

**THE ATMOSPHERIC PATHWAY FOR OXIDES  
OF NITROGEN**

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## **NOTICE**

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### Introduction

Oxides of both sulphur and nitrogen can lead to acidification of the environment at locations well removed from the original sources of these pollutants. Although oxides of sulphur have received much attention in recent studies of the long range atmospheric transport and deposition of acidifying pollutants, nitrogen oxides ( $\text{NO}_x$ ) are also important because:

- a) they play a role in the production of oxidants (known to have effects upon agricultural crops);
- b) their atmospheric chemistry is inextricably intertwined with that of sulphur;
- c) the accumulation of nitrates in snow causes an increase in ground surface and runoff acidification during the melting of the snowpack in the spring.

The atmosphere provides the pathway from source to receptor for nitrogen oxides. This paper briefly describes what is known about the physical and chemical processes affecting nitrogen oxides along the atmospheric pathway.

### Sources of Oxides of Nitrogen

The anthropogenic sources of atmospheric nitrogen oxides are high temperature combustion processes during which the nitrogen in the combustion air is oxidized. Table 1 (from MOI, 1982a) shows that, in Canada, the transportation sector accounted for about 61% of the  $\text{NO}_x$  emissions in 1980.

The geographic distribution in eastern North America of  $\text{NO}_x$  emissions is shown in Figure 1 (from Altshuller and McBean, 1978). It is not expected that the distribution has changed substantially since 1978. The density of emissions follows that of population, with maxima along the eastern seaboard of the United States, the Ohio Valley and the lower Great Lakes basin.

### Atmospheric Transport and Diffusion

When any pollutant is emitted into the atmosphere, it is subjected to the physical processes of transport and diffusion. Transport is due to the mean motion of the

TABLE 1 CANADA NATIONAL CURRENT AND PROJECTED NO<sub>x</sub> EMISSIONS  
(10<sup>6</sup> tonnes/year)<sup>a</sup>

	Current 1980	Projected 1990	Projected 2000
Electric Utilities	0.25	0.19	0.26
Industrial Fuel Combustion	0.30	0.30	0.33
Residential/Commercial Fuel Combustion	0.09	0.07	0.07
Non-ferrous Smelters	0.01	0.01	0.01
Other Industrial Processes <sup>b</sup>	0.07	0.07	0.07
Transportation	1.11	1.34	1.67
<b>TOTAL</b>	<b>1.83</b>	<b>1.98</b>	<b>2.41</b>

<sup>a</sup> Source of Projections: The projected emission estimates are based on the 1980 emissions and were developed by Environment Canada using energy consumption projections provided in National Energy Board reports. From MOI (1982a).

<sup>b</sup> Includes process emissions from petroleum refining, natural gas processing, tar sands operations, other industrial processes and miscellaneous sources.

air, or mean wind, and results in the motion of the centre of gravity of the pollutant cloud over distances which may be only a few kilometres (as in the case of short range transport) or several hundred to 2000 kilometres or more (as in the case of long range transport). Figure 2 (from Shaw, 1982) shows the mean motion of the air at a height of 1.5 km, a typical height for transport of pollutants near the earth's surface. The mean motion is from southwest to northeast, although on any given day the movement of air pollutants around travelling cyclones and anticyclones could be in any direction, resulting in a certain "smearing" of the concentrations and depositions around a source area.

Deviations of air motion about the mean wind velocity are called turbulence. Turbulence occurs in both horizontal and vertical directions. In the horizontal, turbulence can occur on scales of the size of the plume or on much smaller scales. The former scale of turbulence causes the plume to meander about its mean centreline, the small scale turbulence causes the plume to diffuse and broaden horizontally. In the vertical, the turbulence is of a scale smaller than that of the plume and has the effect of causing the vertical depth of the plume to increase with distance travelled downwind. This vertical spreading is not unlimited, however, and is almost always confined to a mixed layer next

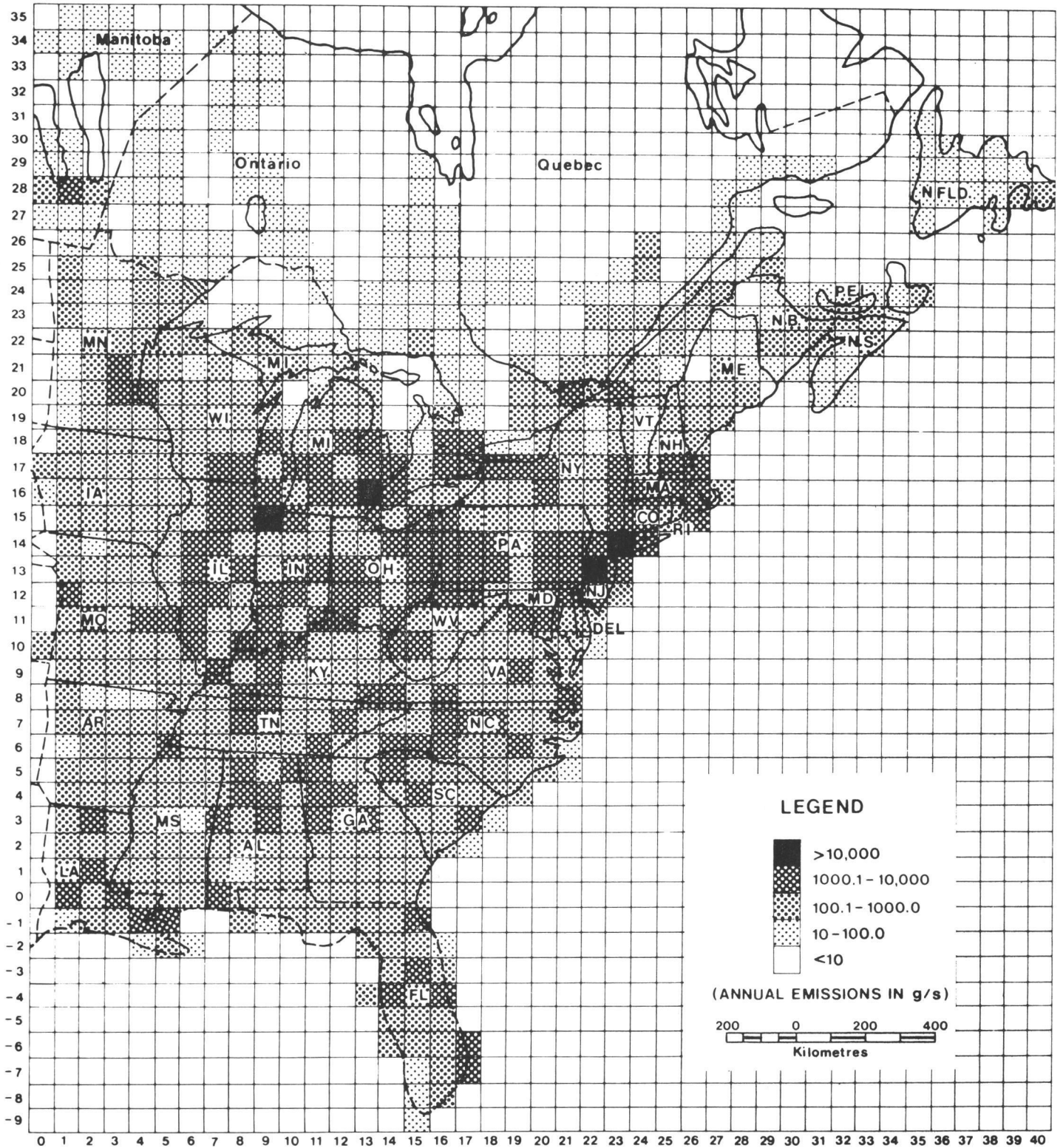


FIGURE 1 MAGNITUDE AND DISTRIBUTION OF EMISSIONS OF NITROGEN OXIDES ( $NO_x$ ) IN EASTERN NORTH AMERICA (Altshuller and McBean, 1979)

Source: U.S.A. emissions from SURE II data base. Canadian emissions from Environment Canada.

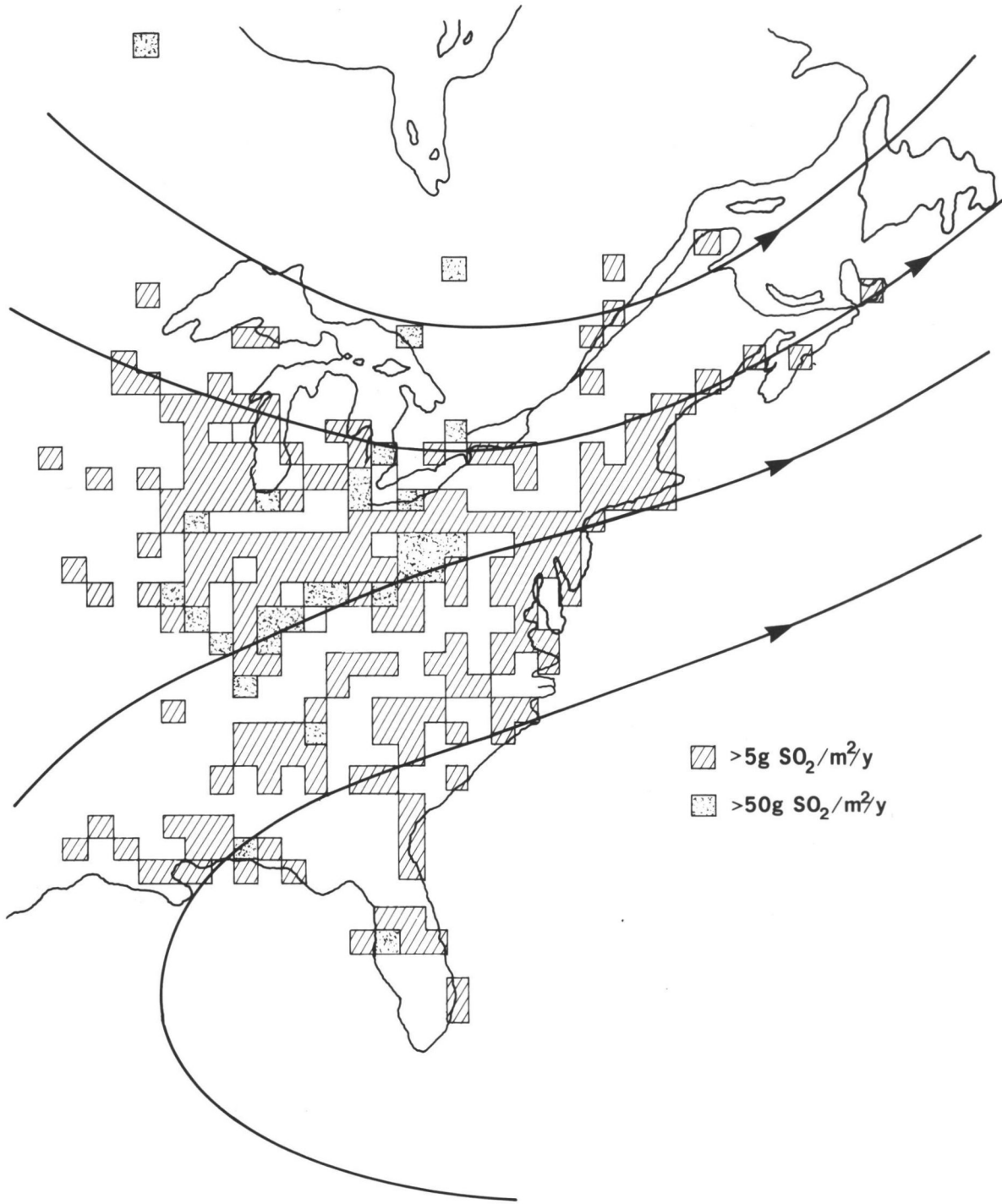


FIGURE 2 MEAN MOTION OF AIR AT 1.5 km ABOVE EARTH'S SURFACE

to the earth's surface which is capped by an inversion or a stable layer. The vertical extent of the surface mixed layer, or "mixing height", is an important parameter which directly affects the concentration of the pollutant and the rate of deposition to the surface.

Nitrogen oxides are emitted from vehicles at ground level, in contrast to industrial emissions which are released from tall stacks of up to several hundred metres in height. This factor makes vehicle emissions less subject to long range transport than industrial emissions because considerable impaction and deposition may occur relatively close to the source before the vehicle emissions are thoroughly diluted in the surface mixed layer. Consequently, changes in automobile emissions are likely to have a more localized effect than changes in industrial emissions.

### **Atmospheric Chemical Transformations Affecting Oxides of Nitrogen**

The chemistry of  $\text{NO}_x$  in a polluted atmosphere is extremely complex and is not completely understood. It is inextricably intertwined with the chemistry of oxidants and of sulphur oxides, as shown in simplified form in Figure 3 from MOI (1982 b). The oxidant cycle on the left hand side of Figure 3 indicates that the steady-state concentration of ozone depends upon the ratio of  $\text{NO}_2$  to  $\text{NO}$ .

The  $\text{NO}_2$  in Figure 3 also takes part in the central loop of reactions which involve volatile organic compounds (VOCs). The  $\text{NO}_x$ -VOC cycle has a determining influence on the  $\text{OH}$  and  $\text{HO}_2$  concentrations. The  $\text{OH}$  radical is an important gas phase (i.e., outside of cloud and rain) reactant for both  $\text{SO}_2$  and  $\text{NO}_x$ . Furthermore,  $\text{HO}_2$  is essential for the formation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), a very strong oxidant for  $\text{SO}_2$  in cloud and rain droplets. It is believed by some chemists that liquid phase oxidation of  $\text{SO}_2$  may be the dominant pathway for producing sulphate. Therefore, the  $\text{NO}_x$ -VOC chemistry has a strong influence on the oxidation of  $\text{SO}_2$ .

Finally, as mentioned above,  $\text{NO}_2$  itself is oxidized to nitric acid ( $\text{HNO}_3$ ) by the  $\text{OH}$  radical. On an annual basis, nitrates contribute about 35% of the precipitation acidity, while sulphates contribute the balance (Galloway and Dillon, 1983). During the winter months it is reported that the nitrate contribution is about 50% in areas receiving the heaviest deposition in Canada (from AES CANSAP data, 1984).

### **Deposition Processes for Oxides of Nitrogen**

Surface deposition of acidifying pollutants can occur via diffusion and absorption in the absence of precipitation ("dry" deposition), or by precipitation ("wet"

## FREE RADICAL INITIATORS

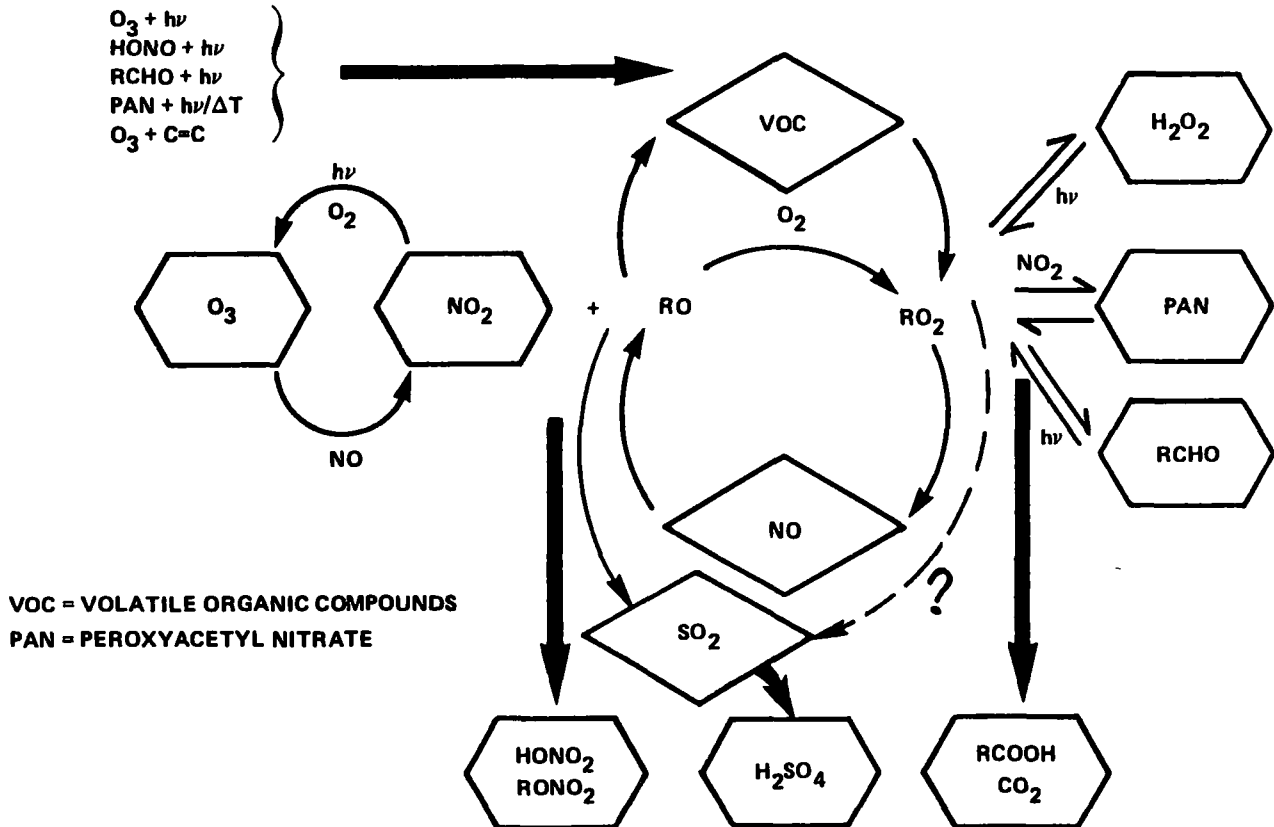


FIGURE 3 SCHEMATIC OF THE POLLUTED ATMOSPHERIC GAS-PHASE PHOTOOXIDATION CYCLE (MOI, 1982b)

deposition). The latter can be directly measured by collecting precipitation samples or can be estimated in models by multiplying the concentrations by a factor called the "scavenging coefficient". No method yet exists for directly measuring dry deposition; its flux is usually estimated by assuming it to be proportional to ambient concentration. Because of the units involved, the constant of proportionality is called the "dry deposition velocity".

Values for the scavenging coefficient and deposition velocities for  $NO_x$  are not as well known as they are for oxides of sulphur. Even for sulphur oxides, they can vary over several orders of magnitude depending upon the atmospheric stability, the type of precipitation (i.e., snow or rain) and the nature of the surface, among other things (McMahon and Denison, 1979). Therefore, it is not yet possible to make model predictions of  $NO_x$  and nitrate deposition.



Observations have been made, however, of regional patterns of nitrate deposition by precipitation as shown by Figure 4 from MOI (1982b). The pattern of wet deposition is elongated in a southwest-northeast orientation in accordance with the prevailing atmospheric flow in the lower layers. The area of maximum deposition is located somewhat downwind of strong source regions in the mid west and over strong source regions in the Lower Great Lakes region. Although the pattern is smoothed by the low density of observations and probably by "smearing" of the plumes by passing cyclones and anticyclones, there is a suggestion of an extension of the maximum toward the strong source area in the New York/New Jersey area. The close correspondence of deposition patterns to emission patterns suggests that changes in NO<sub>x</sub> emissions manifest themselves relatively close to the source.

An approximate estimate of the contribution of NO<sub>x</sub> emitted from light duty vehicles to wet deposition can be made as follows: light duty vehicles account for about 26% of NO<sub>x</sub> emissions in eastern Canada (MOI, 1982a), and nitrate deposition accounts for about 35% of total acid deposition annually. Therefore, light duty vehicles account for about 9% of acid deposition from all sources. Because the nitrate contribution to deposition increases in the winter, it might be expected that the portion attributable to light duty vehicle emissions also increases.

### **Effects of Changing NO<sub>x</sub> Emissions on Atmospheric Concentrations and Depositions**

Models have been devised to simulate the long range atmospheric transport and deposition of sulphur compounds. These models have been moderately successful in predicting large scale patterns of the wet deposition of sulphur in North America. Despite the simplifications used in the models, such as linear processes of chemical transformation and of deposition, source-receptor matrices linking emissions in 40 source areas to wet deposition at nine receptor points have been developed (MOI, 1982b).

Opinion is divided as to whether or not the modelling is advanced enough that the source-receptor matrices can be used to separate the contributions of the various source regions to sulphur concentration and depositions at a given point. Some groups, such as the National Academy of Science in the United States, say that they are not, whereas some other workers believe that one can formulate sulphur emission control strategies based upon broad geographical areas using models (Streets *et al*, 1983; Shaw and Young, 1983).

No such transfer matrices exist for nitrogen oxides because of the great lack of knowledge of their rates of chemical transformation and deposition. However,

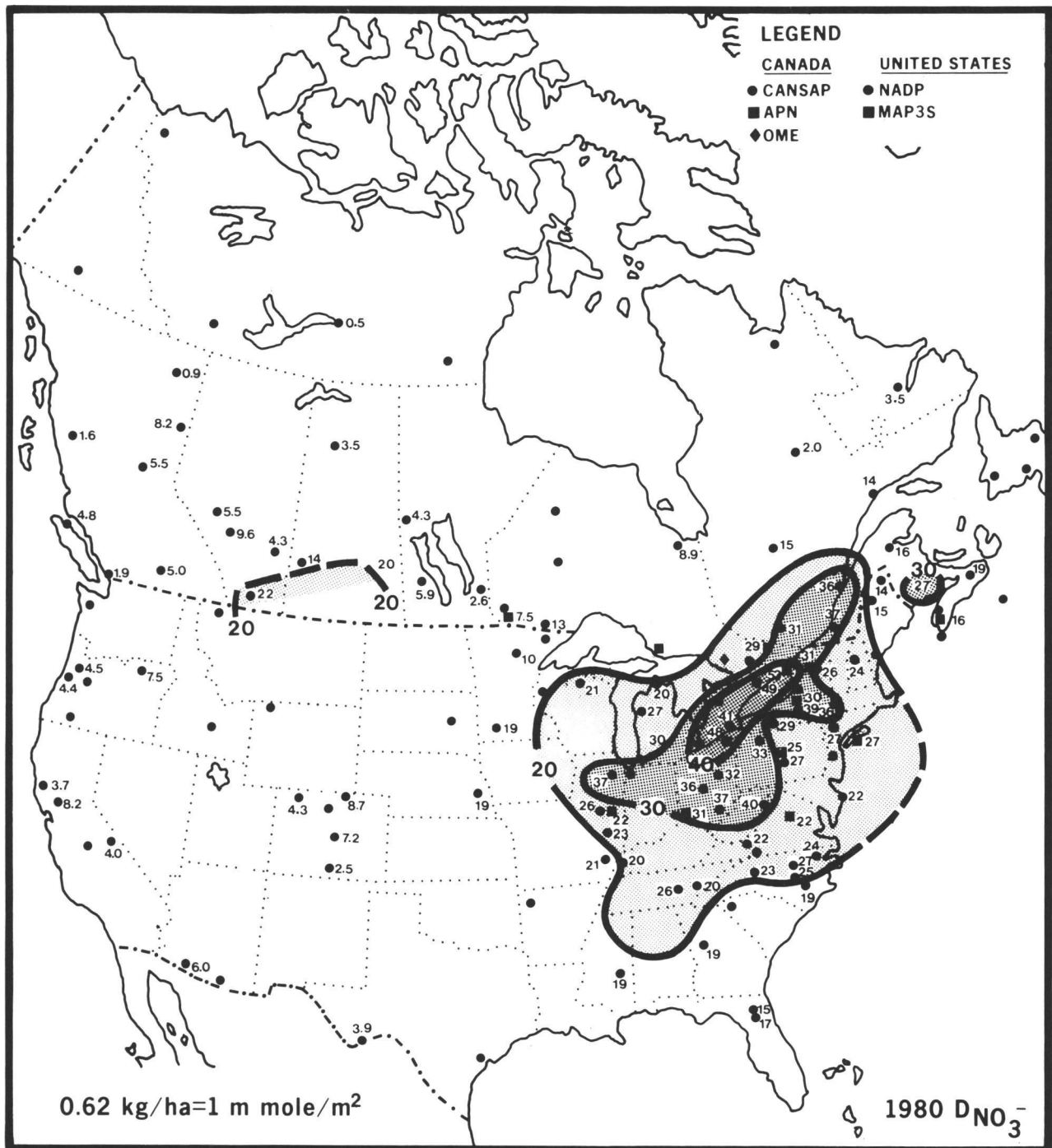


FIGURE 4

PRECIPITATION AMOUNT - WEIGHTED MEAN NITRATE ION DEPOSITION FOR 1980 (m moles per square metre). From MOI (1982b).

qualitative predictions can be made of the results of reducing NO<sub>x</sub> emissions. These are as follows:

- a) Reduction of NO<sub>x</sub> emissions should lead to a reduction in the formation and deposition of nitric acid. The formation of nitric acid in polluted air masses is believed to occur within the first 10-15 hours of travel, whereas the formation of sulphuric acid takes place more slowly over several tens of hours (Rodhe et al, 1981; Calvert and Stockwell, 1983). The deposition patterns for nitrate ion in Figure 4 seem to be closely tied to the distribution of NO<sub>x</sub> sources. Therefore, the reduction of NO<sub>x</sub> emissions in Canada should lead to less deposition and storage of nitrates in snowpacks, thereby reducing the "pH shock" during the spring snowmelt in ecologically sensitive areas.
- b) As stated above, the steady state concentration of ozone depends upon the ratio of NO<sub>2</sub> to NO. Therefore, the effect upon ozone of reducing NO<sub>x</sub> emissions will depend upon how that ratio changes. At certain VOC/NO<sub>2</sub> ratios, reduction of NO<sub>x</sub> emissions may actually increase ozone concentrations in urban areas (Innes, 1981). On a regional scale, however, decreases in NO<sub>x</sub> emissions will probably reduce ozone concentrations in downwind rural areas (Singh, 1979).
- c) The effect of a change in NO<sub>x</sub> emissions on the production and deposition of atmospheric sulphates is difficult to predict because of the complex relationships between sulphur and nitrogen chemistry. SO<sub>x</sub> and NO<sub>x</sub> are both oxidized in the gas phase by the OH radical; reducing NO<sub>x</sub> should lead to less OH formation and lower the formation rate of sulphate. On the other hand, reducing NO<sub>x</sub> will increase the concentrations of HO<sub>2</sub> and the liquid-phase oxidant H<sub>2</sub>O<sub>2</sub>, thereby increasing the rate of formation of sulphates. Such changes in emissions would have the effect of altering the zone of deposition of sulphates rather than changing the absolute value of the amount deposited.

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