

# **Incidents of Widespread Elevated Nitrate Concentration in Southern Ontario**

## **A Case of Long-Range Transport**



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Concentration in Southern Ontario  
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by

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# Incidents of Widespread Elevated Nitrate Concentration in Southern Ontario - A Case for Long-Range Transport

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## Abstract:

Measurement of inorganic nitrate in Ontario is concentrated along a NE- SW line from Windsor through Toronto to Kingston. In addition, the cities of Windsor, Sarnia, Hamilton and Toronto have intra-city networks. Sampling is on a six-day or three-day schedule. Three cities have daily monitoring of nitrate. Collection of samples is on glass-fiber filters by the standard hi-volume sampler technique.

An arbitrary minimum concentration of  $9.9 \mu\text{g}/\text{m}^3$  was chosen to define "high" daily nitrate concentrations. This was chosen because it represented the upper 10% of concentrations at all sites and thus reduced the probability of widespread, simultaneous occurrences of these concentrations occurring by chance.

The cold months of the year had the most occurrences of nitrate  $>9.9 \mu\text{g}/\text{m}^3$  (717), nearly twice as many as warm months. Episodes of high nitrate concentrations showed 10 of 11 occurring in cold months. Nine of the eleven episode days occurred when an anticyclone lay over or to the east of southern Ontario.

During the period 5 to 20 February 1977, nitrates were measured in excess of  $9.9 \mu\text{g}/\text{m}^3$  68 times. On 12, February, this concentration was exceeded at 33 monitoring stations and on 18 February 21 stations were in excess. The daily monitoring at Hamilton, Toronto, and Pickering showed nitrate concentrations rose and fell with the movement of anticyclones.

On the 5<sup>th</sup> of February, the movement of air from the north gave a network average nitrate concentration of 1.7  $\mu\text{g}/\text{m}^3$ . On the 12<sup>th</sup> and 18<sup>th</sup> with flow from the south, the network averages were 17.4  $\mu\text{g}/\text{m}^3$  and 12.5  $\mu\text{g}/\text{m}^3$  respectively. Trajectory analysis showed that on these two days the air entering Ontario had traveled over high nitrogen oxide emission regions in the lower Great Lakes.

The nitrate concentrations measured when an anticyclone lay over Ontario were averaged for those anticyclones which moved from the north, south, or west. The northern anticyclones averaged 3.12  $\mu\text{g}/\text{m}^3$  at Toronto and 2.42  $\mu\text{g}/\text{m}^3$  at Pickering. For the southern air mass, the averages were 5.92  $\mu\text{g}/\text{m}^3$  and 5.17  $\mu\text{g}/\text{m}^3$  for Toronto and Pickering. The difference of about 2.8  $\mu\text{g}/\text{m}^3$  at both sites was significant at the 99% confidence level.

The low variability within the network sample during days of high nitrate concentration coupled with the trajectory and air mass movement studies indicates that a significant amount of nitrate is transported into southern Ontario from sources located south of the Great Lakes.

# **Incidents of Widespread Elevated Nitrate Concentration in Southern Ontario - A Case for Long-Range Transport**

## **Introduction**

The case for long-range transport of ozone, sulphates, sulphur dioxide, and particulate in Ontario, eastern Canada, and the northeastern United States has been well documented in recent years<sup>1-7</sup>. Less attention has been paid to inorganic nitrates despite the realization that they are involved in acidic precipitation.

In a previous study of nitrate synoptic climatology in southern Ontario<sup>8</sup>, it was found that nitrates were high in concentration after the passage of an anticyclone centre across the region and low in concentration with the passage of cyclones or just before the arrival of an anticyclone ridge. In each case, the variability of the concentrations across the Ontario network was low indicating that similar processes were at work across the region.

During the course of the aforementioned study, it was apparent that nitrates in suspended particulate in southern Ontario reached very high concentrations across the network on certain days. Widespread elevated concentration are indicative of similar meteorological and emission factors at network sites and points to the likelihood of advection of nitrates into and across southern Ontario.

## **The Measurement of Nitrate in Ontario**

Regular measurement of nitrate began in Ontario in 1976 at 36 stations. In 1979, the network had expanded to 82 stations. The majority of stations lie along a SW-NE axis from Windsor to Toronto to Kingston (Figure 1). Monitoring mini-networks within the cities of Windsor, Metropolitan Toronto, Hamilton, and Sarnia are also in operation. Frequency of measurement varies within the network. All follow a schedule sampling every sixth day. Some selected stations, however, monitor on a three-day schedule which coincides with

the six-day schedule. Three cities (Toronto, Hamilton and Pickering) run daily monitoring at special sites.

Nitrate measurement in Ontario utilizes the standard high-volume sampling technique with particulate collection on glass-fibre filters. The soluble nitrate collected on these filters is extracted and the nitrate concentration determined. It has been suggested by this method of analysis collects both nitric acid as well as aerosol nitrate<sup>9</sup>. The use of the term "nitrate" in this paper, therefore, will refer to the concentrations of these two forms of the nitrate radical.

### **Incidents of Widespread Elevated Nitrate Concentration in Southern Ontario**

The data for this study were drawn from the nitrate measurements in the Ontario network south of 45° N latitude during the period 1976-1979. A minimum concentration of 9.9 µg/m<sup>3</sup> was chosen to define a day with high concentrations. This arbitrary criterion was chosen because it represented the upper 10% of measurements at most stations, and, therefore, the probability of widespread simultaneous occurrences of nitrate concentrations 9.9 µg/m<sup>3</sup> would be small if only local sources were important.

Days with nitrate levels in excess of 9.9 µg/m<sup>3</sup> show a strong bias toward the cold months (Table 1). During the four-year period, the months October to March accounted for 717 station-days over the 9.9 µg/m<sup>3</sup> criterion, twice the number in the April to September period. (A station-day is defined as one station measuring nitrate levels greater than 9.9 µg/m<sup>3</sup> on a given day). Because of the mini-networks within several of the cities, high concentrations within a single city may give undue emphasis to a single day. (For example, Toronto contributes 10 station-days to the 33 station-days reported on 12 February 1977).

Therefore, to eliminate this bias, the city-day is defined as at least one station within a city measuring nitrate in excess of 9.9 µg/m<sup>3</sup>. (On 12 February 1977, therefore, Toronto contributes one city-day). Incident-days are defined as those days with at least 3 city-days and episode days are defined as those days with at least 9 city-days. The

monthly breakdown of these three categories are shown in Table 1. The same nearly 2 to 1 excess of station-days in the cold season versus the warm season are also evident in city-days and incident-days. All but one episode-day came in the cold season. These results are consistent with those from SURE which found a winter maximum for average nitrate concentrations in the Great Lakes region<sup>10</sup>.

The average network concentration and the coefficient of variability (network standard deviation divided by network average expressed as a percentage) on the eleven episode days are given in Table 2. Nine of the eleven days occurred when southern Ontario was under or to the west of an anticyclonic ridge. One episode day occurred when a stationary front lay over Ontario and another when an extended cold front trailing from a low near Newfoundland crossed Ontario.

To illustrate the weather situation in relation to high nitrate concentrations, we will look closely at the period 5-20 February, 1977.

During the period 5 to 20 February, 1977, nitrates were measured in excess of 9.9  $\mu\text{g}/\text{m}^3$  at 68 stations. Most of these occurred on two of the three regular nitrate sampling days (6-day, high-volume sampling schedule). On 12 February, 33 stations exceeded the 9.9  $\mu\text{g}/\text{m}^3$  level, and on 18 February, 21 stations were in excess. The daily monitoring network at three sites (Hamilton, Toronto and Pickering) shows that elevated levels lasted for several days with fairly good correlation among the three sites (Figure 2).

On the 5<sup>th</sup> of February, a large cold air mass in northern Manitoba began pushing southward into the northern Mississippi Valley. During the three day period 5 to 7 February, strong winds from the northwest and cold temperatures dominated southern Ontario. The mean temperature measured during the period at Toronto international Airport was - 14.6°C. Prevailing winds were from the northwest at 20.5 km/hr. Nitrate levels were quite low. The nitrate network of 30 reporting stations averaged 1.7  $\mu\text{g}/\text{m}^3$  on 6 February.

Figure 3a shows the synoptic weather pattern over the Great Lakes basin on 6

February. Also indicated on this Figure (3b) are back-trajectories from Toronto, London, and Windsor calculated from 2400 EST for 12 and 24 h (indicated by x). Trajectories indicate the flow is generally over low-population density areas in the north.

From eastern Iowa, the air mass moved eastward across Illinois, Ohio, and Pennsylvania before turning south on 9 February. As the system moved to the east, the nitrate levels rose at the daily monitoring sites, exceeding  $15 \mu\text{g}/\text{m}^3$  at Hamilton and Toronto on the 10<sup>th</sup> (Figure 2). A low pressure cell crossed the region on the 11<sup>th</sup> leaving a stationary front across northern Ontario on the 12<sup>th</sup> (Figure 4a). An intensifying storm system lay to the west of Lake Superior on the morning of the 12<sup>th</sup> and the cold high had settled off the Carolina coast. Temperatures in southern Ontario rose above the freezing mark with moderate WSW winds.

Across the network (figure 5), nitrate levels were reported on the 12<sup>th</sup> in excess of  $9.9 \mu\text{g}/\text{m}^3$  at 33 sites. The average for the 35 sites reporting was  $17.4 \mu\text{g}/\text{m}^3$ . The coefficient of geographical variability Cvg on this day was 27%, quite low variability (Table 2).

The 24 h back trajectories in Figure 4b show that the air entering southern Ontario had passed over northwestern Ohio. The London trajectory shows that the air had passed over Lake Erie and rural Ontario after crossing Ohio. Since nitrate inputs over the lake and a rural area in winter are unlikely to be of consequence, the source for high nitrate levels is likely to originate in the air mass south of the lake. Nitrate levels are of similar concentration in Windsor (in excess of  $20 \mu\text{g}/\text{m}^3$ ) and the trajectory shows air originating in nearly the same location.

As the storm system moved across the region, nitrate levels fell at the daily monitors (Figure 2). With the establishment of a northerly flow pattern in the wake of the storm and ahead of another cold air mass in northern Manitoba, nitrate levels fell to values similar to the 5 to 7 February period. This anticyclone moved along the same general path as the previous one. By the 18<sup>th</sup> (Figure 6a), the region was again in the return circulation of the anticyclone with a low pressure system approaching from the

north of Lake Superior. Nitrate levels again rose (Figure 7) averaging  $12.5 \mu\text{g}/\text{m}^3$  with 21 of 32 reporting stations in excess of  $9.9 \mu\text{g}/\text{m}^3$ .

Trajectories to all three sites (Figure 6b) show flow again across northwestern Ohio. With the passage of the cold front and return to northerly winds on the 19<sup>th</sup>, nitrate concentrations dropped to less than  $5 \mu\text{g}/\text{m}^3$ .

The trajectory analyses above and the results of a previous study<sup>8</sup> which showed nitrate concentrations increased when southerly flow was initiated as high pressure systems moved to the east of Ontario, when coupled with the low concentrations found when the air originated to the north of the Great Lakes, strongly indicate a source region for nitrates south of the Great Lakes. Source inventories for eastern North America (figure 8) show that two of the largest emitting areas of nitrogen oxide gases are located in the Toledo, Ohio - Detroit, Michigan and Chicago areas - locations to the southwest of southern Ontario.

Since there is a large difference in the amount of nitrogen oxide gases emitted in the area north and south of the Great Lakes, tracing the direction of movement of an anticyclone centre should give an indication of source contributions of the two areas.

Since the centre of an anticyclone is generally a stable parcel of air, nitrogen oxides injected into the air mass as it passes over the source region will likely remain and be converted to nitrates within the air mass. In this manner, nitrates will accumulate and be transported over long distances until removed by dry or wet deposition or chemical transformation.

Anticyclone centres were partitioned according to the direction from which they approached southern Ontario (north, south, or west) during the 1976-1978 period. When an anticyclone remained over southern Ontario, only the first day was included in the data sample to avoid the possibility of excessive nitrate formation from locally emitted nitrogen oxides.

Two locations were chosen for this study: the downtown Toronto and the rural Pickering stations - both daily monitors. The average nitrate concentration on days when anticyclone arrived from the north or northwest was  $3.12 \mu\text{g}/\text{m}^3$  for 58 occasions in Toronto and  $2.42 \mu\text{g}/\text{m}^3$  for 50 cases in Pickering. When the anticyclones came from the south or southwest, concentrations rose to  $5.92 \mu\text{g}/\text{m}^3$  (for 48 days) in Toronto and  $5.17 \mu\text{g}/\text{m}^3$  (for 46 days) in Pickering. The difference of about  $2.8 \mu\text{g}/\text{m}^3$  at both sites was significant at a 99% confidence level. Centres originating in the west (i.e. those which had no definite movement from a south or north direction) had concentrations of  $3.74 \mu\text{g}/\text{m}^3$  for 36 cases and  $3.73 \mu\text{g}/\text{m}^3$  for 31 cases for Toronto and Pickering respectively.

## **Conclusions**

During episodes of high nitrate concentrations across the southern Ontario monitoring network, variability of the concentrations was low. The days on which these episodes occurred were often synoptically characterized by either an anticyclone of southern origin over the region or an anticyclone to the east of the region with south-southwest flow into Ontario. Since the region from which this air entering Ontario came emits large quantities of nitrogen oxides (the nitrate precursor), it is likely that much of the nitrate collected in Ontario was transported from source regions at a distance.

A study of the nitrate burden of air masses moving from the north and the south showed a concentration from the southerly air masses nearly twice those in the northerly air mass.

Nitrates, therefore, are transported into southern Ontario from sources located south of the Great Lakes in significant quantities.

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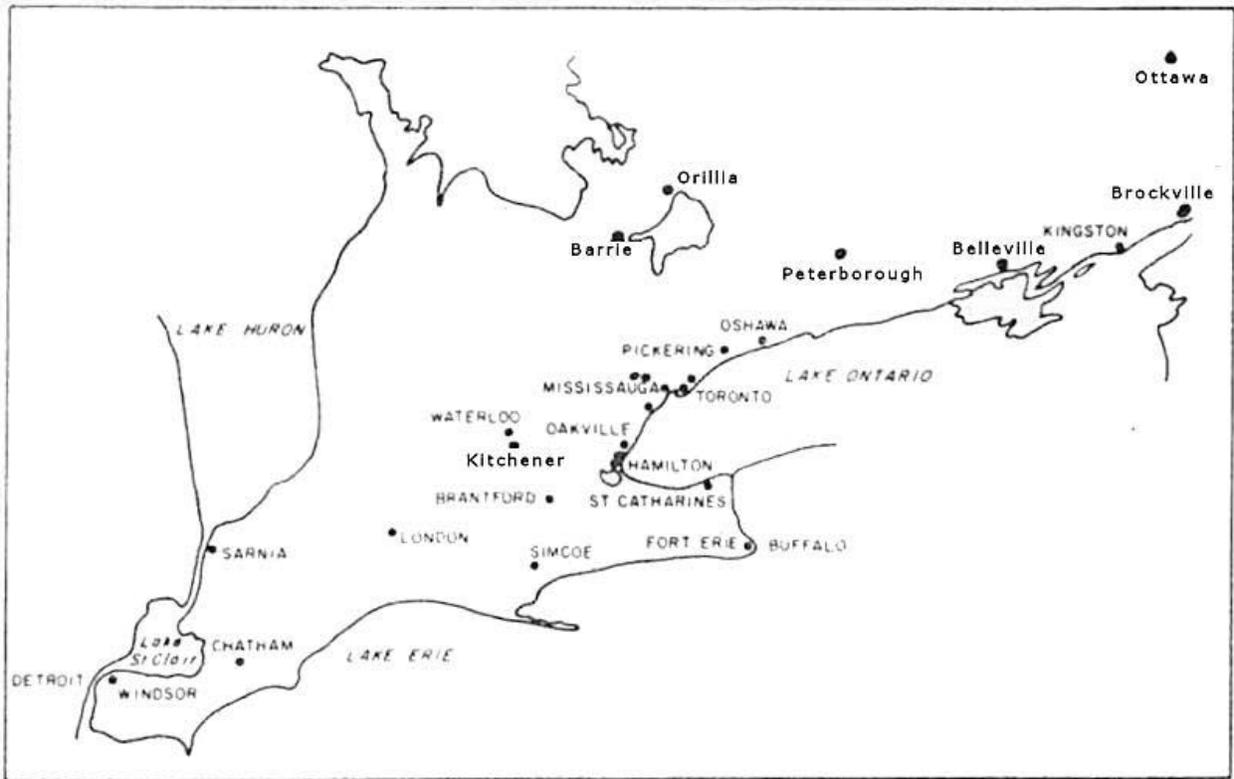


Fig. 1. Cities in southwest Ontario for which nitrate measurements are available.

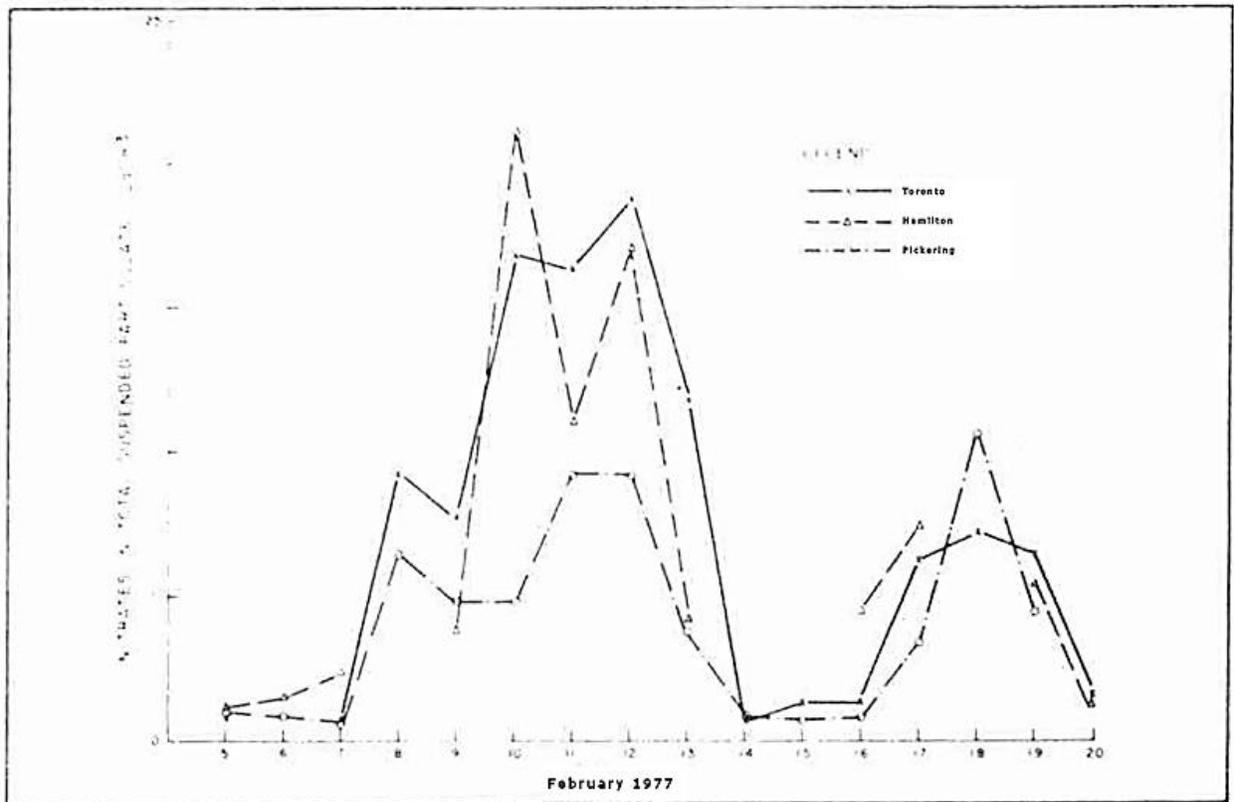
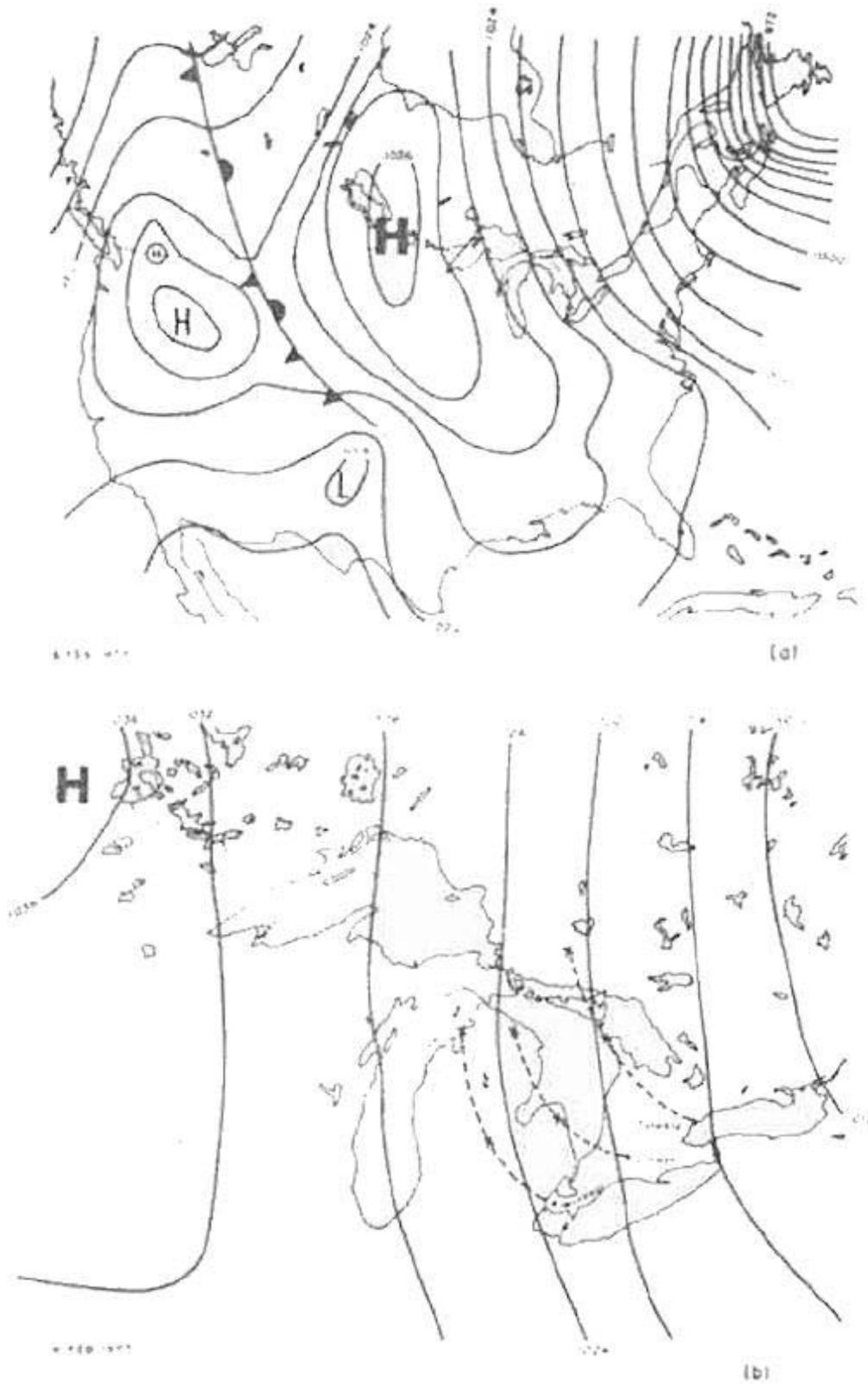
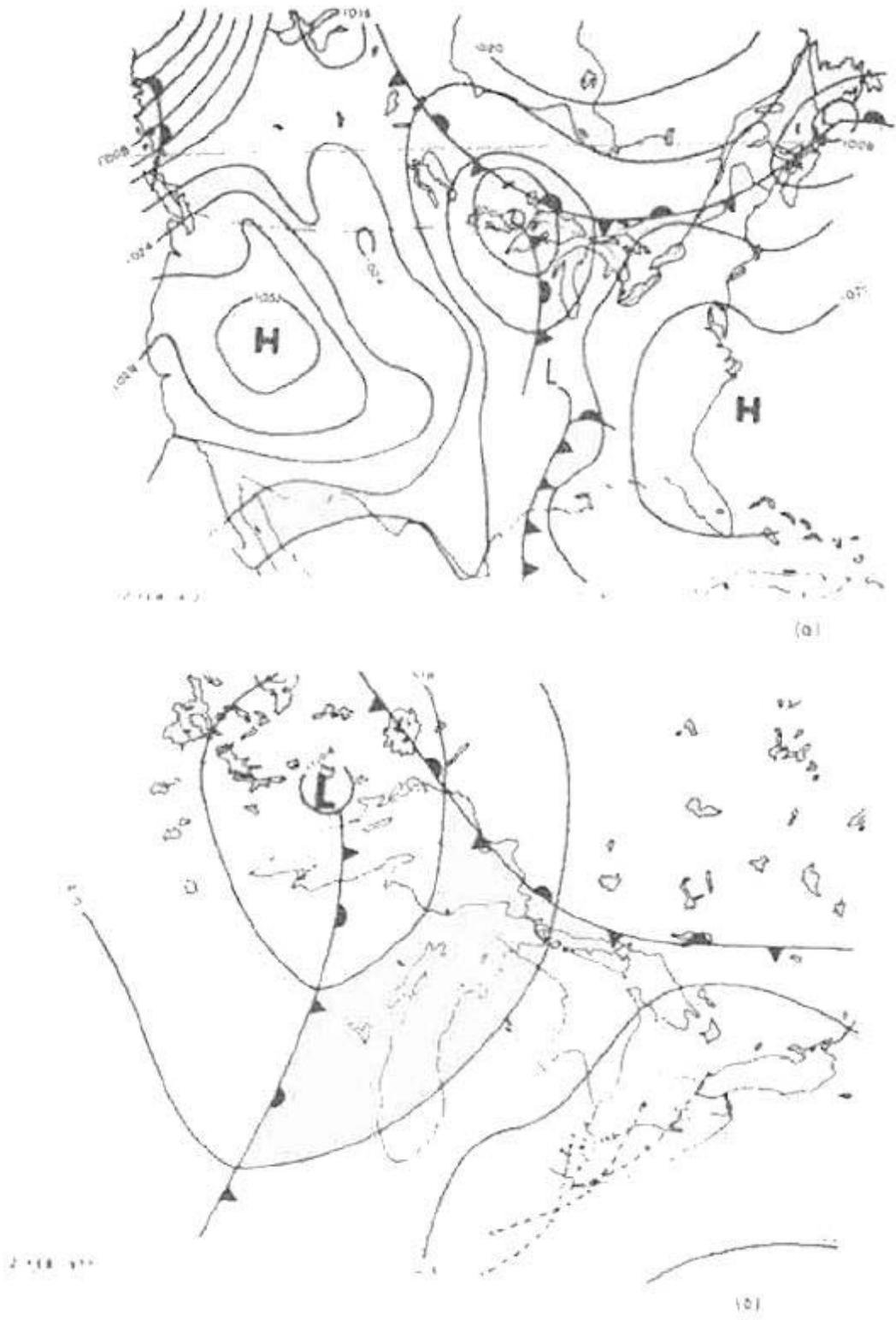


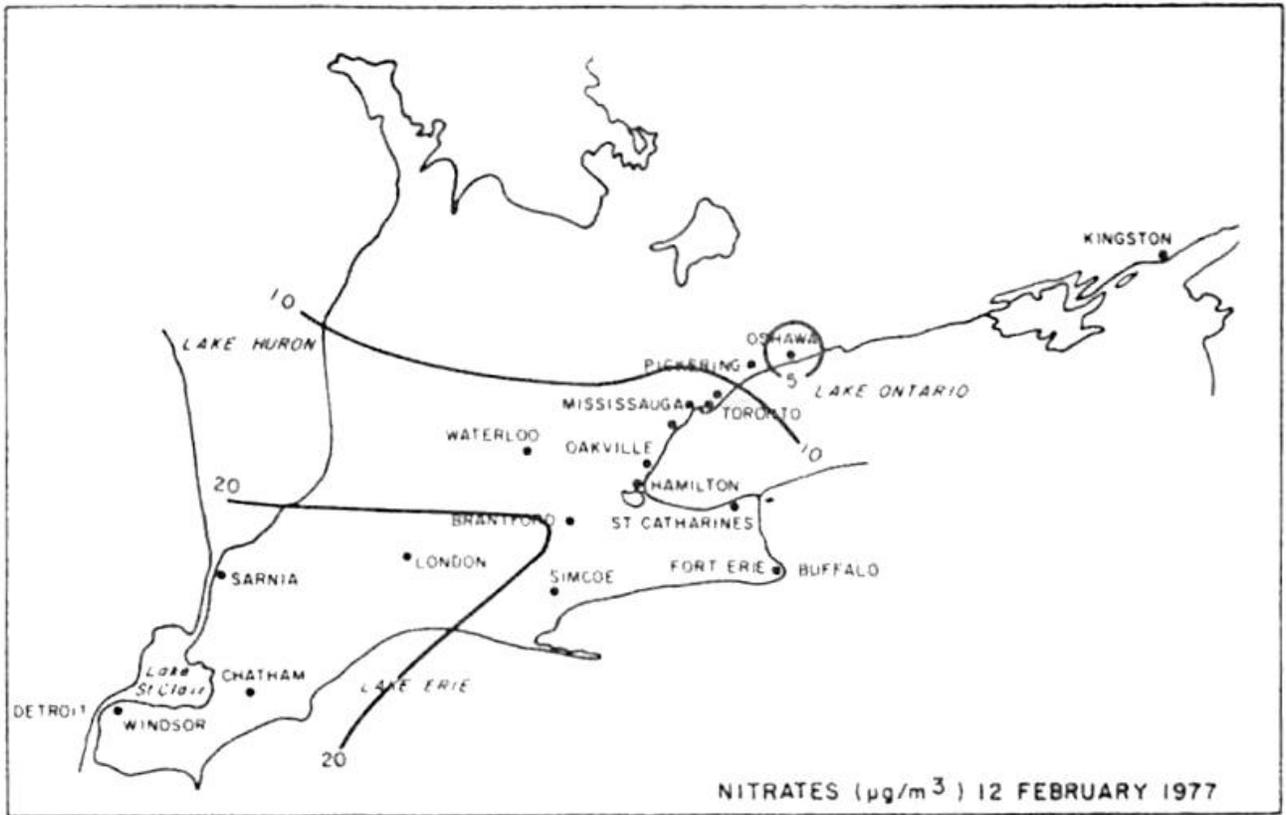
Fig. 2. Daily nitrate concentration for three cities for 5-20 February, 1977.



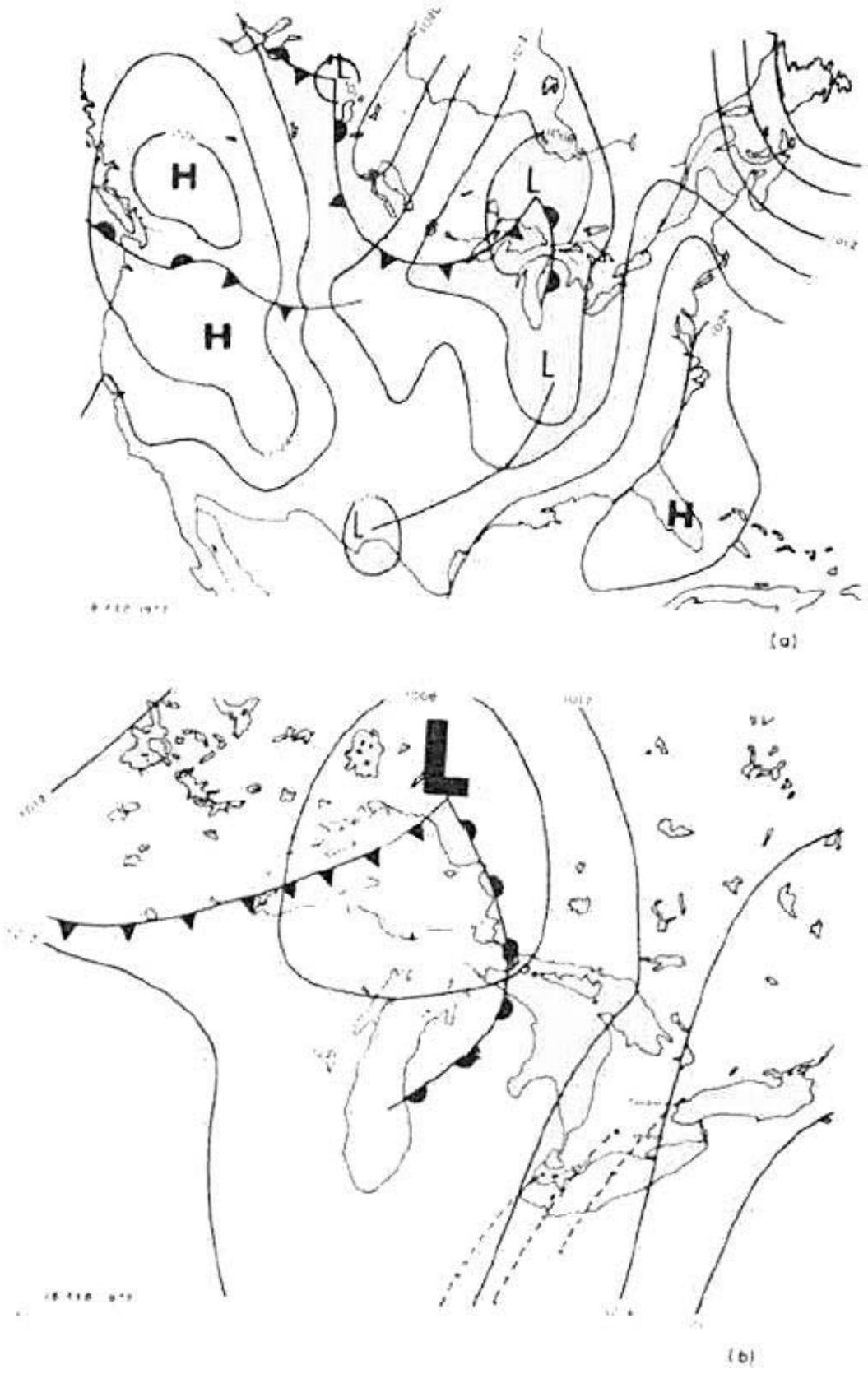
**Fig. 3.** (a) Synoptic weather conditions at 0700 EST b February, 1977. (b) Dashed line indicates back-trajectories from 2400 EST for past 12 and 24h from Windsor, London, and Toronto.



**Fig. 4.** (a,b) Same as Figure 3 for 12 February, 1977.



**Fig. 5.** Nitrate concentrations ( $\mu\text{g}/\text{m}^3$ ) for 12 February, 1977.



**Fig. 6.** (a,b) Same as Figure 3 for 18 February, 1977.

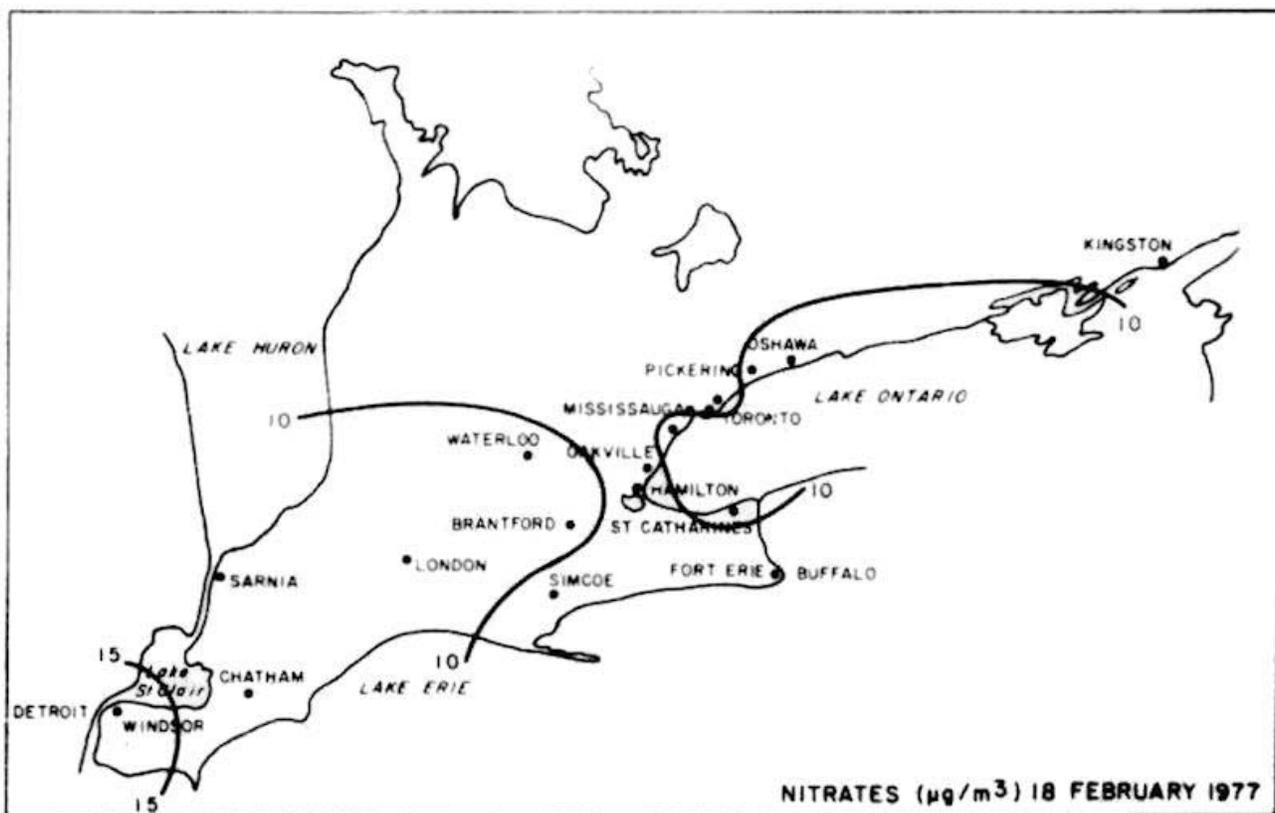
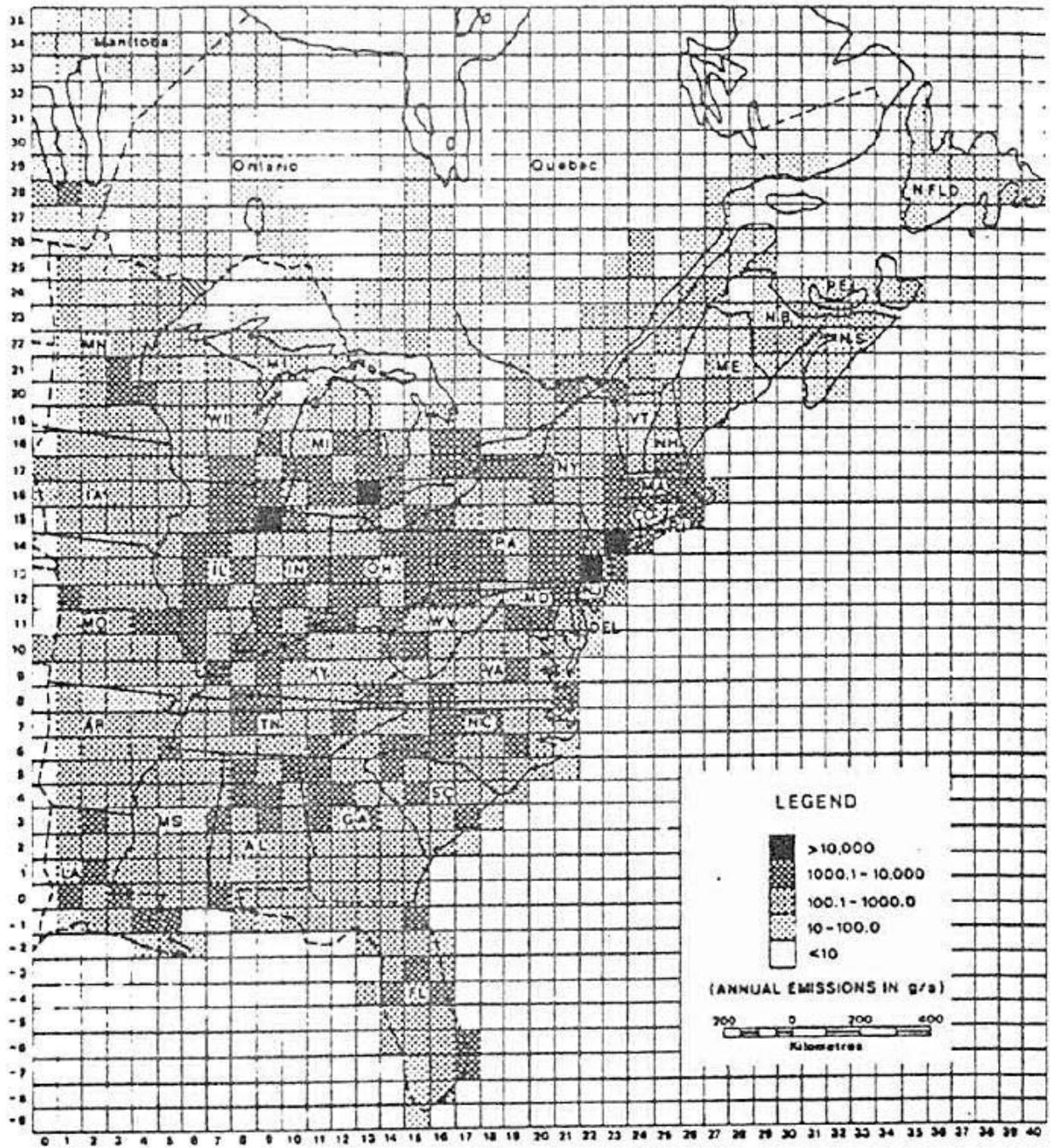


Fig. 7. Nitrate concentrations ( $\mu\text{g m}^{-3}$ ) for 18 February, 1977.



**Fig. 8.** Magnitude and Distribution of Emissions of Nitrogen Oxides in Eastern North America (after LRTAP Research Consultation Group, 1979).

**TABLE 1.** Annual Distribution of Nitrate Concentrations Greater than 9.9 µg/m<sup>3</sup>.

Month	1976-1979			
	Station-Days <sup>1</sup>	City-Days <sup>2</sup>	Incident Days <sup>3</sup>	Episode Days <sup>4</sup>
January	67	47	6	0
February	181	110	12	2
March	230	145	17	4
April	89	47	8	1
May	73	55	4	0
June	54	41	3	0
July	48	41	4	0
August	47	40	1	0
September	45	38	2	0
October	34	33	3	0
November	152	97	7	3
December	53	43	3	1
October-March	717	475	48	10
April- September	356	262	21	1

## Definitions:

1. Station-Day: One station reporting a nitrate concentration of 9.9 µg/m<sup>-3</sup> on a given day.
2. City-Day: One or more stations reporting a nitrate concentration of 9.9 µg/m<sup>-3</sup> on a given day in a city.
3. Incident-Day: Three or more cities reporting nitrate concentrations of 9.9 µg/m<sup>-3</sup> at one or more stations on a given day.
4. Episode-Day: Nine or more cities reporting nitrate concentrations of 9.9 µg/m<sup>-3</sup> at one or more stations on a given day.

**TABLE 2.** Nitrate Episodes in Southern Ontario, 1976-1979.

Date	Average Concentration ( $\mu\text{g}/\text{m}^3$ )	Cvg (%)	No. of Reporting Stations	No. of Stations $9.9 \mu\text{g}/\text{m}^3$	Synoptic Weather Type
12 FEB 77	17.4	27	35	33	back of anticyclone
18 FEB 77	12.5	54	32	20	centre of anticyclone
8 MAR 77	11.5	38	36	21	centre of anticyclone
9 MAR 78	13.8	66	39	22	back of anticyclone
4 NOV 78	12.8	44	34	26	back of anticyclone
10 NOV 78	9.7	44	36	17	extended cold front
16 DEC 78	9.3	27	41	14	stationary front
16 MAR 79	10.1	40	43	22	centre of anticyclone
22 MAR 79	14.0	49	44	35	centre of anticyclone
21 APR 79	8.7	54	44	20	back of anticyclone
17 NOV 79	13.6	34	49	42	back of anticyclone