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Atmospheric decay distances and times for sulphur and nitrogen oxides estimated from air and precipitation monitoring in eastern Canada

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ABSTRACT

Previous estimates of residence times for sulphur species have been made mainly from the overall box budget approach by considering the various deposition and conversion terms in a "static" reservoir. This paper will use a "dynamic" approach by considering daily filter-pack and precipitation observations taken at several eastern Canadian monitoring sites over a period of several years. Some of these sites are lined up from southwest to northeast along the most frequent wind direction for pollutant transport episodes. Concentrations can thus be examined in the Lagrangian sense starting at the edge of the major North American emission region and ending at a remote site in Newfoundland over 2000 km away. Plots of concentration of the monitored species in air and precipitation against distance from the emissions region, show a good fit to an exponential curve. The decay distances, defined as the distances for the initial concentration to fall to 1/e of its original value, can thus be determined. These are in air: 480 km for SO_2, 1280 km for $SO_4^=$, 720 km for total sulphur ($SO_2 + SO_4^=$) and 540 km for total nitrate (HNO_3 + particulate nitrate). In precipitation the decay distances are 1700 km for $SO_4^=$ and 1100 km for NO_3^-. Using mean velocities for southwesterly trajectories across the region, the decay distances can be converted to decay times. These are estimated for air concentrations to be: 14 h for SO_2; 58 h for $SO_4^=$; 24 h for total sulphur and 16 h for total nitrate. In the case of SO_2 and total sulphur, the decay times are equivalent to residence times.

1. Introduction

When considering the global distribution of trace gases and aerosols, knowledge of their decay distances or residence times in the atmosphere is important from several points of view. Firstly, these parameters provide information on the depletion (transformation or deposition) rates in the atmosphere. Secondly, the geographical zone of influence of major emission regions can be determined and this has a direct practical application to the consideration of regional control strategies for various pollutants. Thirdly, the steady-state balance in remote regions, and the possibility of an increase in the global atmospheric burden of pollutants, is related to residence times.

Early discussions of the concept of residence times in natural reservoirs by Eriksson (1961, 1971) focussed on the average age of particles within the reservoir. The discussion was broadened by Bolin and Rodhe (1973) to consider the concepts of age distribution, transit time distribution, turn-over time, average age and finally average transit time which they considered to be the "residence time". The discussion included the development of simple relationships between these terms and a classification of reservoirs in terms of the relationships. The concepts were then applied in detail to budgets and turn-over

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times of atmospheric sulphur compounds by Rodhe (1978), using steady-state box models. The discussion was further developed by Schwartz (1979) to include time-dependent rates of SO_2 to $SO_4^=$ conversion and dry deposition.

All of the above approaches considered a fixed reservoir, either the global atmosphere or the atmosphere over a large region such as Europe. Rodhe (1978) discusses the optimum size for boxes to be used in budget studies depending on the magnitude of the input-output terms and the residence time of the species being considered, which may not in fact be known beforehand. The approach to be used in this paper overcomes some of the difficulties and assumptions in the static, fixed box method and instead considers the measured changes in concentration in a dynamic, Lagrangian sense as air moves from the pollutant source region across eastern Canada. In this way decay distances, decay times and in some cases residence times can be estimated more directly.

2. The Lagrangian approach

2.1. The monitoring data used

Several monitoring networks have been operating in eastern Canada starting in the late 1970's. Most measure only precipitation, but two networks have a small number of sites measuring air concentration of sulphur and nitrogen oxides at a height of 10 m. The Air and Precipitation Network (APN) operated by Environment Canada began with three stations late in 1979 and had expanded to eight stations by the end of 1982 before it was incorporated in the Canadian Air and Precipitation Monitoring Network (CAPMoN) in 1983. A brief description of the APN network is given by Barrie et al. (1984) with fuller details in Barrie et al. (1980). Essentially the same daily sampling protocols are used in CAPMoN, although in this case not all sites monitor air concentrations. The Ontario Government has also operated two networks under the Acid Precipitation in Ontario Study (APIOS) since 1982 (Chan et al., 1982) and at four sites daily average air concentrations are measured.

Both networks measure airborne concentrations of sulphur dioxide (SO_2) and sulphate ($SO_4^=$) which accounts for most of the atmospheric sulphur compounds found in this polluted region, and the sum of the two will be referred to as total sulphur (T-S). In the case of nitrogen, only nitric acid (HNO_3) and particulate nitrate (p-NO_3^-) are measured and will together be referred to as total nitrate (T-NO_3^-). Since NO_2 and PAN are not measured routinely in these networks, only a portion of the oxidation end-products of the anthropogenic NO_x emissions are accounted for. Measurements by Brice et al. (1988) show that close to the NO_x source region at LWD in southern Ontario, the average molar ratio of PAN to T-NO_3^- is 0.35, but further downwind at a site in southern Nova Scotia the ratio is between 0.4 and 0.5. During a mid-winter field study in central Ontario NO_x concentrations (mainly as NO_2) were found to always exceed HNO_3 concentrations, sometimes by as much as a factor 5 (Daum et al., 1988). Thus, total airborne nitrogen cannot be considered.

The selected monitoring sites used in the paper are shown in Fig. 1. These stations were chosen because they are lined up in sequence along the path of the predominating long-range transport episodes of pollutants originating in the lower Great Lakes area and being advected across

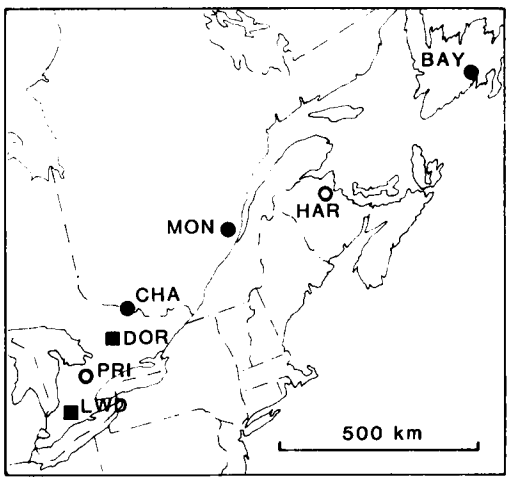

Fig. 1. Map showing the locations of the sites from which daily observations of SO_2, $SO_4^=$ and NO_3^- in air and $SO_4^=$ and NO_3^- in precipitations were used. Atmospheric Environment Service: ● Air and Precipitation, ○ Precipitation only. Ontario Ministry of Environment: ■ Air and Precipitation.

eastern Canada. Thus, the change in pollutant concentrations in both air and precipitation can be observed as air parcels pass over stations successively further downwind. In principle it should be possible to follow individual episodes, but the long sampling period of 24 hours, compared to the typical time of 1 to 3 days for an episode to pass over a station, precludes this approach as illustrated below.

The average spacing of the air monitoring stations between LWD and MON is 325 km which is about half of the average 24 h displacement of air parcels in episodes (650–800 km) as discussed later in section 3.2 and Fig. 6. Consider the simple case of a square-wave pulse of pollution, with constant concentration C on a background of zero, propagating across the domain as illustrated schematically on a time-distance graph in Fig. 2. If the pulse arrives at station A exactly at the beginning of a 24 h sampling period the concentration recorded there will be C in sampling period 1 and zero in sampling period 2. If the pulse is travelling at a speed equivalent to twice the sampler spacing in 24 h then at station B it will be recorded as an average concentration C/2 in both sampling periods 1 and 2. At station C, the passage of the pulse again corresponds exactly with the sampling period 2 and a 24 h average concentration of C is again recorded. If the time of arrival of the pulse at station A is now displaced successively by 2.4 h increments over 10 cases, it can be seen that each station will record 2 cases each of 24 h average concentrations of C, 0.9C, 0.8C, 0.7C . . . 0.1C. Over 10 episodes of real constant concentration C, each station would record exactly the same statistical distribution of measured concentrations with a median of 0.5C and a 95 percentile value of 0.95C. If the concentration in the pollution pulse had been decreasing with time as it crossed the domain, then this would be reflected as a direct proportional decrease in all the percentile values at each successive station. In other words, the 95 percentile value would fall by a factor 2 over exactly the same distance as required for the median value to fall by a factor 2.

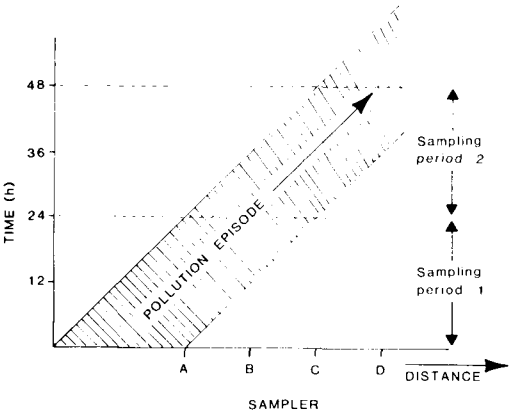

Fig. 2. Schematic representation of a square-wave pollution episode pulse moving across a line of sampling station A to D spanning two 24 h sampling periods.

In the real world, there is no evidence, or meteorological reason, for a preferred time of arrival of episodes at the first sampling station. Thus, with varying times of arrival, and with lengths of episodes and speeds of propagation distributed randomly about their mean value, the differences in the statistical distributions of the observed 24 h concentrations along the line of monitoring stations gives a direct measure of the proportional decrease in concentrations within the episodes, and the decay distance can be obtained from any of the percentiles. However, it is essential that the data used represents only those cases where the episodes pass over each monitoring station in succession.

2.2. Air mass trajectories

A separate study of the trajectory climatology associated with various pollution levels observed at the APN/CAPMoN sites, has shown very distinctive patterns, consistent with the known SO_2 and NO_x emission field (Summers, 1987). For air concentrations, the 925 mb trajectories were used because this height is (a) near the middle of the surface mixed layer, (b) was shown to represent the mean motion of the tracer released during the Cross Appalachian Tracer Experiment (CAPTEX-83) better than either the 1000 mb or 850 mb levels, and (c) accurately depicts the plumes from isolated SO_2 sources in western Canada (Summers, 1987). Haagenson et al. (1987), also using CAPTEX data, showed that for three trajectory models the tracer motion was predicted best by the 950 mb level flow. An example pattern, superimposed on the SO_2 emissions field, is shown in Fig. 3a for the case of all

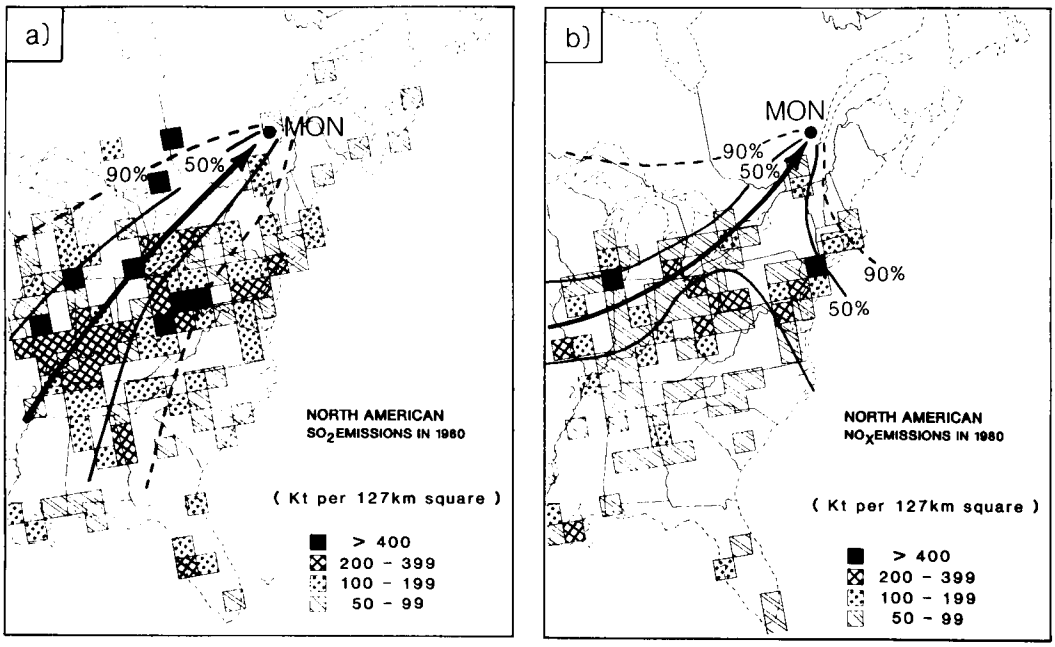

Fig. 3. Climatology of the 925 mb air mass trajectories arriving at Montmorency, Que., (MON) when air concentrations exceed the 95 percentile value: (a) for $SO_4^=$, (b) for NO_3^- (as $HNO_3 + p\text{-}NO_3^-$). Heavy line with arrow represents the median trajectory, regular solid line represents the envelope of 50% of the upwind trajectory hours, and the dashed line represents envelope of 90% of the upwind trajectory hours.

air concentrations in excess of the 95 percentile value (6.5 $\mu g\ SO_4^=\ m^{-3}$) for $SO_4^=$ over the period 1980–1984 at Montmorency, Quebec (MON). It can be seen that the trajectories are contained within a well defined sector, enclosing the major SO_2 sources in southern Ontario and the states south of the Great Lakes. The median trajectory path to MON passes almost directly over the stations to the southwest shown in Fig. 1. Similarly, a trajectory plot (not shown) for the $\geqslant 95$ percentile $SO_4^=$ concentrations at Chalk River, Ontario (CHA) indicates the median pathway over the two stations to the SW of that site. As the concentration cut-off is relaxed, for example to the 90 percentile, the trajectory envelopes becomes wider and with further relaxation eventually to the point where the assumption that the sampling stations gives a representative measure of the concentrations along the pathway becomes invalid. Thus, only the $\geqslant 95$ percentile values will be considered here. Air concentration episodes of $SO_4^=$ are very infrequent at Bay d'Espoir (BAY) in Newfoundland, and when they do occur, the major pathway is up the east coast of North America rather than along the St. Lawrence Valley. Thus, air concentration data from BAY are not used.

The main pathway for $\geqslant 95$ percentile values of air T-NO_3^- is similar to that for $SO_4^=$, but there is a secondary pathway to MON (see Fig. 3b) from the high NO_x emissions along the US east coast from Washington to Boston. However, the distance upwind from MON along the two predominating pathways is about the same to the edge of major NO_x source regions in S. Ontario and lower New York State.

For analysis of $SO_4^=$ and NO_3^- concentrations in precipitation, the selection of an appropriate trajectory height is not possible without much more knowledge of the storm types and their dynamics. Pollutants can be incorporated into precipitation at different heights, thus pollutants transported at all levels in the lower troposphere can make a contribution. In addition, significant

amounts of precipitation are always associated with vertical motion in the atmosphere. A simpler approach is, therefore, used based on the fact that (a) most of the precipitation and wet deposition of $SO_4^=$ in the northeastern North America occurs with southwesterly winds in the lower troposphere (Wilson et al., 1982), and (b) maps of annual wet deposition of $SO_4^=$ and NO_3^- (Barrie and Hales, 1984) suggest a broad "plume" of deposition extending northeastwards from the major SO_2 and NO_x source regions centred in the lower Great Lakes area out to Newfoundland. The axis of this plume lies very close to the line of monitoring stations in Fig. 1, therefore, the average of all rain events at all stations will be used to estimate the decay distance.

3. Results

3.1. Decay distances for air concentrations

The 95 percentile concentrations for SO_2, $SO_4^=$, T-S and T-NO_3^- are shown in Table 1 for the four air monitoring stations LWD to MON. The year 1984 is used since it is the latest year for which high quality data are available. As can be seen from Fig. 3a, once the median trajectory has passed over Lake Erie it follows a track north of Toronto to MON and, compared to the initial SO_2 emissions input, picks up very little additional SO_2 enroute. In the case of the high NO_3^- trajectories (see Fig. 3b) there probably is some further input of NO_x enroute. In Fig. 4, the concentrations in Table 1 are plotted versus distance from the south shore of Lake Erie and in all cases show what appears to be an exponential decay.

The curves for $SO_4^=$ and SO_2 represent the observed decay in concentrations once the air has left the main source region, but since SO_2 is still being converted to $SO_4^=$, the $SO_4^=$ curve represents the net result of depletion by deposition and addition by transformation from SO_2. The curve for T-S, however, is independent of the SO_2 to $SO_4^=$ conversion rate and this does represent the decay of S due to deposition only.

It is assumed that there is little or no removal by precipitation enroute otherwise extreme values of air concentration would not penetrate as far as the CHA and MON stations. Also the effects of horizontal dispersion are minimal because the data used do not represent individual source plumes, but regional scale episodes of the order of 1000 km in horizontal extent in which the pollutants are well-mixed downwind of a large area source itself several hundred km across. The horizontal concentration gradients are very small near the centre of these polluted zones, therefore, decreases in concentration due to diffusion are negligible compared to the other loss terms.

In Fig. 5, the logarithm to base e (ln) of the concentrations is plotted against distance for each of the species and the least-squares best fit regression lines shown. The correlation coefficient for each line is greater than 0.99 and, in spite of there being only four points, all correlations are significant at $\geqslant 99\%$ confidence level. The decay distance, defined in the conventional manner, as the distance for the initial concentration to fall to 1/e of its original value, (i.e., the inverse of the slopes in Fig. 5), is shown for each species in the top half of Table 2. In this case, the decay distance represents the net effect of all the processes of transformation and dry deposition.

Table 1. *The 95 percentile concentrations for SO_2, $SO_4^=$, total S ($SO_2 + SO_4^=$) and T-NO_3^- ($HNO_3^- + p\text{-}NO_3^-$) at four monitoring sites in eastern Canada in 1984*

Station	Distance* (km)	SO_2 ($\mu g\ SO_2\ m^{-3}$)	$SO_4^=$ ($\mu g\ SO_4^=\ m^{-3}$)	T-S ($\mu g\ S\ m^{-3}$)	T-NO_3^- ($\mu g\ NO_3^-\ m^{-3}$)
LWD	150	30.8	14.1	17.7	11.0
DOR	480	16.4	10.8	11.5	6.7
CHA	632	13.0	9.3	8.0	3.7
MON	1128	4.1	6.5	4.7	1.9

* Measured from south shore of Lake Erie.

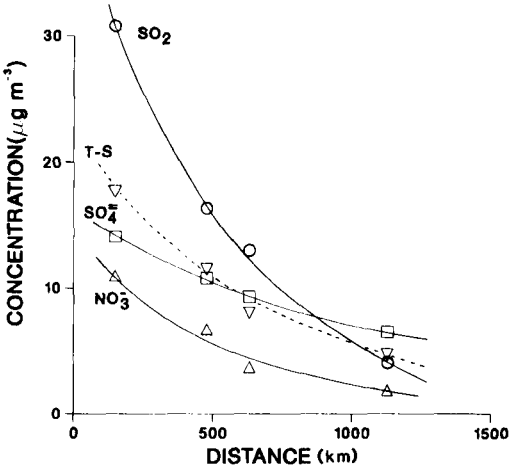

Fig. 4. The 95 percentile air concentrations plotted versus distance from the south shore of Lake Erie.

Table 2. *Summary of estimated decay distances and decay times of S and N oxides in air and precipitation*

Species	Decay distance (km)	Decay time (h)
In air		
SO_2	480	14*
$SO_4^=$	1280	58
T-S ($SO_2 + SO_4^=$)	720	24*
T-NO_3^- (HNO_3 + p-NO_3^-)	540	16
In precipitation		
$SO_4^=$	1700	
NO_3^-	1100	

* Identical to the residence time.

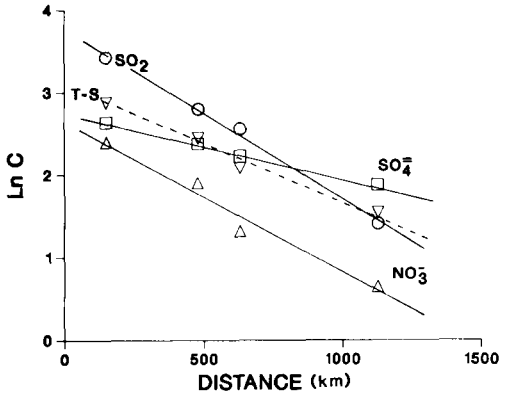

Fig. 5. Logarithm of the 95 percentile air concentrations plotted versus distance from the south shore of Lake Erie. The inverse of the slope gives the decay distance shown in Table 2.

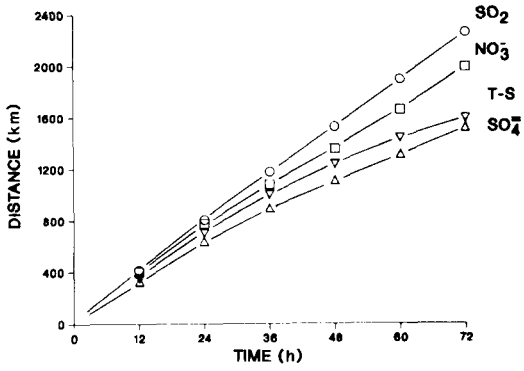

Fig. 6. Mean distance versus time graph for the 925 mb back trajectories arriving at MON at the mid-time of the sampling period for those days when the air concentrations of each of the species exceeded the 95 percentile values.

3.2. Transport velocity and decay time

In order to estimate the decay time it is necessary to establish the time taken for the air parcels to travel the decay distance across the measurement domain. This was done by considering the 925 mb trajectories arriving at MON at the mid-time of the sampling period for the days with concentrations greater than the 95 percentile value i.e. the same days from which the curves in Figs. 4 and 5 were prepared. For the set of trajectories associated with each of the species, the average travel distance upwind of MON is plotted versus time in 12 h increments as shown in Fig. 6.

Note that in Fig. 6 the average air parcel trajectory speed associated with the highest SO_2 concentrations at MON is substantially higher than the speeds associated with the highest $SO_4^=$ concentrations. The reason is that in order for the SO_2 to reach MON in high concentrations, losses due to dry deposition and conversion to $SO_4^=$ must be minimized and this occurs when the transport time is short. On the other hand, high $SO_4^=$ concentrations at MON require a longer transport time in order to maximize the amount

transformed from SO_2. In fact, the $SO_4^=$ case shows that the wind speeds are substantially lower (as indicated by the slope in Figure 6) in the period 36 to 72 h prior to arrival at MON than in the period 12 h before arrival. This then suggests a period of relative stagnation in the SO_2 source region, followed by advection, as a necessary condition for high $SO_4^=$ values at MON. This phenomena was identified by Hidy et al. (1978) as being one of the two major meteorological situations for build-up of $SO_4^=$ over the northeastern United States based on the results of Sulphate Regional Experiment (SURE).

The decay time for each species is obtained by reading off in Fig. 6 the time associated with the appropriate decay distance. The results are given in the last column of Table 2.

3.3. *Residence time for sulphur*

The concept of residence time can only be applied to the period that molecules spend between the time of emission into, or formation within, the atmosphere and the time at which they are removed by transformation or deposition. Thus, from the discussion in subsection 3.1, only the data for SO_2 and T-S can be used to infer the residence time. For these two species the residence time is in fact identical to the decay time. Since the conversion of SO_2 to $SO_4^=$ is a one-way reaction along the pathway, the $SO_4^=$ concentration decays less rapidly than it would if no SO_2 were present. Thus, the decay time for $SO_4^=$ shown in Table 2 represents the upper limit of the residence time for a $SO_4^=$ molecule once formed and being depleted by deposition only. Residence times for the measured N species cannot be inferred from the decay times shown in Table 2. In addition, it cannot be stated whether these times represent to upper or lower limit of residence time because of the complicated two-way reactions involving the various N species which are not measured i.e., NO_2 and PAN.

3.4. *Decay distances for precipitation concentrations*

The decay distance for concentrations of chemical species in precipitation can be defined in exactly the same way as for air. It is simply a statement of the distance over which observed concentrations fall by a factor of 1/e in the region

Table 3. *The average concentrations of $SO_4^=$ and NO_3^- in precipitation at seven monitoring sites in eastern Canada for the period 1984–1986*

Station	Distance (km)	$SO_4^=$ (mgl^{-1})	NO_3^- (mgl^{-1})
LON	150	3.18	2.47
PRI	300	2.50	2.04
DOR	480	2.32	2.34
CHA	632	2.46	2.00
MON	1128	1.63	1.26
HAR	1650	1.31	0.68
BAY	2280	0.83	0.38

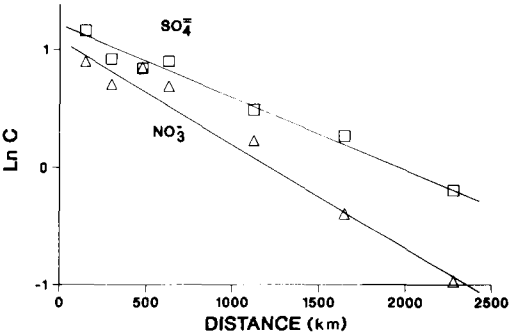

Fig. 7. Logarithm of the average precipitation concentrations of $SO_4^=$ and NO_3^-, for the 3-year period 1984–1986, plotted versus distance from the south shore of Lake Erie. The inverse of the slope gives the decay distances shown in Table 2.

downwind of the injection of the pollutants. However, the interpretation of the distance is more difficult because of the inherent discontinuous nature of the precipitation behaviour. A parcel of air containing a precipitating cloud, within which SO_2 is being continually depleted by aqueous-phase conversion to $SO_4^=$ or by cloud and precipitation scavenging, would not move as a coherent entity across the whole domain from southern Ontario to Newfoundland. Thus the data in Table 3 represent the average of all precipitation events during the period 1984–1986 at each sampling location regardless of whether each event was associated with an event at an adjacent site or not. The plots of $\log_e C$ for both $SO_4^=$ and NO_3^- in precipitation against distance in Fig. 7 show an excellent fit to an

exponential decay with correlation coefficients both greater than 0.98 significant at greater than the 99% level. The decay distances are shown in the bottom of Table 2.

4. Discussion

It should be pointed out that there are seasonal biases in the results shown for air concentrations. There is a strong out-of-phase seasonal cycle of the air concentrations of SO_2 and $SO_4^=$. Thus the selection of the 95 percentile values produces a strong winter bias for the SO_2 data with all days between late November and early April, and a strong summer bias for the $SO_4^=$ with all days (except one) between April and October. The T-S data shows a more even annual distribution, but with two weak frequency maxima in winter and later summer. The T-NO_3^- data shows peak values in all months except August with a frequency maximum in winter/spring. It is thus obvious, and important to note, that the data used for each species do not come from the same sub-set of days from the annual set.

The technique used here gives smaller residence times for both SO_2 and T-S in air than most of the previous estimates summarized by Rodhe (1978) although the relative magnitudes [approximately 1:2] are the same. The differences could be due to the methodology but are more likely due to the fact that the budget approaches give annual average residence times. Also the meteorology and underlying surface (affecting dry deposition rates) is different over eastern Canada compared to Europe where most of the other estimates have been made.

In contrast, the results here give slightly larger decay distances than those recently obtained from the western Atlantic Ocean experiment (WATOX) where Hastie et al. (1988), using a similar Lagrangian approach, found first-order decay distances of 340 and 620 km respectively for SO_2 and T-S, as pollutants moved off the east coast of North America towards Bermuda. Using a mean wind speed of 8 ms^{-1} the residence times where estimated to be 12 h and 22 h respectively, very close to those shown here in Table 2.

For nitrogen, Hastie et al. (1988) obtained more of the separate species than routinely measured in eastern Canada and obtained decay distances (times) for NO_x and total N of 500 km (17.5 h) and 550 km (19 h) respectively. The value for T-NO_3^- (comprising a large fraction of the T-N) shown in Table 2 is not inconsistent with these values.

Very few previous estimates of decay distances for sulphur or nitrogen in precipitation have been made. Church et al. (1982) discussed changes in precipitation chemistry between Lewes, Delaware on the Atlantic coast and Bermuda 1300 km to the SE. Although not calculated by them, first-order decay distances for non sea-salt $SO_4^=$ and NO_3^- in precipitation can be estimated as approximately 1400 km and 975 km respectively. Whelpdale et al. (1988) examined average precipitation chemistry data across the whole North Atlantic Ocean and from a simple model of exponential decrease obtained a distance constant of 2400 km. The value for $SO_4^=$ in Table 2, thus lies between these previous results.

As pointed out in subsection 3.4 interpretation of the decay distances in precipitation is difficult and conversion to a decay time or residence time is questionable, so the latter will not be attempted here. The $SO_4^=$ concentration in precipitation represents the net effect of the scavenging of both gaseous SO_2 and particulate $SO_4^=$, i.e., the total S in precipitation. It is clear from the results presented in Table 2 that total S falls off by a factor of at least 2 more rapidly with distance in air than in precipitation. In the case of nitrogen species, no direct comparison can be made between decay in precipitation and in air because of the large role played by NO_2 which is not measured and the uncertainty of how much is converted to NO_3^- in precipitation. PAN is also a significant fraction of the N in air but, because of its low scavenging efficiency, does not make a significant contribution to the total NO_3^- in precipitation. However, it is interesting to note that for the reduced species contributing to the acidity of precipitation the NO_3^- falls off 35% more rapidly, with distance from the emissions source region, than $SO_4^=$.

In eastern Canada, precipitation occurs only about 5% of the total time and measurable amounts occur about every third day. Thus, on average, pollutants are transported long distances before encountering a precipitating cloud system. During the night-time the air flow aloft is often decoupled from the ground and thus no depletion

Table 4. *Mean trajectory velocity at different heights for SW flow over the 48 hr period prior to arrival at MON, and for W flow over the 96 hr period prior to arrival at BAY, based on meteorological wind field data for the period 1980–1985*

Height (mb)	Average trajectory velocity (km h^{-1}) MON	BAY
1000	15.1	16.8
925	19.9	19.5
850	26.3	23.8

takes place due to dry deposition. Air at higher levels also travels faster than at the ground as shown for southwesterly trajectories at MON and BAY in Table 4. Both these factors combine to allow for a longer decay distance in air travelling at 925 mb and 850 mb levels. Since the pollutant concentrations in precipitation reflect the integrated result of scavenging from air at all levels in the lower troposphere then the decay distances in precipitation are larger than those for air concentrations at ground level.

5. Conclusions

A simple approach, using observations from a series of monitoring stations lined-up downwind of a major anthropogenic SO_2 and NO_x source region has been used to estimate atmospheric decay distances and decay times for S and N oxides, and residence times for SO_2 and T-S.

The residence times for SO_2, and T-S in air of 14 h and 24 h respectively are found to be less by about a factor two than those obtained from the box-budget approach used by Rodhe and others. However, they are similar in magnitude to more recent estimates made from data over the North Atlantic Ocean.

For precipitation concentrations, the decay distance of T-NO_3^- is only 65% that of T-S, indicating that, for the particular terrain, underlying vegetation and precipitation regime in of eastern Canada, these nitrogen compounds are depleted from the atmosphere faster than the sulphur compounds.

This approach, tested on one year of air concentration data, provided useful results and has the potential for further application. In particular, as more quality-assured data become available, it will be possible to subdivide into seasonal sets and look for seasonal differences in the decay distances for each of the oxides.

Finally, routine measurements of NO_2 and PAN at all sites are needed in order to establish the decay functions for each of the end-products of anthropogenic NO_x emissions, and the behaviour of nitrogen as a whole.

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REFERENCES

Barrie, L. A., Wiebe, H. A., Fellin, P. and Anlauf, K. G. 1980. APN the Canadian air and precipitation monitoring network: a description and results for November 1978 to November 1979. *Report No. AQRB 80-002-T*, Atmospheric Environment Service, Toronto, Canada.

Barrie, L. A., Anlauf, K. G., Wiebe, H. A. and Fellin, P. 1984. Acidic Pollutants in air and precipitation at selected rural locations in Canada. *Acid Precipitation Series, Vol. 4* (ed. J. Teasley). Ann Arbor Science, pp 15–36.

Barrie, L. A. and Hales, J. M. 1984. The spatial distributions of precipitation acidity and major ion wet deposition in North America during 1980. *Tellus 36B*, 333–355.

Bolin, B. and Rodhe, H. 1973. A note on the concepts of age distribution and transit time in natural reservoirs. *Tellus 25*, 58–62.

Brice, K. A., Bottenheim, J. W., Anlauf, K. G. and Wiebe, H. A. 1988. Long-term measurements of atmospheric peroxyacetylnitrate (PAN) at rural sites in Ontario and Nova Scotia; seasonal variations and long-range transport. *Tellus 40B*, 408–425.

Chan, W. H., Orr, D. B. and Vet, R. J. 1982. Acidic Precipitation in Ontario Study. An Overview: the event wet/dry deposition network. *Report ARB-164-83-ARSP*, Ontario Ministry of the Environment, Toronto, Canada.

Church, T. M., Galloway, J. N., Jickells, T. D. and Knap, A. H. 1982. The chemistry of Western Atlan-

tic precipitation at the mid-Atlantic coast and Bermuda. *J. Geophys. Res. 87*, 11013–11018.

Daum, P. H., Kelley, T. J., Tanner, R. L., Tang, X., Anlauf, K., Brice, K., Bottenheim, J. and Wiebe, A. 1988. Winter measurements of trace gas and aerosol composition at a rural site in southern Ontario. *Atmos. Environ.*, in press.

Eriksson, E. 1961. Natural reservoirs and their characteristics. *Geofisica International 1 (2)*, 27–43.

Eriksson, E. 1971. Compartment models and reservoir theory. *Annual review of Ecology and Systematics 2*, 67–84.

Haagenson, P. L., Kuo, Y-H, Skumanich, M. and Seaman, N. L. 1987. Tracer verification of trajectory models. *J. Climate and Appl. Met. 26*, 410–426.

Hastie, D. R., Schiff, H. I., Whelpdale, D. M., Peterson, R., Zoller, W. H., Anderson, D. L. and Artz, R. S. 1988. Nitrogen and sulphur over the western Atlantic Ocean. *Atmos. Environ. 22*, 2381.

Hidy, G. M., Mueller, P. K., Lawery, T. F. and Warren, K. K. 1978. Assessment of regional air pollution over the eastern United States: Results from the regional sulphate experiment (SURE). *Report. No. 538*, World Meteorological Organization, Geneva, Switzerland, 65–76.

Rodhe, H. and Grandell, J. 1972. On the removal time for aerosol particles from the atmosphere by precipitation scavenging. *Tellus 24*, 442–454.

Rodhe, H. 1978. Budgets and turn-over times of atmospheric sulfur compounds. *Atmos. Environ. 12*, 671–680.

Schwartz, S. A. 1979. Residence times in reservoirs under non-steady-state conditions: applications to atmospheric SO_2 and aerosol sulfate. *Tellus 31*, 530–547.

Summers, P. W. 1987. Empirical source-receptor relationships in eastern Canada determined from monitoring data and airmass trajectory climatologies. *Proc. EMEP Workshop on Data analysis and presentation*, Cologne, F.R.G., 15–17 June 1987.

Whelpdale, D. M., Eliassen, A., Galloway, J. N., Dovland, H. and Miller, J. M. 1988. The transatlantic transport of sulphur. *Tellus 40B*, 1–15.

Wilson, J. W., Mohnen, V. A. and Kadlecek, J. A. 1982. Wet deposition variability as observed by MAP3S. *Atmos. Environ. 16*, 1667–1676.