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The spatial distributions of precipitation acidity and major ion wet deposition in North America during 1980

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ABSTRACT

Observations are presented of the mean annual concentration and deposition of H^+, $SO_4^=$, NO_3^- and NH_4^+ ions in precipitation in North America during 1980, the first year that a reasonably compatible merger of US and Canadian federal network data was possible. The maximum concentration and wet deposition of H^+, $SO_4^=$ and NO_3^- occurred in—and south of—the great lakes region near maximum anthropogenic emissions of sulphur and nitrogen oxides. The NH_4^+ maximum, however, was located in the north central US where American livestock feedlots are concentrated. Peak H^+ concentrations were 60–80 μmole l^{-1}. In the region of maximum emissions, 1980 observations of H^+, $SO_4^=$ and NO_3^- wet deposition are within 25% of the 5-year mean for 1977–1981. The respective fraction of anthropogenic sulphur and nitrogen oxides released in eastern North America that are wet deposited in the same area is 24 ± 6 and 25 ± 6%. On a smaller scale, in the high sulphur and nitrogen oxide emissions area of the northeastern US, the deposition was 13 and 18% of emissions, respectively. Trends in emissions as well as in $SO_4^=$ and NO_3^- concentrations in precipitation support the conclusion that a real increase in acidity of precipitation of 30–37 μmol l^{-1} has occurred in the southeastern US since 1955/56.

1. Introduction

Air pollution from anthropogenic sources is thought to influence the ionic content of precipitation out to hundreds and even thousands of kilometres downwind. Surprising levels of acidity in Scandinavian precipitation were reported in the 1950s (Eriksson, 1952a, b; Barrett and Brodin, 1955). Later, evidence was presented linking the acidity to distant sources (Odén, 1968; Bolin, 1971). Granat (1972) showed that sulphate, nitrate, ammonium and calcium were the major ions associated with hydrogen ion in European precipitation. An understanding of the nature and origin of acidic rain in Europe was aided at all stages in its evolution by an extensive set of precipitation-chemistry network measurements made routinely since the 1950s.

Networks have served to enhance our understanding of acidic precipitation on the North American continent as well. An assessment of the magnitude and extent of acidification in the eastern United States, first made by Cogbill and Likens (1974), used measurements from two short-lived networks. One was operated in 1955–56 (Junge, 1958; Junge and Werby, 1958) and the other in 1965–66 (Lodge et al., 1968). Several attempts were made to extend these analyses during the early seventies (e.g., for 1972–73 by Likens, 1976; for 1975–76 by Likens et al., 1979). Because of the lack of a unified set of network data, however, it was necessary to piece together the geographical distribution of acidity in North America using uncoordinated measurements from a number of networks. These analyses demonstrated that precipitation has indeed been acidic in eastern North America (annual mean pH 4.1–5.0) since at least the mid 1950s and suggested that an increase had occurred in the magnitude and areal coverage of acidic precipitation in the eastern United States

between 1955 and the early 1970's (Likens and Butler, 1981). Uncertainties in the data bases caused by lack of standardized procedures and absence of long-term records, however, resulted in correspondingly large uncertainties pertaining to trends (i.e., Hansen and Hidy, 1982). On the basis of these analyses, it was obvious that routine measurements spanning decades at many locations would be necessary to:

(1) assess the effects of major ions associated with acid rain;
(2) improve atmospheric models;
(3) determine the variability in the spatial distribution of acidity caused by meteorological fluctuations.

Four national precipitation chemistry networks were established in North America during the late 1970s, two in Canada and two in the United States. Measurements made by these networks enable us to describe the geographical distribution of North American precipitation quality on a finer spatial scale than ever before. Until 1980, however, differing sampling protocols gave rise to significant inconsistencies between the networks which resulted in some rather severe artifacts. These were detected and rectified by quality-control and cross-check procedures, so that in 1980 protocols were adopted which led to a demonstratably more consistent collection of most of the major ionic species*.

The primary objectives of the present paper are to:

(1) examine the spatial variability of North American precipitation chemistry using this newer and more consistent data base;
(2) compare conclusions from this analysis with those from earlier investigations, with the goal of elucidating any artifacts which may have arisen from the use of inconsistent data sets.

These objectives will be fulfilled by examining the 1980 data set from the four national networks for the chemical species $SO_4^=$, NO_3^-, H^+, and NH_4^+. A brief description of these four networks is provided in the next section, which is followed by the comparative analysis.

* Artifact Ca^{++} and NO_3^- ions still pose some problems in merging the Canadian CANSAP data with results from other North American networks. These artifacts which serve to raise the uncertainty of acidity estimates somewhat, are discussed later in the text.

2. Precipitation collection and analysis

In 1980, four national networks were in operation in North America.

1. *CANSAP, The Canadian network for sampling precipitation*

At 46 locations scattered across Canada, monthly precipitation samples are collected in a Sangamo wet-only collector. Monthly composite sampling has been employed since January 1, 1980. With this procedure, the contents of the collector bucket are emptied into a large, refrigerated polyethylene bottle after each event, and at the end of the month the accumulated sample volume is measured and an aliquot shipped to Toronto for analysis. A recent assessment and analysis of the CANSAP network measurements (Barrie and Sirois, 1982), showed that the introduction of monthly-composite sampling improved the quality of CANSAP measurements to a point where observed $SO_4^=$ and NO_3^- concentrations were directly comparable with those from other high-quality networks.

2. *APN, The Canadian air and precipitation monitoring network*

In 1980, five stations were operational in eastern Canada collecting precipitation on a daily basis in a Sangamo wet-only sampler. Daily samples are bottled individually, stored at 4 °C and shipped in a cooled container by express mail to the laboratory in southern Ontario. Samples are analyzed using the same techniques as those used for CANSAP samples. A detailed description of APN network operations can be found elsewhere (Barrie et al., 1980, 1984).

3. *MAP3S*

During 1980, eight stations of the United States MAP3S network were in continuous operation. In this network, samples are collected on an event basis and are bottled individually and stored under refrigeration until chemical analyses can be performed. During early years, the special MAP3S refrigerated wet-only sampler was employed for sample collection, but more recently this design has been replaced by standard Aerochem. Metrics units. Presently the MAP3S network is continuing operation, a ninth station having been added near Oak Ridge, Tennessee. A more detailed descrip-

tion of the MAP3S network can be found in MAP3S/RAINE (1982).

4. *NADP, The national atmospheric deposition program network*

In 1980, 50 stations were in operation for at least two thirds of the time, collecting precipitation on a weekly basis in a wet-only Aerochem Metrics sampler. Each week, samples are shipped in the sealed collector bucket by regular post to the central NADP laboratory at Urbana, Illinois. For a detailed description of collection and analysis procedure, the reader is referred to Stensland et al. (1980).

3. Results

Precipitation-amount-weighted averages and deposition amounts were calculated for the year 1980. Because of the tendency for seasonal cycling (cf. MAP3S/RAINE, 1982), data from stations operating for less than two-thirds of the year were rejected. Our acceptance of data from stations having down-times of up to one-third of a year was a necessary compromise between spatial definition and temporal accuracy. If all stations having less than a full-year's operation were rejected, useful information would be unnecessarily sacrificed to the detriment of spatial resolution. The error arising from the acceptance of fractional-year data can introduce an uncertainty at individual locations of up to 20%. Since most stations had close to a complete data set, the composite uncertainty will be much less than this maximum value.

Isopleth plots of species concentrations are shown in Figs. 1–5. These correspond to precipitation-weighted values computed from the equation.

$$\bar{C}_i = \sum_{j=1}^{N} C_{ij} P_j / \sum_{j=1}^{N} P_j, \qquad (1)$$

where C_{ij} is the individual sample concentration of species i and P_j is the corresponding precipitation amount. The weighted average is taken over all N of the samples obtained during the year. P_j was obtained from standard rain or snow gauges in the case of the Canadian data; corresponding values were obtained directly from the precipitation chemistry samplers for the US counterpart. This difference in procedure was necessitated by differences in collection and reporting methods, and introduces only a small discrepancy in the results (Barrie and Sirois, 1982).

At this point, the relative consistency of the 1980 US–Canadian data should be re-emphasized. Pack (1980) reported that along the border, CANSAP sulphate data of 1978 did not match those of the MAP3S and EPRI/SURE (Hakkarinen, 1979) networks. The isopleth plots of Semonin and Bowersox (1983), based upon the total ensemble of CANSAP/NADP data (1977–1980), show a rather dramatic increase in precipitation-borne pollutant in the vicinity of the Canadian border—an effect ostensibly caused by sampling artifacts existing in the data set prior to 1980. A recent analysis of CANSAP data by Barrie and Sirois (1982) revealed that before 1980, sample collection procedures in the network were the cause of a discrepancy which was largely eliminated by the introduction of monthly composite sampling on January 1, 1980. To support this conclusion, they used a comparison of APN and CANSAP results prior to and after the initiation of composite sampling, a comparison of transboundary measurements (discussed in Subsection 5.1) and results of special studies of CANSAP sampling techniques. It was also found that, even after composite sampling began, calcium concentrations observed by CANSAP in the Great Lakes–St. Lawrence basin were unrealistically higher by a factor of 2–3 than those obtained by APN and MAP3S. The anomalous behavior of CANSAP calcium measurements apparently originates from sites being situated too close to roads, which are sanded under snow conditions. Assuming calcium to be in the form of carbonates, Barrie and Sirois (1982) estimate that this artifact influence on acidity measurements was to reduce its concentrations by 20–40% (approximately 0.1 pH unit). Since the Ca^{++} appears to be associated with Na^+ and Cl^- ions, this will be the maximum effect of contamination on acidity.

3.1. Acidity

Acidity can be represented in terms of the hydrogen ion concentration or the negative of its logarithm to the base ten (pH). Below we discuss the spatial distribution of precipitation acidity in terms of hydrogen ion concentration (Fig. 1), but the comments also apply to the pH distribution (Fig. 2). Concentrations are highest in eastern North

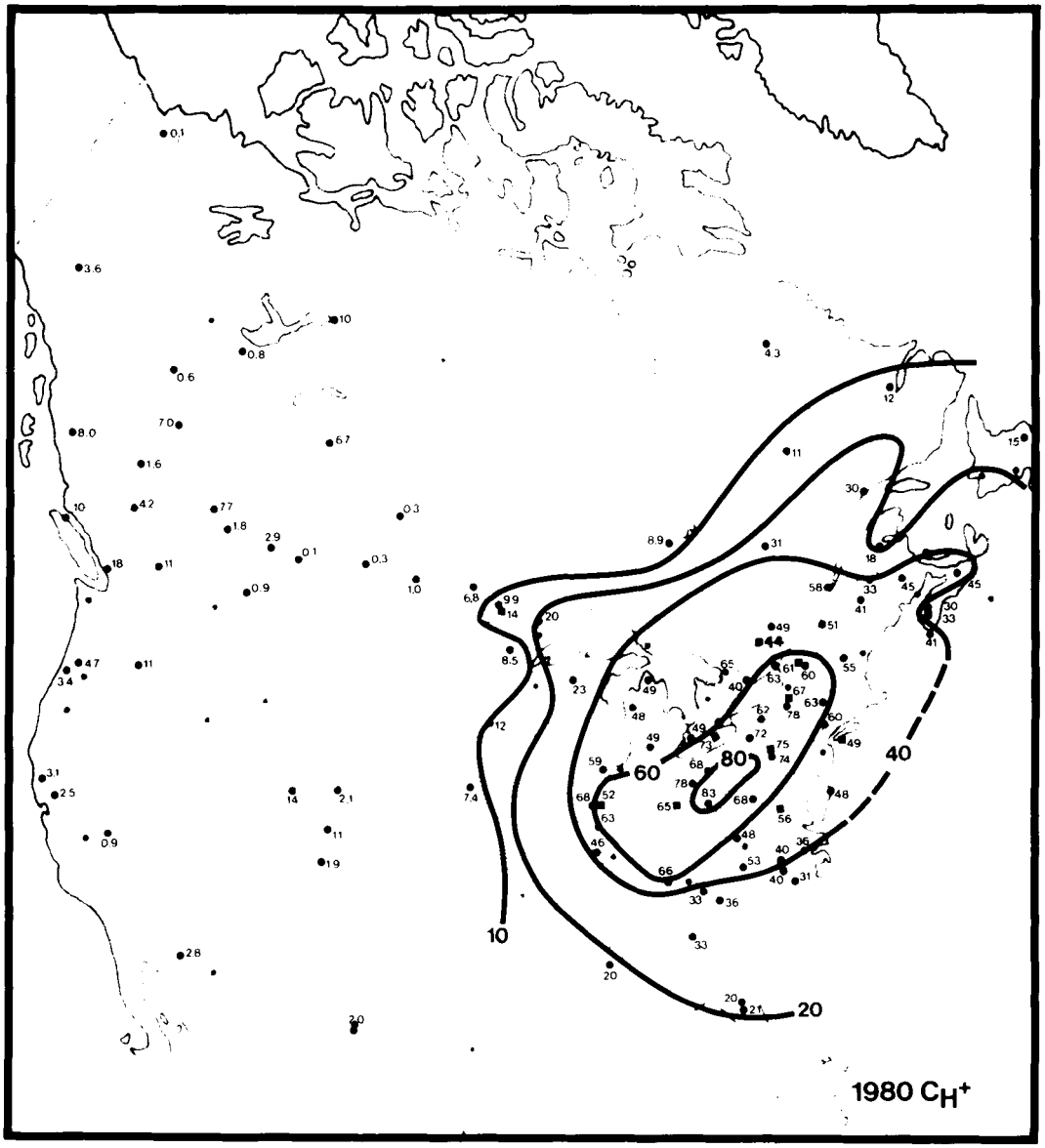


Fig. 1. The spatial distribution of the precipitation-amount-weighted annual mean hydrogen ion concentration (μmole l^{-1}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

America, ranging from 60 to 80 μmole l^{-1} (pH 4.2 to 4.1) over a large area covering a roughly rectangular region 600 km wide and 1500 km long stretching from western Illinois and Kentucky northeastward through New York and southern Ontario.

3.2. Sulphate

Precipitation-borne sulphate exhibits a rather well-defined spatial distribution as indicated in Fig. 3. For visualization purposes, it is convenient to consider this as a spatially variable pattern superimposed on a more-or-less uniform background of

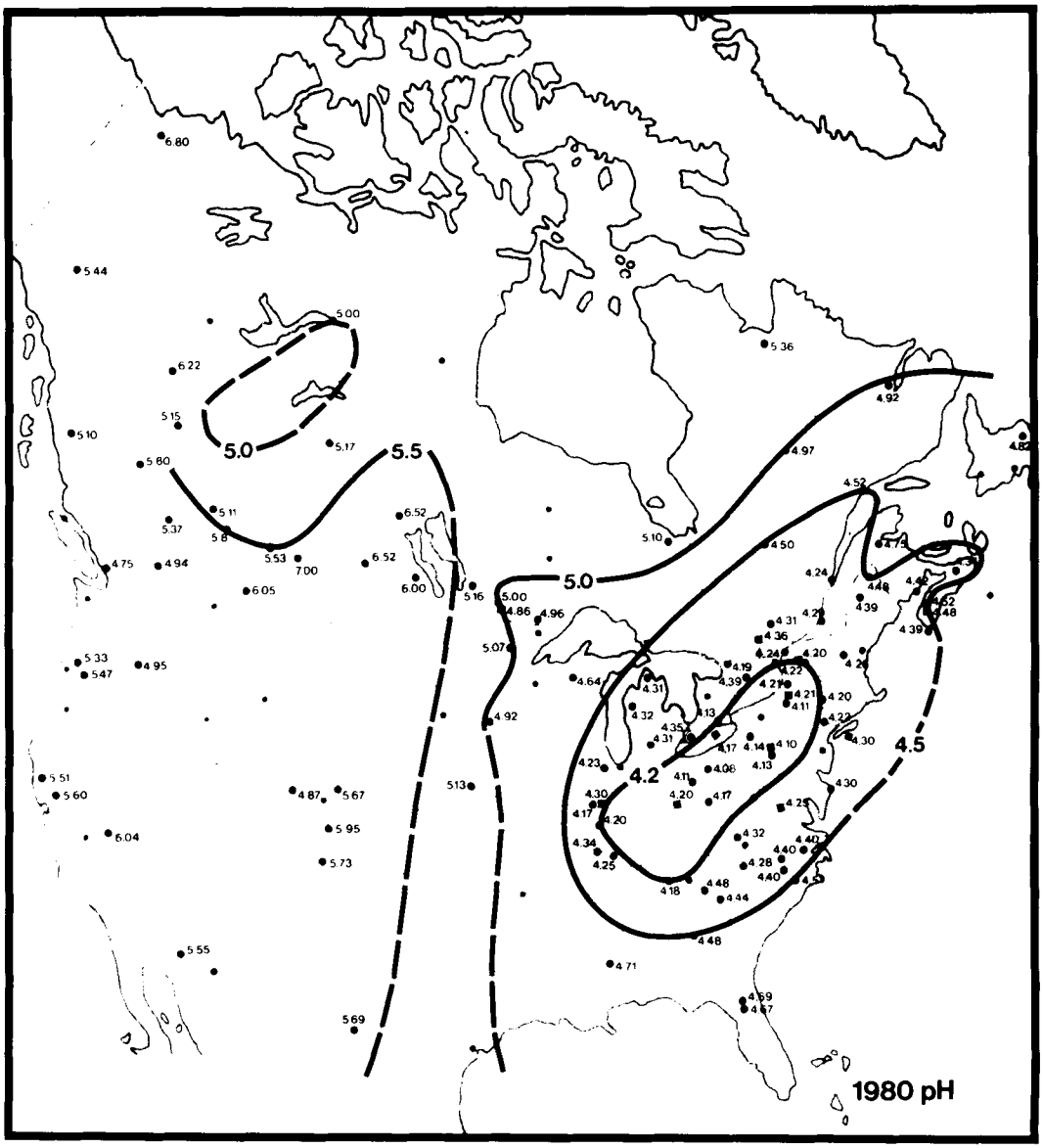


Fig. 2. The spatial distribution of the precipitation-amount-weighted annual mean hydrogen ion concentration expressed as pH in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares), in the United States: NADP (circles) and MAP3S (squares).

3–10 μmole l^{-1}, although our use of the term "background" in this context should not be taken to imply a particular association with natural sources or a relationship to any true global background loading (if one can indeed by defined). This low, relatively-uniform distribution is evident in northern Canada and the Pacific coast of North America. In comparison, concentrations in eastern North America are greater than 20 μmole l^{-1}. A maximum of about 40 μmole l^{-1} occurs in an area approximately 1000 by 250 km covering Ohio and southern Ontario. An ion-balance analysis using

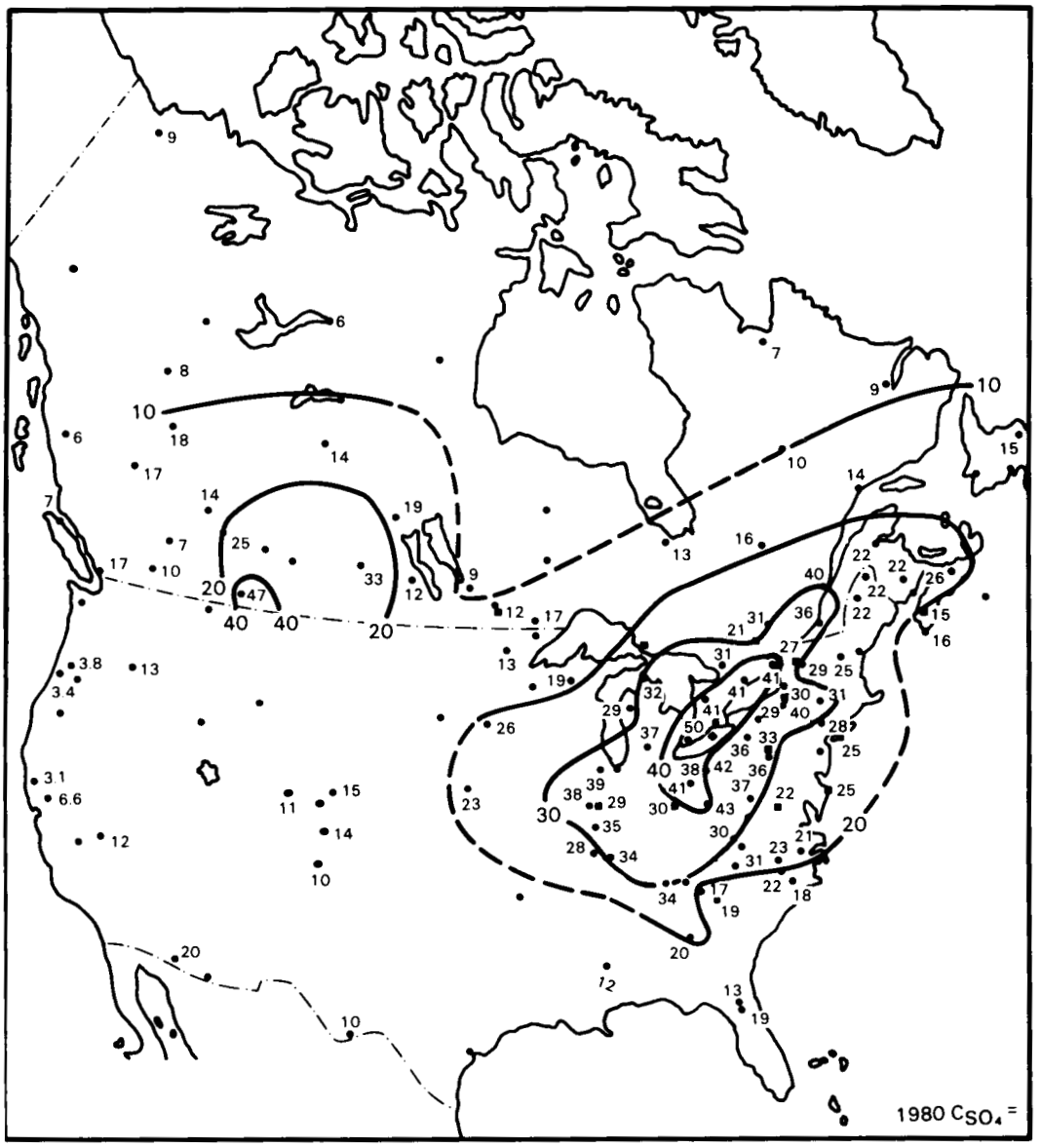


Fig. 3. The spatial distribution of the precipitation-amount-weighted annual mean sulphate ion concentration (μmole l^{-1}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

data in Figs. 1, 3, 4 and 5 indicates that high concentrations in western Canada are associated with non-acidic materials, whereas most of the sulphates in eastern North America originate from acidic compounds. Reported sulphate concentrations have been corrected for sea-salt contributions using sodium. Corrections are generally negligible (<5%) except at a few locations within 5 km of open ocean areas where corrections were 10 to 30%.

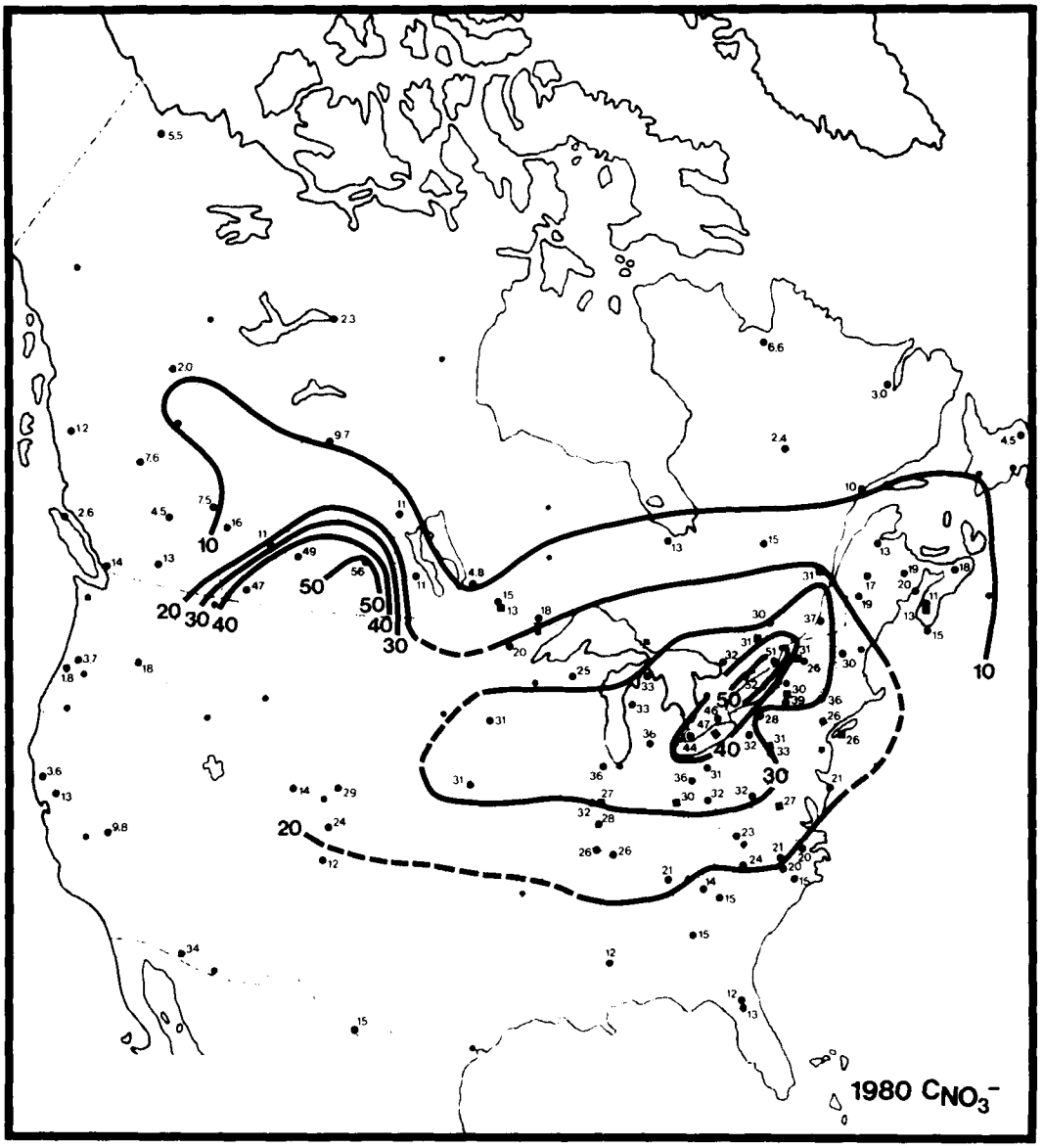


Fig. 4. The spatial distribution of the precipitation-amount-weighted annual mean nitrate ion concentration (μmole l^{-1}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

3.3. Nitrate

Nitrate concentrations in North American precipitation (Fig. 4) have minimum values of 2–4 μmole l^{-1}. In contrast, they are 20 to 50 μmole l^{-1} in areas around and downwind of major sources in the eastern half of the continent. In western Canada, elevated nitrate concentrations are associated with wind-blown dust as indicated by low levels of acidity and high levels of calcium (Barrie and Sirois, 1982). On the other hand, in the eastern

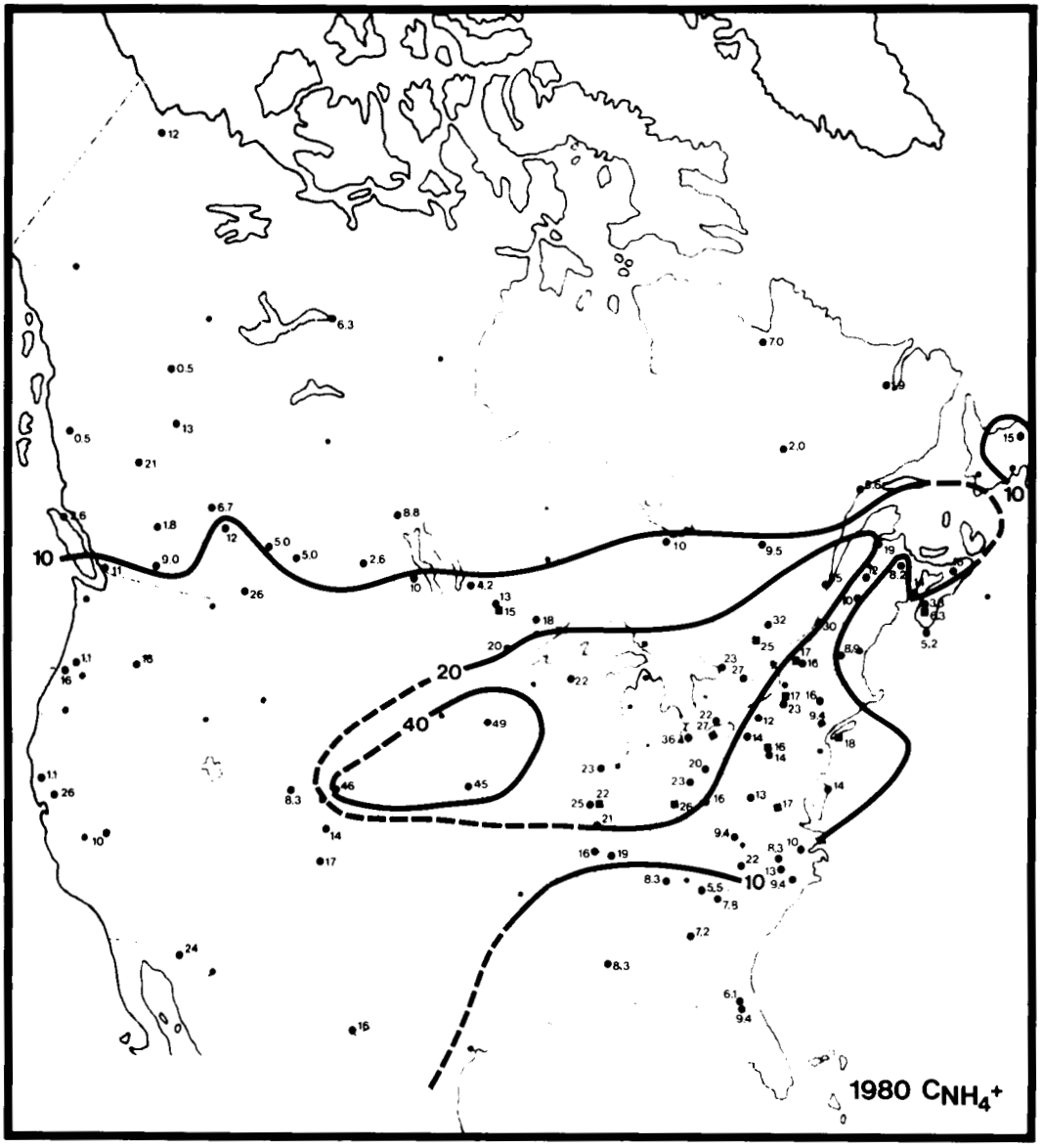


Fig. 5. The spatial distribution of the precipitation-amount-weighted annual mean ammonium ion concentration (μmole l^{-1}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

half of the continent, elevated levels of nitrate parallel high levels of acidity (Fig. 1). Concentrations are above 30 μmole l^{-1} in most of the Great Lakes states and in southern Ontario and Quebec, with highest values (40–50 μmole l^{-1}) occurring in a 1000 km long strip approximately 200 km wide covering southern Ontario. There is some indication that even after composite sampling was instituted in CANSAP in January 1980, nitrate levels remained 10–15% higher than in co-located

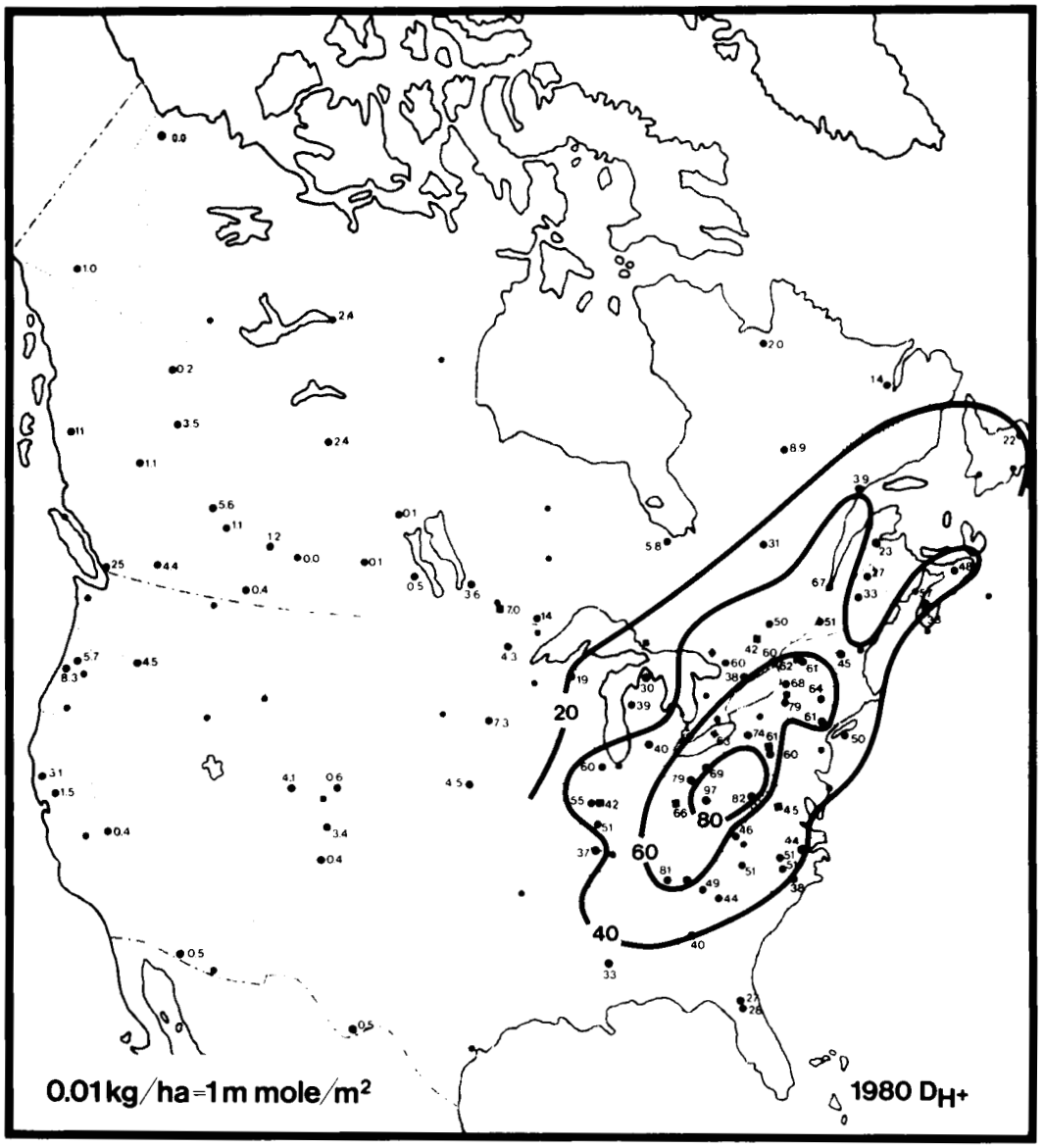


Fig. 6. The spatial distribution of annual wet deposition of hydrogen ion (mmole m^{-2}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States NADP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

US samplers. Consequently the position of the nitrate maximum should be viewed with caution.

3.4. Ammonium

Ammonium concentrations for precipitation in northern Canada and on the west coast range from 0.5–21 μmole l^{-1} (Fig. 5). The spatial distribution of ammonium-ion concentration is different from that of the hydrogen, nitrate and sulphate ions. Concentrations maximize (>40 μmole l^{-1}) in and downwind of the northern plains of the United States in which livestock feed lots, a major source

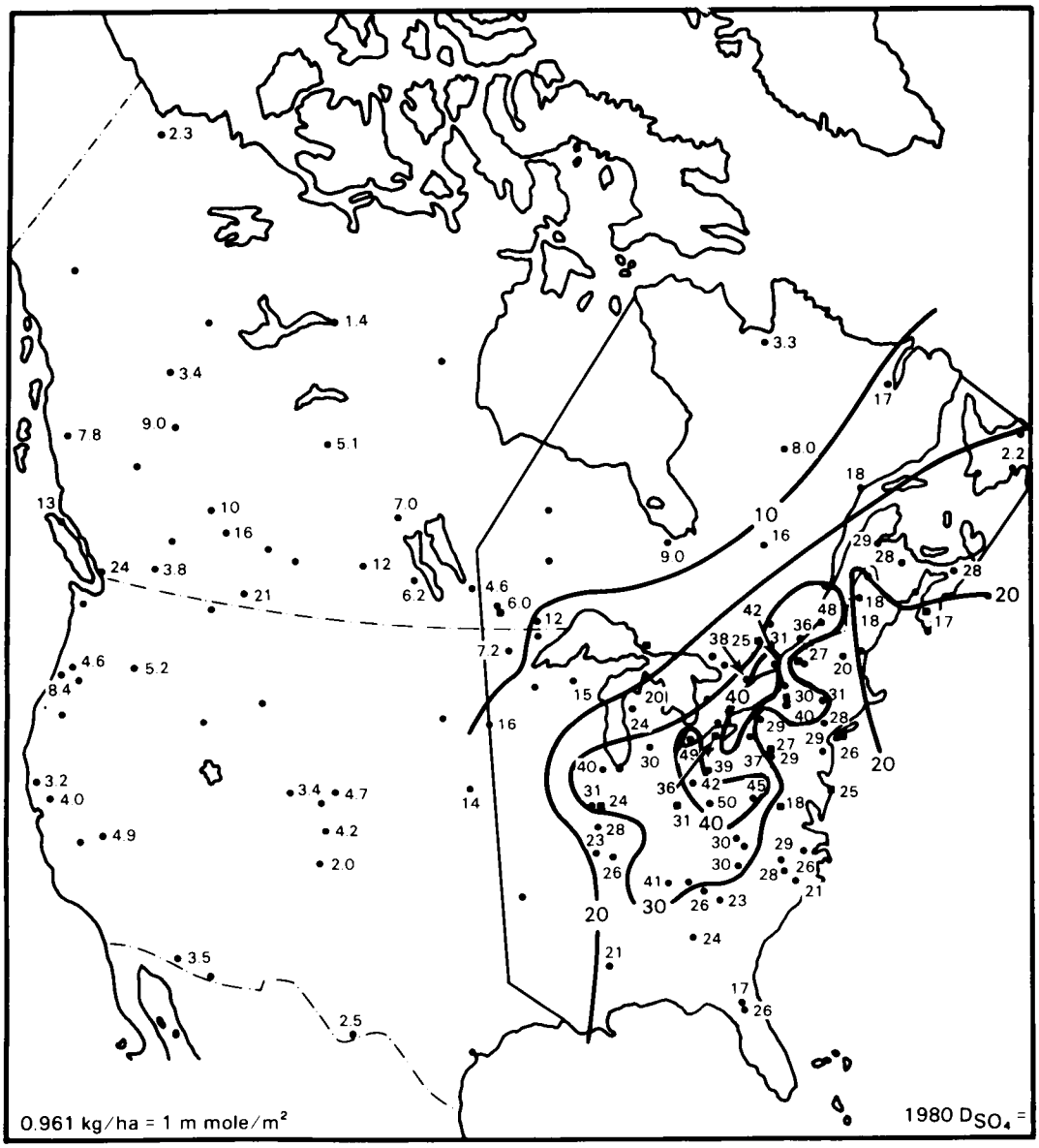


Fig. 7. The spatial distribution of annual wet deposition of sulphate ion (mmole m^{-2}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares). The boundary of the area of eastern North America used in the sulphur-budget calculations (Table 2) is also shown.

of ammonia (Husar and Holloway, 1982), are abundant. Intermediate levels (20–40 μmole l^{-1}) occur in the Great Lakes–St. Lawrence lowlands. A similar spatial distribution of NH_4^+ concentration was observed in 1955/56 in the United States by Junge (1958).

4. Spatial distribution of deposition

The spatial distributions of wet deposition of H^+, $SO_4^=$, NO_3^- and NH_4^+ ions in North America were calculated using observed precipitation-amount-weighted mean concentrations reported in Section

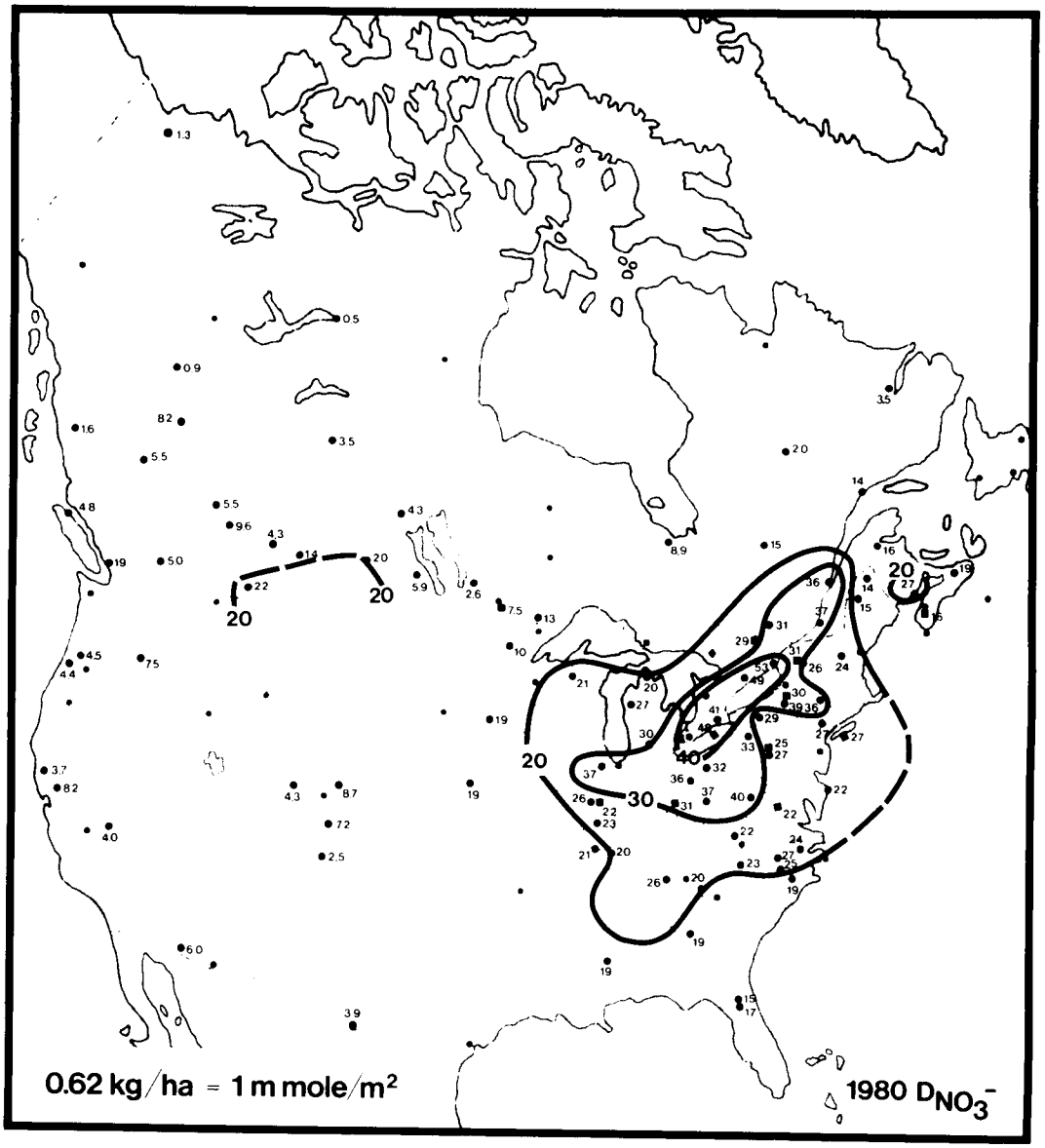


Fig. 8. The spatial distribution of annual wet deposition of nitrate ion (mmole m^{-2}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

3 and two sets of precipitation amount data, one measured by precipitation chemistry networks and one by meteorological networks. Deposition is the product of weighted concentration (eq. (1)) and precipitation amount. Granat (1978) found that the spatial variation in the concentration field was less than that of the precipitation amount field. Consequently, more measurements are necessary to define precipitation amount fields than concentration fields. Recognizing this fact, precipitation amount data from chemistry networks were augmented by those from the national weather services.

The procedure used to multiply concentration

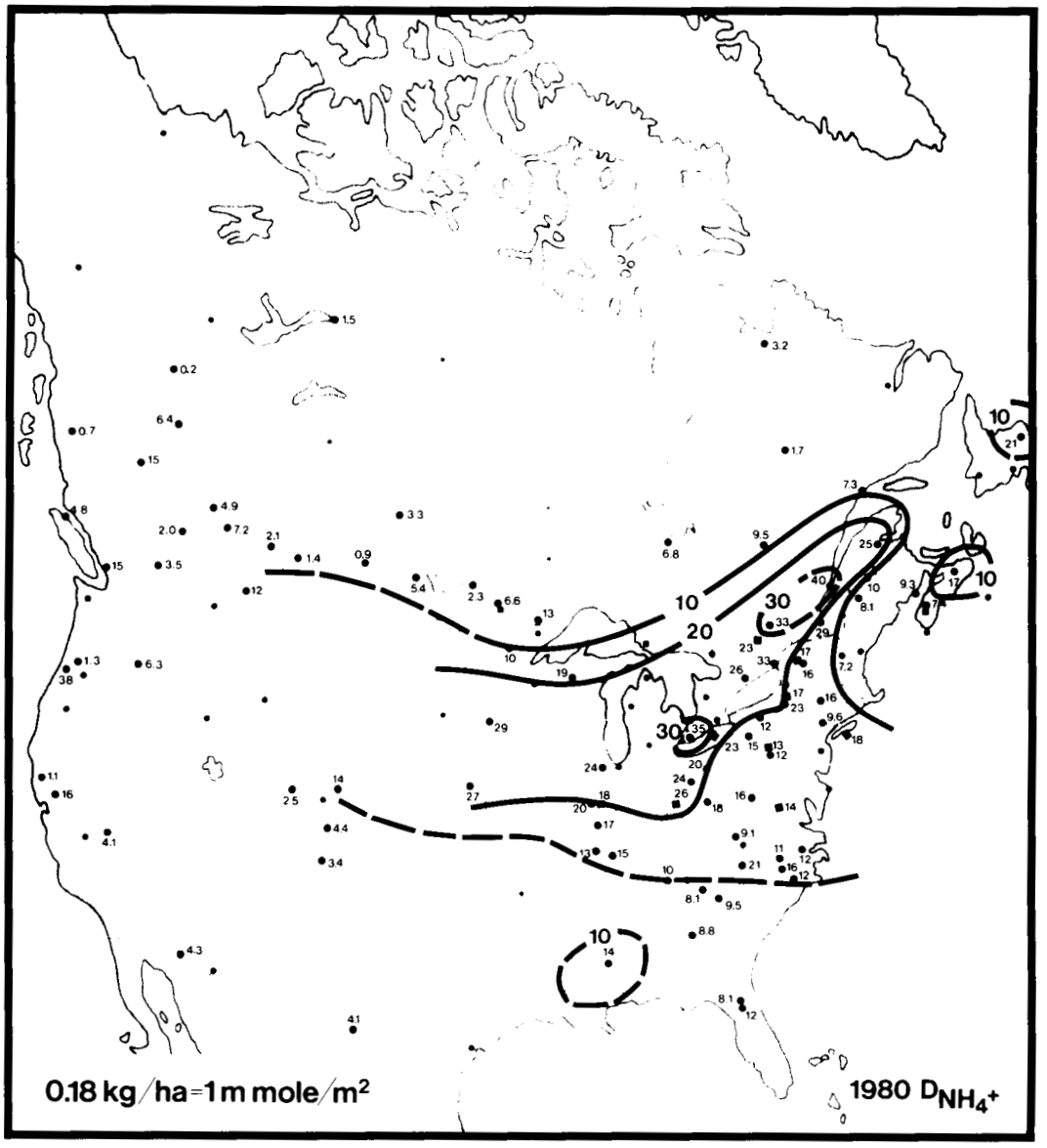


Fig. 9. The spatial distribution of annual wet deposition of ammonium ion (mmole m^{-2}) in North America in 1980. Data from 4 networks are plotted, in Canada: CANSAP (circles) and APN (squares); in the United States: NADP (circles) and MAP3S (squares).

and precipitation amount fields differed between Canada and the United States. In Canada, concentrations were obtained by linear interpolation of the concentration fields (Figs. 1–5) for approximately 250 climatological stations measuring precipitation amount. Then the deposition field was drawn by hand using values calculated at climatological sites as well as those measured by APN and CANSAP. In the United States, the field was obtained by plotting the deposition (i.e., the product of C_i, eq. (1) and the standard-gauge-precipitation amount) measured at each NADP and MAP3S station and then drawing isolines by hand. As guidance in drawing isolines between points, a gridded field of deposition was used. This was produced by interpolating fields of concentration (Figs. 1–5) and

standard gauge precipitation amount for 1980 (US Weather Service) to the intersection points of a grid of spacing ~100 km that was laid over the eastern half of the country. Their product, the deposition, was then calculated. The gridded field was especially helpful in positioning isolines in mountainous regions such as the Appalachians, where gradients in precipitation amount were high, as well as in areas where the density of chemistry-monitoring sites was low.

Deposition fields calculated using the above approach are shown in Figs. 6–9. From these it is evident that regional patterns of wet deposition are quite similar to those for concentrations. Prior to more detailed interpretation of these plots, it is important to emphasize two major areas of uncertainties. The first of these areas relates to the positioning of the isolines, which involves substantial amounts of uncertainty arising from sampling and analysis errors, areal and temporal representativeness and incomplete network coverage. When errors in sampling and analysis are taken into account, it is quite possible that the uncertainty in an annual mean deposition or concentration measurement is ±20%; depending on the location and density of stations, this would translate into a positional uncertainty ranging from 50 to several hundred kilometres (Finkelstein and Seilkop, 1981; Barrie, 1982).

The second major area of uncertainty is related to changes in the spatial deposition pattern from one year to the next, that is, the climatological representativeness of this single-year data set. The correspondence of one year's distribution to that of another depends on meteorological variability and temporal changes in emissions. As mentioned in Section 1, the influence of either factor has not been thoroughly investigated due to lack of high quality, long-term data bases. The question of how representative 1980 is of other years is discussed in Section 5.

5. Discussion

5.1. *Inter-network consistency*

Improvement in post-1979 inter-network consistency can be demonstrated by comparing spatial distributions of $SO_4^=$ and NO_3^- concentrations in 1979 (Fig. 10) and 1980 (Figs. 3 and 4). As noted

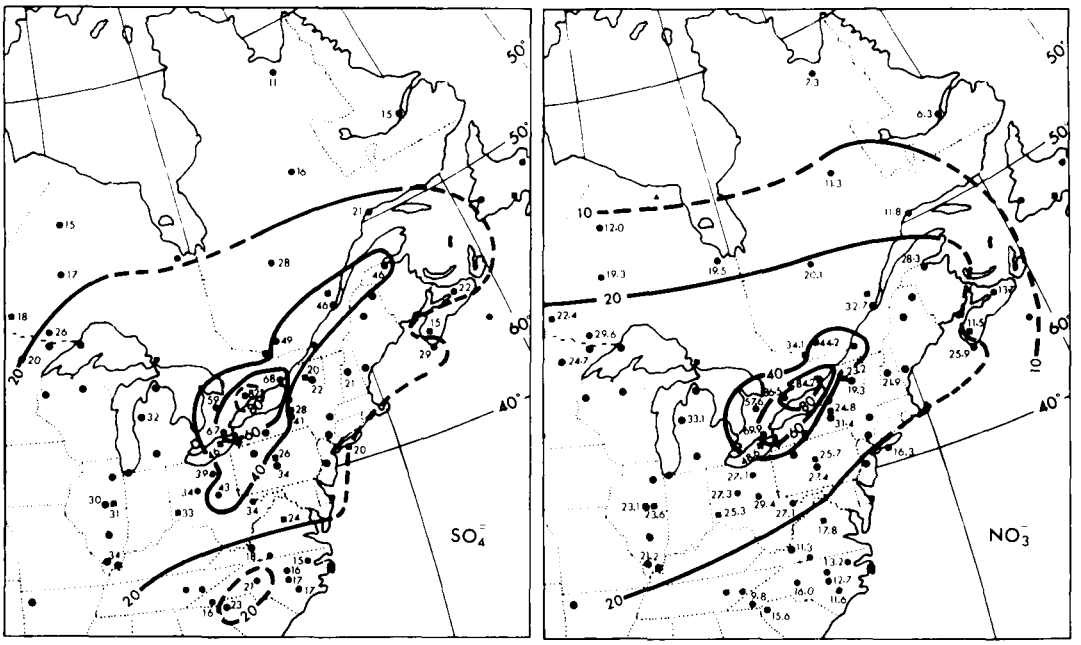


Fig. 10. The spatial distributions of annual precipitation-amount-weighted mean SO_4 and NO_3 concentrations in eastern North America in 1979. These are based on CANSAP observations that are too high as a result of inadequate sampling techniques prior to 1980 (Barrie and Sirois, 1982).

previously, the 1979 distributions are based on CANSAP data before composite sampling was introduced to reduce biases. The region of maximum concentration shifts south between 1979 and 1980 and stems ostensibly from improvements in the quality of CANSAP measurements (cf. Barrie and Sirois, 1982).

5.2. *Representatives of 1980 deposition observations*

Many different types of pollutant impact analyses are forced by necessity to estimate long-term deposition on the basis of limited data sets, such as the one under discussion here. Because of this, it is appropriate to question the confidence levels associated with such extrapolations. While such a question cannot be resolved to total satisfaction, some insight can be gained by comparison of the given data set to selected historical measurements so that a partial time series can be constructed. Temporal variations occur both in precipitation amount, P and pollutant concentration $\bar{C}_i$; it is sometimes beneficial in such analyses to take advantage of the weak correlation between these two variables (cf. MAP3S/RAINE. 1982) and formulate long-term estimates of the product, $P\bar{C}_i$.

The deviation of P in 1980 from the climatological mean for North America is shown in Fig. 11. In the eastern half of the continent where the highest sulphate and nitrate ion deposition occurs, P was approximately 25% above average in the southern states and in the Great Lakes–St. Lawrence river basin. P was below normal by about 25% in the central and eastern part of the eastern United States as well as in northern Ontario.

Since precipitation chemistry observations have only recently commenced, we are unable to provide an estimate of the deviation of $\bar{C}_i$ from the long-term normal. We can, however, examine 5 years of observations from 3 stations in the MAP3S network as an indication of how typical 1980 was of the 5-year normal for the high deposition region of the northeast. The deviation (D) of P and $\bar{C}_i$ in 1980 from the 5-year mean (1977 to 1981) is shown in Table 1.

In 1980 in the northeastern United States, P was 8–16% below the 5-year normal. This is about the same as the deviation from the longer term climatological normal (Fig. 11). The deviation of ionic concentrations from normal was not consistently in one direction. At the Whiteface and Penn State sites, for example, H^+ and $SO_4^=$ concentrations were above normal thus offsetting the influence on deposition of below-normal precipitation. On the other hand, at Ithaca they were above-normal, thus enhancing the influence on deposition of below-normal precipitation. In general, NH_4^+ and NO_3^- concentrations were above normal, with the exception of Penn State. During 1980 in the high deposition area of the northeast, the deposition of the major ions H^+, $SO_4^=$, NO_3^- and NH_4^+ was within 25% of the 5-year normal.

5.3. *Deposition relative to emissions*

A particularly important aspect of acidic pollutant emissions pertains to the question of the fraction of pollutant released that is wet-deposited in prescribed areas surrounding the sources. Although the present data set is too limited to apply to an extensive analysis of source-receptor phenomena, it is still useful for examining overall features in a semi-quantitative manner. In applying the 1980 data for this purpose, we have focused on a specific geographical region wherein emissions and wet deposition rates for sulphur and nitrogen oxides can be compared. The boundary of the "budget area" (see Fig. 7) was chosen to be the same as that used by Galloway and Whelpdale (1980). Most North American anthropogenic sulphur and nitrogen oxides are released within this area. The emissions for 1980 were obtained from the Canada/US Working Group 3B (1982) and wet deposition from our observations (Fig. 7 and 8). Table 2 compares these values for the total budget area and for the two national regions, eastern Canada (area 3.9×10^{12} m^2) and eastern United States (area 2.1×10^{12} m^2). It should be emphasized that wet deposition can be subdivided into two components: (i) a contribution arising solely from anthropogenic emissions in the area and (ii) a contribution resulting from natural emissions inside the area combined with natural and/or anthropogenic emissions from outside. Within eastern North America, natural sulphur emissions are expected to be negligibly small compared to anthropogenic ones (Rice et al., 1981). If on the basis of observations in northern Canada and other remote locations on the periphery of the budget area such as Bermuda (Galaloway et al., 1982),

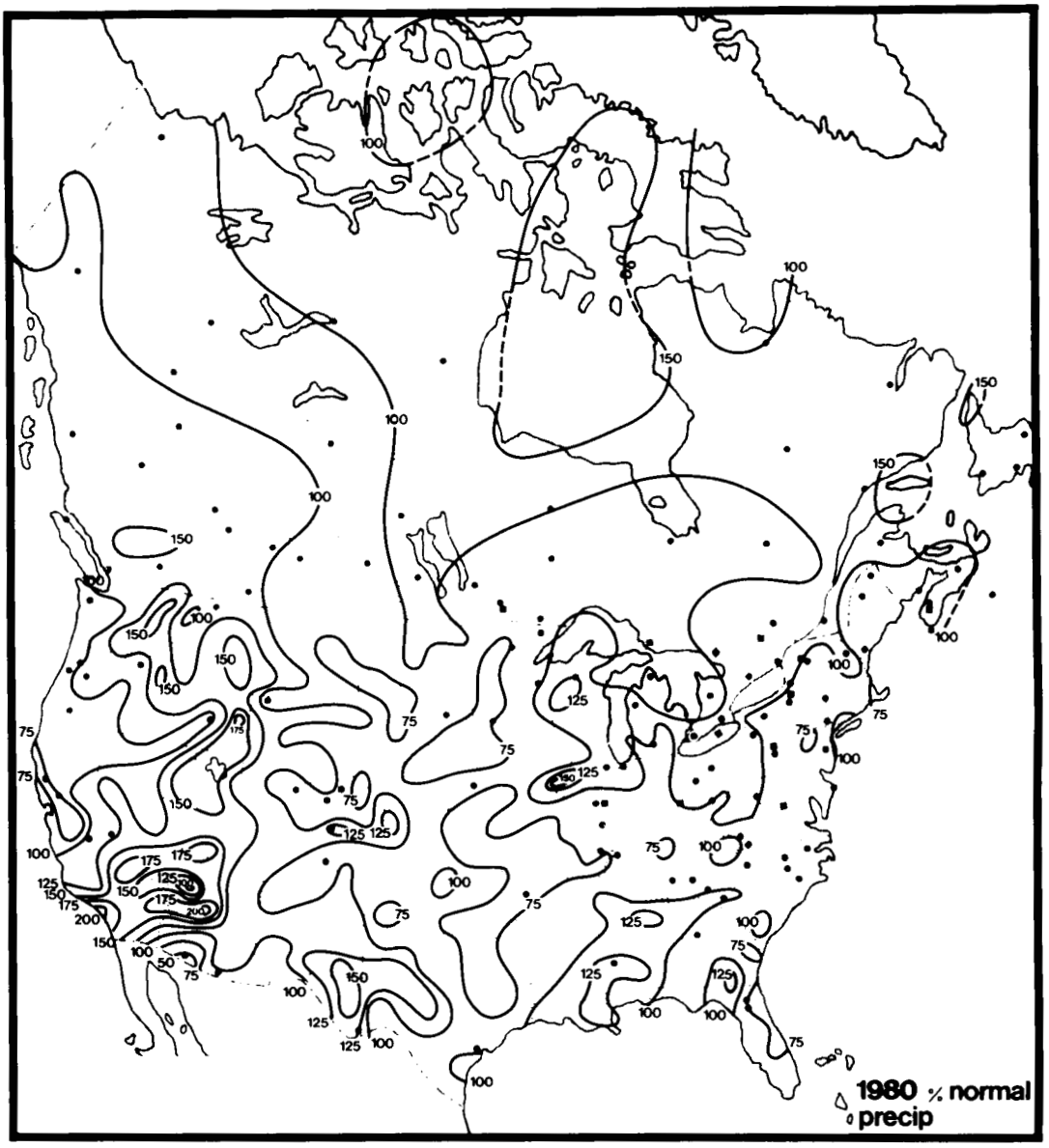


Fig. 11. The % deviation of precipitation amount in 1980 from the long-term mean in North America.

one assumes a background[1] deposition of 3 m mole m^{-2} yr^{-1} (based on background sulphate concentrations of 3–10 μmole l^{-1} in the area), the background component of total wet deposition can be estimated. It is 17 and 20% of the $SO_4^=$ and NO_3^- wet deposition in eastern North America, respectively.

Within the eastern North American budget area, wet deposited sulphur comprised 29% of the total anthropogenic emissions. Considering the uncertainties involved, this agrees well with an estimate of 32% based on 1978 data made by Galloway and Whelpdale (1980). The ratio of wet deposition to

[1] Background in the sense described in Subsection 3.2.

Table 1. *A comparison of the annual mean precipitation amount P and concentration of major ions $\bar{C}_i$ for 1980 at three sites in the MAP3S network in the northeastern United States with those of other years; D is the deviation of 1980 observations from the 5-year mean*

Year	P (cm)	H^+	$SO_4^=$	NO_3^-	NH_4^+
Site: Whiteface (73°51′ W, 44°23′ N)					
1977	116	46	22	22	11
1978	80	60	29	26	17
1979	107	50	20	19	11
1980	95	61	27	26	17
1981	124	37	21	18	12
D(%)	−9	20	25	17	25
Site: Ithaca (76°43′ W, 42°23′ N)					
1977	99	69 (66)	30	29	13
1978	78	84	34	31	16
1979	102	70	28	25	15
1980	91	67	30	30	17
1981	124	70	37	31	17
D(%)	−8	−7	−6	3	9
Site: Penn state (77°57′ W, 40°47′ N)					
1977	105	73 (79)	33	31	15
1978	94	78	21	31	13
1979	132	58	26	26	15
1980	88	75	33	31	16
1981	104	59	35	30	25
D(%)	−16	−9	7	4	−4

Table 2. *A comparison of the nitrate and sulphate wet deposition D (10^{10} mole) in the eastern Canada, eastern United States and eastern North America during 1980 with emissions E (10^{10} mole); the boundary of the budget area is shown in Fig. 7*

	Eastern Canada			Eastern USA			Eastern North America		
	D	*E*	*D/E*	*D*	*E*	*D/E*	*D*	*E*	*D/E*
S	5.5	5.4	1.01	5.0	30.6	0.16	10.5	36.0	0.29
N	4.0	2.3	1.74	4.9	25.8	0.19	8.9	28.1	0.32

emissions in the target area was roughly the same for NO_3^- as for $SO_4^=$ (32 vs 29%, respectively). After adjusting for background, these respective values were 25 and 24%. Uncertainties in these ratios, however, make it difficult to draw any firm conclusions from them regarding the relative gross scavenging efficiencies. If one takes into account uncertainties in the measured deposition (Section 4) and in the emissions (Laulainen, 1982), the standard error in an estimated wet-deposition/emissions ratio is approximately 25%.

Some additional insight can be gained by considering the emission/deposition ratio for subregions of the budget area. In the high emission subregion including Ohio, Pennsylvania, Indiana, Kentucky, West Virginia and Tennessee, for example, background-adjusted wet-deposition of $SO_4^=$ and NO_3^- accounted for 13% and 18% of the corresponding emissions, respectively. Although there is a variety of ways one can interpret these results, they suggest rather strongly that NO_x is being wet-removed somewhat more efficiently than SO_x over this more limited spatial domain. This suggestion is consistent with results of a number of earlier authors (e.g., Pack and Pack, 1979). Another way of demonstrating the differences in precipitation scavenging of oxides of sulphur and nitrogen on a subarea basis is to compare the S/N mole ratio in wet deposition to that in emissions (Fig. 12). In the high emission areas of the eastern United States, this ratio is generally lower in precipitation (1.2–1.6) than in emissions (1.5–1.9).

It is instructive as well to intercompare multiple subregions within the budget area. Sulphate and nitrate wet-deposition rates in the eastern-Canada subregion, for example, were observed to be about the same as corresponding emission rates (corrected for background, a ratio of 0.8 for S and 1.2 for N). In contrast, the eastern US subregion is characterized by ratios of about 0.15 for both elements. Quite obviously these differences are related to the complex relationship between sources, receptors and transport patterns within the budget area.

In the design of an emission control strategy, it is important to consider the relative contribution of sulphur and nitrogen oxides to the acidity of precipitation, in addition to their relative effects once they are deposited. This is especially true since both transportation and stationary sources contribute strongly to the nitrogen oxide burden. The

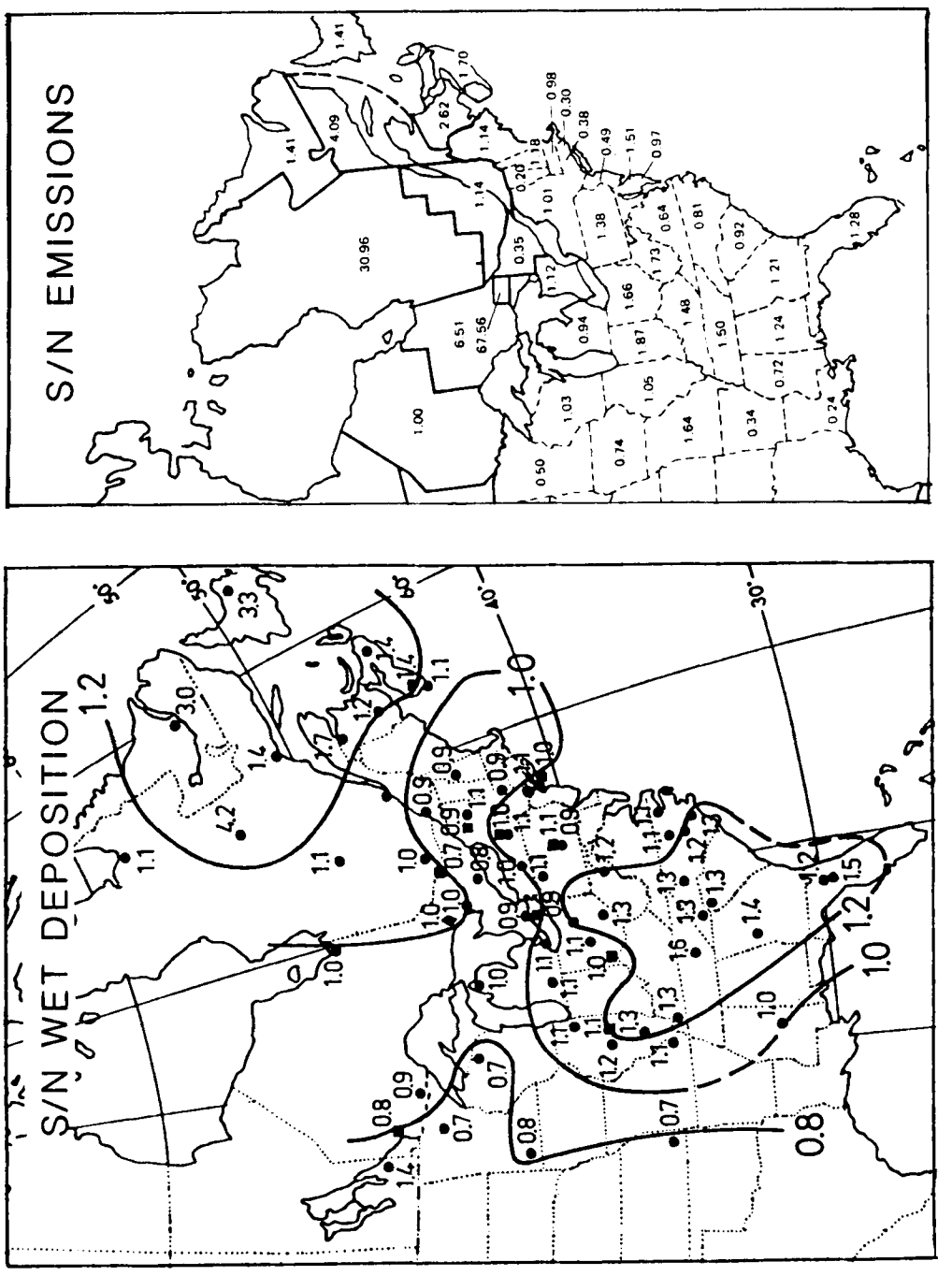


Fig. 12. A comparison of the spatial distribution of the mole ratio of sulphate to nitrate in precipitation in 1980 with that in emissions (from US/Canada Working Group 3B 1982 reported in NAS 1983).

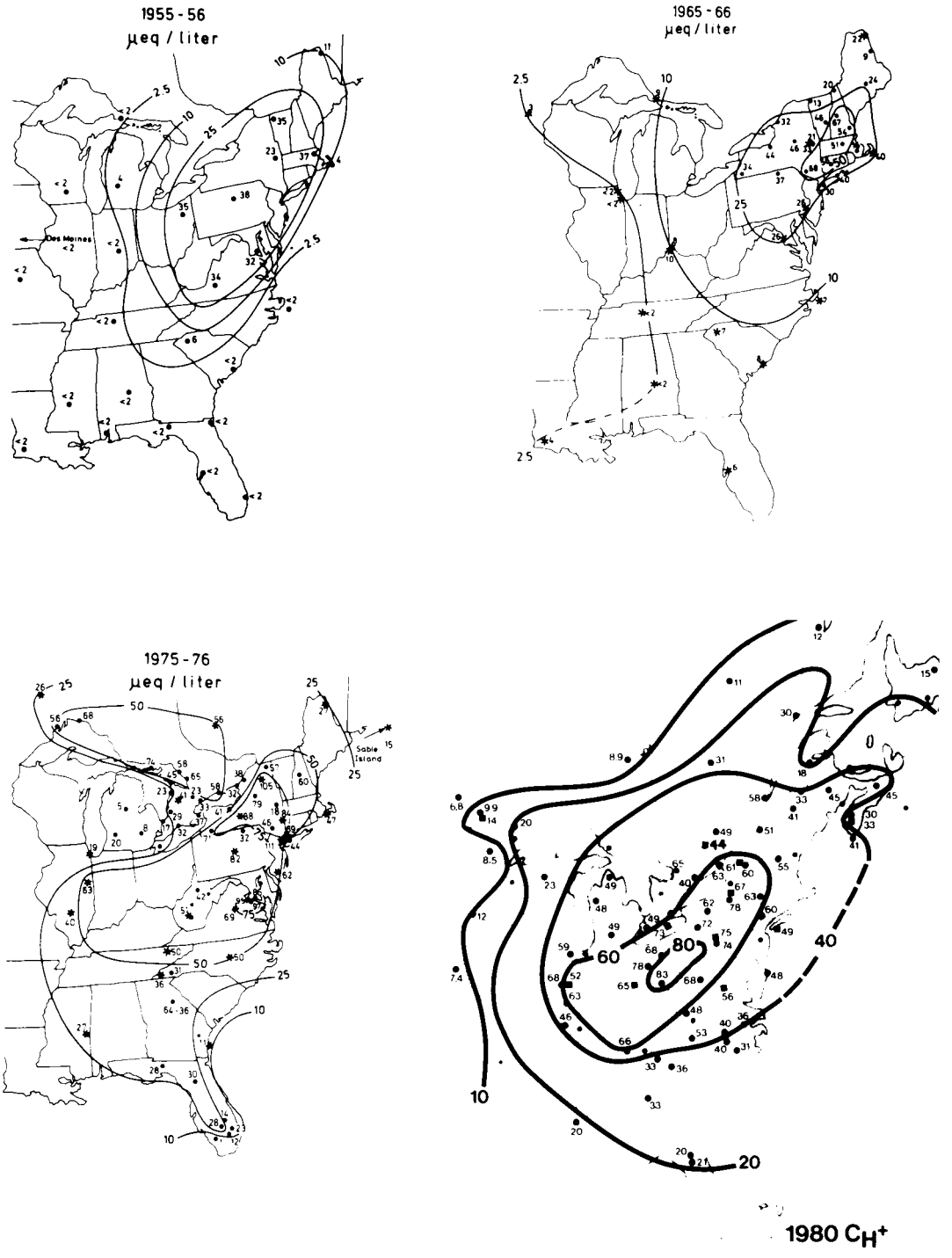


Fig. 13. A comparison of the spatial distribution of H^+ concentration for 1980 with those reported for previous years by Likens and Butler (1981).

transportation sector contributes little to sulphur emissions but comprises about 50% of the nitrogen oxide emissions (Benkovitz, 1982; Laulainen, 1982). Mole ratios of sulphur to nitrogen (S/N) in wet deposition exhibit a distinct spatial pattern in eastern North America, as demonstrated by Fig. 12. There are two regions of maximum values, one in the central eastern United States (1.3–1.4) and one in remote eastern Canada (1.2). These are separated by a region of minimum values (0.8–1.0) in southern Canada and New England. Since sulphur potentially contributes twice as many hydrogen ions to solution as nitrogen oxides do, this suggests that the oxides of sulphur are currently at least 1.6 times as important as nitrogen oxides for the acidification of precipitation on an annual basis.

5.4. Precipitation acidity in 1980 compared to previous years

A comparison of the spatial distribution of precipitation acidity during 1980 with that for other years (summarized by Likens and Butler, 1981) is made in Fig. 13. In this context, it should be re-emphasized that earlier data have many sources

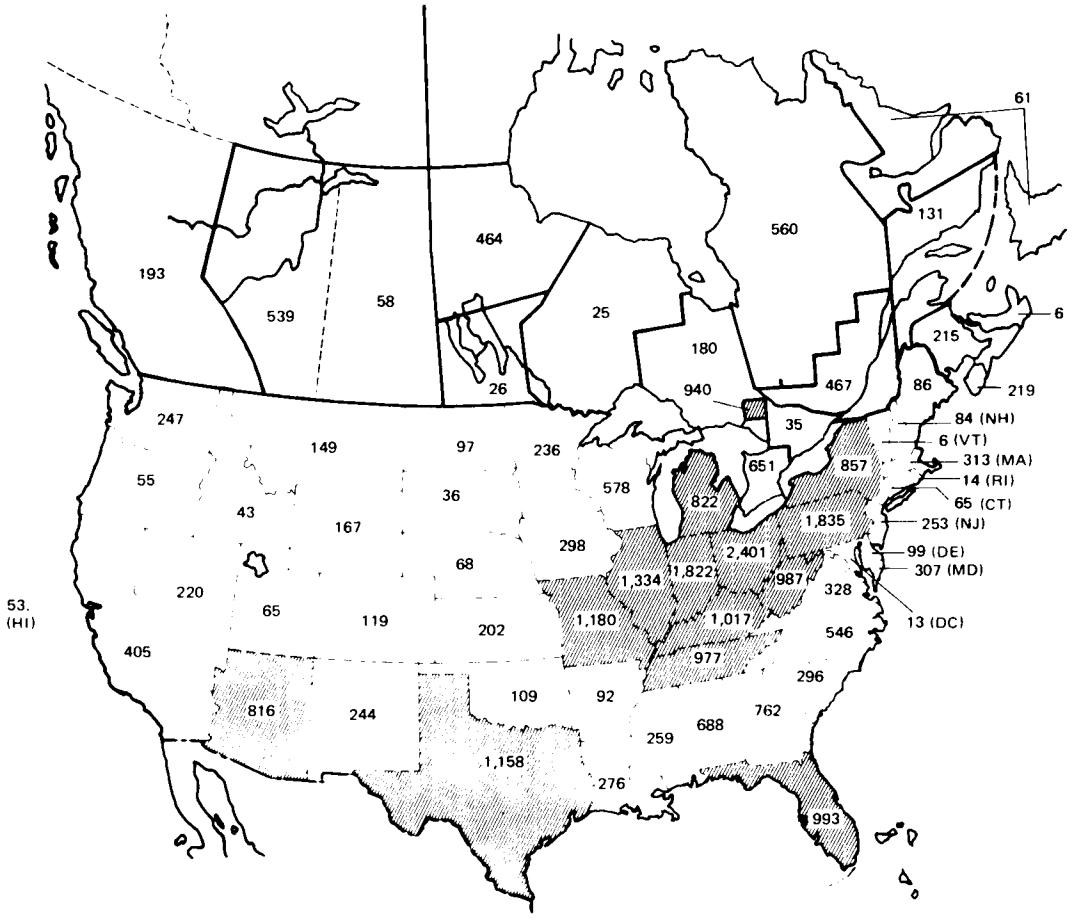


Fig. 14. Emissions of sulphur oxides in the United States and Canada in 1980 (thousands of metric tonnes of SO_2). From US/Canada Working Group 3B, 1982 reported in NAS 1983.

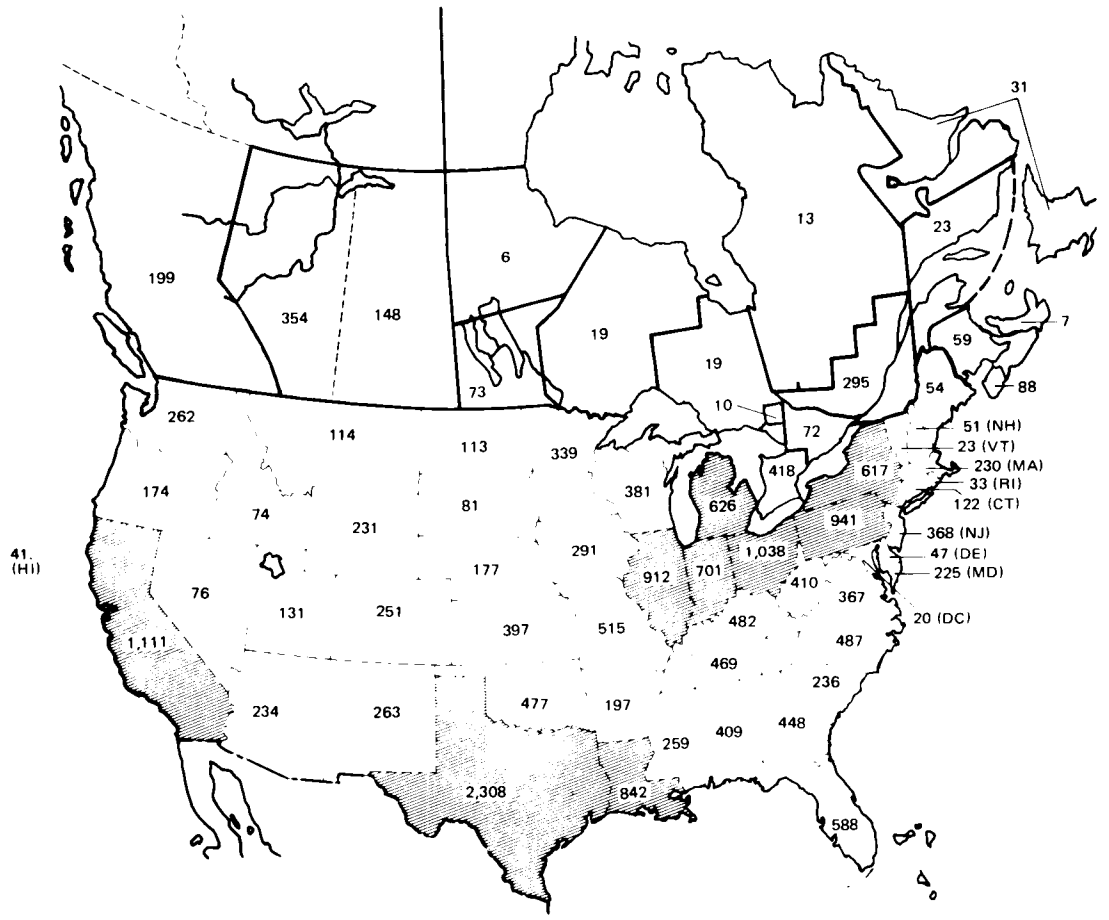
of uncertainty that the 1980 data base does not (cf. Hansen and Hidy, 1982), in particular:

(i) the 1955–56 H^+ concentrations were calculated from an ion balance rather than measured, and samples were collected in bulk collectors;

(ii) the 1965–66 data are limited in spatial extent and were often collected at sites in urban areas that were not regionally representative;

(iii) the 1975–76 data represent measurements from many different networks using a variety of sample collection techniques whose consistency is suspect.

Because of the above factors, one must be extremely cautious in drawing any conclusions about the spatial distributions and temporal trends. With confidence, it can be said that in the high emission region of eastern North America, precipitation has been much more acidic than in remote clean air regions since at least 1955–56. Furthermore, the 1980 data support the previous conclusions of Likens et al. (1979) on the basis of measurements made in the mid-seventies regarding the increase in precipitation acidity in the southeastern United States since the 1950s. There are indeed large uncertainties associated with historical observations, and natural fluctuations in



NO_x Emissions in 10^3 Tonnes (1980)

Fig. 15. Emissions of nitrogen oxides in the United States and Canada in 1980 (thousands of metric tonnes of NO_2). From US/Canada Working Group 3B (1982) reported in NAS (1983).

precipitation chemistry. Despite these uncertainties, however, it is difficult to attribute the H^+ increase in the southern US (2–9 μmole l^{-1} in the 1950s and 1960s to 20–40 μmole l^{-1} in the 1970s and 1980) to any cause other than increased human activity in that region.

This conclusion is supported by changes in concentration of $SO_4^=$ and NO_3^- ions in precipitation and in emissions of oxides of sulphur and nitrogen in the region since the mid-1950s. $SO_4^=$ and NO_3^- concentrations observed in the southeastern states by Junge (1958) and Junge and Werby (1958) were compared with those for 1980. The arithmetic mean of annual concentrations in northern Florida, Georgia, Alabama, North Carolina, South Carolina and Tennessee has changed by 22 μeq l^{-1} for $SO_4^=$ and 14 μeq l^{-1} for NO_3^-. This is sufficient to explain the observed increase in H^+ ion of 30–37 μeq l^{-1} in the same area. According to the US/Canada Working Group #3B (1982), emissions of sulphur and nitrogen oxides have increased by a factor of 2.5 and 2.4 between 1955 and 1978, respectively, in the area covered by Alabama, Florida, Georgia, Mississippi, Kentucky, North and South Carolina and Tennessee.

Based on the available data, we cannot draw any firm conclusion regarding temporal trends of acidity in the high-emission area of the US northeast. This is not, however, needed to establish the link between emissions and precipitation acidity. The good, qualitative correlation of the more accurately known 1980 spatial distributions of sulphur and nitrogen oxide emissions (Figs. 14 and 15) and acidity is sufficient (Fig. 1) to conclude that this link does indeed exist.

6. Conclusions

Several conclusions regarding precipitation chemistry in eastern North America can be drawn on the basis of this analysis. A number of these conclusions are unique to this investigation, while others support contentions by previous authors. These are itemized as follows.

(1) The concentration and deposition of H^+, $SO_4^=$ and NO_3^- in precipitation are highest in eastern North America, where the majority of anthropogenic sulphur and nitrogen oxide emissions occur.

(2) A definite southward shift in $SO_4^=$ and NO_3^- maxima occurs in 1980, as compared to merged-network data from previous years. This apparent shift is caused primarily by sampling artifacts in the older CANSAP data.

(3) Precipitation is most acidic, 60–80 μmole/l^{-1} of H^+, in the region covering the states of New York, Pennsylvania, Ohio, Indiana, Illinois, Kentucky, West Virginia and the southern half of the province of Ontario. This same region receives the highest wet deposition of H^+, $SO_4^=$ and NO_3^- and is the source of sulphur and nitrogen.

(4) Of the anthropogenic sulphur and nitrogen oxides released in the eastern North American budget area (Fig. 7), 24 $\pm$ 6 and 25 $\pm$ 6% are removed by precipitation in the same area, respectively. The rest are dry deposited or discharged from the area.

(5) There is evidence that nitrogen oxides are wet removed somewhat more efficiently than sulphur oxides within selected subregions of the eastern North American budget area. This combined with conclusion (4) suggests that changes in relative scavenging efficiencies may be occurring as distance scales increase.

(6) The concentration and deposition patterns of $SO_4^=$, NO_3^- and H^+ are similar to each other but differ from those of NH_4^+. The former are influenced by emissions of anthropogenic oxides of sulphur and nitrogen while the latter originates mainly from natural sources with a maximum source strength in the centre of the continent.

(7) Precipitation acidity has increased in the southeastern United States since the 1950s.

(8) In the region of maximum deposition, 1980 observations of annual wet deposition of H^+, $SO_4^=$ and NO_3^- are within 25% of the 5-year mean.

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