. The ratio in (4.1) is related to the F-ratio in the analysis of variance. Although strictly speaking, no critical values can be used to assess the significance of the values obtained in view of the obvious spatial correlation of the data for closely located sites, nevertheless, intuitively one feels that a ratio greater than or equal to 1 would cast doubt on the use of site data for trend detection. The within site variability in that case would mask the variation between years. As seen from Tables 1 and 2, for several sites in the high deposition region we observe annual ratios greater than 0.4. At Dorset, the ratios are close to or greater than 1. These results indicate that the narrow use of the site data alone may not be sufficient for detecting trends unless changes of the order of 40 percentage points or more are expected.

The data used in the rest of this study were obtained from the ADS data base and satisfy a level 1 or 2 criteria as outlined by the Unified Acid Deposition Committee

Table 3. Number of sites for the analysis of sulfate and nitrate deposition

Year	Annual	Winter	Spring	Summer	Fall
1980	38	47	51	64	76
1981	48	63	69	81	58
1982	70	79	101	117	107
1983	82	87	120	113	119
1984	90	100	111	120	107

(Olsen et al. (1989)). For wet sulfate, the units are in kg/ha of sulfur whereas for nitrate they are in kg/ha of nitrogen. The number of sites used which varied from season to season are shown in Table 3. It can be seen that there were fewer sites available in 1980–1981 than in later years.

5. Detecting Shifts in Patterns

In order to detect changes in the position and orientation of the spatial patterns suggested by the measurements we computed on the basis only of the site data, both the centroids and the angle of the first principle components with axes anchored at the centroid. Let x_i represent the vector co-ordinate indicating the location of the ith site and let z_i denote the corresponding deposition measurement. Then, the centroid c is defined to be the weighted average of the coordinates of the site data with weights proportional to the deposition

$$c = \sum w_i x_i,$$

where

$$w_i = z_i / \sum z_i, \quad i = 1, \ldots, n.$$

This choice of weights permits comparisons between patterns in different seasons. The angle of the first principal component, measured clockwise from north, is determined from a weighted principal component analysis performed on the coordinates of the monitoring sites with weights proportional to deposition. Principal component analysis as applied in this case, treats the coordinates of the sites as variables and considers a covariance function different from that used in kriging. The goal of this analysis is to determine spatial rotations in the patterns. The use of these measurements the context of acid deposition data was first investigated in the ISDME study (Voldner et al. (1988); Clark et al. (1989)). The statistical package SAS was used to perform this analysis.

6. Kriging

The interpolation method known as kriging is favoured over other methods because it permits a quantification of the uncertainty in the interpolation estimate. Various authors have provided details of the technique (Delhomme (1978), Journel and Huijbregts (1978), Ripley (1981)) and only a brief description of simple kriging will be presented here. Consider a two-dimensional spatial domain R. Let $Z(x)$ be a real valued stochastic process describing the deposition at position x where x takes values in R. Suppose that deposition is measured at monitoring sites $x_1, \ldots, x_n$. Let the deposition over a region A be denoted by $Z_0 = \int Z(x)\, d(x)$, where the integration is over A. The case where A consists of a single point is included in this formulation. Set $Z' = (Z_1, \ldots, Z_n)$ where $Z_i = Z(x_i)$. A linear estimator of Z_0 is an estimator of the form $\alpha^t Z$, where α is a vector of weights. Simple kriging as frequently used in practice (Delhomme (1978); Finkelstein (1984); Seilkop and Finkelstein (1987); Eynon and Switzer (1983)), assumes that:

1. $EZ(x) = m$, a known constant and
2. $\Gamma(x_i, x_j) = 1/2E(Zi - Z_j)^2$ is a function only of the distance $\| x_i - x_j \|$.

The function Γ is called the semi-variogram and is related to the covariance function in the case where the process Z has finite variance. The weights α are chosen so as to minimize the expected square error $E(\alpha^t Z - Z_0)^2$.

Since the process is assumed to have constant drift, the estimator will be unbiased (i.e., $E\alpha^t Z = m$) if and only if the weights sum to 1 (i.e., $\Sigma_i \alpha_i = 1$). The use of the semi-variogram eliminates the need to know

the drift for estimating either the semi-variogram or the deposition Z_0. The approach has been criticized by Venkatram (1988) and by Fedorov (1989) for the assumptions made about both the trend surface and the intersite correlation. Venkatram (1988) suggests that the assumption of constant drift can be substantially weakened by substituting for the drift the estimate provided by a simple long range transport model which would take into account the atmospheric processes. The approach espoused by Venkatram (1988) is misleading because it presupposes that the drift can be estimated without error by a simple long range transport model. As seen in the recent ISDME study (Clark et al. (1989)), care must be taken in choosing a simple long range transport model. Models which grossly under or over estimate the deposition may result in a poor spatial pattern. The suggestion does have merit, however, although it would be preferable to incorporate the inital estimate of the drift obtained from a comprehensive model within the framework of a Bayesian kriging analysis as detailed by Omre (1987). This was not attempted in this study.

Fedorov (1989) makes the argument that the estimate of the semi-variogram from site data is inadequate and that assumption 2 is unwarranted in most applications in environmental studies. In order to validate the variogram model in our case, residuals were computed by successively deleting the site data, only one at a time, and computing an estimate on the basis of the remaining sites. The differences between the estimate and the known value at the site were then computed. We report in Figure 1 a typical analysis for 1980 annual data. Predicted values are plotted against site data and the correlation R of the regression is shown. It can be seen that

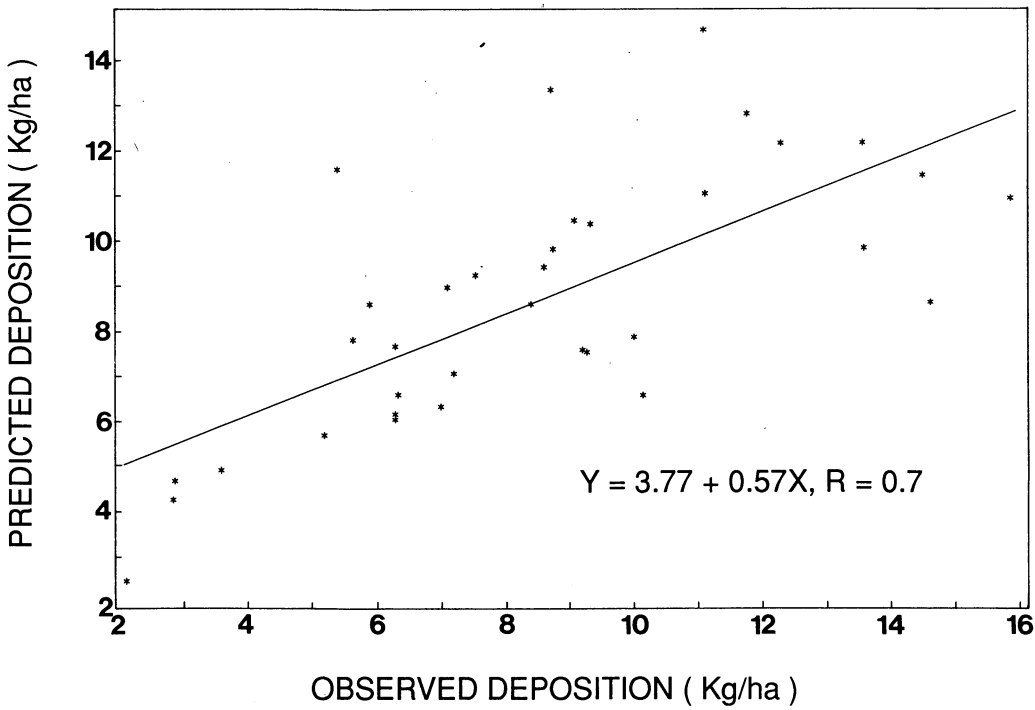

Fig. 1. Predicted and observed 1980 annual sulfate deposition

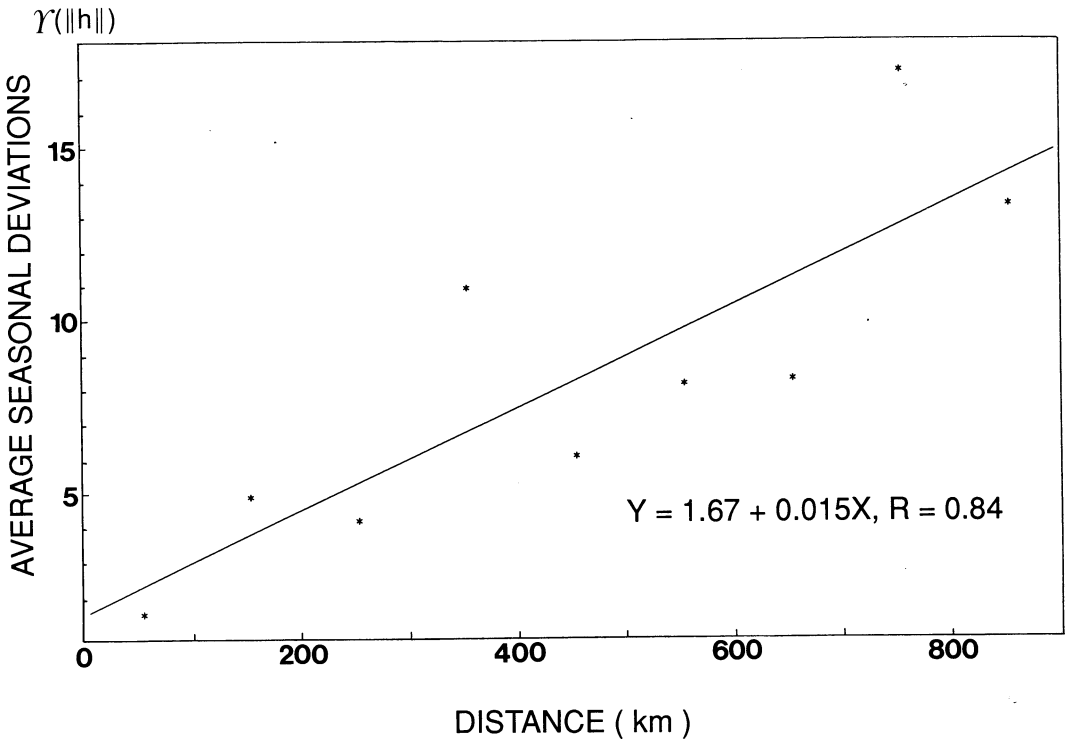

Fig. 2. Typical semi-variogram for seasonal depositions

a straight line provides a reasonable fit. Standardized residuals were computed and shown to lie mostly within ± 2.

In order to estimate the semi-variogram, we computed for several distances $\|h\|$, the average of the squared deviations between measurements at a distance $\|h\|$

$$\gamma(\|h\|) = 1/2 \sum \{Z(x + h) - Z(x)\}^2 / N(h),$$

where $N(h)$ represents the number of pairs of sites at a distance $\|h\|$ apart and the sum is taken over all such pairs. These values were then regressed against distance. In our analysis, owing to the sparsity of data in some regions, regional estimates of deposition were determined separately but using a common variogram, one for each season. In Figure 2, a typical variogram is shown along with a straight line fitted using a linear regression. The correlation coefficient R of the regression line is also indicated. Similar variograms were fitted by Finkelstein (1984) and by Seilkop and Finkelstein (1987) for annual data. The semi-variogram typically is positive when $\|h\| = 0$. This implies that two distinct points even though close to one another will exhibit a difference measured by the discontinuity of the semi-variogram at 0. In the literature, this phenomenon is called the "nugget effect" and is the result of local effects. The use of directional variograms did not substantially alter either the pattern or the variance estimates and consequently were not employed in this study. Similar findings were reported in Seilkop and Finkelstein (1987). Finally, it should be stated that Fedorov ((1989), p. 182) in his discussion proposes to weaken the assump-

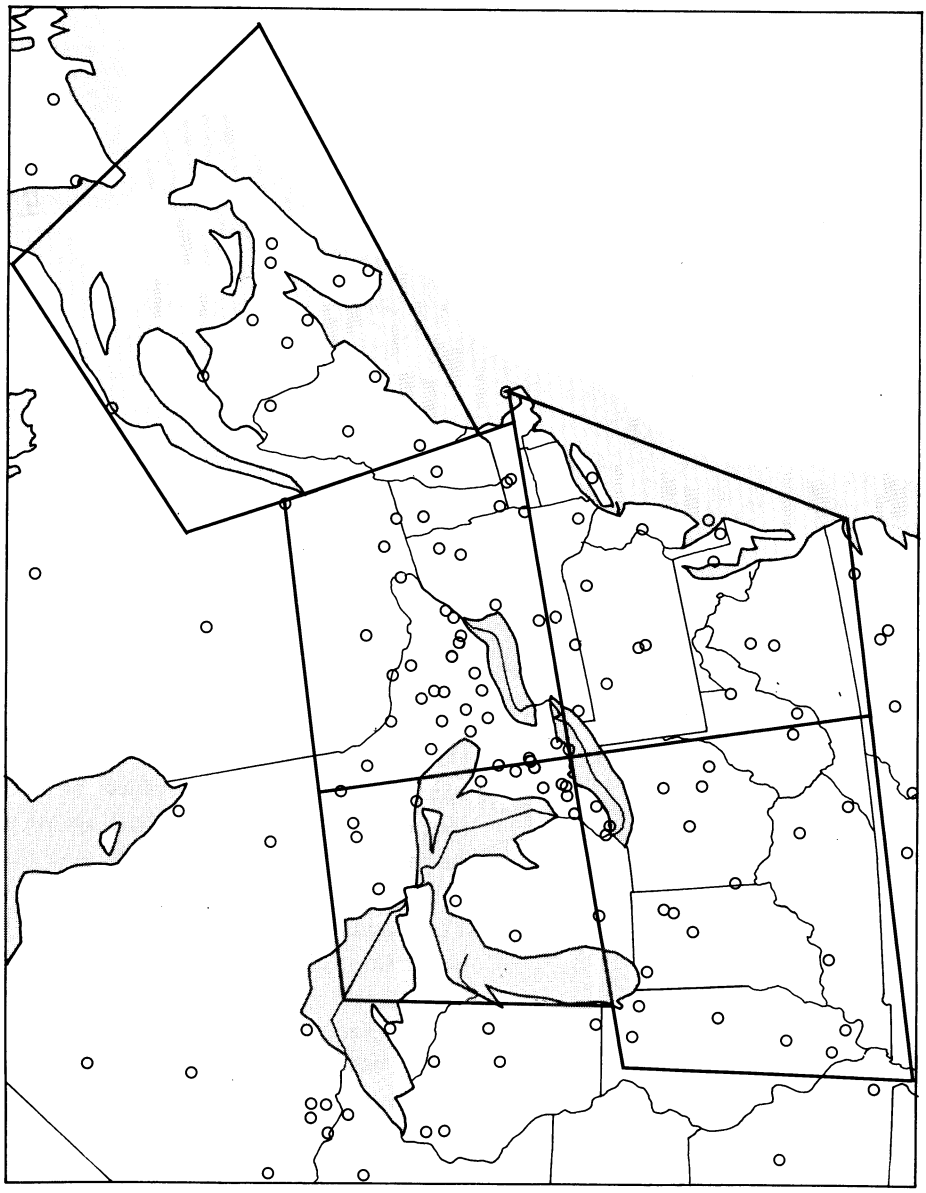

Fig. 3. Monitoring sites and regions used in eastern North America

tions made in simple kriging but only by proposing others which to quote the author are "practically nonverified."

7. Partitioning the Eastern North American Region

The eastern North American region was partitioned into five regions chosen to take into account the spatial resolution of the sites and the natural geographical boundaries. These along with the location of the sites are shown in Figure 3. The North region, which has an area of $6.7 \times 105\,km^2$ includes Lake Superior, Lake Michigan, Lake Huron and parts of Lake Erie. It encompasses the large urban centres of Michigan and Illinois. The North Central region is of the same size and includes Lake Ontario, part of Lake Erie and the region of south eastern Ontario. The North East region has an area of $8.1 \times 105\,km^2$ and includes the Maritimes and part of Newfoundland. The South region, having an area of $7.1 \times 105\,km^2$, includes the states of Ohio, Tennessee and the rest of Illinois. It represents a high emission region as noted for example by Zemba et al. (1988). Finally, the South East region is the smallest with an area of $4.8 \times 105\,km^2$. It includes the eastern states of Pennsylvania, West Virginia as well as the Appalachian mountain range. For the purposes of interpolation, grid sizes of approximately $1° \times 1°$ were chosen.

8. Results

The evaluation of the centroid for both wet sulfate and nitrate reveals that the seasonal variability is of the order of one degree in latitude and slightly greater in longitude. The centres of the patterns in winter are somewhat further north than for the other seasons. Consequently, the seasonal patterns do not exhibit any pronounced shifts in overall location pointing perhaps to the stability of the wind patterns. The principle component angles for both sulfate and nitrate, shown in Figure 8, exhibit an intra-year variability of less than ten degrees. The inter-season variability is of the order of five degrees. The principal angle for nitrate is slightly more towards the east than the angle for sulfate. The overall stability of the location of the patterns indicates that there have been no significant spatial shifts. Hence, it is reasonable to proceed with an analysis of temporal trends in the regions chosen.

Contours of both sulfate and nitrate deposition (reported in kg/ha sulfur and nitrogen respectively) were determined for each season for the period 1980–1984 using simple kriging as described in Section 6. Hence, for each season, a single mean and a single variogram were used for all five regions. To illustrate the results, the contours for 1984 are shown in Figures 4–7. These resemble concentric ellipsoids whose orientation is generally south-west to north-east. For annual deposition, this was previously noted by Seilkop and Finkelstein (1987) and by Endlich et al. (1986). It can be seen that the deposition values for sulfate (respectively for nitrate) in both spring and summer are comparable. In those seasons, the maximum for sulfate is seen to occur in west Pennsylvania. For fall and winter, the deposition values for sulfate and nitrate are much lower. Generally, the contour levels for deposition are lower during the period 1983–1984 compared to 1980–1981 as are the corresponding estimates of uncertainty. In part, this may be due to the fewer number of monitoring sites and valid data available during the period 1980–1981. The deposition values at the sites may vary by a factor of three from one year to the next. This is especially true in the high deposition regions of West Virginia, Pennsylvania, and the

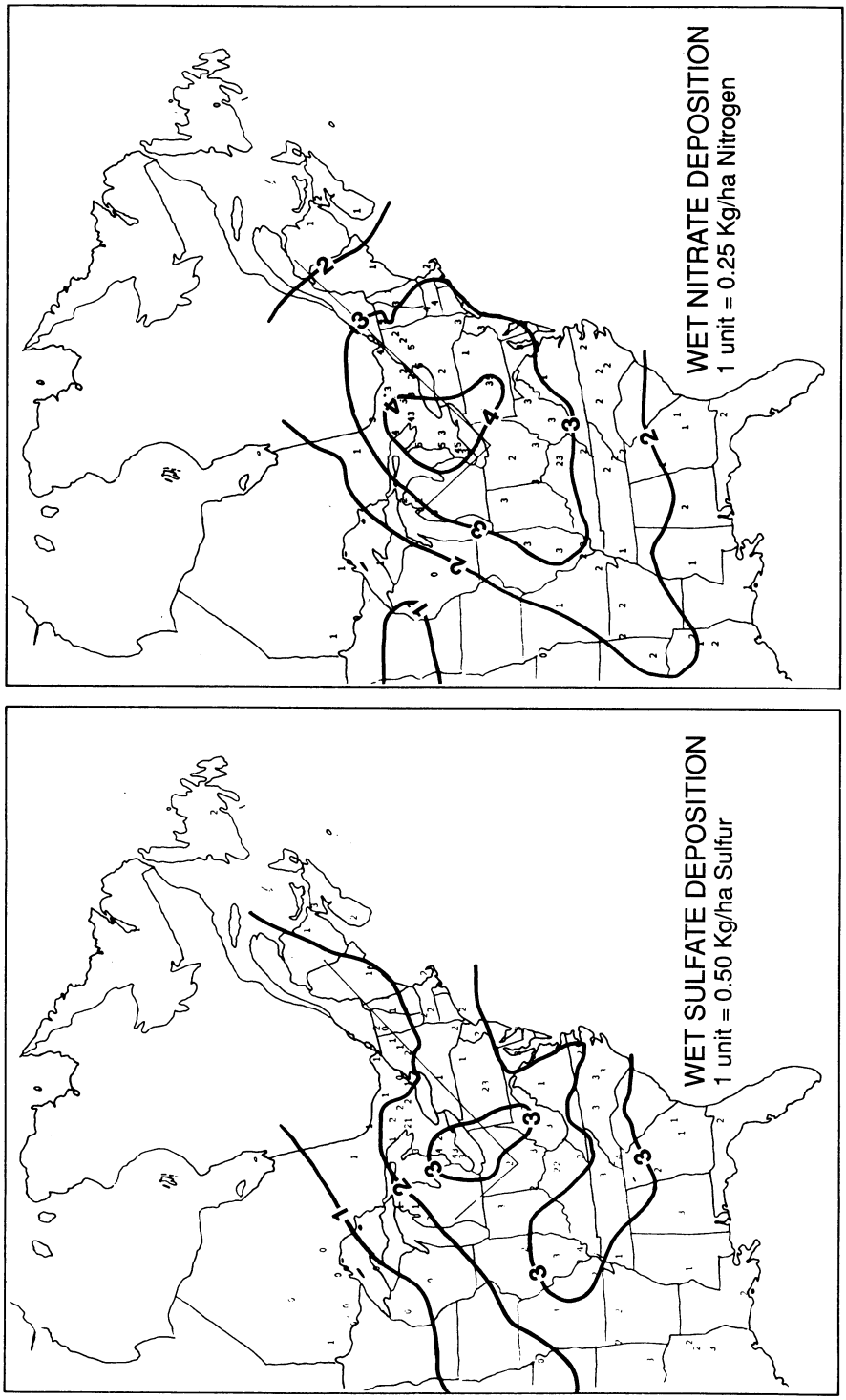

Fig. 4. Contour plots for 1984 winter sulfate and nitrate depositions

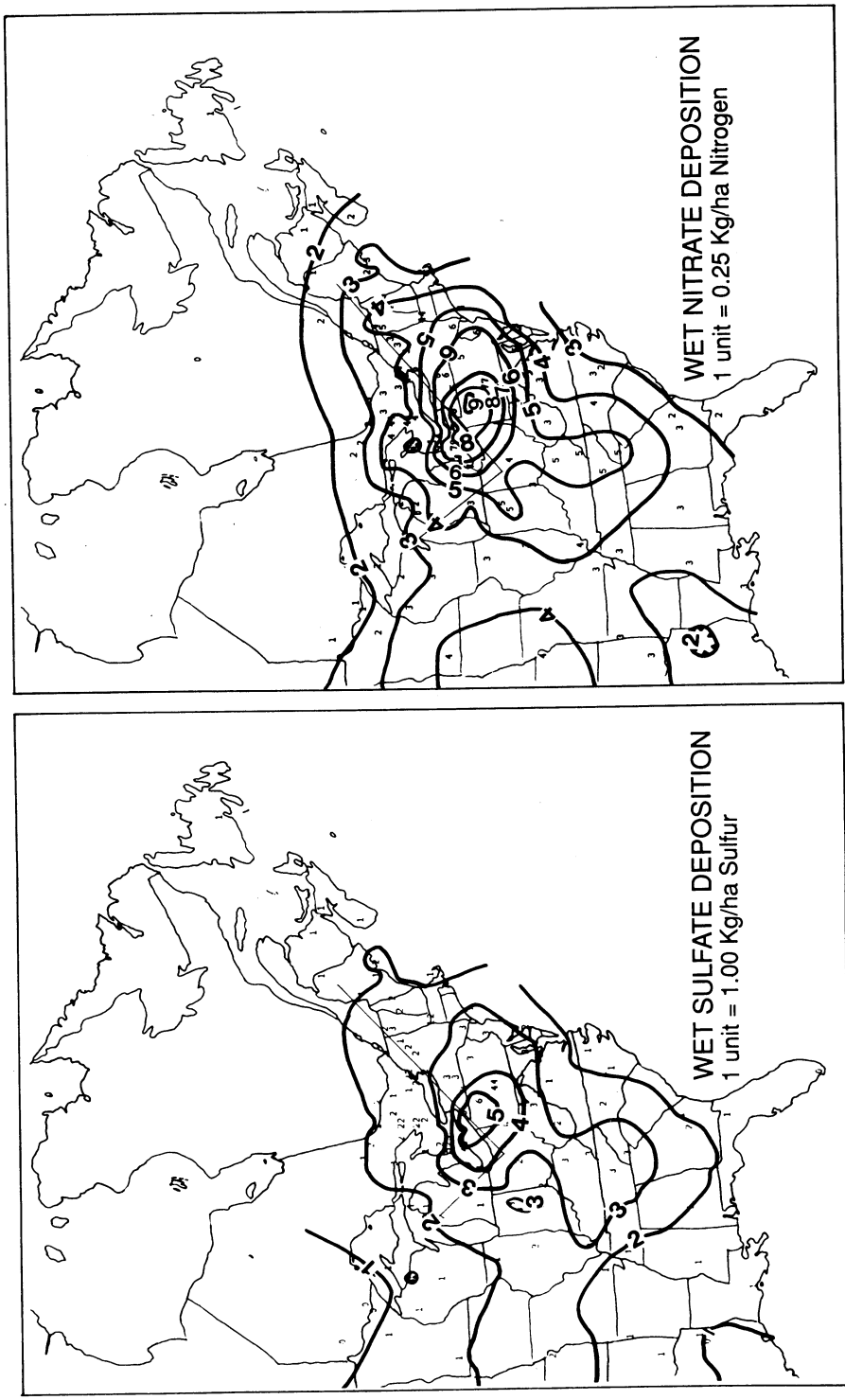

Fig. 5. Contour plots for 1984 spring sulfate and nitrate depositions

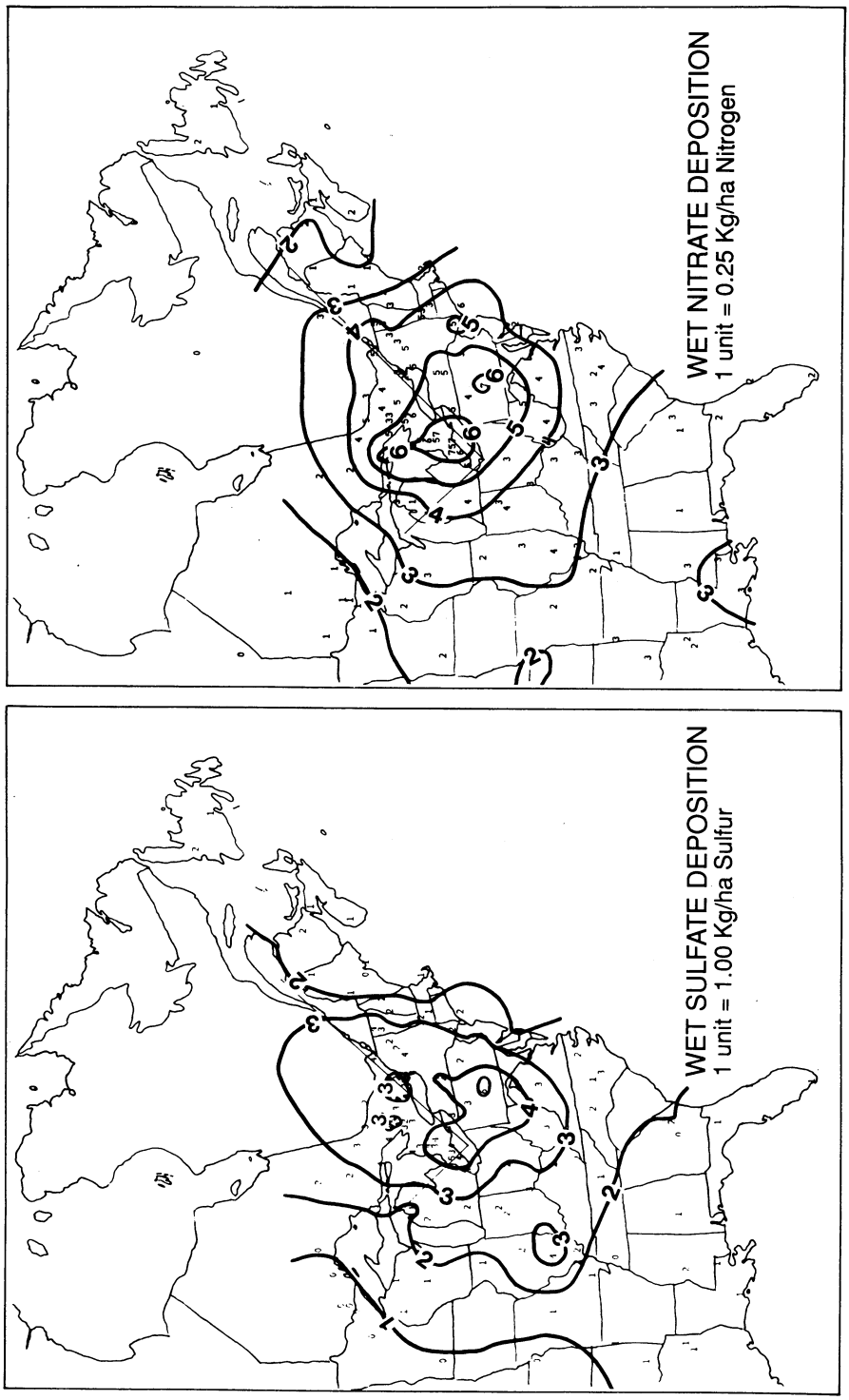

Fig. 6. Contour plots for 1984 summer sulfate and nitrate depositions

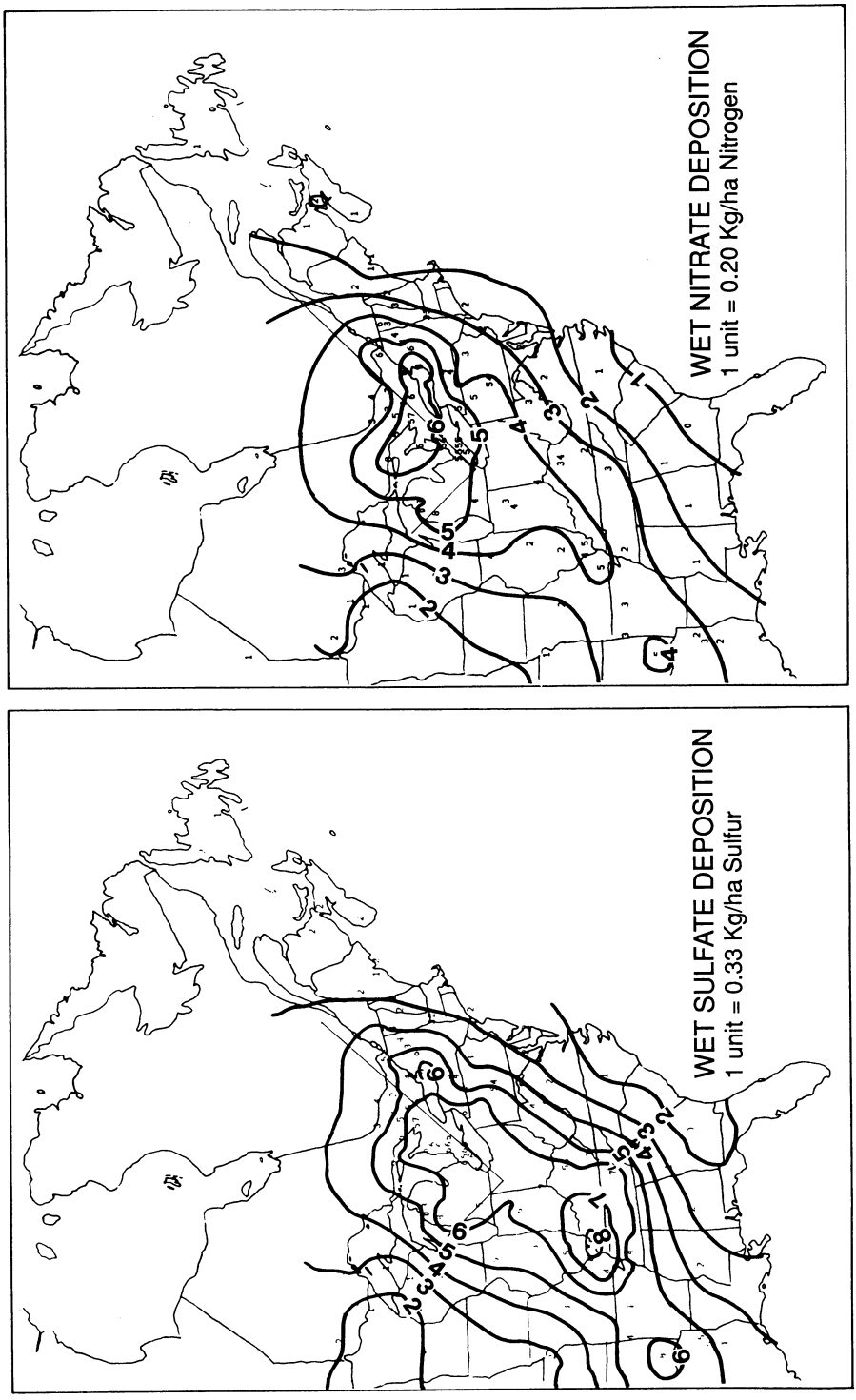

Fig. 7. Contour plots for 1984 fall sulfate and nitrate depositions

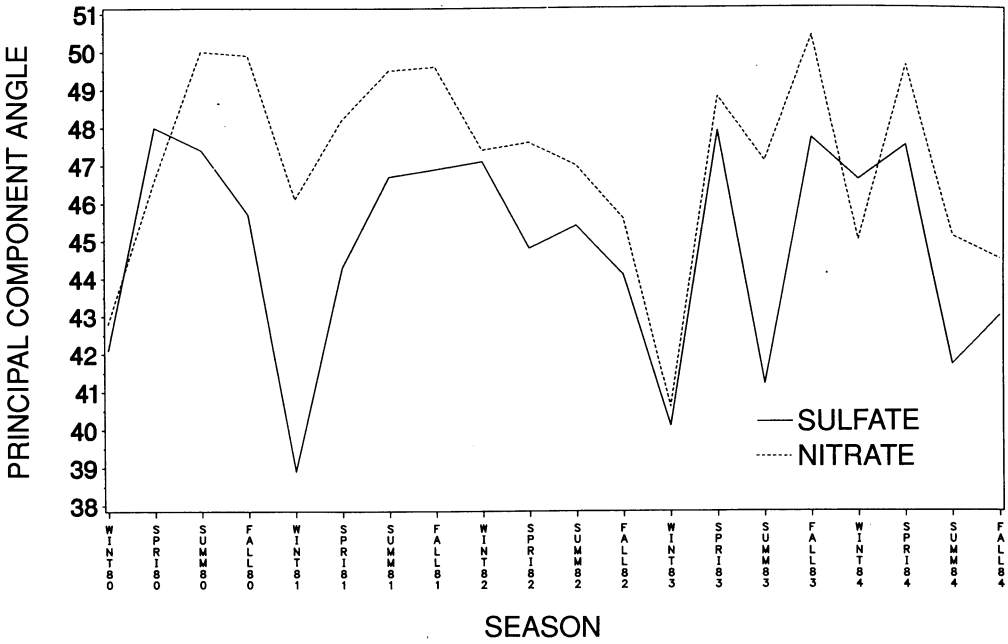

Fig. 8. Angle of principal component for sulfate and nitrate

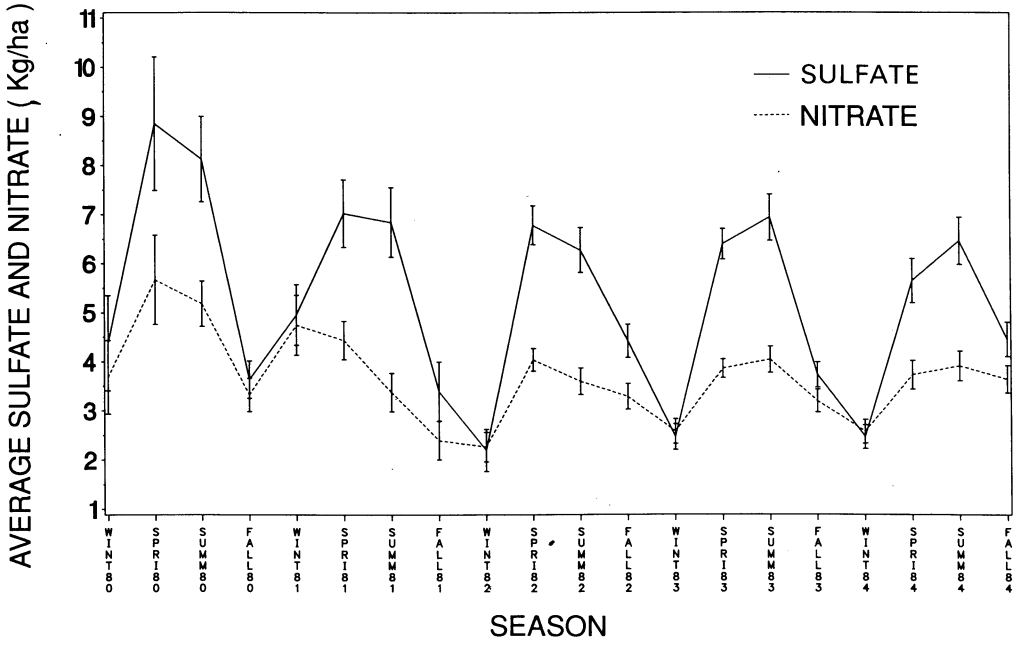

Fig. 9. Average sulfate and nitrate depositions in Kg/ha. North Region

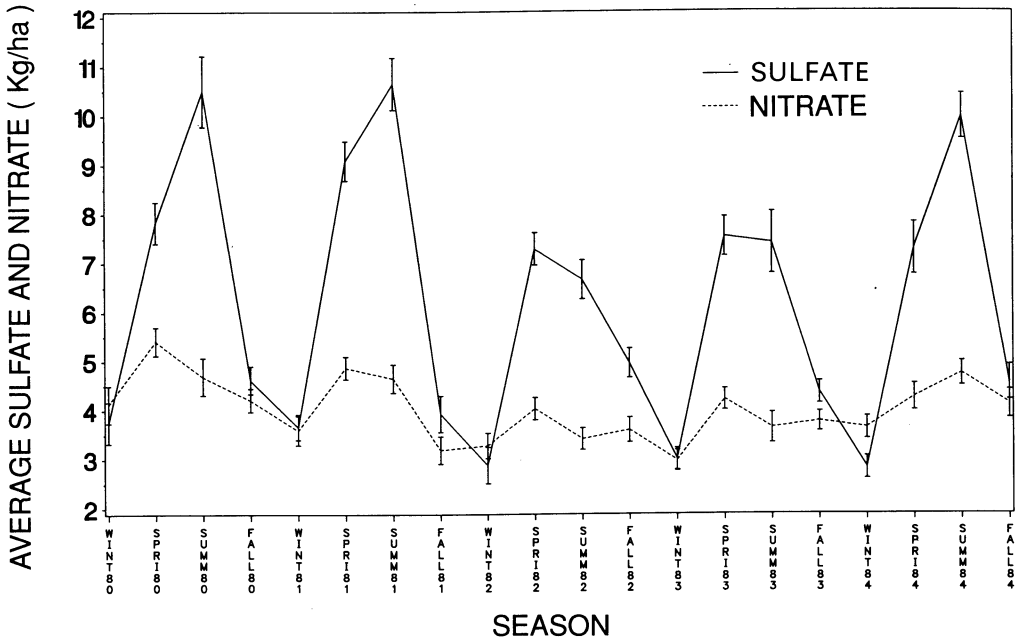

Fig. 10. Average sulfate and nitrate deposition in Kg/ha. North Central Region

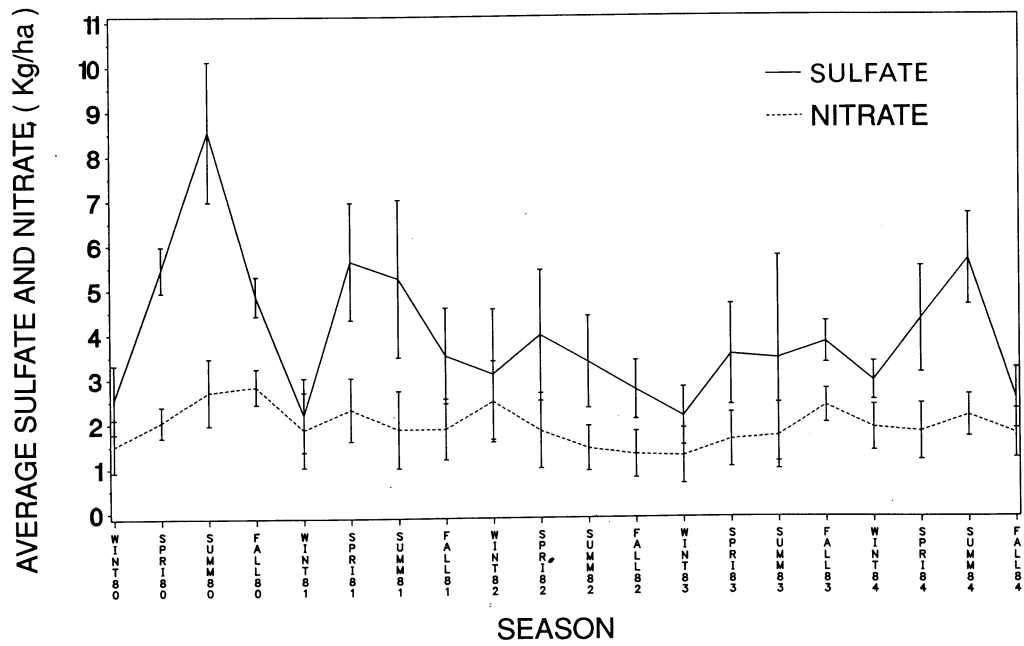

Fig. 11. Average sulfate and nitrate deposition in Kg/ha. North East Region

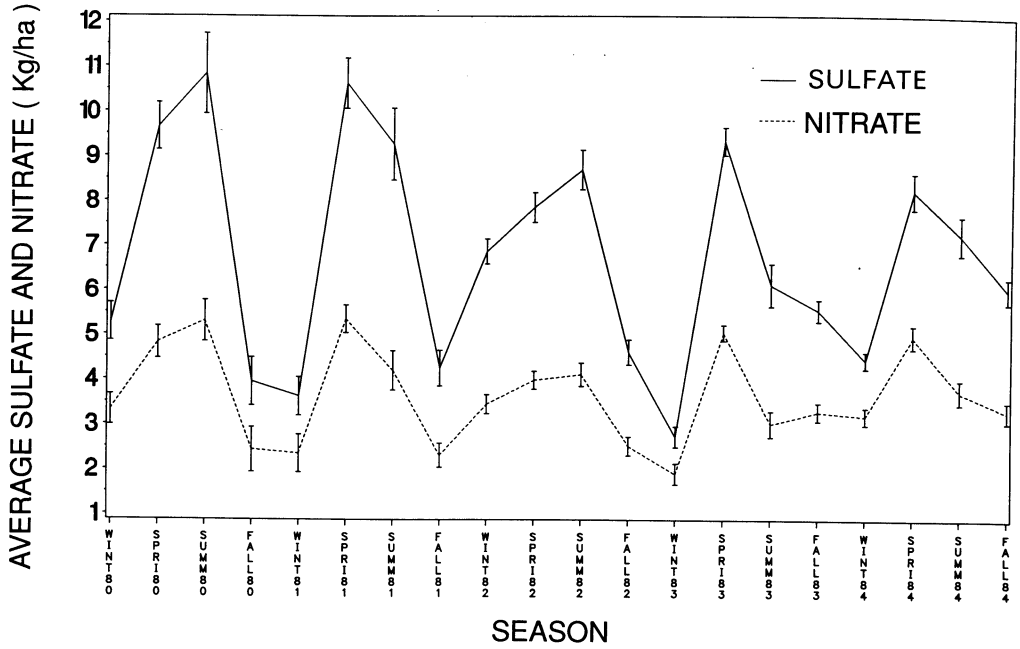

Fig. 12. Average sulfate and nitrate deposition in Kg/ha. South Region

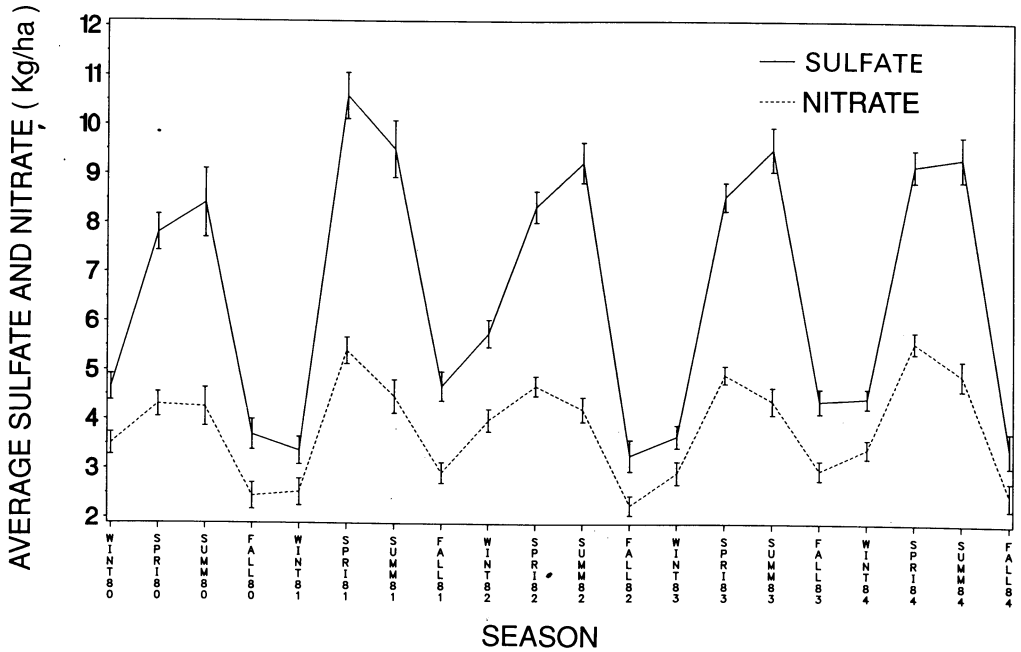

Fig. 13. Average sulfate and nitrate deposition in Kg/ha. South East Region

Great Lakes. Regional estimates derived from kriging, as from other interpolation methods, are particularly sensitive when relatively large or small values occur in isolation far removed from other site data. In those cases, the contours tend to be circular and to exhibit strong gradients.

Separate regional estimates of average sulfate (in kg.S./ha) and nitrate (in kg.N./ha) depositions were determined for each season and are displayed in Figures 9–13. The estimates of the corresponding uncertainties are indicated as error bars (the estimate plus or minus one standard deviation). The figures indicate that there is a strong seasonal component which naturally is obscured when attention is restricted to annual data. Moreover, sulfate and nitrate exhibit a strong correlation, although the former is more variable. The deposition values are greatest in the South as noted previously by Zemba et al. (1988). The uncertainties are small owing to the large number of sites in that region. The depositions in the North East region are the smallest but the uncertainties are large in view of the fewer number of sites. The estimates obtained in the South East region which includes Ontario support the findings of Ro et al. (1988) who reported sulfate depositions exceeding 20 kg/ha/yr, a "value considered critical for the acidification of sensitive water bodies." The uncertainties in the South and South East regions range from about 5% to 10% of the estimate itself. For the North and North East regions, the uncertainty can be as high as 40% in winter.

In Tables 4 and 5, we present the results of the Run test. It can be seen that there are significant decreasing temporal trends for the North Central region for both wet sulfate and nitrate. Since the Run test does not take into account the uncertainties in the seasonal estimates, a further investigation was made on the basis of a paired comparison study. This confirmed the existence of a trend from mid 1981 to early 1984. We note that during that period there were significant annual decreases of 18% and 14% for sulfate and nitrate respectively. Most of these changes occurred in summer when the reduction exceeds 20%. It is interesting to note that there appear to be no trends in the high deposition region nor in the North East. This observation does not support the findings of Seilkop and Finkelstein (1987) who analyzed annual data for much smaller regions.

In order to investigate the reasons for the observed trends in sulfate and nitrate in the

Table 4. Results of the Run test on deseasonalized wet sulfate deposition for the period 1980–1984

Region	1980 W S S F	1981 W S S F	1982 W S S F	1983 W S S F	1984 W S S F	Runs
North	+ + + −	+ + + −	− + − +	− − + −	− − − +	11
North Central	+ + + +	+ + + −	− − − −	− − − +	− − + +	5*
North East	− + + +	− + + +	+ − − −	− − − +	+ − + −	9
South	+ + + −	− + + −	+ − + −	− + − +	− − − +	13
South East	+ − − −	− + + +	+ − − −	− − + +	− + + −	8

*Significant at the 5% level
+The deviation is above the median
−The deviation is below the median

Table 5. Results of the Run test on deseasonalized wet nitrate deposition for the period 1980–1984

Region	1980 W S S F	1981 W S S F	1982 W S S F	1983 W S S F	1984 W S S F	Runs
North	+ + + +	+ + − −	− − − +	− − + +	− − − +	7*
North Central	+ + + +	+ + + −	− − − −	− − − −	− − + +	3*
North East	− + + +	+ + + −	+ + − −	− − − +	+ − + −	9
South	+ − + −	− + + −	+ − − −	− + − +	+ + − +	13
South East	+ − − −	− + + +	+ − − −	− − − +	+ + + −	6*

*Significant at the 5% level
+ The deviation is above the median
− The deviation is below the median

North Central region, we compared the number and the location of the reporting sites in 1981–1983. There were more monitoring sites around Lake Huron in 1982–83 especially in the north west part of the region where depositions are lower. Consequently, the observed trend may be due to changes in network protocol, in emissions, in meteorology or a combination thereof. Emissions of oxides of sulfur and nitrogen in the United States dropped about 8% and 4% respectively between 1981 and 1980 and then remained steady until 1984. Although much smaller in magnitude, sulfur dioxide emissions in eastern Canada decreased about 2% between 1980–82 and then rose about 12% between 1982–84. Emissions of nitrogen oxides in Canada decreased slightly over the period 1980–84 (NAPAP (1987)). We conclude that in order to interpret the observed changes, one needs a comprehensive model based on an understanding of the physical and chemical processes in the acid deposition system. Finally, it should be noted that the within site variability in the North Central region may be quite large as evidenced from the Dorset site.

9. Summary and Conclusions

In this study, interest was centered on detecting trends in wet sulfate and nitrate deposition for the period 1980–1984 based on an intercomparison of patterns and their features. Generally, although our results support the findings of previous authors, they are more specific and they permit a quantification of the observed changes. Eastern North America was partitioned into five regions. Estimates of seasonal deposition were determined for each region using a simple kriging interpolation technique. The non-parametric Run test was first applied to the deseasonalized estimates. It was shown that there were significant decreases in the North Central region but not in the high deposition region. This was confirmed using a pairwise analysis which took into account the estimates of uncertainty provided from kriging. It was revealed that these changes occurred from 1981 to 1982–83. A further examination of the actual data indicated that there were fewer sites in 1981 than in 1982–83. Hence, part of the detected change may be attributed to this. Changes may also be due to changes in emission levels or in meteorology. To deal with the effect of precipitation and other meteorological factors, we need a comprehensive physically-based model. This is beyond the scope of this study. The technique proposed however, may be useful for detecting trends in deposition.

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