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Temporal variation of oxides of sulphur and nitrogen in ambient air in eastern Canada: 1979–1994

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ABSTRACT

The temporal variation of daily ambient concentrations of particulate SO_4^{2-}, NO_3^-, NH_4^+ and gaseous SO_2 and HNO_3, and total-NO_3 (i.e. HNO_3+NO_3) in eastern Canada was studied by fitting (using the maximum likelihood statistical technique) a temporal model that included long-term trend, long-term cycles, seasonal cycles and an auto-regressive model. The technique allowed for missing data and used kernel smoothing and spectral analysis to facilitate the selection of the right model. It was first found that the long-term trends were neither linear nor monotonic. Between the beginning of the 80s and 90s, SO_2 ambient air concentration decreased by 21 to 43% at 5 of the 8 sites. During the same period HNO_3 and total-NO_3 concentrations increased at 7 of the 8 sites. For the other compounds, no systematic variations were found for that period and any overall increases or decreases were small. Long-term cycles were found for 70% of the time-series but their amplitudes were small and they represented only a small fraction of the total variance for each time-series. Seasonal cycles with large amplitudes were found only for SO_2. For the other compounds, statistically significant seasonal cycles were obtained but they had small amplitudes. Auto-regressive models of order 2 were necessary for most of the time-series. For some SO_2 and NO_3^- time-series, auto-regressive models of order 1 were sufficient. For the other compounds, auto-regressive models of order 3 were necessary for some of the time-series. These results indicate that the air masses that arrived at the sites were less homogeneous in the case of SO_2 and NO_3^- than for the other compounds.

1. Introduction

Daily integrated ambient air concentrations have been measured in Canada since the autumn of 1978 when the Air and Precipitation Monitoring Network (APN) began operation with three sites. Other sites were added in the subsequent years and some were eliminated after several years of operation. In the summer of 1983, the APN sites were integrated into the new Canadian Air and Precipitation Monitoring Network (CAPMoN). Some modifications to the network have occurred since that time. By the end of 1994, the CAPMoN network comprised 11 sites across Canada at which ambient air concentrations were measured.

To measure the ambient air concentrations, a filter pack system, consisting of several air filters mounted in series at the top of a 10 m tower, was used. Prior to December 1982, a two-stage filter pack system was employed (Barrie et al., 1980). The upstream filter was a Whatman 40 cellulose filter which was analyzed for particulate SO_4^{2-}, Cl^-, Na^+, K^+, NH_4^+ and NO_3^- as well as vapor-phase nitric acid (HNO_3). The downstream filter was a Whatman 41 filter, impregnated with K_2CO_3-glycerol which collected only gaseous sulphur dioxide (SO_2). The filters operated for 24-h periods starting at 1200 GMT (0600–0800 h local time). In December 1982, the two-filter system was replaced by a three-filter system (Sirois and Fricke, 1992) which enabled the separate measurement of

particulate NO_3^- and gaseous HNO_3 rather than just their sum (as was the case for the two-filter system). In the three filter system, the upstream filter was a Teflon filter that was analyzed for particulate SO_4^{2-}, Cl^-, Na^+, K^+, NH_4^+ and NO_3^-. The central filter was a nylon filter that collected gaseous HNO_3 and a small fraction of SO_2. The third filter was an Whatman 41 impregnated with K_2CO_3-glycerol that collected SO_2.

Ambient air concentrations were measured in CAPMoN mainly to enable the estimation of dry deposition using estimates of the dry deposition velocity (Voldner et al., 1986) and to study atmospheric source-receptor relationships and processes (Summers and Fricke, 1989). Estimates of dry deposition can be found in Barrie et al. (1984), Barrie and Sirois (1986), Sirois and Barrie (1988), Sirois and Vet (1988) and Sirois and Summers (1989). Some studies of the ambient air concentrations have also been reported (Anlauf et al., 1980; Barrie et al., 1984; Sirois and Fricke, 1992) as have several papers on the temporal variation of the ambient air concentrations (Sirois and Summers, 1989; RMCC, 1990; Sirois, 1994).

Most of the aforementioned studies of temporal variations of the ambient air concentrations were for single sites and/or for periods before 1990. In the present paper, a complete study of the temporal variation of the oxides of sulphur and nitrogen at 8 sites in eastern Canada is reported after a brief description of the data and the statistical techniques used. The results are then related, in a broad way, to the known changes in SO_2 and NO_x emissions in the USA and Canada. Since no information about NH_3 emissions could be obtained by the author, such an analysis could not be performed in the case of NH_4^+.

2. Data

A complete description of the sampling equipment, procedures and analytical techniques is published in Anlauf et al. (1985) and Sirois and Fricke (1992). Therefore, only a brief summary is presented here.

As mentioned earlier the ambient air concentrations were measured using a vacuum system consisting of 2 or 3 filters mounted in series at the top of a 10-m tower. The filters were mounted in an open-face Teflon filter pack connected to a flow meter or flow controller and vacuum pump. The filters were loaded into the filter packs in a clean room. Each Tuesday morning, eight new filter packs were placed in the filter pack holder at the top of the 10-m tower. Every day thereafter, at about 1200 GMT, the filter pack though which air was forced was switched automatically. Only seven of the filter packs were used during the week, the eighth filter pack served as a field blank.

Upon receipt of the filters by the laboratory, they were extracted with different solutions depending on the filter (Anlauf et al., 1985; Sirois and Fricke, 1992) and analyzed by ion chronotography.

As mentioned earlier, a set of 7 filter packs, one of which actively sampled each day, was exposed to the atmosphere each week. During the 6 days that air was not being drawn through each filter, particles and gases still had the opportunity to reach the filters through diffusion. Since diffusion is dependent on the ambient pollutant concentration and the atmospheric characteristics of temperature and pressure, the filter loading due to diffusion could and did vary from day to day and from filter to filter. Contamination could also occur from the original matrix and from filter handling. To correct for these effects, a weekly "blank" filter pack was used. This filter pack was identical to the others except that no air was forced through it. The blank filter pack data were used to blank-correct the active filter pack data. Details are given in Sirois and Fricke (1992).

It has been known for some time that filter pack measurements of nitrate and nitric acid are prone to errors due the volatilization of ammonium nitrate (NH_4NO_3) as ammonia (NH_3) and nitric acid (HNO_3) from the front Teflon filter. This produces a negative artifact in the particulate nitrate measurements and a positive artifact in the gaseous nitric acid measurements. Several studies comparing filter pack and denuder measurements have indicated that, typically, total-nitrate measurements compare to within a few percentage points while HNO_3 is overestimated in the filter pack measurements (by up to about 10%) and NO_3^- is underestimated by about 10 to 20% (Sickles et al., 1990; Benner et al., 1991; Harrison and Kitto, 1990). These inherent uncertainties in the filter pack data must be considered when evaluating the nitrate, nitric acid and total-nitrate

temporal variations. The results for these three variables are presented here.

Because of technical problems in the laboratory, the 1983 SO_2 concentrations for Montmorency, ELA and Kejimkujik could not be used in the analyses presented in this paper.

3. Statistical model and techniques

Sirois and Fricke (1992) have shown that the ambient air concentrations of oxides of sulphur and nitrogen are approximately log-normally distributed. Therefore, to use techniques like least-squares or generalized linear models (which assume that the data are normally distributed; see Miller, 1986) to fit a temporal model to the data, one must use a geometric (or log-normal) model. A second characteristic of ambient air concentrations is that the data are highly correlated in time; therefore the time variation model should include an auto-regressive part.

A geometric time variation model was used to describe the temporal variation of the daily ionic concentrations. It included a long-term trend, long-term cycles, seasonal cycles and a daily component with auto-correlation in time. It is written algebraically as follows:

$$\log(C(t_i)) = C_0 + f^{\mathrm{T}}(t_i) + f^{\mathrm{C}}(t_i) + f^{\mathrm{S}}(t_i) + f^{\mathrm{D}}(t_i), \tag{1}$$

where C_i is the concentration on day "i" and t is the time in days.

The long-term trend, f^{T}, was approximated by either a low-order polynomial in t, namely,

$$C_1^{\mathrm{T}} t_i + C_2^{\mathrm{T}} t_i^2 + \ldots + C_K^{\mathrm{T}} t_i^K \tag{2}$$

where K is the order of the polynomial, or by sinusoidal waves, i.e.,

$$\sum_{m=1}^{M_{\mathrm{T}}} \left(C_{sm}^{\mathrm{T}} \sin\left(\frac{2\pi t}{365.25\lambda_m}\right) + C_{cm}^{\mathrm{T}} \cos\left(\frac{2\pi t}{365.25\lambda_m}\right)\right), \tag{3}$$

with periods, λ_m, greater than or equal to 6 years, where M_{T} is the number of waves. The long-term cycles, f^{C}, were approximated with the same equation but with M_C periods between 1 and 6 years. The seasonal cycles were approximated by:

$$\sum_{m=1}^{M_{\mathrm{S}}} \left(C_{sm}^{\mathrm{S}} \sin\left(\frac{2\pi mt}{365.25}\right) + C_{cm}^{\mathrm{S}} \cos\left(\frac{2\pi\, mt}{365.25}\right)\right), \tag{4}$$

where M_{S} is the number of waves used. Up to 4 waves (i.e., M_{S} between 1 and 4) were used. The daily variation, f^{D}, was approximated by the auto-regressive model:

$$f^{\mathrm{D}}(t_i) = a_1 f^{\mathrm{D}}(t_{i-1}) + a_2 f^{\mathrm{D}}(t_{i-2}) + \ldots + a_N f^{\mathrm{D}}(t_{i-N}) + \varepsilon_i, \tag{5}$$

where N is the order of the auto-regressive model; ε_i is the random noise component drawn from a distribution with mean zero and variance σ^2.

This model, extended by the inclusion of an auto-regressive component, is similar to the one used on weekly precipitation chemistry data by Sirois (1993). The presence of the auto-regressive component prevented the use of exactly the same model-fitting technique as Sirois (1993). The presence of missing days in the time series also complicated the problem. Therefore, a more complex statistical technique had to be used.

For given values of K, M_{T}, M_C, M_{S} and N, the parameters θ_j of the temporal model (i.e., C_0, C_1^{T}, ..., $C^{\mathrm{T}}{}_K$, $C_{sm,\ \ldots,}^{\mathrm{T}}$ a_1, ..., a_N) were estimated by maximizing its log-likelihood, $\log(L)$ (Harvey and Phillips, 1979; Kohn and Ansley, 1985). Note that it is assumed here that the ε_i are normally distributed. If the number of data is large, the technique gives unbiased estimates even if the ε_i are not normally distributed (this results from the central limit theorem; see Silvey, 1975). Because there were missing data (which will always be the case in ambient air data), the log-likelihood was maximized using the method given by Kohn and Ansley (1986), which involves the application of the Kalman filter to a state-space representation of the model. In the present study, the S-Plus function "arima.mle", which implements the method of Kohn and Ansley (1986), was used.

To test that the estimated values of the parameters, θ_j^* (the star indicating that they are estimated values), are statistically different from zero, their covariance matrix, $\mathbf{V}$, was estimated as (Shumway, 1984; Silvey, 1975):

$$\{v_{ij}\} = \left\{ -\left[\frac{\partial^2 \log(L)}{\partial\theta_i \partial\theta_j} \right]_{\theta^*} \right\}^{-1}, \tag{6}$$

where $\{v_{ij}\}$ indicates the matrix $\mathbf{V}$ with element v_{ij}. The second derivative of the log-likelihood is obtained at the estimated values of the temporal model. For large n, equal to the number of data, it can be shown (Silvey, 1975) that the random vector θ follows a multidimensional normal distri-

bution with mean **0** and covariance **V** even if the distribution of the ε_i is not normal. As more than one parameter is tested simultaneously for each species, the Bonferroni's multiple testing technique at a 90% confidence level was used (Miller, 1981).

One of the main problems of the present analysis was to determine the model that best fit the data. The values used for K, M_T, M_C, M_S and N (and, in the case of the long-term trend, whether a low order polynomial or a sinusoidal wave should be used) all needed to be evaluated as well as which of the different coefficients defined in equations (2) to (5) were different from zero. One technique was to try various combinations of the functions to determine the ones most appropriate for the model for each species. For example, for $f^T(t)$, polynomials from order 0 up to order 4, and sinusoids with periods between 6.5 and 15 years were tested. Ultimately, the statistically significant model that explained the greatest fraction of the total variance was selected. However, such a technique was labour intensive as the possible number of different models was large. To reduce that number, two techniques can be used separately or in combination.

The first technique was used by Sirois (1993). It consists of using the results of kernel smoothing regressions to guide the choice of the time-series models. Fig. 1 gives examples of the estimation of the long-term trends of particulate SO_4^{2-} and gaseous SO_2 at Chalk River using the kernel smoother described in Sirois (1993) with a bandwidth of 4 years. This technique is most useful for determining the long-term trend.

The second technique, useful for estimating the long-term and seasonal cycles, is spectral analysis. Since missing data were present, the spectral analysis technique described in Sirois et al. (1995) was used. The smoothed power spectra for particulate SO_4^{2-} and gaseous SO_2 at Chalk River are shown in Figs. 2a, c. Figs. 2b, d are for the same data but after eliminating the kernel smoothing estimates of the long-term trends shown in Fig. 1. For both SO_4^{2-} and SO_2, the power spectra indicated the presence of long-term trends and even long-term cycles (see frequency less than about 0.002 days^{-1}). Once the estimated long-term trends were eliminated, the presence of a long-term cycle with a frequency of about 0.0008 days^{-1} (wavelength $\approx$3.4 years) was clear (Figs. 2b, d). In the case of SO_4^{2-}, the power spectrum indicated also that the seasonal cycles were composed of waves of about the same amplitude with wavelengths of 1 year (frequency $\approx$0.0027 days^{-1}) and half a year (frequency $\approx$0.0055 days^{-1}). For SO_2, the one year wave dominated (Fig. 2c). In these plots, the net decrease in the power (especially between frequency 0.001 days^{-1} and 0.5 days^{-1}) indicated the presence of auto-correlation in the data (Sirois et al., 1995).

In summary, these two techniques can help in identifying the best model that fit the data. Once the model has been fitted to the data, it remains to verify if the residuals (the ε_i in eq. (5)) are independent and normally distributed. The first hypothesis was verified by calculating the auto-correlation coefficients up to lag 100 and comparing them to the limit $1.96/\sqrt{n}$, where n is the number of data (see Chatfield, 1984). Because of the presence of missing data, the technique described by Dunsmuir (1984) was used. The hypothesis of normality was checked using normal probability plots and the Kolmogorov–Smirnov test (Hollander and Wolfe, 1973). The hypothesis of normality had to be rejected for most of the species and sites (for only 9 out of 48 tests the P-value of the Kolmogorov-Smirnov test was greater than 0.05). However as mentioned earlier the technique can tolerate some deviation from normality because the number of data was large. Examples of the normal probability plots are given in Fig. 3. Although the hypothesis of normality has to be rejected for Chalk River (Fig. 3a), the deviation from normality is small. In the case of Montmorency, the hypothesis of normality could not be rejected (P-value of the Kolmogorov-Smirnov test equal 0.14). Similar plots for the other compounds and sites indicated than the deviations from normality were usually small and the effects on the analyses were minimal.

4. Results

The model and techniques described in the preceding section were used for particulate SO_4^{2-}, NO_3^-,and NH_4^+ and gaseous SO_2 and HNO_3, and total-NO_3 (i.e., $HNO_3+NO_3^-$) concentrations at 8 sites across eastern Canada. The locations of the sites are given in Table 1 and shown in Fig. 4. The percentage of the total vari-

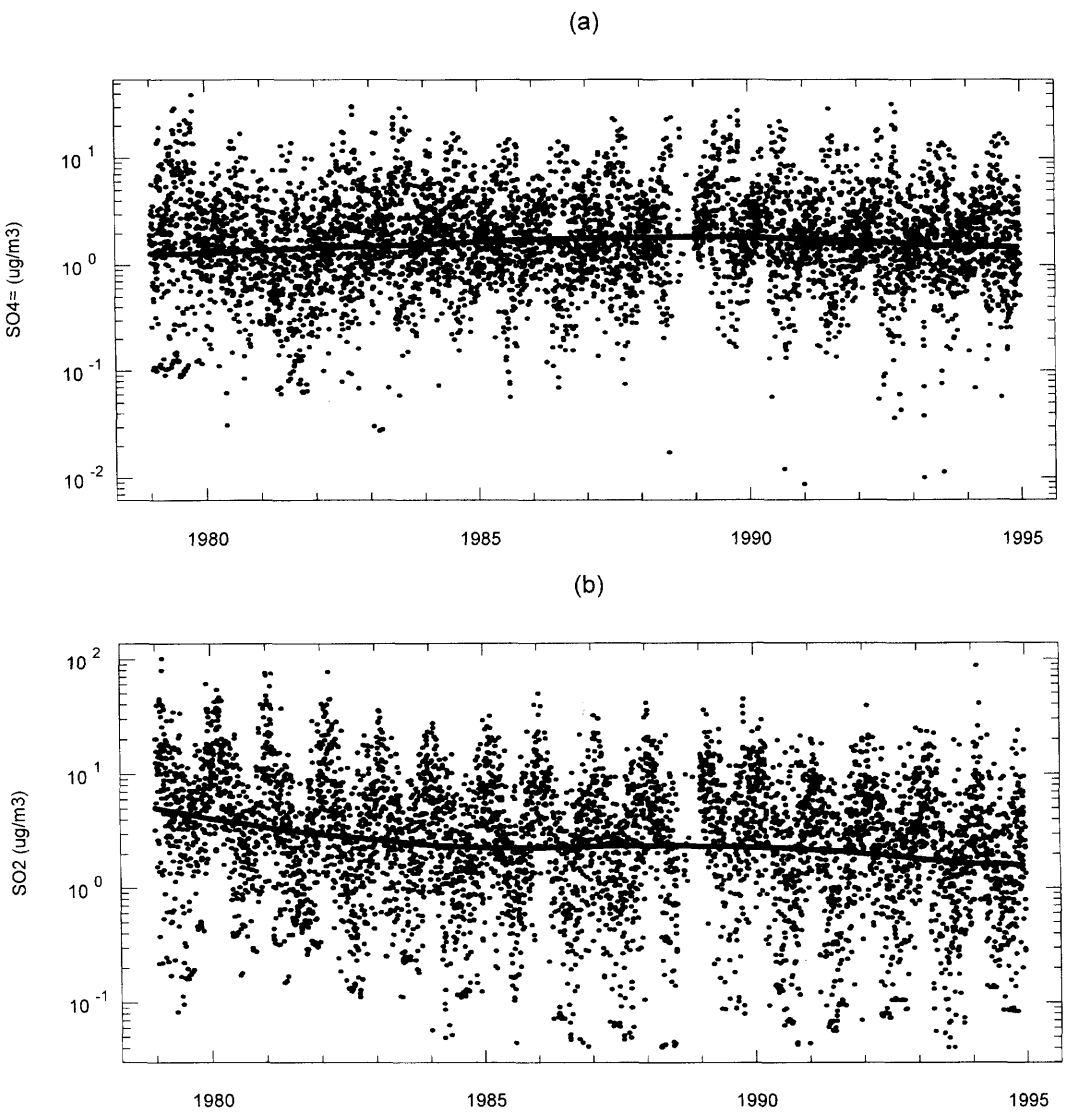

Fig. 1. Temporal variation of particulate SO_4^{2-} and gaseous SO_2 at Chalk River. The solid line is the kernel smoothing regression estimate of the long-term trend.

ance explained by the model (R^2) is given in Table 2, which also gives the percentages of the total variance explained by the long-term trend, long-term cycles, seasonal cycles and auto-regression. The number of available data is also given.

From Tables 1, 2, it can be seen that only between 2 and 10% of the data were missing. Exceptions occurred at ELA, Kejimkujik and Montmorency for SO_2 for which the number of missing data varied between 11 and 15%. This was due to the fact that, as mentioned earlier, the 1983 SO_2 data were completely eliminated at those sites.

The R^2 values indicate that the models could explain between 18 and 51% of the total variance in the data, with the fit being slightly better for SO_2, HNO_3, NH_4^+, and total-NO_3 than for

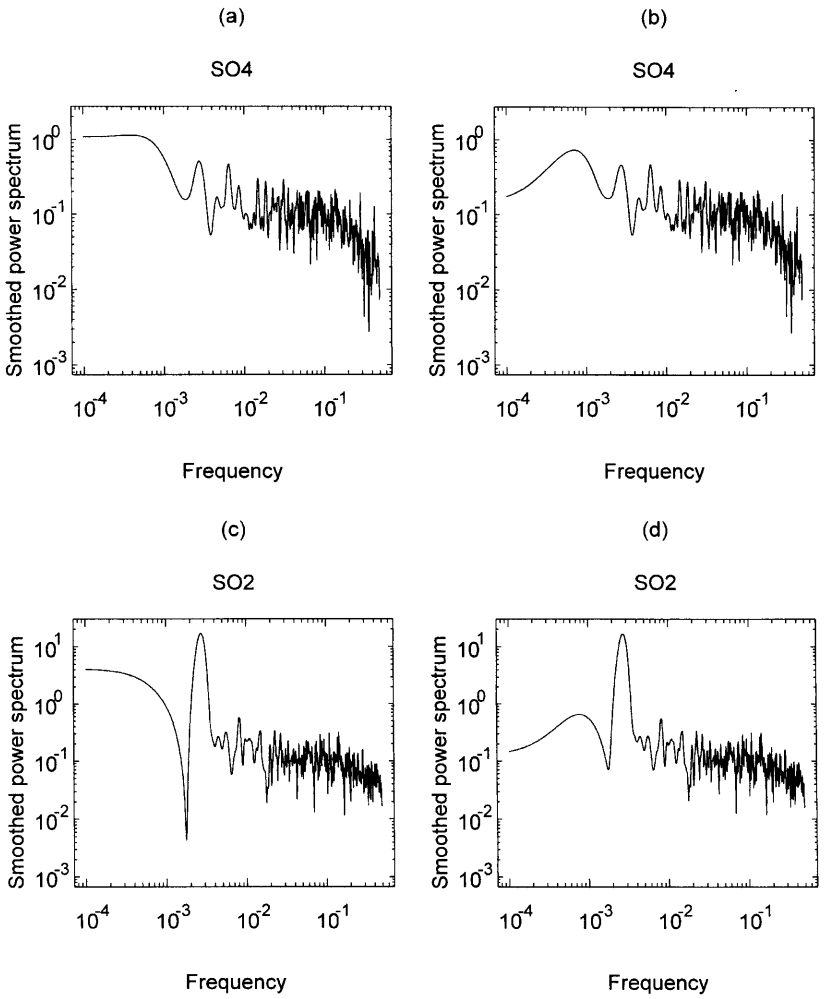

Fig. 2. Smoothed power spectrum for SO_4^{2-} and SO_2 at Chalk River, for original data (a) and (c) and after eliminating the kernel-smoothed regression estimate of Fig. 1 (b) and (d). Frequency in days^{-1}.

SO_4^{2-} and NO_3^-. The fit was also slightly better at ELA and Kejimkujik than at the sites in Southern Ontario which are closer to the major SO_2 and NO_x sources in Canada and the USA. The percentages of the total variance explained by the model although being less than 50% were quite good considering the complexity of the physical processes involved (e.g., the temporal and spatial variation of emissions, the temporal variation of meteorology) and the simplicity of the statistical model used. Table 2 indicates that the auto-correlation term and the seasonal cycles are the most important factors to explain the total variance at most sites. We will discuss in detail each of the model components in the following sections.

4.1. *Long-term trends* ($f^T(t)$)

The long-term trends explained between 0 and 8% of the total variance (Table 2). The fit is generally better for SO_2 and HNO_3 than for SO_4^{2-} and NO_3^-. For all species except SO_4^{2-} and total-NO_3, the percentage of the total variance explained by the long-term trend was lowest in southern Ontario and highest further from the

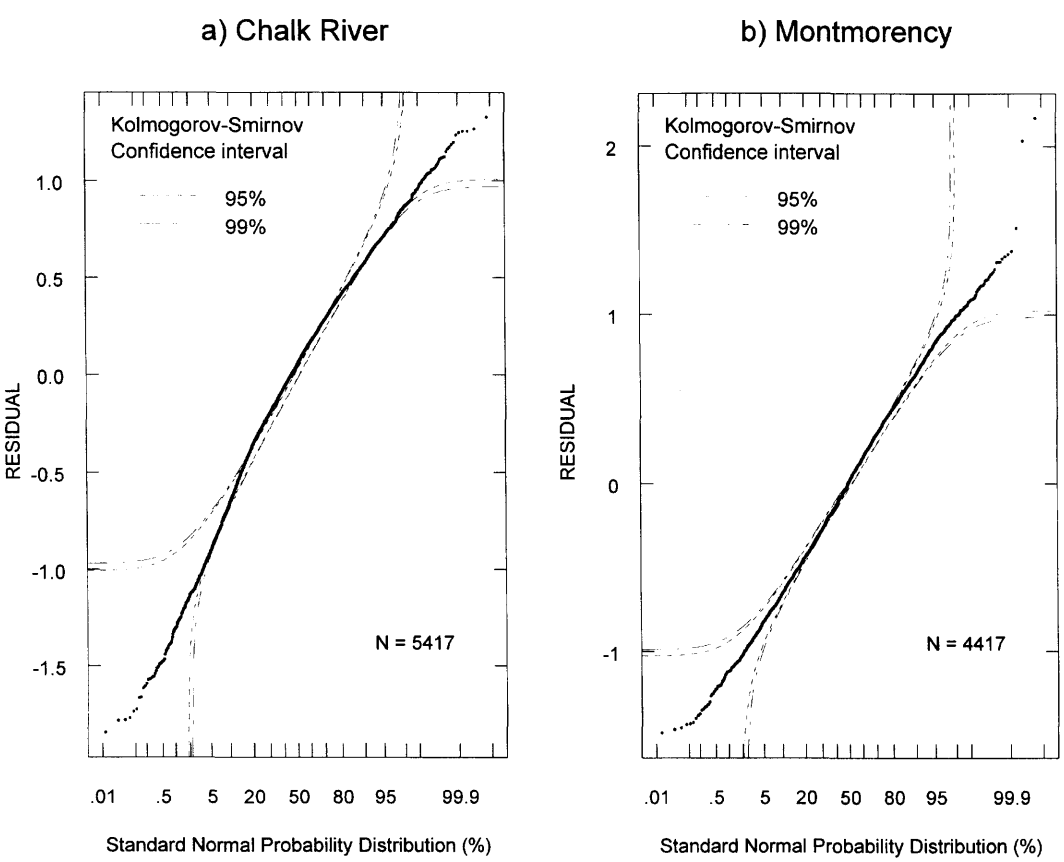

Fig. 3. Normal probability plots of the residuals for SO_2 at Chalk River (a) and Montmorency (b). The dashed and dotted lines indicate the 95 and 99% confidence bands for the Kolmogorov-Smirnov test for normality, respectively.

Table 1. *Site information*

Site	Location		Province	Beginning date[a]	Number of days[b]
	Longitude	Latitude			
Algoma	84° 23′	47° 02′	Ontario	29 Sept 1980	5207
Chalk River	77° 24′	46° 04′	Ontario	1 Jan 1979	5844
Egbert	79° 47′	44° 14′	Ontario	26 Jul 1988	2350
ELA	93° 43′	49° 40′	Ontario	1 Jan 1979	5844
Kejimkujik	65° 12′	44° 26′	Nova Scotia	5 Nov 1979	5714
Longwoods	81° 28′	42° 53′	Ontario	5 Jan 1983	4379
Montmorency	71° 9′	47° 19′	Quebec	4 Dec 1980	5141
Sutton	72° 41′	45° 04′	Quebec	7 Jan 1986	3281

[a] Beginning date for NO_3^- and HNO_3 is December 2, 1982 for all sites that opened before that date.
[b] Number of calendar days between the beginning date and 31 December, 1994. For NO_3^- and HNO_3, the number of days is less or equal to 4413.

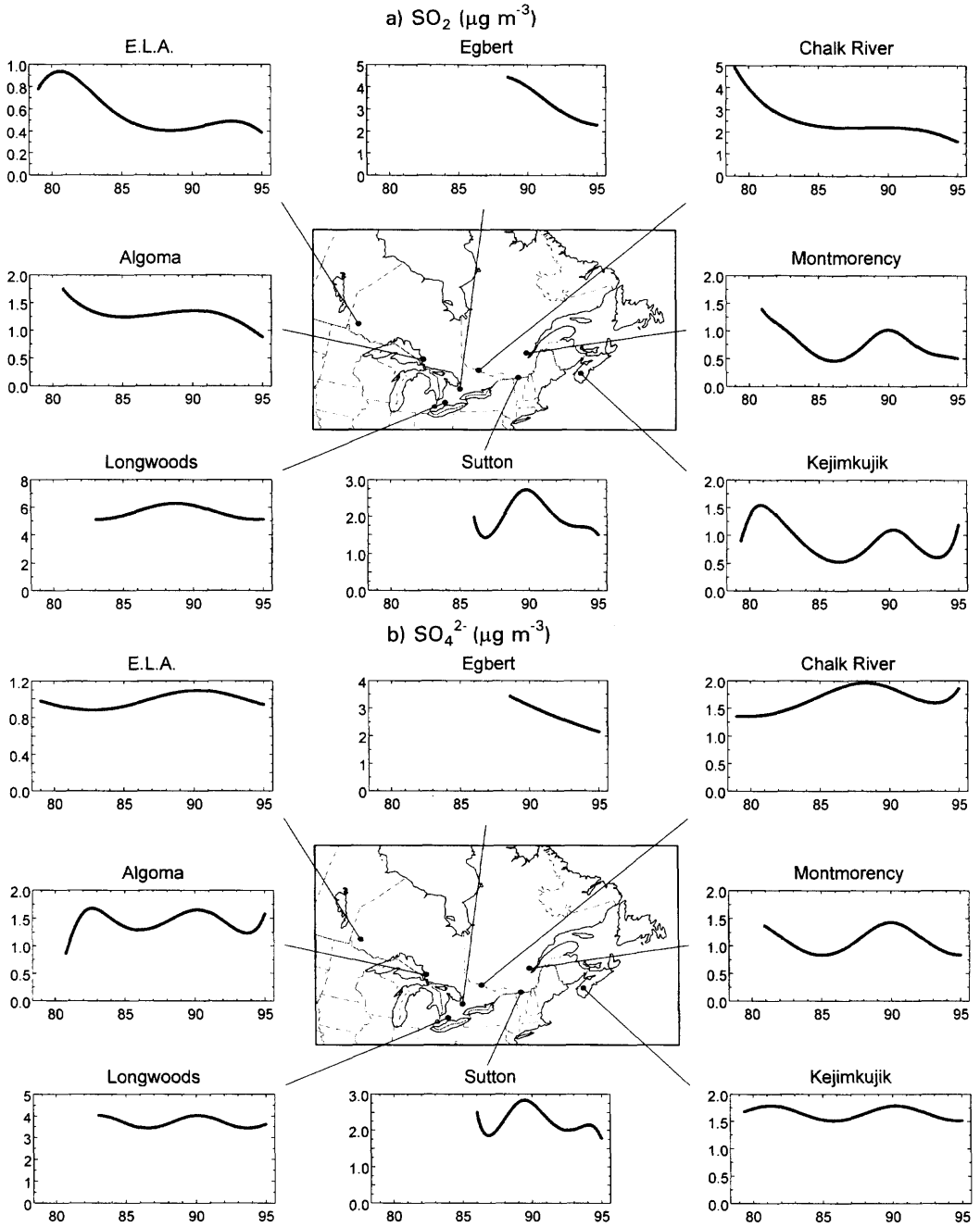

Fig. 4. Estimated long-term trends for SO_2 (a) and particulate SO_4^{2-} (b) at the 8 sites.

Table 2. *% of total variance explained by each term of the statistical model; the number of data* n *and the* R^2 *are also given; note that the values are not given when not statistically significant*

				% of total variance explained by			
Site	Ion	n	R^2	Long-term trend	Long-term cycle(s)	Seasonal cycle	Auto-regression
Algoma	SO_4^{2-}	4832	0.267	0.8	0.2	2.8	23.0
	SO_2	4816	0.248	1.0	0.2	13.3	10.3
	NO_3^-	4115	0.185	1.6		2.5	14.3
	HNO_3	4119	0.292	3.3	0.5	0.9	24.6
	total-NO_3	4821	0.282	2.4	0.3	1.8	23.8
	NH_4^+	4810	0.283	1.4	0.5	1.3	25.2
Chalk River	SO_4^{2-}	5424	0.178	1.0	0.7	0.7	15.2
	SO_2	5417	0.331	2.0	0.4	22.3	6.1
	NO_3^-	4060	0.197	0.8	0.6	11.8	6.7
	HNO_3	4064	0.243	1.6	0.4	5.5	17.1
	total-NO_3	5413	0.254	2.0	0.7	8.1	14.7
	NH_4^+	5388	0.204	0.6	0.7	0.4	18.8
Egbert	SO_4^{2-}	2271	0.251	2.1		2.7	20.1
	SO_2	2269	0.232	2.9	0.8	13.8	5.8
	NO_3^-	2267	0.183	0.7		7.5	10.1
	HNO_3	2268	0.217	1.1		5.2	15.8
	total-NO_3	2268	0.193	1.2		1.9	16.4
	NH_4^+	2270	0.228	1.2		3.2	18.2
ELA	SO_4^{2-}	5276	0.311	0.8	0.5	10.8	19.0
	SO_2	4969	0.513	5.7	0.6	30.9	14.0
	NO_3^-	4040	0.279	3.2		10.0	15.8
	HNO_3	4054	0.320	2.2	0.9	6.3	22.6
	total-NO_3	5363	0.310	2.3	0.5	10.3	18.1
	NH_4^+	5371	0.329	4.0	0.4	4.8	23.6
Kejimkujik	SO_4^{2-}	5503	0.206	0.3	1.1	2.5	16.5
	SO_2	5086	0.384	5.9	1.6	20.5	10.6
	NO_3^-	4322	0.236	3.8	0.3	8.5	11.2
	HNO_3	4326	0.253	1.6	2.9	5.5	15.5
	total-NO_3	5499	0.196	0.5	1.6	1.4	16.1
	NH_4^+	5485	0.264	2.0	1.0	5.0	18.4
Longwoods	SO_4^{2-}	4023	0.262	0.6	0.4	4.0	21.4
	SO_2	4022	0.207	0.6	0.3	14.9	5.1
	NO_3^-	4021	0.240	0.3	0.2	14.0	9.5
	HNO_3	4024	0.233	0.3	0.3	11.0	11.7
	total-NO_3	4021	0.217	0.7		3.7	16.9
	NH_4^+	4021	0.234	0.3	0.7	2.3	19.8
Montmorency	SO_4^{2-}	4765	0.266	2.0	1.2	3.2	20.2
	SO_2	4417	0.379	5.6	0.8	20.7	10.8
	NO_3^-	4065	0.170	1.2	2.5	1.3	11.9
	HNO_3	4088	0.289	7.9		1.3	19.7
	total-NO_3	4737	0.279	5.3	0.8	1.6	20.2
	NH_4^+	4757	0.283	4.0	0.7	2.6	21.0
Sutton	SO_4^{2-}	2961	0.236	2.1		2.5	18.7
	SO_2	2954	0.462	2.3		34.2	9.7
	NO_3^-	2958	0.291			20.4	8.7
	HNO_3	2957	0.209	2.7		4.1	13.8
	total-NO_3	2953	0.241	1.6		9.8	12.4
	NH_4^+	2956	0.210	0.9	0.7	1.2	17.9

main emission sources. For particulate SO_4^{2-}, the percentage of the total variance explained by the long-term trends was highest in south-east Ontario and southern Quebec. For total-NO_3, it was lowest in southern Ontario and in Nova Scotia. The reason for such patterns is not clear. However, it seems not to be related to the variation in the variance as the variance of the logarithm of the concentration showed a net north-south gradient being minimum at the southern sites.

The estimated long-term trends are shown in Figs. 4–6. As can be easily seen, the long-term trends were neither linear nor monotonic. In the case of SO_2, there was a net decrease between the beginning of the 80s and the beginning of the 90s except at Longwoods and Sutton. This was not the case for the other compounds. For particulate SO_4^{2-}, only small increases or decreases over the full period were observed. The same was also true for NO_3^- with the exception of Kejimkujik where there was a marked decrease in the late 1980s to early 1990s (Fig. 5). In contrast, HNO_3 and total-NO_3 concentrations increased at all sites except Egbert (Fig. 5). For particulate NH_4^+, the air concentrations decreased during the 80s at all sites except Chalk River at which it remained constant (see Fig. 6). During the late 80s and the beginning of the 90s, NH_4^+ concentrations increased at all sites except Chalk River where it remained about the same (Fig. 6).

To illustrate the importance of the variation in the daily air concentrations, the mean values of the long-term trends for three periods were calculated and compared (i.e. the arithmetic mean values of $f^T(t)$ in eq (1) were calculated for each year. Then, these yearly mean values were transformed by taking the antilogarithm. Finally, the arithmetic mean values for the three periods were then obtained and the absolute and relative differences could be calculated). The three periods were the beginning of the 80s (1980 to 1983), the second half of the 80s (1985 to 1988) and the beginning of the 90s (1991 to 1994). Note that for NO_3^- and HNO_3, only 1983 data represented the first period as the separated measurements were only started in December 1982 at all sites. The results of the analyses are given in Table 3. No calculations were made for Egbert as not enough years of data were available. Note that only the long-term trends shown in Figs. 4–6 were tested for statistical significance. The number given in Table 3 were not tested. They are given only as illustration as mentioned earlier.

For SO_2, the concentrations decreased between the beginning of the 80s and the beginning of the 90s at all sites except Longwoods. Most of the reduction occurred between the beginning of the 80s and the end of the 80s. At ELA, Montmorency and Kejimkujik, this was followed by a small increase between the second half of the 80s and the beginning of the 90s (there was also an increase at Sutton during the same period). For sites closer to the most important Canadian single SO_2 point sources (Algoma and Chalk River), the air concentration continued to decrease between the second half of the 80s and the beginning of the 90s but at a smaller rate. Longwoods is quite different from the other sites in that it shows an increase between the beginning of the 80s and the second half of the 80s and then a decrease between this latest period and the beginning of the 90s.

No general pattern exists in the case of the SO_4^{2-} concentrations. At Algoma, Longwoods, Montmorency and Kejimkujik, the concentrations decreased between the first and second period and re-increased slightly between the 2nd and 3rd period, resulting in a net decrease of less than 11% between the beginning of the 80s and 90s. At Chalk River, the opposite is true, a strong increase occurring during the 80s followed by a decrease in the early 90s. The same decrease is also observed at Sutton. At ELA, SO_4^{2-} concentrations increased slightly during the 80s and beginning of the 90s.

The difference in behavior between the SO_2 and SO_4^{2-} concentrations is likely related to the former being a primary emitted gas influenced largely by local sources and the latter being largely an oxidation product affected mainly by more distant sources. We will return to this point later.

Except at Chalk River and Montmorency, NO_3^- concentrations decreased in the 80s but re-increased in the beginning of the 90s. The net effect was only small changes in concentration between the beginning of the 80s and 90s except at Kejimkujik for which the 90s increase was too small to counter-balance the earlier decrease. At Chalk River, an increase in the 80s was followed by a slight decrease in the beginning of the 90s. NO_3^- air concentrations increased throughout the entire period at Montmorency, the increase being

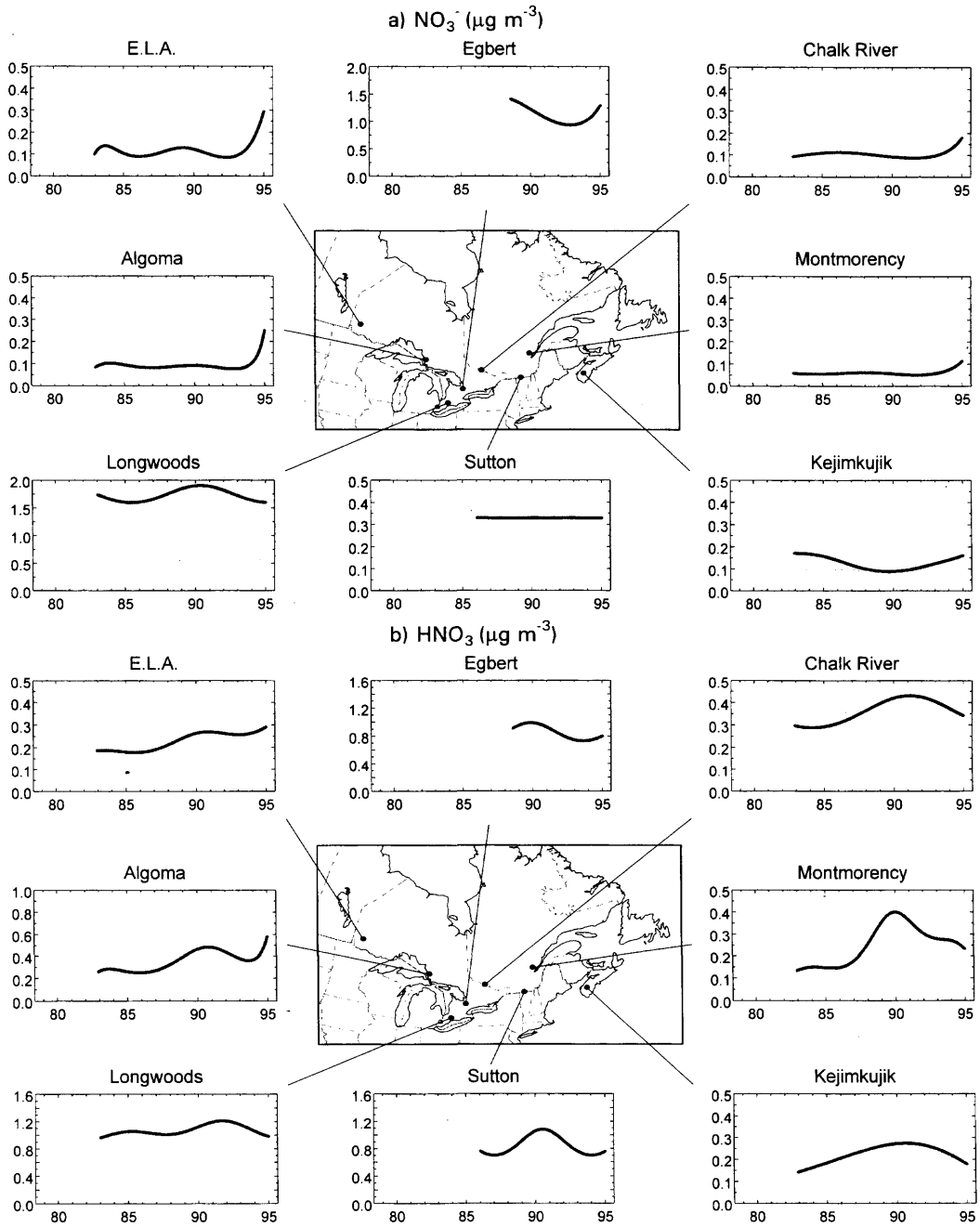

Fig. 5. Estimated long-term trends for particulate NO_3^- (a) and gaseous HNO_3 (b) at the 8 sites.

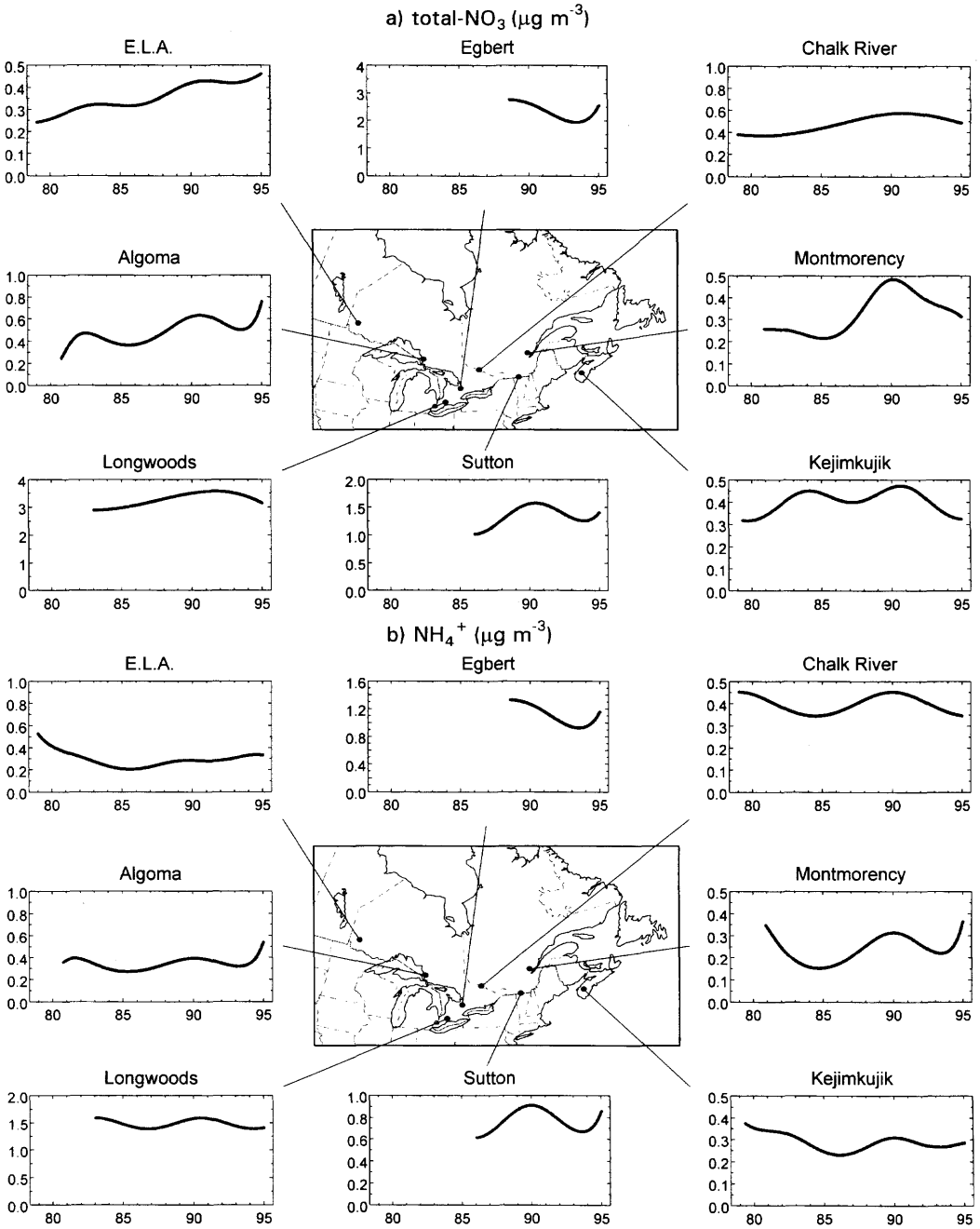

Fig. 6. Estimated long-term trends for total NO_3 (a) and NH_4^+ (b) at the 8 sites.

Table 3. *Differences ($\mu g\ m^{-3}$) and in % between 3 times period at 7 of the sites*

Ion	[a]	Site						
		E. L. A.	Algoma	Longwoods	Sutton	Chalk River	Montmorency	Kejimkujik
SO_2	I	−0.3843	−0.2031	0.8238		−0.7799	−0.5439	−0.6463
		−46.8	−13.7	16.1		−26.1	−48.4	−50.8
	II	0.0284	−0.1165	−0.6024	0.0416	−0.2411	0.0539	0.1471
		6.5	−9.1	−10.1	2.3	−10.9	9.2	23.5
	III	−0.3558	−0.3196	0.2215		−1.0210	−0.4804	−0.4991
		−43.3	−21.5	4.3		−34.2	−42.8	−39.3
SO_4^{2-}	I	0.1065	−0.0144	−0.4160		0.4439	−0.1291	−0.1489
		11.9	−1.0	−10.4		30.8	−11.1	−8.6
	II	0.0193	0.0057	0.0140	−0.1262	−0.2217	0.0004	0.0296
		1.9	0.4	0.4	−5.7	−11.7	0.0	1.9
	III	0.1259	−0.0087	−0.4020		0.2222	−0.1288	−0.1194
		14.1	−0.6	−10.1		15.4	−11.0	−6.9
NO_3^-	I	−0.0275	−0.0119	−0.0125		0.0107	0.0027	−0.0493
		−21.0	−12.2	−0.7		10.8	4.8	−29.0
	II	0.0215	0.0134	0.0476	0.0000	−0.0014	0.0053	0.0046
		20.8	15.5	2.8	0.0	−1.2	8.9	3.9
	III	−0.0059	0.0014	0.0351		0.0093	0.0080	−0.0447
		−4.5	1.5	2.1		9.4	14.1	−26.3
HNO_3	I	0.0104	0.0102	0.0390		0.0458	0.0611	0.0732
		5.6	3.6	3.9		15.7	42.5	46.7
	II	0.0690	0.1279	0.0979	0.0622	0.0610	0.0833	0.0117
		35.1	44.0	9.5	8.2	18.1	40.6	5.5
	III	0.0794	0.1381	0.1370		0.1068	0.1444	0.0849
		42.7	49.2	13.8		36.6	100.4	55.3
total-NO_3	I	0.0406	0.0344	0.2864		0.1199	0.0436	0.0298
		13.6	8.8	9.9		1.7	17.5	7.8
	II	0.0894	0.1387	0.2716	0.1725	0.0421	0.0863	−0.0224
		26.3	32.6	8.5	14.4	8.4	29.4	−5.4
	III	0.1300	0.1732	0.5581		0.1620	0.1299	0.0074
		43.5	44.3	19.3		42.8	52.04	1.9
NH_4^+	I	−0.0856	−0.0498	−0.1505		−0.0001	−0.0147	−0.0743
		−26.9	−13.9	−9.5		−0.0	−6.5	−22.9
	II	0.0732	0.0496	0.0291	0.0193	0.0001	0.0429	0.0259
		31.4	16.1	2.0	2.7	0.0	20.2	10.4
	III	−0.0124	−0.0002	−0.1214		0.0000	−0.0283	−0.0483
		−3.9	−0.0	−7.7		0.0	12.5	−14.9

[a] Comparison I betwen 1980–83 and 1985–88 periods; II between 1985–88 and 1991–94; III between 1980–83 and 1991–94. Note that for NO_3^- and HNO_3 the 1980–83 period include only 1983.

more important between the second half of the 80s and the beginning of the 90s.

At all sites, HNO_3 concentrations increased between the beginning of the 80s and the 90s. At more than half the sites the increase was more important between the second and third periods than between the first and second. Because of the volatilisation problem, those results are difficult to interpret especially as the NH_3 concentration is not known.

The results for total-NO_3 are similar to the one for HNO_3 except at Kejimkujik and Longwoods. This is not surprising as HNO_3 dominated over NO_3^- at most sites. The median values of the daily HNO_3/total-NO_3 ratio varied between 0.4 at Longwoods and 0.8 at Montmorency. At Kejimkujik, the median values of the daily ratio was equal to 0.6. Part of the difference in the results was also due to the fact that the data for HNO_3 only started in December 1982 and therefore, as mentioned earlier, only the long-term trends for 1983 were available for the first period.

The uncertainties on the long-term trends for that year would be therefore large.

Except at Chalk River, NH_4^+ concentrations decreased during the 80s and increased between the second half of the 80s and the beginning of the 90s. Taken over the full period, the concentrations changed little at all sites except Montmorency and Kejimkujik where they increased and decreased, respectively.

4.2. *Long-term cycles* ($f^C(t)$)

Statistically significant long-term cycles were present for more than 70% of the time-series studied (Tables 2, 4). The percentage of the total variance explained by the long-term cycles was small varying between 0.2 and 2.9%. For more than 79% of the time-series with long-term cycles, the explained variance was less than 1%. The % of the total variance explained by the long-term cycles was generally more important at the eastern sites (i.e., Montmorency and Kejimkujik) than at the other sites.

The wavelengths of the significant long-term cycles are given in Table 4. They varied between 1.9 and 5.1 years (Note that, as mentioned earlier, the limit between long-term cycles and long-term trends was set equal to 6 years). They are not consistent among compounds or sites. For most of the time-series (28 out of 34) only one wave was present and there seemed to be no geographic pattern to the wavelength values. At the same site, the statistically significant long-term cycle could have a similar wavelength for all compounds, e.g., ELA, or a very different wavelength, e.g. Algoma (see Table 4).

The presence of these long-term cycles is now well confirmed either by the use of smoothing regression (Sirois, 1993) or by spectral analysis (Fig. 2). However, the physical processes that engendered these long-term cycles are not known. The two most plausible sources would be that they are present in the emission sources and/or are result of meteorological processes. In fact, the observed long-term cycles could be the result of a complex interaction of both, which is more probable as one will expect the same long-term cycles to show up for all compounds at a site if meteorology was the dominant factor.

4.3. *Seasonal cycles* ($f^S(t)$)

The seasonal cycles are shown for all compounds and sites in Figs. 7 to 9. The % of the total variance explained by the cycles are given in Table 2. The most important seasonal cycles were found for SO_2 (Fig. 7a) for which concentrations were highest in winter and lowest during the summer. These strong seasonal cycles are likely related to higher rates of transformation and dry deposition in summer than in winter. The percentage of the total variance explained by the seasonal cycles varied between 13 and 35%. It was lowest in southern Ontario and increased further from the emission sources.

SO_4^{2-} concentrations exhibited less important seasonal cycles than SO_2 (Fig. 7b). These seasonal cycles were not simply the inverse of the SO_2 seasonal cycles as they would be if the transformation rates were the only factor influencing the relative importance of SO_2 and SO_4^{2-} air concentrations at a site. The percentage of the total variance explained by the seasonal cycles varied between 0.7 and 11% although it was between 2.5 and 4% for 6 of the 8 sites. The shape of the seasonal cycles also changed with the location. At ELA, where the seasonal cycle is the most important, SO_4^{2-} concentrations were maximum in March-April and minimum during the summer. At the sites east of the main sulphur emission sources (Montmorency, Longwoods, Sutton and Kejimkujik), the SO_4^{2-} concentrations were highest in winter and summer and lowest in spring and autumn.

The amplitudes of the seasonal cycles for NO_3^- (Fig. 8a) concentrations were generally more important than those for SO_4^{2-} but less than those for SO_2. Like the latter, the concentrations of NO_3^- were maximum in winter and minimum in summer. The percentage of the total variance explained by the seasonal cycles varied between 1.3% at Montmorency and 20.4% at Sutton. No clear geographical pattern for that statistic was found.

There seemed to be no simple relationship between the seasonal cycles of the HNO_3 and NO_3^- concentrations. The amplitude of the cycles was lower for the former than for the latter (Fig. 8b). The shape of the seasonal cycles was not the same at all sites. At ELA and Algoma, the HNO_3 concentrations were minimum in autumn

Table 4. *Long-term cycle wave length (years) and auto-correlation coefficients*

		Long-term cycle wave length		Auto-correlation coefficients		
Site	Ion	1st	2nd	lag 1	lag 2	lag 3
Algoma	SO_4^{2-}	4.70		0.55	−0.16	
	SO_2	3.15		0.37		
	NO_3^-			0.42	−0.10	
	HNO_3	2.00		0.58	−0.20	0.04
	total-No_3	2.00		0.58	−0.20	0.06
	NH_4^+	2.50		0.58	−0.19	0.05
Chalk River	SO_4^{2-}	3.30		0.42	−0.06	
	SO_2	3.20		0.29		
	NO_3^-	2.60		0.29	−0.08	
	HNO_3	3.50		0.48	−0.17	0.04
	total-NO_3	3.50		0.44	−0.12	0.05
	NH_4^+	4.65		0.48	−0.11	
Egbert	SO_4^{2-}			0.51	−0.16	
	SO_2	2.60		0.28	−0.07	
	NO_3^-			0.35	−0.16	
	HNO_3			0.44	−0.14	
	total-NO_3			0.44	−0.20	
	NH_4^+			0.48	−0.15	
ELA	SO_4^{2-}	3.00		0.48	−0.04	
	SO_2	3.60		0.44	0.07	
	NO_3^-			0.44	−0.04	
	HNO_3	3.00		0.54	−0.07	
	total-NO_3	2.60		0.48	−0.05	
	NH_4^+	3.00		0.55	−0.08	
Kejimkujik	SO_4^{2-}	5.00		0.44	−0.05	
	SO_2	3.50		0.39		
	NO_3^-	2.50		0.36		
	HNO_3	3.20	5.00	0.44	−0.06	
	total-NO_3	3.00	4.50	0.42	−0.05	
	NH_4^+	3.70	5.10	0.47	−0.06	
Longwoods	SO_4^{2-}	3.00		0.54	−0.20	0.05
	SO_2	3.15		0.25	−0.12	
	NO_3^-	2.55		0.36	−0.10	
	HNO_3	4.20		0.40	−0.12	0.05
	total-NO_3			0.48	−0.20	0.06
	NH_4^+	2.90	4.10	0.52	−0.19	0.05
Montmorency	SO_4^{2-}	5.00		0.50	−0.09	
	SO_2	4.10		0.40	−0.04	0.04
	NO_3^-	2.50	3.05	0.36		
	HNO_3			0.51	−0.14	0.07
	total-NO_3	1.92	4.00	0.51	−0.11	0.07
	NH_4^+	4.00		0.52	−0.12	0.06
Sutton	SO_4^{2-}			0.49	−0.12	
	SO_2			0.42	−0.06	
	NO_3^-			0.34		
	HNO_3			0.42	−0.09	
	total-NO_3			0.41	−0.07	
	NH_4^+	3.80		0.42	−0.10	

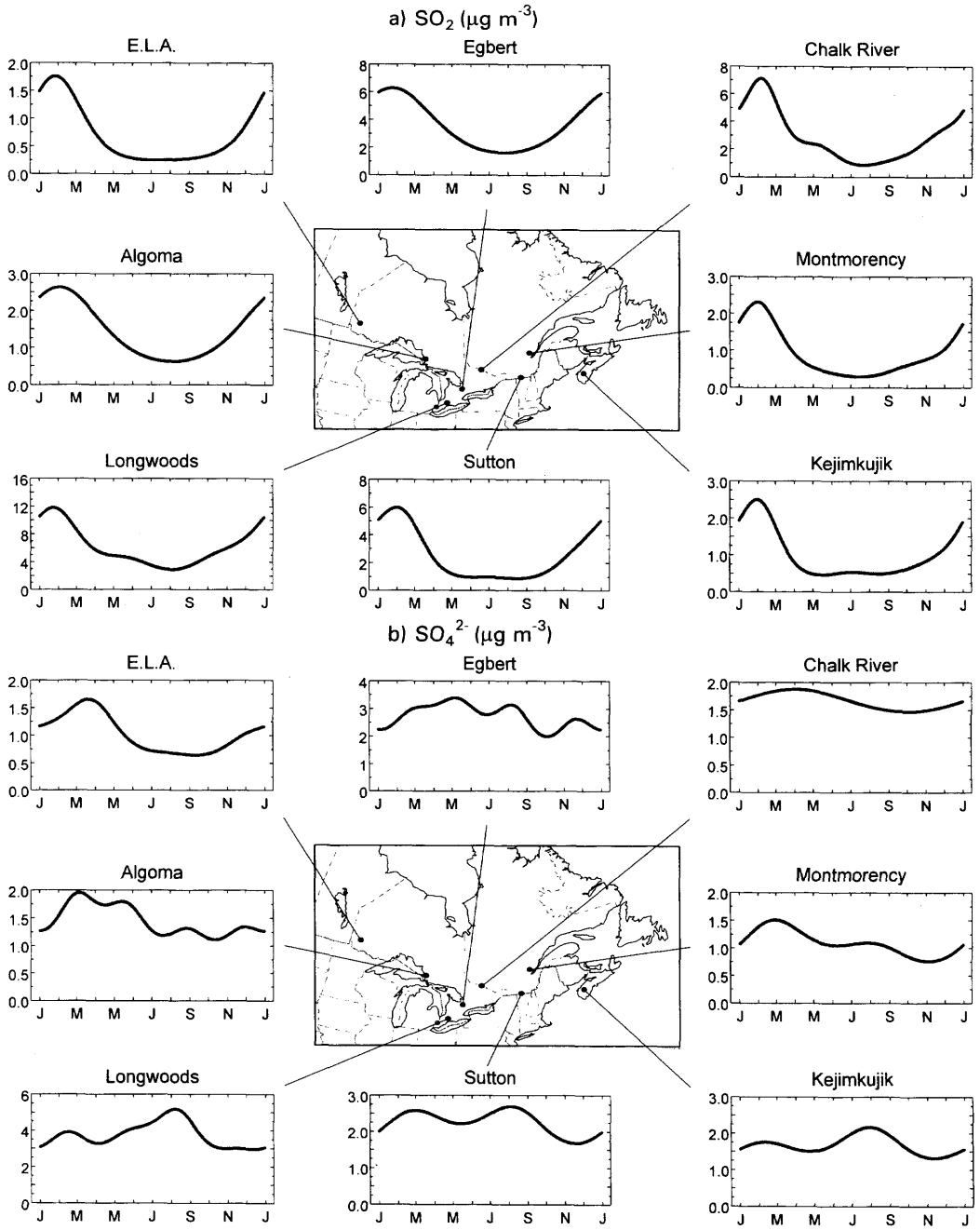

Fig. 7. Estimated seasonal cycles for gaseous SO_2 (a) and particulate SO_4^{2-} (b) at the 8 sites.

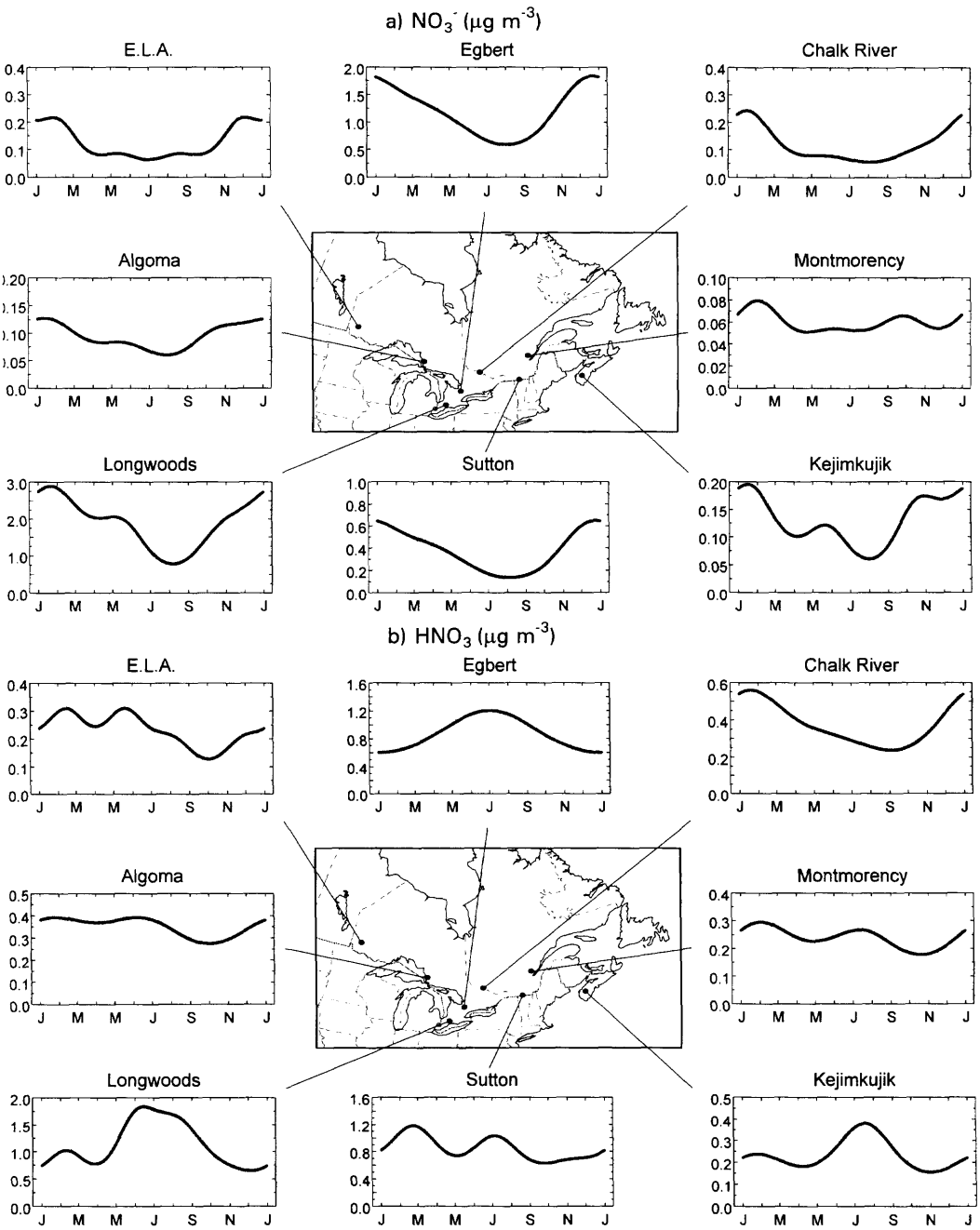

Fig. 8. Estimated seasonal cycles for particulate NO_3^- (a) and gaseous HNO_3 (b) at the 8 sites.

and maximum in winter. The minimum shifted to late summer — early autumn at Chalk River. At Montmorency, Longwoods, Sutton and Kejimkujik, the concentrations were maximal in winter and summer and minimal in spring and autumn like the SO_4^{2-} concentrations. At Egbert, the concentrations were maximum in summer and minimum in winter. The percentage of the total variance explained by the seasonal cycles varied between 0.8% at Algoma and 11% at Longwoods.

The seasonal cycles for total-NO_3 are similar at most sites to the one for HNO_3. The similitude between the seasonal cycles were due to the fact, as mentioned earlier, that HNO_3 dominated over NO_3^- at most sites. There were however some marked differences like at ELA and Kekimkujik (Figs. 8b, 9a). At 5 of the sites, the percentage of the total variance explained by the seasonal cycles was larger for total-NO_3 than for HNO_3.

The amplitude of the seasonal cycles for NH_4^+ concentrations was small and no general pattern could be discerned (Fig. 9b). The percentage of the total variance explained by those seasonal cycles varied between 0.4 and 5.0%, the smallest of the compounds studied here.

4.4. *Auto-regressive model* ($f^D(t)$)

The auto-regressive model was, along with the seasonal cycles, the most important component of the general model for explaining the total variance. The percentage of the total variance explained by the auto-regressive model was between 5.1 and 25.2% (Table 2). For 37 of the 48 time-series, this component was the most important with the seasonal cycles component being more important for SO_2 at all sites and for NO_3^- at three sites. The %s were lowest for SO_2 and NO_3^- and largest for NH_4^+. For all compounds except SO_4^{2-}, they were lower in southern Ontario and southwestern Quebec. For SO_4^{2-}, the opposite was true.

The order of the auto-regressive models and the estimated coefficients are given in Table 4. For 29 out of 48 of the time-series, an auto-regressive model of order 2 was necessary. For 6 of the remaining time-series, an auto-regressive model of order 1 was sufficient. An auto-regressive model of order 3 was necessary for the other 13 time-series. The first coefficients of the auto-regressive models varied between 0.25 and 0.59. All the statistically significant coefficients for the second lag except for SO_2 at ELA were negative and varied between -0.04 and -0.20. The 13 statistically significant coefficients for lag 3 were all small and positive, being between 0.04 and 0.07.

Based on the auto-regressive model, the 6 compounds could be divided into two groups. The first group consists of SO_2 and NO_3^-, for which an auto-regressive model of lag 1 was sufficient at 3 sites. The remaining sites had models of order 2. The coefficients for the first lag varied between 0.28 and 0.44 being lower than for the other compounds. The same was true for the second coefficient. For the other three compounds, models of order 2 and 3 were necessary. The coefficients for the first lag were also greater being between 0.40 and 0.59. The coefficients of the second lag were also larger in absolute value at many of the sites, reaching -0.20 for some sites and compounds. Those results indicate that the concentrations in the air masses reaching the sites were more homogeneous for SO_4^{2-}, HNO_3, total NO_3 and NH_4^+ than for SO_2 and NO_3^-.

5. Summary and conclusions

Results of the modeling of the temporal variation of the daily ambient air concentrations of particulate SO_4^{2-}, NO_3^-, and NH_4^+, gaseous SO_2 and HNO_3 and total-NO_3 at 8 sites in eastern Canada were presented. The main conclusions of the study are as follows:

- The long-term trends are not linear or even monotonic.
- SO_2 ambient air concentrations decreased between the beginning of the 80s and the beginning of the 90s at 5 of the 8 sites by 21 to 43%. Most of the decreases occurred in the 80s. At Longwoods and Sutton, sites closest to the major sources regions, SO_2 concentrations increased slightly.
- For particulate SO_4^{2-}, NO_3^-, NH_4^+, only small changes (increase or decrease of less than 15%) occurred at most sites between the beginning of the 80s and 90s.
- HNO_3 and total-NO_3 concentrations increased at most sites between the 80s and 90s.
- Long-term cycles were present for about 70% of the time-series although they explained only a small fraction of the total variance.

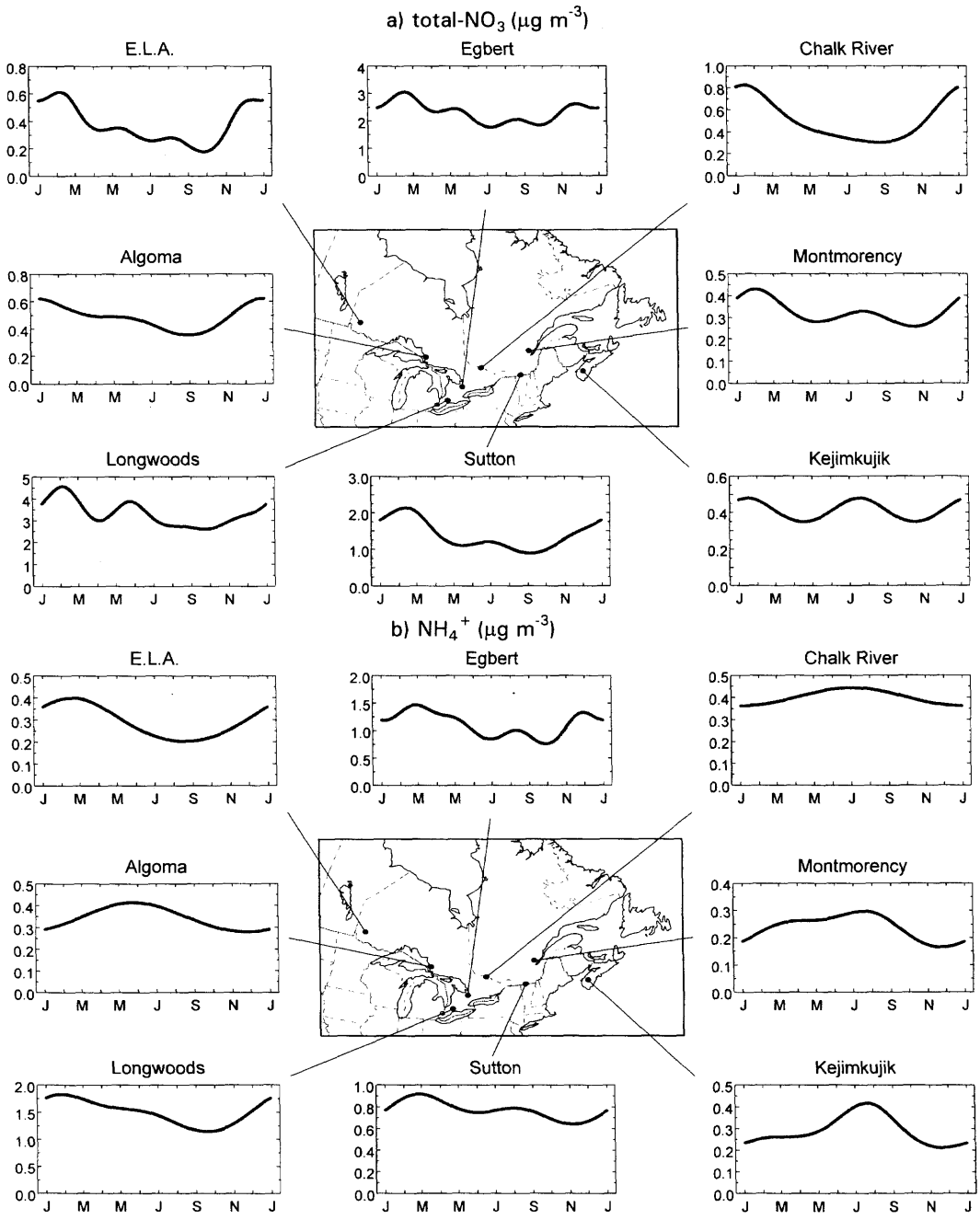

Fig. 9. Estimated seasonal cycles for total-NO_3 (a) and NH_4^+ (b) at the 8 sites.

- Important seasonal cycles were found for SO_2 concentrations. They explained between 13 and 35% of the total variance. Less important seasonal cycles were present in the case of the other compounds.
- For most of the time-series, an auto-regressive model of lag 2 was necessary. For some SO_2 and NO_3^- time-series, auto-regressive models of order 1 were sufficient. For the other compounds, auto-regressive models of order 3 were necessary at some sites.

SO_2 emissions are not distributed uniformly across North America (Misra et al., 1989); the largest emissions occur in the USA midwest and East and in southern Ontario and Quebec. Some strong local sources also exist in northern Ontario (e.g. Sudbury, Ontario) and in northern Manitoba. The emission source strengths also changed in time. Generally in North America, SO_2 emissions decreased strongly in the first half of the 80s (RMCC, 1990; Sirois, 1993). However since 1985, they changed only slightly in the USA (EPA, 1994). In some regions, SO_2 emissions decreased, but they increased in others (EPA, 1994). In Canada, they remained about constant between 1985 and 1988 but decreased between 1988 and 1994 (Environment Canada, 1994). This reduction was not uniform across eastern Canada. Present estimates indicate that SO_2 emissions, between 1990 and 1993, decreased strongly in Ontario, slightly increased in Manitoba and Nova Scotia, and remained about the same in Quebec (Environment Canada, 1994).

In trying to relate the observed long-term trends in air concentrations to the reported trends in emissions, it seems clear that the difference between the long-term trends of SO_2 and SO_4^{2-} may be related to the fact that the former is influenced mainly by local and near emission sources (Canadian sources) and the latter by more distant sources (USA sources). For SO_2, the large decrease observed at all sites, except Longwoods (the site closest to the high emission areas of the USA), between the beginning and the second half of the 80s (Table 3) paralleled a decrease in the SO_2 emissions. Furthermore, sites at which SO_2 concentrations increased between the mid-80s and the beginning of the 90s (i.e., ELA, Sutton, Montmorency and Kejimkujik, see Table 3) are generally influenced by regions where the emissions increased or remained about the same. At all other Ontario sites, SO_2 decreased during that period (Table 3). For SO_4^{2-}, a link between changes in emission and observed changes in concentration at a site is less obvious and would necessitate the use of back-trajectories information.

NO_x emissions are also not distributed uniformly across eastern North America. The highest emissions occur in the mid-western USA, along the Atlantic coast between Washington DC and Boston, and in southern Ontario (Olson et al., 1992). Those emissions have not changed much during the last 15 years in the USA (EPA, 1994) or in Canada (based on preliminary results; personal communication, Environment Canada, Environmental Protection Service, Pollution Data Analysis Division, Ottawa, Ontario, Canada). This is consistent with the observation that the NO_3^- concentration did not change much at most of the sites. Exceptions are Kejimkujik, Chalk River and Montmorency where it decreased at the former and increased slightly at the latter (Table 3).

In the present study, the fact that the daily data represent the ambient concentrations in air masses coming from different source regions was not considered. A logical continuation of the present investigation would include the separation of each of the time-series into 3 to 5 time-series that represent air masses having similar characteristics. Such an approach should allow to take into account the non-uniform distribution of emissions across Northern America. An attractive method which has been used before is using back-trajectories (RMCC, 1990; Bottenheim and Sirois, 1996). As the statistical theories used here compensated for the presence of missing data, the use of the same models and techniques to the trajectory-separated time-series should not present major difficulties.

6. Acknowledgements

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