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An estimate of the importance of dry deposition as a pathway of acidic substances from the atmosphere to the biosphere in eastern Canada

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ABSTRACT

The relative importance of dry and wet deposition of sulphate and nitrate over southeastern Canada is examined using daily air and precipitation chemistry observations made at 6 rural stations of the Air and Precipitation Monitoring Network (APN) during the period 1979 to 1982. Dry deposition was calculated from these air concentrations using deposition velocity information on land-use types, on atmospheric wind speed and stability and on dry deposition rates from over 80 published studies. Despite the large uncertainty in dry deposition estimates which is associated with the complexity of the process, valuable conclusions emerge. It is estimated that total annual deposition varies between 10 to 86 mmole m^{-2} and 13 to 62 mmole m^{-2} for $SO_4^=$ and NO_3^-, respectively. To eastern Canada 22% and 30% of the total $SO_4^=$ and NO_3^- deposition is dry deposited, respectively. Depending on location, the contribution of SO_2 to the dry deposition of sulphur ranges from 37% to 78%. It tends to decrease with increasing distance from major sources. In eastern Canada, the best estimate of the fraction of the total dry deposition of nitrogen contributed by NO_2 and HNO_3 is in the range 50% to 60% and 31% to 45%, respectively, depending on location. The uncertainty in the NO_2 estimate is large, approaching a factor of 3.5. Even if PAN dry deposition velocities are equal to that of NO_2 (they are expected to be lower), the contribution of PAN to total nitrate deposition is negligibly small. Both dry and wet deposition are episodic in nature. It is estimated that the top-20% deposition events yield 47% to 70% of the total deposition.

1. Introduction

Deposition of acidic sulphates and nitrates from the atmosphere to aquatic and terrestrial ecosystems in Canada is of serious environmental concern. It takes place via three processes: removal by rain and snow (wet deposition), direct uptake of particles and gases at the earth's surface (dry deposition) and fogwater deposition. Budget estimates of atmospheric sulphur and nitrogen for two major source regions of acidic compounds in the world, Europe (Rodhe and Granat, 1983; Bonis et al., 1980) and eastern North America (Galloway and Whelpdale, 1980; Logan, 1983) have indicated that dry deposition is a substantial fraction of the total deposition. In North America, these budget estimates were based on relatively limited information. Since the inception of acid rain research programs, new information is available to enable more accurate estimates to be made and to examine the seasonal variation and episodic nature of wet and dry deposition in eastern Canada.

In late 1978, a research network was established in Canada with the aim of measuring atmospheric pollutant inputs to sensitive ecosystems. Measurements related to fogwater deposition were not made. As of December 1982, the Air and Precipitation Monitoring Network (APN) consisted of 6 stations (Fig. 1). Four (ELA, Algoma, Montmorency, Kejimkujik) were located in calibrated watersheds of the federal acid rain research program. We will discuss measurements made during the period 1979 to

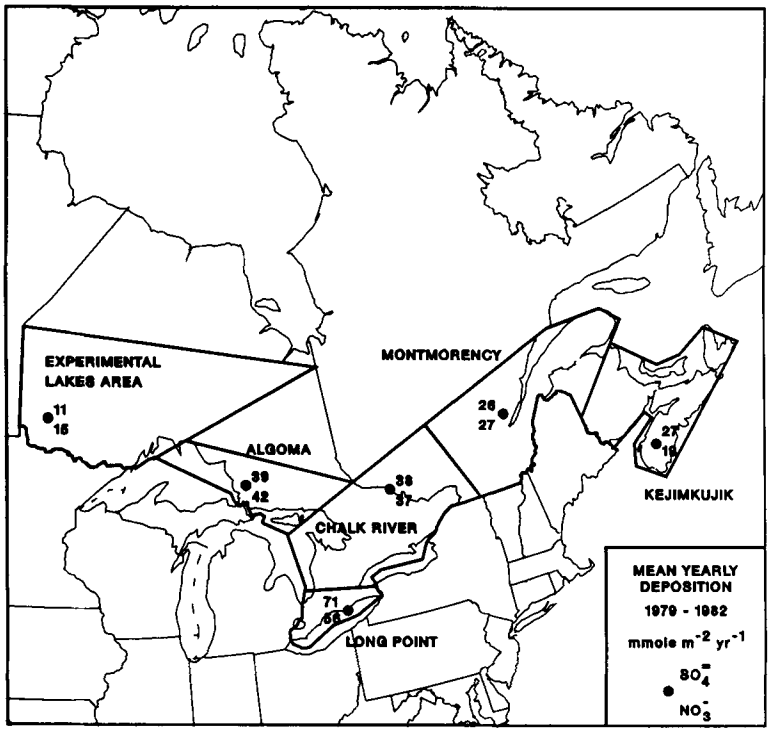

Fig. 1. Location of the 6 APN sites, the areas represented by them and the mean yearly total depositions of $SO_4^=$ and NO_3^- (neglecting NO_2 contributions) in mmole m^{-2} yr^{-1}.

1982. Various aspects of the data have been analyzed and reported elsewhere (Barrie et al., 1980, 1984; Anlauf et al., 1980; Barrie, 1982a) but not until recently has it been possible to address quantitatively the absolute value and relative magnitude of wet and dry deposition at all sites in eastern Canada for an extended period of time. It is our purpose in this paper to "estimate" the importance of dry deposition as an atmospheric input pathway of acids to ecosystems. This topic has also been briefly addressed by Barrie and Sirois (1986). We emphasize "estimate" since the complexity of the dry deposition process leads to substantial uncertainty. Whenever possible an attempt has been made to estimate the uncertainty in the calculated dry deposition. One might argue that attempting to quantify such a highly complex process on the basis of current knowledge is futile. If this were indeed the case then one could justifiably argue that the attempts at global or regional budgets cited above were equally futile, which is obviously not the case.

2. Observations

A detailed description of the sampling equipment, procedures and analytical techniques is published elsewhere in a series of data reports (DATA). A brief description is presented here. Each site is located remote from local sources of contamination in accordance with currently accepted siting criteria (that is, each site is as regionally representative as possible). Both air and precipitation chemistry measurements were made on a daily basis beginning and ending at 12.00 GMT (i.e., early morning).

Precipitation was collected with a wet-only Sangamo collector in a black plastic bucket that was carefully rinsed with deionized water each morning. Analysis for $SO_4^=$ and NO_3^- was done using the automated methyl thymol blue and cadmium reduction techniques, respectively. No attempt was made to prevent oxidation of dissolved SO_2 in the sample. Consequently, the $SO_4^=$ measured represents total $SO_4^=$. Precipitation amount was measured using standard Canadian

meteorological service rain and snow gauges (specially designed snow gauges are necessary since rain gauges undercollect snow in windy situations).

Concentrations of ambient $SO_4^=$, SO_2 and total NO_3^- (particulate NO_3^- plus HNO_3) concentrations were measured at a height of 10 m by: (i) drawing approximately 30 m^3 of air over a 24 hour period through two filters in series (Whatman 40 and Whatman 41 impregnated with K_2CO_3-glycerol), (ii) extracting the filters in deionized water and (iii) analyzing the extracts using liquid ion chromatography and, in the case of the Whatman 41 extract, using the automated Thorin method (Persson, 1966).

Two technical studies pertinent to application of the measurements have been made. In the first (Anlauf et al., 1986), the collection efficiency of gaseous nitric acid and sulphur dioxide by the filters was tested for temperatures down to $-20°C$ and for a reasonable range of loadings and relative humidities. It was found that Whatman 40 collects HNO_3 with an efficiency close to 100% and is essentially inert to SO_2. Impregnated Whatman 41 collects SO_2 with a high efficiency. In a second study (CSC, 1982), an intercomparison of this methodology with that of the Ontario Ministry of Environment (OME) was made by simultaneously sampling at a field site over a 6-month period (January–March and August–October 1981) and then analyzing all samples at one laboratory. The OME air sampling method differed from the APN system in their use of a teflon–nylon sandwich instead of a Whatman 40 filter. The comparison showed that there was good agreement in measurements of particulate $SO_4^=$, SO_2 and major ions in precipitation but that the total NO_3^- in air measured by us was 20–30% lower than that measured by OME. That may suggest that contrary to results in the laboratory Whatman 40 filter collects most but not all HNO_3.

In the following estimates of deposition of nitrate, it will be assumed that, on a monthly mean basis, the total nitrate observed was partitioned between particulate NO_3^- and HNO_3 in the same proportion as they were in 1983 (Table 1) when a three filter teflon–nylon-Whatman 41 system was used allowing separation of gaseous and particulate NO_3^-. Using this system, there is a tendency to overestimate the fraction of NO_3^- that is in the form of HNO_3 because of the volatilization of particulate NO_3^- from the teflon filter. However, recent observations by Cadle (1985) have indicated that the errors thus incurred are, on a monthly basis, less than 20–30% and lower at colder winter, fall and spring temperatures than at higher summer temperatures. The uncertainty in assuming that on a monthly basis the partitioning of NO_3^- between the gaseous and particulate phases was the same as in 1979 to 1982 as in 1983 was tested by comparing 1983 values with the 1983–84 values (the 1984 data were recently available). With the exception of one case, the old values differed from the new values by less than 35% (being less than 10% in most cases).

Table 1. *The mean and range of monthly averages of the estimated fraction (%) of total nitrate that is HNO_3 (from APN 1983 teflon/nylon filter data)*

	Mean	Range
Chalk River	66	50–78
Long Point*	39	23–59
Kejimkujik	46	26–46
Montmorency	64	45–79
Algoma	69	60–79
ELA	52	19–73

* Estimated using London, Ontario data.

The network provides air concentrations of those compounds in which most airborne sulphur is concentrated (i.e., $SO_4^=$, SO_2). As shown below, this allows us to calculate readily sulphur dry deposition. However, the same does not hold for the nitrogen oxides since the gaseous precursor NO_2 and the oxidation product peroxyacetylnitrate (PAN) were not monitored routinely. The strategy used is to take the routinely observed NO_3^- observations to calculate a lower limit for NO_3^- dry deposition and to use available non-routine NO_2 and PAN measurements to make a rough estimate of the additional contribution of these compounds to NO_3^- dry deposition.

3. The calculation of wet and dry deposition from observations

Daily wet deposition was calculated as the product of the $SO_4^=$ or NO_3^- concentration in the

sample collected from the wet-only precipitation collector and the precipitation amount measured with the standard precipitation gauge. Monthly wet deposition was calculated as the product of the standard-precipitation-amount-weighted concentration and the standard precipitation amount. If all precipitation events were not analyzed during a month, we applied the criterion that those that are available must represent at least 50% of the total precipitation that fell. Then the precipitation-amount-weighted concentration was used as an estimate of the actual value. Otherwise, the monthly deposition is reported as missing. Tests using complete data sets indicate that this approach introduces errors of less than 20% in the monthly wet deposition. The uncertainty in a daily wet deposition measurement at a point is due to uncertainty in the measurement of precipitation amount and in concentration. The standard error in each of these is of the order of 10%. However, if a daily wet deposition measurement is used as an estimator of deposition to an area around a site, there is an additional uncertainty introduced due to sampling representativeness (Barrie, 1982b). This can be extremely large especially for convective storms. Sampling representativeness tends to increase (i.e., uncertainties decrease) as averaging time increases to include a number of events. Thus, we feel that estimates of wet deposition to an area within 100 km of a site for averaging times of less than approximately a month would be very uncertain.

For a given surface and chemical compound, daily dry deposition (D) is calculated as the product of the daily mean air concentration (C), the dry deposition velocity (V) and the averaging time (T). The monthly-mean areal-average $\overline{D}$ to a circular region 100 km in radius about a station is the product of the monthly arithmetic mean concentration ($\overline{C}$), the areal mean monthly dry deposition velocity ($\overline{V}$) and T. If daily air concentration measurements were missing in a month, the criterion was applied that at least 50% must be available to estimate $\overline{C}$, otherwise the deposition was reported as missing. $\overline{V}$ was calculated from the monthly mean $\overline{V}$ values for each surface type in the area about a station by weighting the values according to fractional surface coverage (Table 2). Seasonally-dependent, surface-type and site-specific deposition velocities estimated by Voldner et al. (1986) were used. These deposition velocities embody information on dry deposition of $SO_4^=$, SO_2 and NO_2 from over 80 published studies to various surface types as well as a detailed characterization of surface conditions by season. They take into account stability weighted aerodynamic resistances and surface resistances based on best experimental estimates from the literature. $\overline{V}$ of SO_2, $SO_4^=$, HNO_3, NO_3^- and NO_2 as a function of station and month are shown in Table 3. The ranges of annual mean $\overline{V}$ for SO_2, $SO_4^=$, HNO_3, NO_3^- and NO_2 between locations are 0.19–0.30, 0.25–0.37, 1.09–2.93, 0.35–0.65 and 0.10–0.23 cm s^{-1}, respectively.

There are differences in $\overline{V}$ between sites that depend on the local distribution of surface types (Table 2) and on climate. The annual variation of $\overline{V}$ of SO_2 for each site is shown in Fig. 2. During winter it is a minimum of about 0.08 cm s^{-1} reflecting the poor uptake by snow and dormant forest. The unique maritime location of Kejimkujik leads to only 3 months of low winter $\overline{V}$ values rather than 4 at the other sites. In spring, summer and fall, $\overline{V}$ ranges from about 0.2 to 0.4 cm s^{-1}. It tends to be higher at those sites having the greatest fraction of water in the area. Thus, Kejimkujik is highest with 46% water and

Table 2. *Percentages of surface type coverages within a 100 km radius of the 6 APN sites*

Station	Water	Coniferous forest	Deciduous forest	Swamp	Cultivated	Grassland	Urban
Chalk River	10.1	47.8	36.7	1.2	4.1	0.0	0.1
Long Point	41.8	8.3	3.7	0.5	43.5	0.0	2.2
Kejimkujik	46.2	24.5	24.6	2.5	0.0	2.2	0.0
Montmorency	9.9	38.1	38.2	0.7	0.0	13.0	0.1
Algoma	28.2	0.4	67.8	1.8	0.0	0.0	1.8
ELA	30.1	6.1	61.2	2.1	0.0	0.4	0.1

Table 3. *Monthly areal average (radius 100 km) dry deposition velocities ($\overline{V}$) in cm s^{-1} at 6 APN sites for SO_2, $SO_4^=$, HNO_3 and NO_2; the annual mean is also indicated*

$\overline{V}$ (cm s^{-1}): SO_2

Station	Month												Annual mean
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chalk River	0.07	0.07	0.07	0.24	0.27	0.28	0.28	0.26	0.25	0.20	0.20	0.07	0.19
Long Point	0.09	0.09	0.09	0.76	0.34	0.31	0.29	0.28	0.29	0.32	0.40	0.29	0.30
Kejimkujik	0.08	0.08	0.08	0.41	0.40	0.39	0.37	0.35	0.35	0.35	0.37	0.41	0.30
Montmorency	0.08	0.08	0.08	0.08	0.28	0.30	0.29	0.28	0.27	0.22	0.22	0.08	0.19
Algoma	0.09	0.09	0.09	0.20	0.33	0.32	0.31	0.30	0.30	0.30	0.31	0.09	0.23
Ela-Kenora	0.09	0.09	0.09	0.09	0.33	0.33	0.33	0.31	0.31	0.30	0.21	0.09	0.21

$\overline{V}$ (cm s^{-1}): $SO_4^=$

Station	Month												Annual mean
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chalk River	0.19	0.19	0.20	0.28	0.52	0.53	0.52	0.50	0.48	0.34	0.35	0.19	0.36
Long Point	0.07	0.07	0.07	0.32	0.36	0.33	0.31	0.30	0.31	0.33	0.30	0.27	0.25
Kejimkujik	0.14	0.14	0.15	0.42	0.42	0.50	0.47	0.46	0.45	0.41	0.44	0.48	0.37
Montmorency	0.19	0.20	0.20	0.20	0.32	0.49	0.48	0.46	0.45	0.34	0.34	0.19	0.32
Algoma	0.29	0.29	0.30	0.32	0.44	0.44	0.43	0.41	0.42	0.43	0.43	0.29	0.37
Ela-Kenora	0.26	0.27	0.28	0.28	0.45	0.45	0.45	0.43	0.43	0.42	0.38	0.26	0.36

$\overline{V}$ (cm s^{-1}): HNO_3

Station	Month												Annual mean
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chalk River	2.97	2.94	3.09	3.16	3.08	3.01	2.83	2.68	2.70	2.84	3.03	2.95	2.94
Long Point	0.81	0.77	0.78	1.21	1.44	1.33	1.20	1.14	1.20	1.32	1.19	0.90	1.11
Kejimkujik	2.16	2.15	2.17	2.21	2.23	2.13	1.99	1.92	1.87	2.01	2.15	2.36	2.11
Montmorency	2.80	2.84	2.91	2.83	2.93	2.83	2.61	2.52	2.49	2.67	2.79	2.75	2.75
Algoma	2.58	2.38	2.57	2.66	2.72	2.57	2.49	2.39	2.49	2.67	2.79	2.54	2.57
Ela-Kenora	2.12	2.16	2.32	2.41	2.59	2.57	2.48	2.32	2.42	2.53	2.42	2.13	2.37

$\overline{V}$ (cm s^{-1}): NO_3^-

Station	Month												Annual mean
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chalk River	0.36	0.36	0.37	0.53	0.94	0.95	0.94	0.89	0.87	0.62	0.63	0.36	0.65
Long Point	0.12	0.12	0.12	0.40	0.50	0.48	0.45	0.43	0.44	0.46	0.39	0.30	0.35
Kejimkujik	0.28	0.27	0.28	0.58	0.58	0.75	0.72	0.69	0.67	0.58	0.60	0.65	0.55
Montmorency	0.37	0.37	0.38	0.39	0.58	0.89	0.86	0.82	0.79	0.61	0.61	0.37	0.59
Algoma	0.56	0.55	0.57	0.60	0.72	0.73	0.71	0.68	0.68	0.69	0.71	0.56	0.65
Ela-Kenora	0.49	0.50	0.53	0.54	0.74	0.75	0.74	0.70	0.69	0.67	0.61	0.49	0.62

Table 3—*continued*

$\overline{V}$ (cm s^{-1}): NO_2

Station	Month												Annual mean
	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
Chalk River	0.06	0.06	0.06	0.28	0.35	0.38	0.38	0.35	0.31	0.22	0.22	0.06	0.23
Long Point	0.03	0.03	0.03	0.14	0.15	0.15	0.15	0.14	0.14	0.14	0.09	0.02	0.10
Kejimkujik	0.05	0.05	0.05	0.16	0.18	0.22	0.22	0.20	0.18	0.14	0.14	0.14	0.14
Montmorency	0.06	0.06	0.06	0.06	0.29	0.36	0.36	0.33	0.30	0.22	0.22	0.06	0.20
Algoma	0.07	0.07	0.07	0.26	0.28	0.30	0.30	0.27	0.24	0.23	0.22	0.07	0.20
Ela-Kenora	0.07	0.07	0.07	0.07	0.28	0.29	0.30	0.27	0.24	0.21	0.07	0.07	0.17

Chalk River and Montmorency are lowest with about 10% water. The month of April at Long Point is notable for an SO_2 $\overline{V}$-value more than double that at other sites. This is due to a high deposition velocity to cultivated land and water (the dominant surface types around this station) at this time of year. Later in the spring, cultivated land is covered with crops that react less efficiently with SO_2 than soil does.

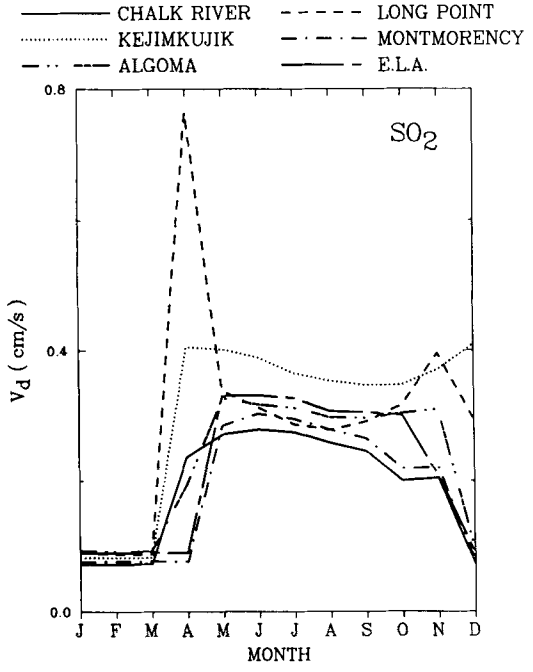

Fig. 2. Temporal variation of the monthly aerial average deposition velocity ($\overline{V}$) (cm s^{-1}) of SO_2 at the 6 APN sites.

4. Uncertainties in dry deposition estimates

Because of the complexity of the dry deposition process, there are large uncertainties in calculating dry deposition; uncertainties which in our opinion are sufficiently small as to make an estimate worthwhile. Relatively speaking the fact that we have integrated considerably more information on air concentrations and dry deposition velocities than was available for previous regional or global budget estimates makes this exercise in itself valuable. In applying the above approach the following assumptions are made.

(1) That dry deposition can be represented by the deposition velocity parameterization involving transfer resistance components. Inherent in this assumption is the presumption that deposition at surface element edges is not seriously misrepresented on average. We feel that estimates of dry deposition made by water-shed mass balances of $SO_4^=$ agree sufficiently well with dry deposition estimates based on this assumption (see discussion section) that the error associated with this assumption is probably less than a factor of 2.

(2) That the product of V and C when averaged over one month can be represented by the product of their averages. In other words, air concentrations and deposition velocities are independent. Mathematically this can be represented as:

$$\overline{VC} = \overline{V}\,\overline{C}(1 + r S_V^{\circ} S_C^{\circ}), \qquad (1)$$

where r is the correlation coefficient between V and C and S° represents the coefficient of variance. It is reasonable to assume that, in general, S° is less than 1 for both deposition velocity and air concentration. In the worst case when there is

perfect correlation between C and V (i.e., $r = 1$) the error in assuming that $\overline{VC}$ equals $\overline{V}\,\overline{C}$ is less than a factor of 2. In reality, with the exception of perhaps HNO_3, we expect this error to be much less than a factor of 2. In a 17-week summer study of SO_2 deposition velocity calculated hourly from meteorological data and surface biological information over forest, Meyers and Yen (1987) concluded that because r was less than 0.1 the second term in brackets is at most 10% of the first term. For ozone in summer the second term is approximately 0.4.

(3) That the molar fraction of total nitrate that is HNO_3 (F_{HNO_3}) is independent of the total concentration of airborne NO_3^- so that monthly average concentration of HNO_3 can be represented by the product of average F_{HNO_3} and of total NO_3^- concentration (i.e., an analogous problem to that in eq. (1) above with V replaced by F). We have found that, based on 1983 and 1984 data, the term $r S_F^\circ S_C^\circ$ was less than 0.15 and conclude that this error is negligibly small.

(4) That the average monthly F_{HNO_3} for 1983 and 1984 is representative of the years 1979 to 1982. Tests described above indicate that the uncertainty introduced by this assumption is less than 35%.

Thus, given the uncertainties associated with the above assumptions, with measured air concentrations (20%) and with the best value deposition velocities (within a factor of 2), it is possible to estimate the bounds of the dry deposition estimates made here. The net uncertainty is less for $SO_4^=$ deposition than for NO_3^- deposition because assumptions 2, 3 and 4 lead to greater uncertainty in NO_3^- deposition. We feel that total $SO_4^=$ dry deposition estimates have a factor of 2 uncertainty while those of NO_3^- (excluding NO_2) are uncertain by a factor of 3.

Our estimates of NO_2 and PAN deposition are even more uncertain possibly a factor of 3.5. However, as will be shown below even this uncertainty enables us to discount PAN as a major source of NO_3^- and to flag NO_2 dry deposition as an important source of dry deposited NO_3^- that is worthy of further study.

5. Results and discussion

In the following discussion uncertainty refers to the most probable error at a confidence level of approximately 90%. This was estimated using a Monte Carlo technique to simulate the propagation of the uncertainties.

Monthly mean wet and dry deposition estimates for each station and for sulphur and nitrogen (neglecting NO_2 contributions to dry deposition) are shown in Tables 4, 5. The seasonal variation of total deposition, its wet and dry components, the fraction of dry deposition conveyed to the surface by the gaseous form SO_2 or HNO_3 and the fraction of total deposition that is dry are shown for each station in Figs. 3–8. Error bars for the last four variables are also included. The annual deposition of $SO_4^=$ and NO_3^- (neglecting NO_2 contributions to dry) and the annual mean fraction of total deposition that was dry is shown in Tables 6, 7, respectively. The numbers in brackets represent estimates of the range of possible values that reflect uncertainties. The calculated deposition based on similar observations in Ontario by Chan et al. (1984, 1985) are also included. They assumed that all NO_3^- was in the form of HNO_3 which, since V of HNO_3 is much higher than that of NO_3^-, will yield an overestimate of deposition. The four-year mean annual total deposition is also given.

Before discussing the results we need to assess the contribution of NO_2 and PAN to NO_3^- dry deposition. Because of the scarcity of observations this only was possible at two sites for each constituent. For NO_2, it was done for the Long Point site using routine air concentrations from Duncan Falls (300 km south) in rural Ohio (SURE, 1981) for the period November 1977 to October 1978 and for the Chalk River site using the Duncan Falls data multiplied by a factor of 0.55. The factor is the ratio of the arithmetic mean NO_2 concentration (6.6 ppb) determined at North Bay Ontario from 16 January to 23 February 1984 (Anlauf, 1987) to the mean concentration at Duncan Falls in January and February. These estimates are probably accurate within a factor of 2. The deposition velocities used for NO_2 are those areally representative ones of Voldner et al. (1986).

For PAN, deposition estimates were made at Long Point and at Kejimkujik using concentrations observed by Bottenheim et al. (1987) during February to October 1983 and June 1984 to June 1985, respectively. Dry deposition velocities were assumed to be the same as for

Table 4. *Monthly wet and dry deposition of $SO_4^=$ in mmole m^{-2} for the 6 APN sites*

$SO_4^=$ (mmole m^{-2})

		Chalk River		Long Point		Kejimkujik		Montmorency		Algoma		Ela-Kenora	
Year	Month	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1979	Jan	0.8	0.5	4.4								0.3	0.2
	Feb		0.7	1.2								0.6	0.4
	Mar	1.3	0.5	2.9								0.8	0.4
	Apr	1.9	0.9	3.0	4.0							1.5	0.2
	May	4.4	1.4	3.2	2.6							1.6	0.2
	Jun	2.6	1.6	3.1	2.4	1.3	0.6					1.1	0.1
	Jul	3.9		3.5	2.8	1.4	0.8					0.3	0.3
	Aug	2.9	1.2	3.1	1.9	3.8	0.6					0.8	0.3
	Sep	4.8	1.2	3.4	2.5	2.1	0.4						0.2
	Oct	4.5	1.1	6.2	3.6							1.4	0.2
	Nov	1.7	0.6	4.4	3.1		0.7						0.2
	Dec	1.3	0.6	1.4	4.5								
1980	Jan	0.7	0.5	0.8	1.1	1.3	0.2						0.1
	Feb	0.4	0.8		1.0	0.5	0.2					0.2	0.2
	Mar	1.5	0.6	5.7	0.9	2.2	0.2					0.3	0.2
	Apr	2.6	1.0	3.7	4.7	1.3	0.4					0.1	0.1
	May	2.2	0.9	2.4	2.0	1.5	0.5						0.2
	Jun	4.1	1.1	3.8	2.2	1.8	0.7						
	Jul	3.5	0.7	5.7	1.9	1.7							
	Aug	3.8	0.8	3.5	2.0	0.7	0.8					0.9	0.2
	Sep	4.3	0.5	4.2	1.5	1.5	0.5					0.8	0.2
	Oct	2.4	0.4	2.0	1.8	2.6	0.4					0.6	
	Nov	1.4	0.7	1.8	3.3		0.4			1.6	0.6	0.1	0.2
	Dec	1.1	0.4	1.9	3.1		0.9		0.4	2.5	0.4	0.2	0.3
1981	Jan	0.3	0.7	0.5	1.5	1.0	0.2	0.5	0.3	0.6	0.3	0.1	0.2
	Feb	1.9	0.7	2.1	1.1	0.9	0.2	1.6	0.4	1.9	0.5	0.1	0.2
	Mar	1.6	0.3		0.5	2.1	0.1	1.3	0.1	5.2	0.3	0.5	0.1
	Apr		0.9	4.9	3.1	2.8	0.5	1.8	0.2	2.1	0.4	0.4	0.1
	May	2.8	0.9	3.4	2.5	1.5	0.5	2.9	0.4	3.2	0.8	0.5	0.3
	Jun	3.5	1.0	6.4	1.8	3.4	0.3	2.9	0.5	9.4	0.5	1.3	0.1
	Jul	5.3	0.7	4.4	1.8	1.9	0.4	1.7	0.4	1.5	0.8	1.0	0.3
	Aug	4.7	0.8	2.7	2.2	1.8	0.6	3.0	0.7	2.3	0.7	0.3	0.3
	Sep	4.9	0.5	8.9	1.7	2.3	0.4	1.5		1.5	0.2	1.5	0.1
	Oct	1.5	0.4		2.8	2.2	0.4	2.0		3.0	0.6	0.9	0.4
	Nov	0.9	0.5		2.7	2.0	0.4	0.5	0.1	1.3	0.8	0.5	0.3
	Dec	0.7	0.3		2.5	1.3	0.5		0.1	1.2	0.3	0.3	
1982	Jan	0.9	0.5		1.2	2.4	0.2		0.2		0.4	0.3	0.2
	Feb	0.5	0.6	4.2	1.4	1.3	0.2	0.4	0.3	1.2	0.3	0.6	0.2
	Mar	1.4	0.7	4.5	0.8	1.7		2.1	0.2	2.7	0.5	1.0	0.3
	Apr	2.0	0.8	4.3	3.9	1.9	0.5	2.7	0.2	2.6	0.5	1.0	0.2
	May	2.4	1.2	8.3		0.9	0.3	1.4	0.3	2.3	1.3	1.4	0.4
	Jun	4.4	0.6	4.6	1.6	2.5	0.6	2.5	0.3	1.6	0.3	0.9	0.2
	Jul	1.3	1.0	2.7	1.4	0.8	0.8	1.5	0.6	3.8	0.6	2.0	0.3
	Aug	1.3	0.5	7.2	1.1	0.8	0.7	2.0	0.2	0.7	0.2	0.6	0.4
	Sep	3.6	1.3	5.4	2.0	1.4	0.7	1.9		2.5	1.0	1.3	0.3
	Oct	2.5	0.8	3.0	2.1	0.8	0.5	1.4		5.7	0.5	1.2	0.3
	Nov	2.1	0.7	5.7	2.1	1.9	0.6	3.1	0.2	2.5	0.4	0.4	0.2
	Dec	2.1				1.5		3.0				0.3	

Table 5. *Monthly wet and dry deposition of NO_3^-, neglecting the contribution of NO_2 and PAN (see text), in mmole m^{-2} for the 6 APN sites*

NO_3^- (mmole m^{-2})

		Chalk River		Long Point		Kejimkujik		Montmorency		Algoma		Ela-Kenora	
Year	Month	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
1979	Jan	1.0	0.5	3.2								0.2	0.3
	Feb		0.8	1.4								0.5	0.5
	Mar	2.1	1.2	3.7								1.2	0.6
	Apr	2.3	0.7	2.1	1.0							1.2	0.4
	May	3.2	1.3	2.4	1.9							1.5	0.2
	Jun	1.6	1.2	2.3	1.5	0.7	0.4					1.8	0.2
	Jul	2.4		3.4	1.3	0.8	0.4					0.4	0.4
	Aug	1.8	0.5	2.4	0.8	2.5	0.2					1.0	0.2
	Sep	3.4	0.7	2.6	1.3	1.7	0.2						0.2
	Oct	4.4	1.4	8.4	1.6		0.2					1.6	0.3
	Nov	3.0	0.7	7.6	1.5		0.3						0.3
	Dec	1.8	0.9	2.1	1.0								
1980	Jan	1.7	0.7	0.8	0.5	0.9	0.1						0.3
	Feb	1.1	0.8		0.6	0.6	0.3					0.2	0.3
	Mar	3.4	1.1	7.3	0.5	1.8	0.1					0.8	0.2
	Apr	3.6	0.6	5.0	1.1	0.9	0.2						0.2
	May	1.8	0.4	2.9	1.7	1.3	0.3						0.4
	Jun	3.2	0.6	4.2	1.6	1.2	0.5						
	Jul	3.2	0.3	5.2	1.3	1.5	0.5						
	Aug	2.6	0.4	2.5	1.1	0.5	0.3					1.1	0.2
	Sep	3.4	0.4	3.7	0.9	1.0	0.3					0.7	0.2
	Oct	2.3	0.5	2.5	0.9	1.5	0.3					1.0	0.1
	Nov	1.8	1.2	2.2	0.8		0.2			2.9	0.8	0.1	0.3
	Dec	1.7	0.7	3.5	0.7		0.3		0.7	3.6	0.5	0.4	0.6
1981	Jan	1.4	0.5	1.9	0.6	1.4	0.2	1.3	0.4	1.4	0.7	0.2	0.5
	Feb	4.1	0.9	2.8	0.4	1.1	0.3	3.1	1.4	4.3	1.5	0.1	0.4
	Mar	2.0	0.2		0.4	2.4	0.3	1.8	0.2	4.8	0.6	0.7	0.2
	Apr		0.5	5.5	0.8	2.7	0.4	2.9	0.6	2.5	0.9	0.6	0.3
	May	3.1	0.4	3.2	1.6	0.5	0.3	1.8	0.4	3.4	0.6	0.5	0.3
	Jun	2.3	0.3	6.0	1.9	1.5	0.1	1.9	0.4	7.4	0.5	1.5	0.1
	Jul	4.2	0.3	3.7	0.9	1.6	0.2	1.0	0.3	1.2	0.7	1.0	0.4
	Aug	3.0	0.2	2.7	1.0	1.4	0.3	1.7	0.4	1.3	0.4	0.3	0.4
	Sep	3.8	0.3	8.8	0.7	1.4	0.2	1.0		1.4	0.2	1.7	0.1
	Oct	1.2	0.5		0.9	0.5	0.2	2.4		2.7	0.9	1.0	0.5
	Nov	1.1	0.4		0.6	0.8	0.2		0.2	1.0	1.5	0.6	0.7
	Dec	2.3	0.7		0.6	1.0	0.2		0.3	3.0	0.9		
1982	Jan	2.1	0.6		0.2	2.1	0.2		0.2		0.6		0.2
	Feb	1.7	0.6	5.5	0.3	0.9	0.2	0.8	0.4	2.9	0.5	0.9	0.4
	Mar	2.8	0.9	5.7	0.2	1.3		3.0	0.4	3.4	1.0	1.1	0.4
	Apr	1.9	0.6	4.0	0.4	1.2	0.3	2.0	0.4	2.4	0.7	1.0	0.4
	May	1.5	1.1	4.9		0.5	0.2	0.9	0.4	2.2	1.3	1.2	0.3
	Jun	3.1	0.5	4.1	0.8	1.5	0.3	1.9	0.3	1.7	0.3	0.9	0.2
	Jul	1.0	0.4	1.6	0.6	0.5	0.4	1.0	0.3	3.1	0.4	2.5	0.2
	Aug	1.0	0.2	3.5	0.6	0.7	0.4	1.7	0.2	1.0	0.2	0.9	0.2
	Sep	2.7	0.6	5.2	0.5	1.0	0.3	1.2		1.7	0.7	1.0	0.2
	Oct	2.1	0.8	2.9	0.8	0.2	0.3	1.1		4.3	1.3	0.8	0.4
	Nov	2.9	1.1	6.2	0.3	1.5	0.2	4.8	0.4	3.5	1.1	0.4	0.5
	Dec	3.0				1.7		3.0				0.5	

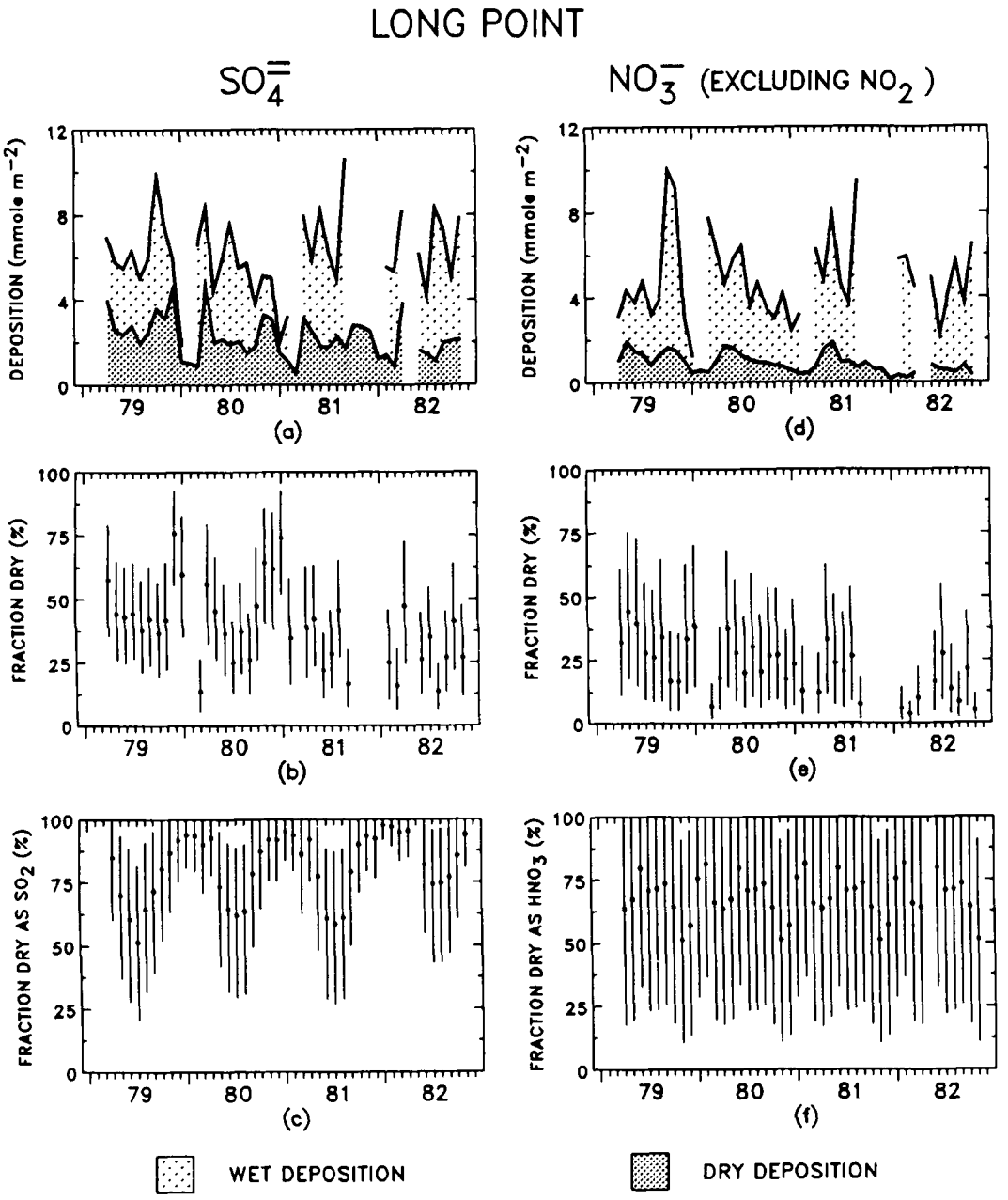

Fig. 3. Monthly variation of total deposition, its wet and dry components (a) and (d), the fraction of total deposition that is dry (b) and (e) and the fraction of dry deposition by gaseous form SO_2 (c) and HNO_3 (f) for $SO_4^=$ and NO_3^- at Long Point. NO_3^- does not include the contribution of NO_2 (see text).

NO_2. Considering the relative reactivity of these two compounds this will definitively lead to an upper limit of PAN dry deposition. The results of the estimates together with uncertainties are shown in Tables 8, 9. A comparison of these results with those in Table 7, leads to the conclusion that deposition of NO_2 but not of PAN is an important component of total nitrate

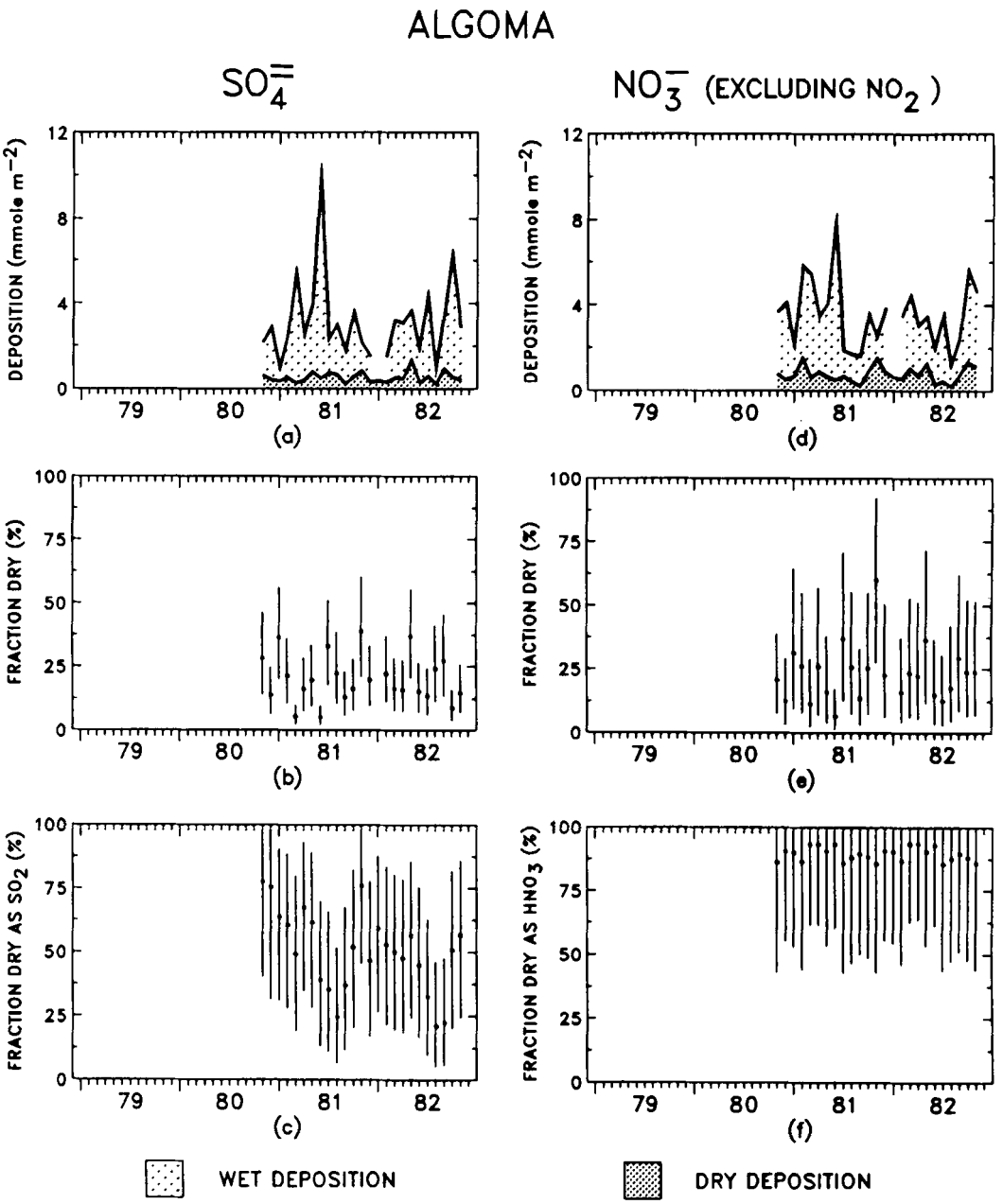

Fig. 4. Same as Fig. 3 for Algoma.

dry deposition. Approximately 49% (most probable range 21% to 78%) and 61% (most probable range 35% to 88%) of total dry deposited nitrate comes down as NO_2 at Long Point and Chalk River, respectively. Qualitatively, the above conclusions are probably valid for the other sites although quantitatively of the contribution of NO_2 may be different. For instance, at Algoma which is near upper Michigan where Cadle et al. (1985) report NO_2 concentrations during winter

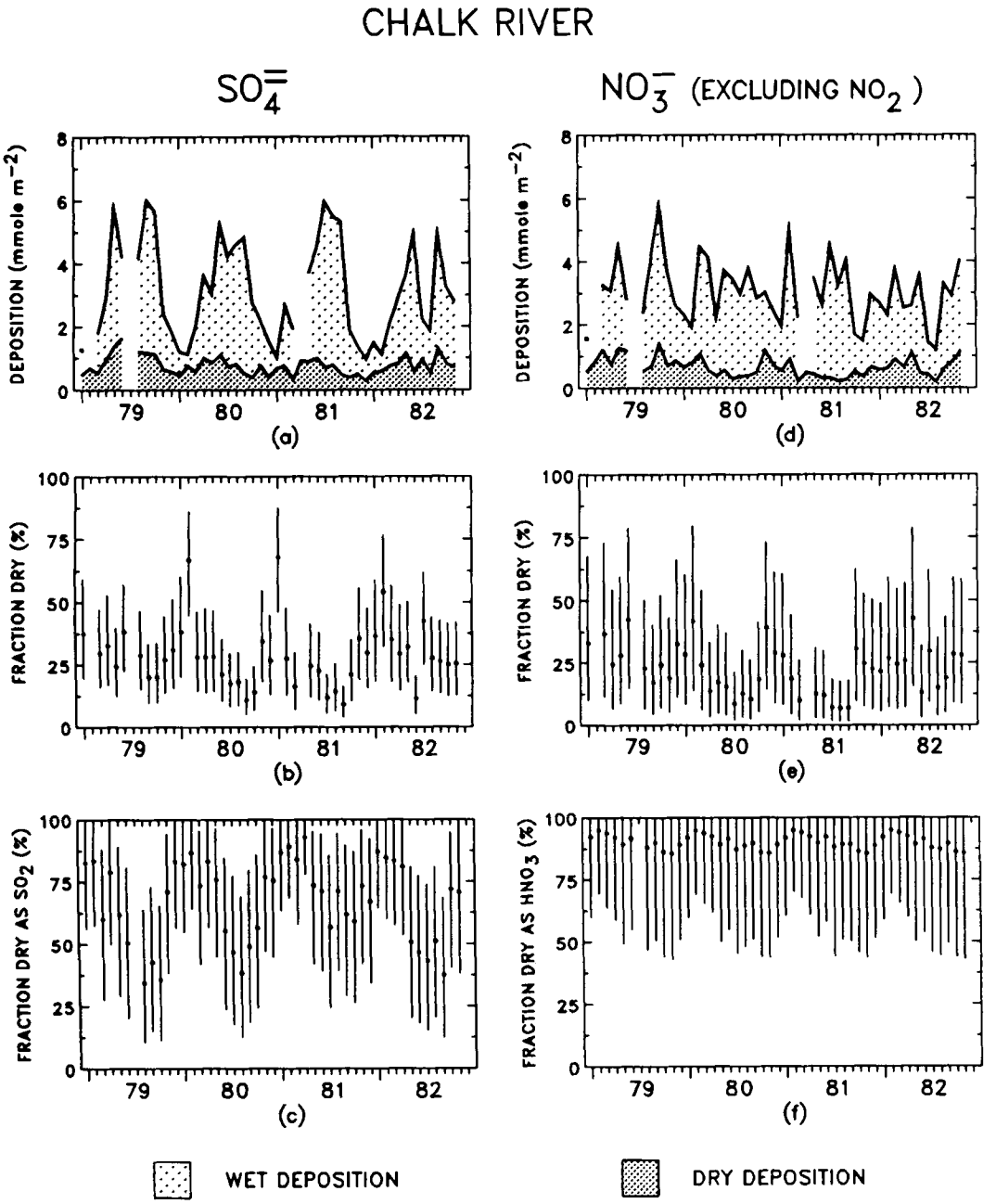

Fig. 5. Same as Fig. 3 for Chalk River.

of 1.9 ppb compared to 6.6 ppb observed at Chalk River during the same season, the relative importance of NO_2 deposition will be less than at Chalk River since the dry deposition from NO_3^- compounds is about the same at both sites.

The four year mean total annual depositions of $SO_4^=$ and NO_3^- (neglecting NO_2 contributions) are plotted in Fig. 1 to show the spatial distribution. The spatial distribution of deposition in eastern Canada is qualitatively consistent with the

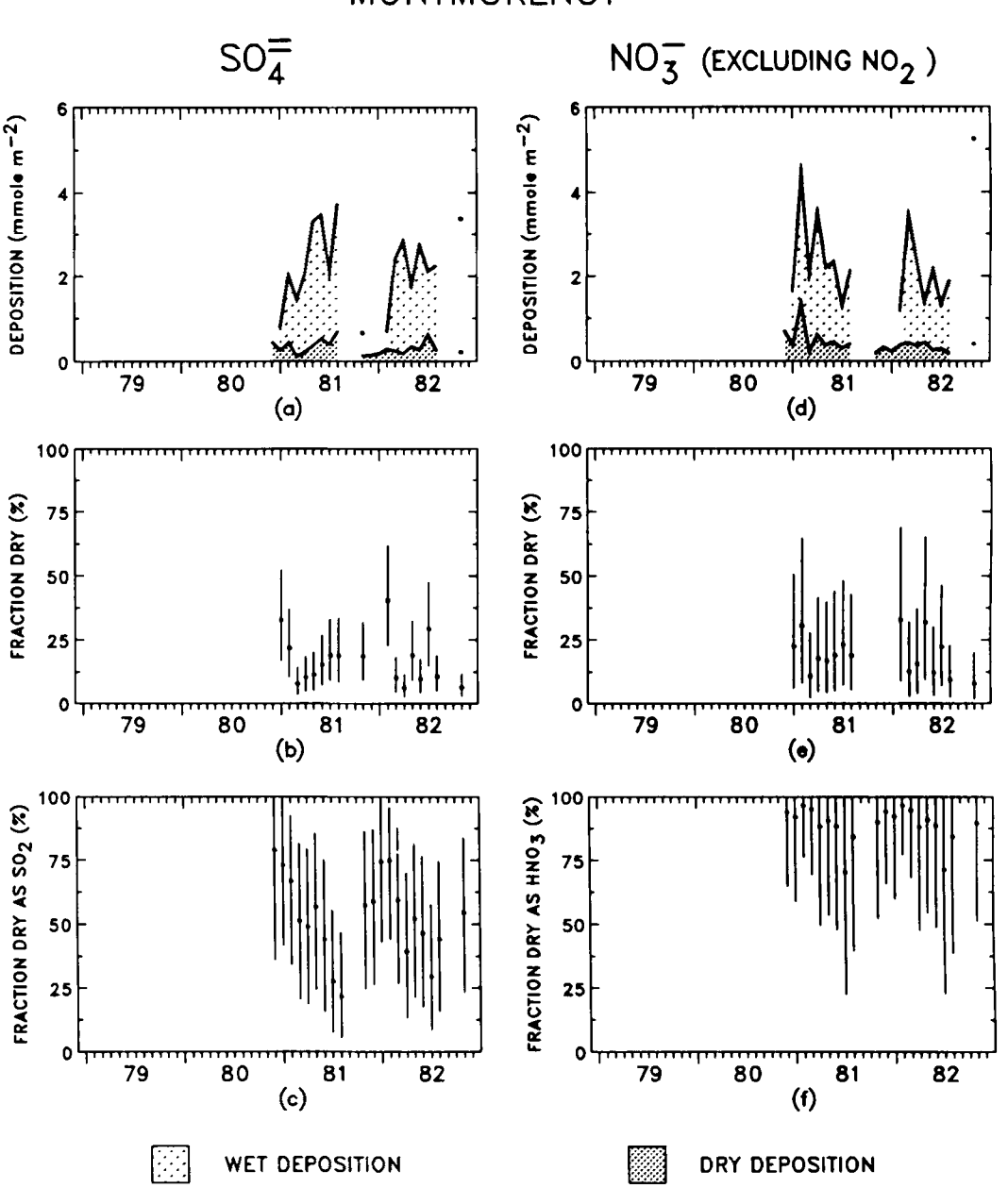

Fig. 6 Same as Fig. 3 for Montmorency.

emissions distribution of SO_2 and NO_x in the region (see Barrie and Hales (1985)). Ranked in order of decreasing sulphur deposition estimates, the stations are Long Point, Algoma/Chalk River, Montmorency/Kejimkujik and ELA. When ranked according to NO_3^- deposition estimates, the stations appear in the same order as above with the notable difference that deposition at Montmorency is 40% higher than at Kejimkujik. However, since NO_2 deposition is

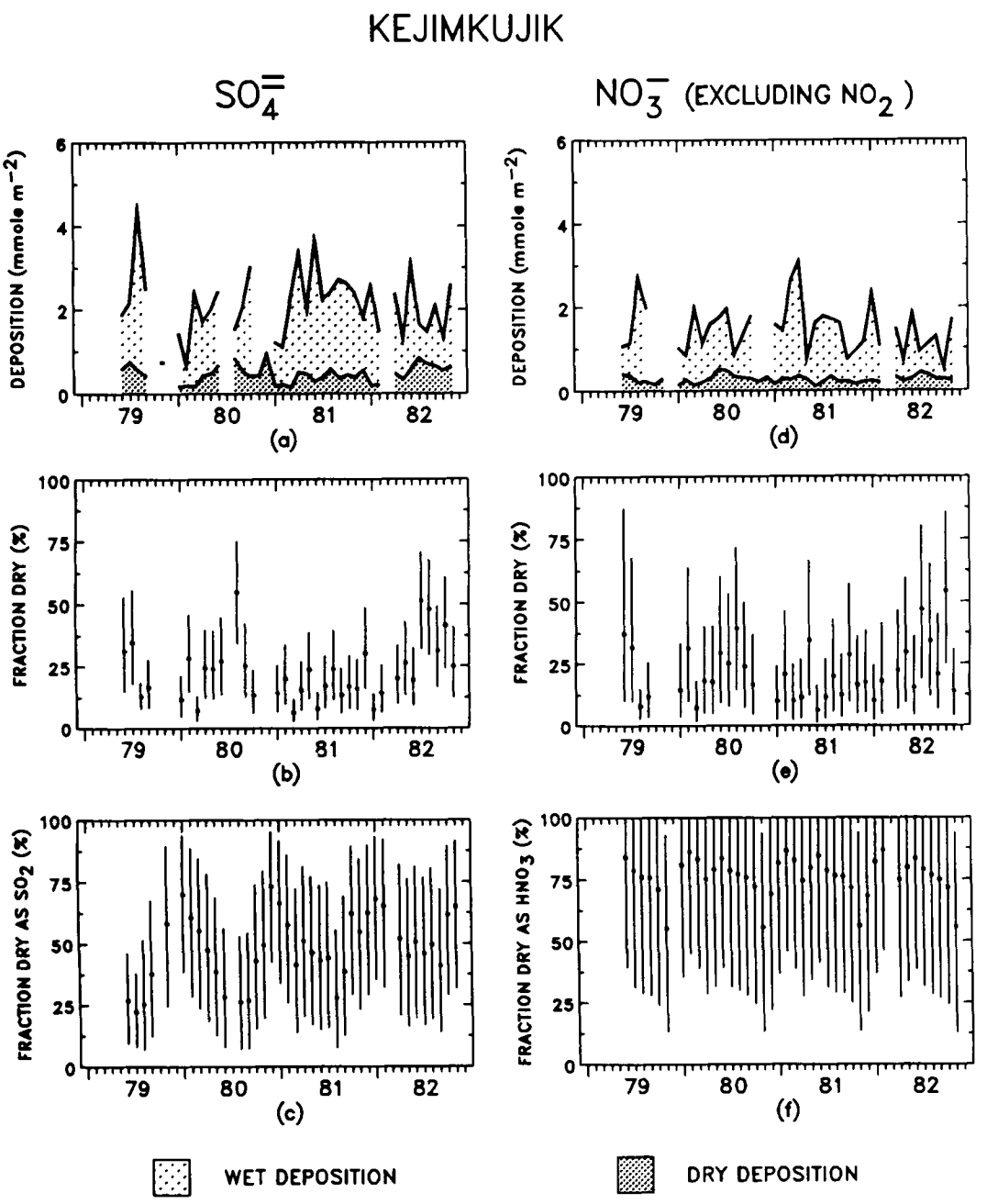

Fig. 7. Same as Fig. 3 for Kejimkujik.

not included, this ranking is somewhat uncertain. The inclusion of NO_2 dry deposition estimates in Table 8 has the effect of increasing total deposition at Long Point and Chalk River by 18% (most probable range 6% to 40%) and 33% (most probable range 11% to 75%), respectively.

Best estimates of the four-year average fraction of total sulphur deposition comprised of dry

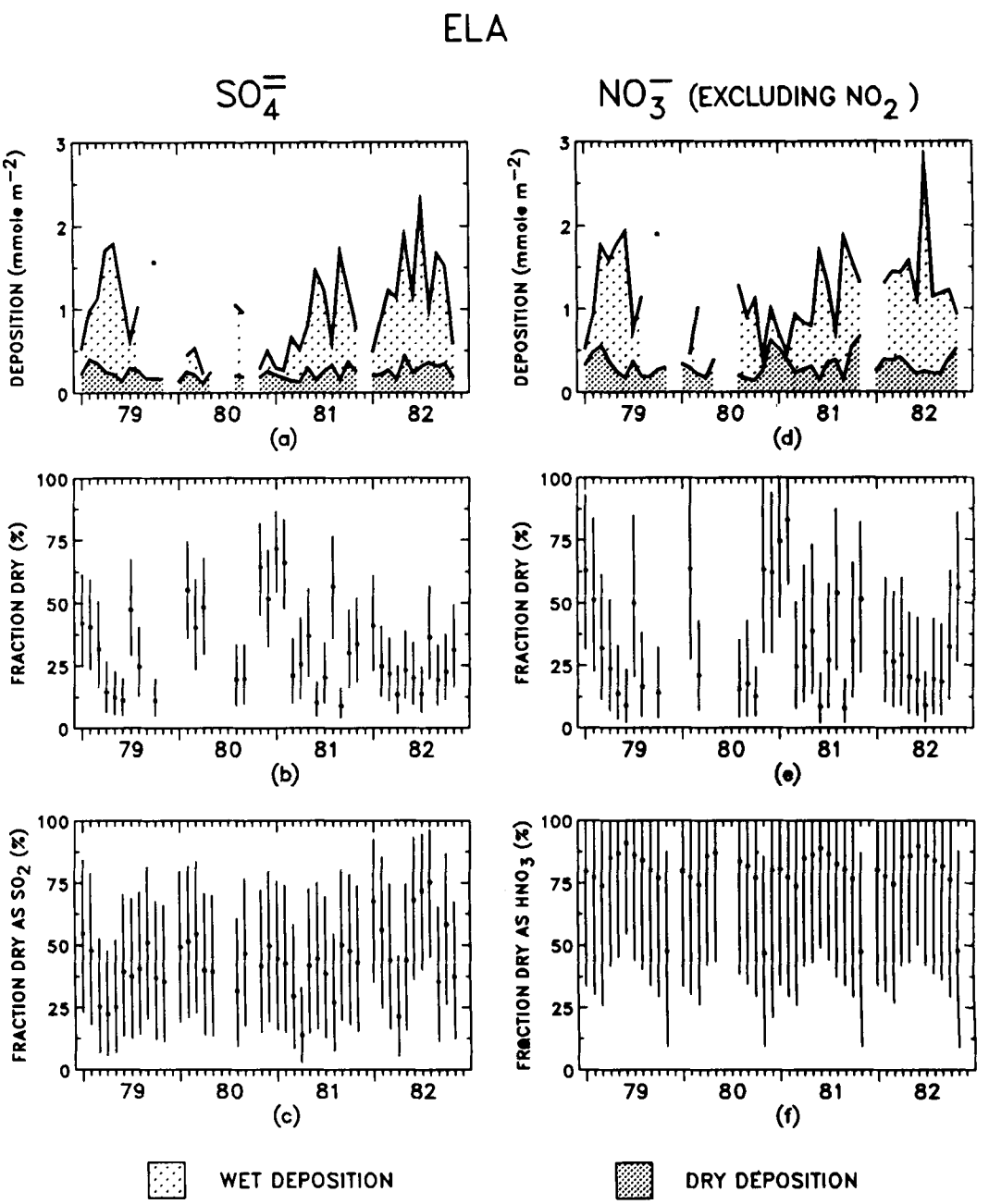

Fig. 8. Same as Fig. 3 for experimental lakes area.

deposition ranges from 12% to 37%. The contribution of dry deposition to total sulphur deposited tends to be highest at Long Point (37%, most probable range 20% to 55%) close to sources, next highest at the remote central North American site of ELA (26%, most probable range 14% to 40%), intermediate at Chalk River (24%, most probable range 13% to 38%) and

Table 6. *The annual total deposition (T) of $SO_4^=$ (mmole m^{-2}) and the fraction that is comprised of dry deposition (D) as measured at APN sites for 4 years in comparison to results measured by Chan et al. (1984, 1985) in Ontario; note that T does not include fogwater deposition*

	APN										Ontario	
	1979		1980		1981		1982		4-year mean		1982	
	T	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)
Long Point	71* (52,98)	43 (24,60)	62 (47,87)	41 (24,61)	65 (50,90)	37 (19,55)	86* (71,109)	26 (12,42)	71 (55,96)	37 (20,55)	58	22
Algoma	NM		ID		40* (35,46)	16 (8,26)	38 (34,44)	17 (9,27)	39 (34,45)	16 (8,26)	27#	20#
Chalk River	43 (36,53)	27 (15,40)	36* (31,44)	23 (13,36)	38 (32,46)	20 (9,33)	34 (28,42)	27 (14,41)	38 (32,46)	24 (13,38)	24	22
Montmorency	NM		ID		25 (22,29)	16 (8,26)	27 (24,31)	12 (6,20)	26 (23,30)	14 (7,23)		
Kejimkujik	ID		28 (24,33)	22 (11,34)	28 (25,32)	16 (8,26)	24 (20,29)	26 (14,40)	27 (23,32)	21 (11,33)	--	
ELA	13 (11,16)	22 (11,34)	8 (6,10)	31 (18,47)	10 (8,12)	27 (15,41)	14 (12,17)	22 (12,35)	11 (9,14)	26 (14,40)	12	13

Numbers in brackets are the most probable range.
ID: insufficient data (see text).
NM: no measurements.
*: precipitation amount estimated.
#: Ontario sampling sites more than 120 km from Algoma.

Table 7. *The annual total deposition (T) of NO_3^- (mmole m^{-2}) and the fraction that is comprised of dry deposition (D) as measured at APN sites for 4 years in comparison to results measured by Chan et al. (1984, 1985) in Ontario in 1982; note that T does not include fogwater deposition; T and D do not include NO_2 dry deposition which can be substantial (see text)*

	APN										Ontario	
	1979		1980		1981		1982		4-year mean		1982	
	T	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)	*T*	*D* (%)
Long Point	55* (44,75)	24 (8,48)	53 (43,71)	22 (7,44)	53 (45,66)	20 (6,42)	62 (55,71)	9 (3,21)	56 (48,66)	19 (9,31)	67	35
Algoma	NM		ID		44* (35,59)	22 (6,48)	41 (33,56)	22 (6,48)	42 (35,54)	22 (9,40)	39#	45#
Chalk River	39 (30,56)	28 (9,59)	37* (30,50)	20 (6,45)	36 (30,45)	15 (4,36)	34 (27,48)	24 (7,51)	37 (31,46)	22 (10,37)	29	25
Montmorency	NM		ID		26 (21,35)	20 (6,45)	28 (24,36)	15 (4,35)	27 (23,33)	17 (7,32)		
Kejimkujik	ID		20 (16,26)	18 (5,39)	19 (16,24)	14 (4,31)	16 (13,22)	20 (6,42)	19 (16,22)	18 (8,30)		
ELA	15 (12,21)	25 (8,51)	ID		13 (9,20)	34 (13,63)	16 (12,22)	25 (8,50)	15 (12,19)	28 (15,44)	19	37

Numbers in brackets are the most probable range.
ID: insufficient data.
NM: no measurements.
*: precipitation amount estimated.
#: Ontario sampling sites more than 120 km from Algoma.

Table 8. *Best estimates of NO_2 dry deposition (DD) at Chalk River and Long Point based on estimated monthly air concentrations ($\overline{C}$) from other measurements and deposition velocities from the calculations of Voldner et al. (1986), see Table 3*

	Chalk River		Long Point	
	$\overline{C}$ (ppb)	*DD* (mmole m^{-2})	$\overline{C}$ (ppb)	*DD* (mmole m^{-2})
Jan	5.9	0.42	10.8	0.39
Feb	7.3	0.47	13.3	0.43
Mar	8.4	0.60	15.4	0.55
Apr	5.0	1.62	9.2	1.49
May	4.1	1.72	7.5	1.34
June	3.0	1.32	5.4	0.94
July	2.7	1.18	5.0	0.90
Aug	2.5	1.05	4.6	0.77
Sept	3.7	1.33	6.7	1.09
Oct	3.7	0.97	6.7	1.12
Nov	5.0	1.27	9.2	0.96
Dec	5.5	0.39	10.0	0.24
Total annual		12.3		10.2
Possible range		3.5–43		3.0–36

Table 9. *Estimates of the upper limit of PAN dry deposition (DD) at Long Point and Kejimkujik based on estimated monthly air concentrations ($\overline{C}$) from non-routine measurements (see text) and deposition velocities equal to that of NO_2 (see Table 3)*

	Long Point		Kejimkujik	
	$\overline{C}$ (ppb)	*DD* (mmole m^{-2}) upper limit	$\overline{C}$ (ppb)	*DD* (mmole m^{-2}) upper limit
Jan	0.34	0.012	0.16	0.010
Feb	0.34	0.011	0.27	0.015
Mar	0.29	0.010	0.32	0.019
Apr	0.28	0.045	0.29	0.054
May	0.28	0.050	0.20	0.043
June	0.30	0.052	0.16	0.041
July	0.31	0.055	0.15	0.039
Aug	0.24	0.040	0.16	0.038
Sept	0.29	0.047	0.18	0.038
Oct	0.25	0.042	0.19	0.032
Nov	0.25	0.026	0.19	0.031
Dec	0.25	0.006	0.11	0.018
Total annual		0.40		0.38
Possible range		0.11–1.4		0.11–1.3

Kejimkujik (21%, most probable range 11% to 33%) and lowest at Montmorency (14%, most probable range 7% to 23%) and Algoma (16%, most probable range 8% to 26%). ELA receives about 40% less precipitation than the other sites. If one excludes the contribution of NO_2 to nitrogen dry deposition, best estimates of the fraction of total NO_3^- deposition that is dry range from 17% to 28% being highest at ELA, Kenora. Of course, the estimated fraction will increase if NO_2 deposition is included. For instance, from the estimates in Table 8, it will increase from 19% to 32% and 22% to 55% at Long Point and Chalk River, respectively.

Even though $SO_4^=$ watershed mass balances are uncertain because of accumulating errors in differencing and assumptions that $SO_4^=$ is conservative, they nevertheless provide an independent source of information on dry deposition. At Hubbard Brook in New Hampshire, Likens et al. (1980) report that the output of $SO_4^=$ exceeded the measured input by about 32% with the difference presumably attributable to dry deposition and fogwater deposition. Studies by Dillon et al. (1982) on forested watersheds near a major point source (Sudbury) attributed 45% to 71% of the $SO_4^=$ flowing out to dry deposition and fogwater deposition. One would expect the fraction of total deposition that is dry to be higher close to a large source than at regionally representative locations at which our measurements were made. At two watersheds nearest these areas, Chalk River and Algoma, we estimate that 24% and 16% of the total deposition is dry. Thus, these estimates are not inconsistent with the watershed mass balance results.

Based on the observed wet and dry deposition at APN sites representing the areas shown in Fig. 1, we estimate that on an annual basis in the southern part of Canada east of Manitoba, 22% (most probable range 12% to 34%) of the total $SO_4^=$ deposited comes down as dry deposition. Using earlier measurements in the literature, Galloway and Whelpdale (1980) estimated that in all of eastern Canada 29% of $SO_4^=$ deposition was dry. In Europe (Rodhe and Granat, 1983), the estimated fraction dry deposited annually is 50% while it is 39% and 61% for the summer and winter half of the year, respectively. In contrast, on a seasonal basis, the estimated contribution of total $SO_4^=$ deposition that is dry in southern

eastern Canada ranged from 21% (most probable range 9% to 31%) to 26% (most probable range 13% to 40%). Differences in the winter/summer contrast between eastern Canada and Europe are due to differences in climate that yield, during winter in Canada, more frequent snow and dormant vegetation surfaces inert to SO_2, than in Europe. Thus even though SO_2 concentrations are highest in both regions during winter, the winter rate of deposition is lower in Canada than in Europe resulting in less winter/summer contrast than in Europe.

For NO_3^- deposition (excluding NO_2 dry deposition), it was calculated that 21% (most probable possible range 8% to 38%) of the total deposition in southern eastern Canada is dry. If as suggested by the estimates in Table 8, NO_2 and particulate NO_3^- contribute equally to nitrogen dry deposition, then the overall fraction that is dry deposition would increase to 30% (most probable range 13% to 53%). A nitrogen budget estimate by Logan (1983) indicates that in eastern Canada and in the eastern United States dry deposition of NO_3^- is in the range 17% to 29% and 49% to 66% of the total, respectively. Our estimated range of deposition for eastern Canada contains Logan's range but allows the possibility for even higher dry deposition contributions. Bonis et al. (1980), neglecting HNO_3 dry deposition, estimate for Europe that on an annual basis the total deposition of NO_x that is dry deposited ranges from 32% to 67%. It is higher than in eastern Canada but comparable to Logan's estimates for the climatologically more similar eastern United States.

In making the above estimates of regional deposition of $SO_4^=$ and NO_3^- it was assumed that the five locations were representative of the main part of each area they center in Fig. 1. Of course, there are cities (covering less than 10% of the area) having elevated concentration and deposition above the regional averages. This would mean that our deposition estimates and those of others may be slightly low.

A comparison of the seasonal variation of total monthly deposition and its wet and dry components of $SO_4^=$ and NO_3^- (excluding NO_2 contributions to dry) can be made using Figs. 3–8. At all locations, there is a marked seasonal variation in $SO_4^=$ wet deposition and to a lesser extent in dry deposition. Wet deposition peaks in the summer and is a minimum in winter. Dry deposition follows a similar pattern except at ELA where little variation is apparent. This is due to the difference between the seasonal cycles of SO_2 and $SO_4^=$ at ELA and the other sites (Barrie et al., 1984). Seasonal variations in total NO_3^- (excluding NO_2 dry) are much less pronounced than those of $SO_4^=$. However if the contribution of NO_2 dry deposition as indicated in Table 8 is taken into account, there is, at least in central eastern Canada, a seasonal variation in total deposition with a summer peak and winter minimum.

Long Point is the only site where there is any indication of a systematic trend superimposed on the seasonal variation. There is a decrease in the dry deposition and an increase in the wet deposition for both sulphur and nitrogen (excluding NO_2 contribution) (Fig. 3). However, the total deposition for both $SO_4^=$ and NO_3^- does not show any marked trend, because opposing variations cancel one another. The decrease in the dry deposition of sulphur is related to a reduction in the mean concentrations of particulate sulphate by a factor of about 2.5 between 1979 and 1982. Gaseous SO_2 does not show any systematic trend. The air concentration of total NO_3^- (excluding NO_2 contribution) also decreased by approximately the same factor as for particulate sulphate. The increase in the wet deposition is due to slight augmentations in both the concentrations of $SO_4^=$ (or NO_3^-) and of the monthly precipitation amount.

With regard to effects on forests, the fraction of sulphur deposited to a forest canopy in the form of SO_2 may be a very important parameter. Since most of the gas is taken up by the stomata (Garland and Branson, 1977) where it most likely is not washed off by precipitation, much of the sulphur being deposited may not be reaching the forest soil directly but rather by transferral via the root system. The same may be true for nitrogen deposited as NO_x or PAN whose uptake by forests is also controlled mainly by stomata (Grennfelt et al., 1983). In contrast, HNO_3 deposition occurs equally well to all forest surfaces and since stomatal area is only a small fraction of the total, it is likely that much of the nitrate thus deposited may be washed to the ground during precipitation as suggested by Cronan and Reiners (1983). The estimated

fraction of dry deposition that is delivered by gaseous SO_2 is shown in Figs. 3c to 8c as a function of time. It has a strong seasonal variation with a winter peak and a summer minimum at all sites but ELA. On average, it is highest at Long Point (78%), next highest at Chalk River (65%), intermediate (50%) at Algoma, Montmorency, Kejimkujik and lowest at ELA (37%). Less can be said with certainty about the seasonal variation of the estimated contribution of HNO_3 deposition to the total dry deposition (excluding NO_2 contributions, Figs. 3f to 8f) because we have used only one year of new data from 1983 to apportion total airborne nitrate into particulate and gaseous forms. On average, it is higher than that of sulphur ranging from about 63% to 90%. If NO_2 and total NO_3^- (particulate $NO_3^- + HNO_3$) contribute approximately equally to dry deposited NO_3^- as was estimated above, the estimated fraction contributed by HNO_3 to total NO_3^- dry deposition would be half that shown in Figs. 3f to 8f. That is, it would range from 31% to 45%. At Chalk River and Long Point, we estimated that the fraction of NO_3^- dry deposited as NO_2 was 61% and 49%, respectively.

Another aspect of acidic deposition that is important in the assessment of effects is its episodic nature. It is useful to know what fraction of wet or dry deposition is delivered by a certain fraction of events or, in other words, the episodicity (E). Episodicity is defined here as the fraction of total wet or dry deposition delivered by the top 20% of the daily events when ranked according to deposition. This is graphically illustrated for $SO_4^=$ dry deposition at Chalk River in Fig. 9. Several years of daily data were used for each station. It should be noted that the monthly mean dry deposition velocity is used to estimate E on a daily basis. However, unless the daily mean concentration and deposition velocity are strongly correlated, this will not introduce a large bias. There is little reason to believe that they are well correlated on a daily basis. For each site, E was calculated for both wet and dry deposition for both $SO_4^=$ and NO_3^- (excluding NO_2) deposition (Table 10). It ranges from 47% to 70%. For $SO_4^=$, estimated E of wet deposition is higher than for dry, especially at Kejimkujik, Algoma and ELA. The reverse is true for NO_3^- especially at Algoma and Chalk River. Inter-site differences are apparent. For both $SO_4^=$ and NO_3^-,

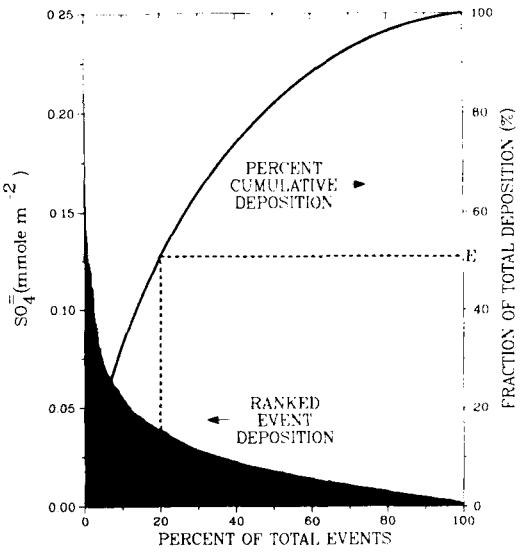

Fig. 9. Total $SO_4^=$ dry deposition at Chalk River ranked by % of total events, and % cumulative deposition. E is the fraction of total deposition contributed by the highest 20% daily events.

estimated E of wet and dry deposition was 10% ± 5% higher at the more remote sites than at Chalk River and Long Point closer to sources (the exception was E of NO_3^- for dry deposition at Chalk River which was similar to that at other sites). This is expected since the closer a rural site is to a major source region, the more uniform the air pollutant concentrations are likely to be.

The relative importance of the oxides of sulphur and nitrogen in contributing to acidic

Table 10. *The estimated episodicity of dry and wet deposition of $SO_4^=$ and NO_3^- (excluding NO_2) as indicated by the fraction of total dry or wet deposition in a period (%) that occurs in the top 20% of deposition events*

	Dry		Wet	
Station	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-
Long Point	51	51	52	47
Algoma	60	68	70	55
Chalk River	51	62	55	46
Montmorency	61	64	63	58
Kejimkujik	51	56	57	59
ELA	49	62	63	58

deposition is an important consideration in developing emission control scenarios for the alleviation of acid deposition. Summers and Barrie (1986) have examined precipitation chemistry data in eastern North America and concluded that in eastern Canada and the northeastern United States, the molar ratio $SO_4^=/NO_3^-$ (S/N) in wet deposition peaks in summer and is a minimum in winter. The data enable this ratio to be examined in not only wet deposition but also dry and total deposition at Chalk River and Long Point. The results for Chalk River region sensitive to acid deposition are shown in Fig. 10. In contrast to the strong summer peak in wet deposition, estimated S/N has little seasonal variation in dry deposition. The S/N dry annual average is 0.46; that is, equal equivalents of $SO_4^=$ and NO_3^- are dry deposited. A pronounced peak in NO_2 dry deposition during summer (Table 8) rather than one for that of particulate NO_3^- plus HNO_3 (Table 5) tends to offset the summer peak in $SO_4^=$ dry deposition (Table 4). The lack of seasonal variability in S/N in dry deposition produces less seasonal variation in total deposition than in wet deposition alone. However, a marked seasonal variation in total deposition remains with a June to September peak of ≈ 1 (i.e., twice as many $SO_4^=$ equivalents deposited as NO_3^-) and a November to February minimum of ≈ 0.5 (equal equivalents). At Long Point, estimated S/N for dry deposition has large fluctuations about a mean of ≈ 1.5 with little evidence of seasonal dependence. It was similar to the annual mean ratio in wet deposition. S/N for the wet deposition has a spring, summer, fall peak of ≈ 1.8 and a winter minimum of ≈ 1.1. The estimated ratio in total deposition was not markedly different from that in wet deposition.

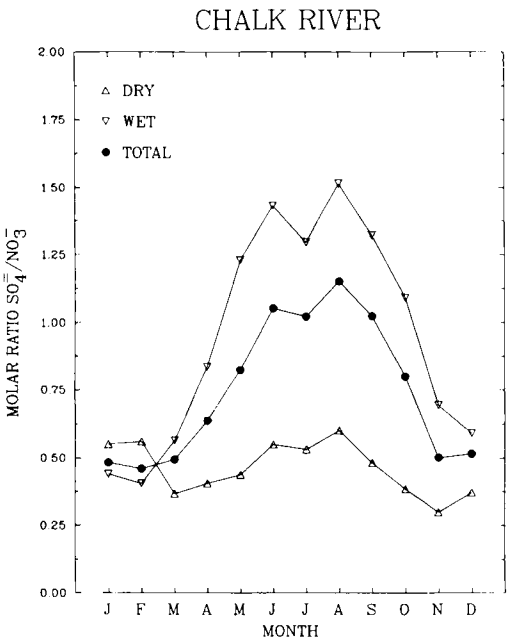

Fig. 10. Seasonal variation of the molar ratio of $SO_4^=$ to NO_3^- for wet, dry and total deposition at Chalk River.

6. Conclusion

Four years of daily air and precipitation chemistry measurements at 6 locations in eastern Canada have been used to examine the contribution of dry deposition to the total deposition of potentially acidic sulphur and nitrogen compounds. Deposition due to fogwater impaction/interception, which in coastal and high elevation areas can be substantial (Barrie and Schemenauer, 1986), was not taken into account.

The complexity of dry deposition processes in complex terrain leads to dry deposition estimates for sulphates and nitrates in eastern Canada that are uncertain by an estimated factor of 2 and 3, respectively. This is despite having: 4 years of routine air concentrations for SO_2, $SO_4^=$ and total NO_3^- at 6 locations, over 80 published studies available on dry deposition of $SO_4^=$, SO_2 and NO_2 and a sophisticated dry deposition model that incorporates information on fractional surface coverage by various surface types classed by season, wind speed and boundary layer stability. Nevertheless, within these limits of uncertainty valuable conclusions can be drawn.

(1) In southern eastern Canada 22% (most probable range 12% to 34%) and 30% (most probable range 13% to 53%) of the total $SO_4^=$ and NO_3^- deposition, respectively, is dry deposited. For $SO_4^=$, the best estimate is somewhat, but not significantly, lower than a previous estimate of 29% for eastern Canada (Galloway and Whelpdale, 1980) while for NO_3^-, it is at the upper end of the range 17% to 29% indicated by a budget estimate by Logan (1983) for eastern Canada.

(2) On an annual basis depending on location, the estimated fraction of $SO_4^=$ dry deposited as SO_2 ranges from 37% (most probable range 15% to 59%) to 78% (most probable range 47% to 100%). It tends to decrease with increasing distance from major sources. Limited NO_2 and PAN air concentration observations indicate that NO_2 contributes up to 61% (most probable range 35% to 88%) of the total NO_3^- dry deposition while PAN deposition is negligibly small. Since much of the SO_2 and NO_2 dry deposition to vegetation is taken up by stomata and likely reaches the soil only after lengthy biological processing, this result may have important consequences on assessment of acid deposition impacts.

(3) The seasonal variation of the molar ratio of $SO_4^=/NO_3^-$ is less for dry deposition than for wet deposition. However, since wet deposition is the dominant deposition pathway, there remains a strong seasonal variation of $SO_4^=/NO_3^-$ in total deposition with a peak in summer and a minimum in winter.

(4) The estimated episodicity of wet and dry deposition of $SO_4^=$ and NO_3^- (excluding NO_2 contributions to dry) on a daily basis in eastern Canada is such that 20% of the top daily events deliver 47% to 70% of the deposition. For $SO_4^=$, the episodicity of wet deposition is higher than for dry deposition, particularly at remote sites while the reverse is true for NO_3^-.

This attempt at integrating a larger body of information on dry deposition into a better estimate of the relative importance of dry deposition has revealed the need for more information that will reduce the uncertainty in an areal average dry deposition estimate. Routine measurements of NO_2 air concentrations are badly needed. In addition, since much of eastern Canada is covered by forest and much of the sulphur and nitrogen deposition is controlled by stomatal uptake (Voldner et al., 1986), there is a need for better parameterization of gaseous dry deposition to forest canopies. Another area for future research is the assessment of the importance of surface element edge effects on the dry deposition to an area. Furthermore, there is a need to develop techniques for estimating dry deposition on an areal basis (e.g., watershed mass balances, tracer studies) that can be used to complement the very valuable micrometeorological techniques currently in use.

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