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Regional and background aerosol trace elemental composition observed in eastern Canada

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ABSTRACT

Measurements of the trace elemental composition of atmospheric aerosols were undertaken at three rural locations in eastern Canada during the autumn of 1984. One aim was to investigate differences in anthropogenic elemental composition between aerosols of regional eastern North American origin and "background" aerosols in air masses moving into the region. Another aim was to identify the origin of aerosol trace elements with the use of air parcel back-trajectories, multivariate analysis, and lead isotope ratios.

Daily aerosol samples taken at Dorset Ontario, Forêt Montmorency Quebec, and Kejimkujik Nova Scotia, were analyzed by instrumental neutron activation analysis and inductively-coupled plasma mass spectrometry for Ti, Br, Mn, In, Na, V, Al, Ca, Se, As, Sb, Pb, Cd, and Pb-206/207 isotope ratios. Average concentrations of Na and V showed the greatest regional diversity and were 8.0 and 5.4 times higher at Kejimkujik than at Dorset, respectively. Factor analysis revealed the presence of a soil, a marine, and a general pollution component in the aerosols, plus additional components specific for a few elements of anthropogenic origin. Comparison of mean concentrations in samples grouped by similarity of the associated back-trajectories showed that In and As were excellent tracers of non-ferrous smelter emissions. Trajectories from prominent coal-burning areas were also enriched in As but were associated with low In concentrations.

Groups of trajectories originating from background areas, i.e., without major anthropogenic sources of aerosols, formed a significant fraction of the samples and accounted for 20%–25% of the classified aerosol samples at each site. Comparison of the mean concentrations in the background groups with each other and with similar aerosol data from the Arctic showed that both local influences, such as the composition of soils in the immediate area, and long-range transport of aerosols can affect the apparent local composition of the background aerosol.

Using recent findings by Sturges and Barrie that there is a significant difference between the Pb isotope ratio in aerosols from smelters, Canadian auto exhaust and American sources, the fraction of Pb originating from each source was estimated for each location. During the 3-month period studied, it is estimated that Pb from automotive emissions in the US accounted for 46%, 28%, and 44% of the atmospheric Pb at Dorset, Forêt Montmorency, and Kejimkujik, respectively, versus 52%, 67%, and 51% from Canadian auto exhaust.

1. Introduction

The chemical composition of atmospheric aerosols is of interest because of the possible presence of toxic elements, and because the composition may give clues as to the origin of the aerosol. This is particularly important for sites distant from industrial or urban sources of aerosols, since it may be possible to use the aerosol composition as a tracer of long-range atmospheric transport of pollutants and to apportion the observed concentrations amongst sources.

An aerosol chemistry survey was undertaken at three regionally representative locations in eastern Canada in the autumn of 1984 partly to address these needs, and partly to test hypotheses regarding regional aerosol composition. Each site

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was in a calibrated watershed dedicated to the study of the effects of the long range transport of acidic pollutants. Each was located at least 100 km from major industrial or urban pollutant sources. Daily hi-volume samples were collected at Dorset, Ontario, from 1 October to 9 December. Additional samplers were operated at Forêt Montmorency, Quebec, and Kejimkujik, Nova Scotia (see Figs. 1–3 for location). At these two sites, daily aerosol samples were collected in two periods (1 October–14 October; 26 November–9 December) and weekly samples were collected from 15 October to 25 November. Samples were later analyzed for a number of potentially useful aerosol tracer elements.

The Dorset data have been analyzed in detail and the results presented elsewhere (Barrie, 1988). This study compares the data collected at the three sites, with emphasis on the applicability of aerosol composition as a long-range transport tracer.

2. Methodology and results

Sampling methodology is described in detail in Barrie (1988). A brief account is given here. Standard Sierra hi-volume samplers with 15 um size-selective inlets were operated to draw air at 1.13 l min^{-1} (at 20°C, 1 atm.) through 20 cm × 25 cm Whatman-41 filters. Field blank filters were taken routinely. Aliquots of filters were analyzed by instrumental neutron activation analysis and inductively-coupled plasma emission spectroscopy. Filter collection efficiency was better than 75% for elements such as Pb in small aerosols, and better than 95% for all other elements. This is consistent with well established filter performance characteristics (Watts et al., 1987). Sampling precision based on 10 triplicate daily samples taken at Dorset was 7% to 18% for Al, As, Pb, Fe, Mg, and 10% to 14% for Ti, Br, Mn, Na, V, Cd, Se. Statistics describing the observed distributions of the element concentrations at each site are presented in Table 1.

3. Multivariate analysis of aerosol concentrations

Multivariate statistical techniques offer a powerful and efficient method of gaining insights into correlations between the dominant aerosol components. However, there are difficulties with the application of readily available techniques. The two main problems are the non-normal distributions of the sample concentrations (arising from the presence of outliers, from high detection limits, or by sampling a non-normal population) and the small sample size. For instance, it has been recommended that the number of samples should exceed the number of variables by 50 or more for reliable results from principal components analysis (Thurston and Spengler, 1985). The number of samples from Dorset meets this requirement, but there are only 28 daily samples available from both Forêt Montmorency and Kejimkujik.

Alternative approaches were devised for use with these data. Factors can be calculated from the decomposition of any product-moment matrix; instead of using the common Pearson product-moments as measures of variable correlation, the Spearman correlation was employed. This is a non-parametric measure of variable correlation based on the correlation of the ranks of the data, which permits variables with decidedly non-normal distributions to be included in the analysis. This is important because several potential tracers of industry-specific aerosols (such as As and In) may be present or above detection limits only in a small number of samples, when these large point sources have their largest impact on the receptor site. Yet these few cases have the highest discriminatory power for identifying these particular source types. Clearly, it is an advantage to include variables even if their concentrations are usually at or below detection limits, because these variables contain a significant amount of information.

Maximum likelihood factor analysis was used to extract the factors from the Spearman correlation matrix because, unlike the much more common principal factor analysis, this method does not require a multivariate normal distribution. Maximum likelihood factor analysis also has desirable statistical properties (Rummel, 1970). The problem of the small number of samples for Forêt Montmorency and Kejimkujik was overcome by performing two factor analyses. The first used only Dorset data.

The Varimax-rotated factor loading matrix from this analysis is shown in Table 2. Five of a

Table 1. *Summary statistics of daily concentrations (ng m^{-3}) observed at the three monitoring sites; Dorset samples were collected during 1 October–9 December 1984; Forêt Montmorency and Kejimkujik samples were collected from 1–14 October and 26 November–9 December 1984*

	Ti	Br	Mn	In	Na	V	Cl	Al	Ca	Se	As	Sb	Cu	Pb	Cd	Fe
Dorset ($n = 70$)																
mean	6.5	6.8	2.8	0.005	54	1.3	*	161	112	1.01	0.84	0.23	6.1	18.8	0.24	55
std. dev.	7.0	6.5	3.0	0.008	57	1.6	*	155	112	1.29	1.09	0.38	4.0	17.7	0.25	53
maximum	33.4	29.1	16.3	0.044	306	6.5	*	785	601	8.02	6.46	2.17	15.9	78.6	1.17	248
75% quartile	8.9	8.2	3.8	0.008	79	1.8	*	219	170	1.26	1.29	0.28	8.5	24.8	0.34	78
median	3.9	5.1	1.8	0.001	34	0.6	*	103	63	0.51	0.43	0.05	4.7	14.2	0.13	35
25% quartile	0.9	2.6	0.9	0.001	15	0.2	*	51	29	0.28	0.12	0.05	3.2	5.9	0.07	23
minimum	0.9	0.5	0.3	0.001	15	0.04	*	23	6	0.06	0.12	0.05	0.4	0.5	0.04	6
Forêt Montmorency ($n = 28$)																
mean	7.1	3.0	1.4	0.005**	52	2.0	34	86	39	0.35	0.55	0.11	4.5	8.5	*	*
std. dev.	16.2	2.6	1.5	0.007	47	2.3	38	84	42	0.49	0.65	0.05	2.9	7.6	*	*
maximum	87.4	12.7	7.5	0.024	225	7.9	136	283	214	2.33	3.12	0.37	11.1	26.1	*	*
75% quartile	5.2	4.1	1.9	0.007	79	3.2	29	150	46	0.42	0.52	0.10	6.2	14.2	*	*
median	3.1	1.9	0.7	0.003	42	1.1	15	40	22	0.16	0.24	0.10	3.3	5.8	*	*
25% quartile	1.4	1.3	0.5	0.002	13	0.4	15	21	15	0.07	0.23	0.09	2.4	2.1	*	*
minimum	1.2	0.6	0.1	0.001	5	0.02	14	5	13	0.05	0.23	0.09	0.9	0.2	*	*
Kejimkujik ($n = 28$)																
mean	4.1	6.2	1.6	0.006	434	7.0	541	74	50	0.57	0.49	0.18	3.8	11.8	*	*
std. dev.	2.9	4.6	1.1	0.004	221	5.9	277	61	23	0.72	0.37	0.18	1.7	13.9	*	*
maximum	16.3	19.5	4.7	0.020	1192	26.6	1123	272	121	3.30	1.55	0.85	9.3	56.4	*	*
75% quartile	5.1	7.5	2.2	0.008	544	6.9	784	108	59	0.82	0.62	0.17	4.3	16.9	*	*
median	3.5	4.2	1.3	0.006	384	6.0	544	60	44	0.28	0.24	0.10	3.5	5.8	*	*
25% quartile	2.4	3.5	0.7	0.005	335	2.8	304	28	32	0.12	0.24	0.09	2.8	4.1	*	*
minimum	1.1	2.4	0.2	0.002	61	1.7	105	10	20	0.06	0.23	0.09	1.8	1.2	*	*

* Data not available.

** After omitting one value because of laboratory analytical uncertainties.

possible 14 factors were considered significant, as determined from consideration of scree plots, eigenvalue magnitude, variance explained, and factor interpretability. Three of these factors represent crustal, marine, and "general urban pollution" (anthropogenic) contributions to the aerosol composition. The identification of the factor with the highest Na loadings as a marine factor may be misleading in the sense that this type of statistical analysis cannot differentiate between long-range transport of small, dry sea salt particles, and Na from re-suspension of NaCl from road-salting operations. There is also an As–In factor representing emissions from smelters (Barrie, 1988), and a unique factor for Cu. There is a slight chance that the latter factor may represent contamination from the hi-volume sampler motor, even though precautions were taken to channel exhaust air away from the samplers. However, the weak loadings for Br and Pb on this factor suggest a source of Cu that is at least partially correlated with automotive emissions.

A second factor analysis was performed on the Forêt Montmorency and Kejimkujik aerosol concentrations. Results are shown in Table 3. Because of the small sample size for each of these two stations, numerical values for the factor loadings are not presented. These are qualitative results based on a limited number of samples, which may change when a larger number of samples were available for analysis. The intent is to present the general pattern of the suspected underlying factors for comparison with the Dorset factors. The "+" sign indicates a high factor loading (greater than about 0.5).

The In/As factor is not as easily interpretable at Forêt Montmorency and Kejimkujik as it is at Dorset. V is associated with this factor at Kejimkujik, which may be reasonable given the

Table 2. *Varimax rotated factor loading matrix from analysis of Dorset data. Factor loadings equivalent to a probability of more than 5% of obtaining a similar correlation coefficient from the same number of independent random samples have been deleted. Loadings equivalent to a probability between 1% and 5% of finding the same correlation between random samples are shown in parentheses*

Dorset

Element	Factor 1 (crustal)	Factor 2 (urban)	Factor 3 (In/As)	Factor 4 (marine)	Factor 5 (Cu)
Ti	0.81	0.33			
Br	0.46	0.78			0.33
Mn	0.74	0.60			
Cu		(0.24)			0.81
In			0.60		
Na	(0.29)			0.93	
V	0.53	0.71			
Al	0.90	(0.29)			
Ca	0.87				
Se	(0.24)	0.77	0.40		
Fe	0.80	0.50			
As		(0.28)	0.90		
Sb	(0.26)	0.69			
Pb	(0.30)	0.89			(0.24)
Variance explained (%)	41	25	16	9	7

Table 3. *Shaded factor loading matrices from analysis of Forêt Montmorency and Kejimkujik data; the "+" sign indicates a high factor loading, and a bracketed (+) sign indicates marginal significance*

Forêt Montmorency

Element	Factor 1 (crustal)	Factor 2 (urban)	Factor 3 (In/As)	Factor 4 (marine)	Factor 5 (Cl)
Ti	+				
Br		+			
Mn	+	+			
Cu					
In			(+)		
Na				+	
V		+			
Cl				+	+
Al	+				
Ca	+				
Se		+			
As			+		
Sb		+			
Pb		+			

Kejimkujik

Element	Factor 1 (crustal)	Factor 2 (urban)	Factor 3 (In/As/V)	Factor 4 (marine)	Factor 5 (Pb)
Ti	+				
Br		+			
Mn	+	+			
Cu		+			
In			+		
Na				+	
V			+		
Cl				+	
Al	+				
Ca	+				
Se		+			
As			+		
Sb		+			
Pb		+			+

higher V emissions from abundant oil combustion along the US East Coast (Rahn and Lowenthal, 1985; Keeler and Samson, 1987), but it is not necessary to conclude the existence of sources which emit high concentrations of all three elements. More likely, this factor represents aerosols from distant smelter sources (In, As) and coal combustion sources (As) which become mixed with V-enriched aerosols from intermediate or local sources.

Pb was associated with two factors at Kejimkujik. As at the other two sites, the general pollution factor included both Pb and Br, but an additional factor for Pb only was derived at Kejimkujik. The absence of Br in this factor suggests that the second factor represents either unique industrial emissions of Pb or, more likely, a minor industrial correction to the predominantly automotive Pb associated with the general pollution factor. The potential impact of industrial Pb emissions at Kejimkujik has implications for the source apportionment based on lead isotope ratios, and will be discussed further in a later section.

Another approach to comparing concentrations at the three sites is shown in Table 4, which contains ratios of the average concentrations at Forêt Montmorency and Kejimkujik

Table 4. *Ratios of average concentrations at Forêt Montmorency and Kejimkujik to the average concentrations at Dorset*

	Ti	Br	Mn	In	Na	V	Al	Ca	Se	As	Sb	Cu	Pb
Forêt Montmorency													
Dorset	0.62*	0.44	0.50	1.0	0.96	1.5	0.53	0.35	0.35	0.65	0.48	0.74	0.45
Kejimkujik													
Dorset	0.63	0.91	0.57	1.2	8.0	5.4	0.46	0.45	0.56	0.58	0.78	0.62	0.63

* After omitting one anomalously high value from the calculation of the mean Ti concentration at Forêt Montmorency.

to the average concentrations at Dorset. The mean Na concentration at Kejimkujik is almost an order of magnitude greater than at the inland stations. At the same time, Cl has an anomalous behaviour at Forêt Montmorency which was sufficiently distinct to define a unique factor for Cl. That is, a marine factor with high loadings for both Na and Cl was evident at Forêt Montmorency but by itself this factor was unable to account for the observed variance in the Cl concentrations. The mean Cl/Na mass ratio at Kejimkujik was 1.29 ± 0.36 versus 0.89 ± 0.66 at Forêt Montmorency. Both are lower than the ratio of 1.80 expected for sea salt. This is likely due to volatilization losses of Cl from marine aerosol that has mixed with acidic aerosols and gases. Na is an involatile element.

At Forêt Montmorency and Kejimkujik, the mean concentrations of pollution-derived elements such as Se, As, Sb, Cu, and Pb, were 35% to 78% of the Dorset mean concentrations. This probably reflects the proximity of Dorset to large urban and industrial sources of these elements in southern Ontario, the US midwest, and the Great Lakes states. However, the mean V and Br values observed at Kejimkujik were much higher than those observed at Dorset or Forêt Montmorency. Cu concentrations at Forêt Montmorency were uncorrelated with the concentrations of any other element, with the result that Cu was poorly modelled by the linearly-additive factor analysis model. This shows up in Table 3 where Cu did not have significant loadings on any of the retained factors at Forêt Montmorency.

The availability of multi-station aerosol samples on a daily basis allows a study of the change in aerosol composition as air parcels traverse a region. An example of such a comparison is shown in Table 5 for two of the trajectories in group K2 of Fig. 3. There was no precipitation recorded at either station for at least two days before and after the samples were collected. Concentrations of all elements tended to increase. Elements associated with the crustal factors (Ti, Al, Ca, Mn) increased by 1.3–2.5 times, while the concentrations of Na (assumed to represent the marine component) were 6 times higher by the time the air had reached Kejimkujik. Modification of the near-surface

Table 5. *Comparison of ratios of concentrations measured at Kejimkujik to the concentrations measured at Forêt Montmorency the previous day. Pb-206/207 is the ratio of abundances of these two isotopes of Pb in each sample. The ratios of these isotopes were then calculated for the consecutive samples at Forêt Montmorency and Kejimkujik*

	Ratios for													
Samples collected at	Ti	Br	Mn	In	Na	V	Al	Ca	Se	As	Sb	Cu	Pb	Pb-206/207
Kejimkujik 10 October	1.8	3.1	2.0	2.3	6.6	39	1.5	1.6	5.4	3.0	1.0	0.8	8.6	1.02
Kejimkujik 11 October	2.3	2.3	2.5	1.8	5.9	11	1.5	1.3	1.8	1.1	3.0	2.5	2.0	1.01

mixed layer probably occurs rather quickly, since the trajectories show that the air in these two cases had only passed over the Bay of Fundy and, possibly, the Gulf of St. Lawrence. The increase in the concentrations of elements associated with the pollution factors was not as consistent, varying from 1 × to 39 ×. V concentrations were much higher at Kejimkujik than at Forêt Montmorency in both samples, most likely reflecting widespread oil combustion along the east coast. Additional measurements are needed for a thorough study of this sort, and would permit a more careful analysis of the effects of precipitation, seasonal differences, etc.

4. Meteorologically-stratified mean concentrations

Five-day 92.5 kPa Lagrangian back-trajectories from each station were organized into similar groups. Trajectories were selected on the basis of uniformity throughout each 24-h sampling period. This was done by examining the five trajectories associated with each sample (beginning of sampling; 6-h, 12-h, 18-h after start of sampling; end of sampling). For a sample to be accepted, all 5 trajectories had to be consistently from the same direction (within 30°) close to the site and have similar paths to the site in the previous 5 days. Samples with meandering trajectories were omitted. Mean concentrations were calculated for each of the groups and are shown in Table 6. The back-trajectories for the middle of each daily sample are plotted by groups in Figs. 1–3. Trajectories were not selected according to the occurrence of precipitation along the trajectory path, so any group may contain concentrations observed during both dry and wet periods.

Groups with the highest Br concentrations (D6, D8, M4, K5, K6) also have the highest mean Pb concentrations, consistent with a predominantly automotive source of these elements. These groups include trajectories which have passed over heavily-populated areas such as southern Ontario, the US midwest, and the New York City area. The Dorset data show that groups with high Pb concentrations (D6, D8) tend to have high mean Cd concentrations. There are exceptions to this tendency. For instance, group D2 has a high mean concentration of Cd and low Pb. Based on the back-trajectories only, D2 might be taken to represent background northerly flow at Dorset, but there is evidence (to be described shortly) of aerosols from non-ferrous smelters in these samples. Crustal elements such as Ti, Al, and Ca are highest in groups associated with flow from the south or southwest at Dorset (D5, D6, D8) although two samples with an easterly flow (D11) were observed to have high concentrations of these elements as well. At Forêt Montmorency and Kejimkujik, the crustal contribution was highest with westerly (M3) and northerly air flow (K1, K2) respectively.

At Kejimkujik, high concentrations of V were observed with trajectories which had crossed New England and southern Quebec (K4, K5) but not with background air from northern regions (K1), although the mean V concentration in the latter group was still higher than that observed in many of the Dorset and Kejimkujik groups. This strongly suggests that there are significant sources of V in this region, presumably from oil combustion. This is supported by the results of Keeler and Samson (1987) as well as by the V concentrations for group D11 samples which are the highest observed at Dorset. It is possible that some of the V in this pair of samples was due to emissions from Quebec City and the Ottawa–Montreal area, which may also have affected the mean V concentrations in K4 and K5. Keeler and Samson (1987) also found elevated V in eastern Canada.

Highest In concentrations at Dorset are associated with trajectory groups (D1, D2, D7, D10) which had passed near the smelter complexes of Sudbury and Noranda-Val d'Or in Quebec. Group D3 and D4 are associated with northwest to southwesterly flow at Dorset, and have In concentrations 6 to 20 times lower. This illustrates the high specificity of In as a tracer of smelter emissions. Concentrations of As were not only high in smelter trajectory groups at Dorset, but also high in groups D6, D7, and D8 with air flow from the US midwest and the Ohio River valley–West Virginia areas. The latter area in particular is noted for abundant coal combustion (Barrie, 1988; Rahn and Lowenthal, 1985; Keeler and Samson, 1987). Concentrations of In in these groups were low or at background levels.

Table 6. *Mean concentrations (ng m^{-3}) in samples grouped by similarity of back-trajectories; the groups indicated correspond to the plotted trajectories in Figs. 4–6*

Group no.	No. of samples	Ti	Br	Mn	In	Na	V	Al	Ca	Se	As	Sb	Cu	Pb	Mg	Zn	Cd	Ba
								Dorset										
D1	2	0.92	0.89	0.5	0.0225	36	0.06	23	26	0.41	0.64	0.05	1.4	5.7	4.5	33	0.25	0.18
D2	7	2.8	3.2	0.7	0.0120	111	0.17	78	57	0.66	1.8	0.11	6.2	7.3	15	16	0.36	1.9
D3	10	2.9	2.2	1.1	0.0012	32	0.22	84	50	0.42	0.68	0.05	5.0	5.2	9.7	24	0.12	0.75
D4	9	5.9	6.7	3.8	0.0012	27	0.86	160	149	0.81	0.50	0.30	6.4	18	19	15	0.21	0.88
D5	6	9.7	10	4.1	0.0023	57	2.5	228	218	1.5	0.67	0.24	5.7	29	28	44	0.31	1.2
D6	5	11	19	6.6	0.0040	92	2.3	241	142	3.1	1.1	0.84	9.0	50	22	35	0.47	1.1
D7	4	2.6	7.3	1.5	0.0068	15	12 5	68	37	1.1	1.8	0.13	9.7	22	4.5	12	0.20	0.73
D8	2	13	15	3.7	0.0010	113	4.3	337	142	2.7	1.3	0.67	6.7	41	33	17	0.47	1.6
D9	1	2.7	6.0	1.8	0.0010	15	0.75	23	16	1.1	0.12	0.19	4.7	20	4.5	20	0.12	0.18
D10	4	5.6	6.4	2.0	0.0138	21	0.88	174	56	0.83	1.1	0.12	11	22	13	18	0.21	2.8
D11	2	19	8.0	5.8	0.0010	123	5.4	378	145	0.35	0.23	0.17	11	25	37	39	0.07	2.8
								Forêt Montmorency										
M1	6	7.6	2.8	1.7	0.0044	74	2.7	140	50	0.19	0.23	0.11	4.0	8.6				
M2	4	4.3	2.6	1.1	0.0097	50	0.61	94	42	0.42	0.92	0.09	2.0	6.9				
M3	11	10	2.2	1.4	0.0059	28	1.4	68	41	0.19	0.74	0.09	5.6	7.0				
M4	2	6.1	9.0	2.2	0.0033	46	4.1	140	29	1.8	0.42	0.23	2.8	21				
M5	2	3.2	4.6	1.0	0.0024*	159	5.0	60	28	0.44	0.24	0.09	9.1	12				
								Kejimkujik										
K1	4	5.0	3.6	2.0	0.0048	568	4.4	81	53	0.11	0.24	0.09	3.2	3.1				
K2	5	6.0	5.0	2.0	0.0077	384	6.5	103	57	0.37	0.59	0.13	3.9	7.6				
K3	1	5.3	5.0	0.8	0.0045	543	2.8	52	45	0.29	0.24	0.09	3.3	5.5				
K4	5	2.8	6.6	1.5	0.0062	443	9.9	73	52	0.47	0.50	0.17	4.1	13				
K5	3	3.7	8.2	1.4	0.0102	285	11	64	49	0.98	0.74	0.28	3.6	27				
K6	1	1.7	8.0	0.7	0.0026	351	6.4	17	29	1.3	0.24	0.19	4.4	20				

* After omitting one value because of laboratory analytical uncertainties.

With some qualifications, the result for In and As from Forêt Montmorency and Kejimkujik are consistent with the Dorset results. The Forêt Montmorency groups with the highest In concentrations (M2, M3) include trajectories which passed near the Noranda-Val d'Or and Sudbury region. Concentrations of As were also high in these groups, but were low in the pair of trajectories comprising group M5 which originated from the oil burning region of the US east coast. Groups K2, K4 and K5 have the highest mean In and As concentrations at Kejimkujik, consistent with emissions from the non-ferrous smelter areas of Ontario and Quebec which these trajectories had passed. These results support the use of In as a potential tracer specific for non-ferrous smelter emissions, which would also be expected to be accompanied by higher As concentrations. The latter, however, are not specific to this type of source and high As concentrations may also arise from aerosols emitted by coal-burning power plants.

In autumn, instances of purely maritime air at Kejimkujik appear to be rare. More typically, continental air masses transport aerosols from inland sources into the near-coastal atmosphere where they undergo rapid modification. As shown earlier in the discussion of the data in Table 5, Na concentrations can increase by a factor of 6 in a 24-h period. The two predominant types of marine modification which occur are illustrated by group K1 and the single trajectory in group K6. In the former, northerly air may pick up additional marine aerosols from the Labrador Sea, which is still open at this time of year, or from the Gulf of St. Lawrence.

In the latter case, cyclonic flow may transport air over the ocean and later bring it back towards

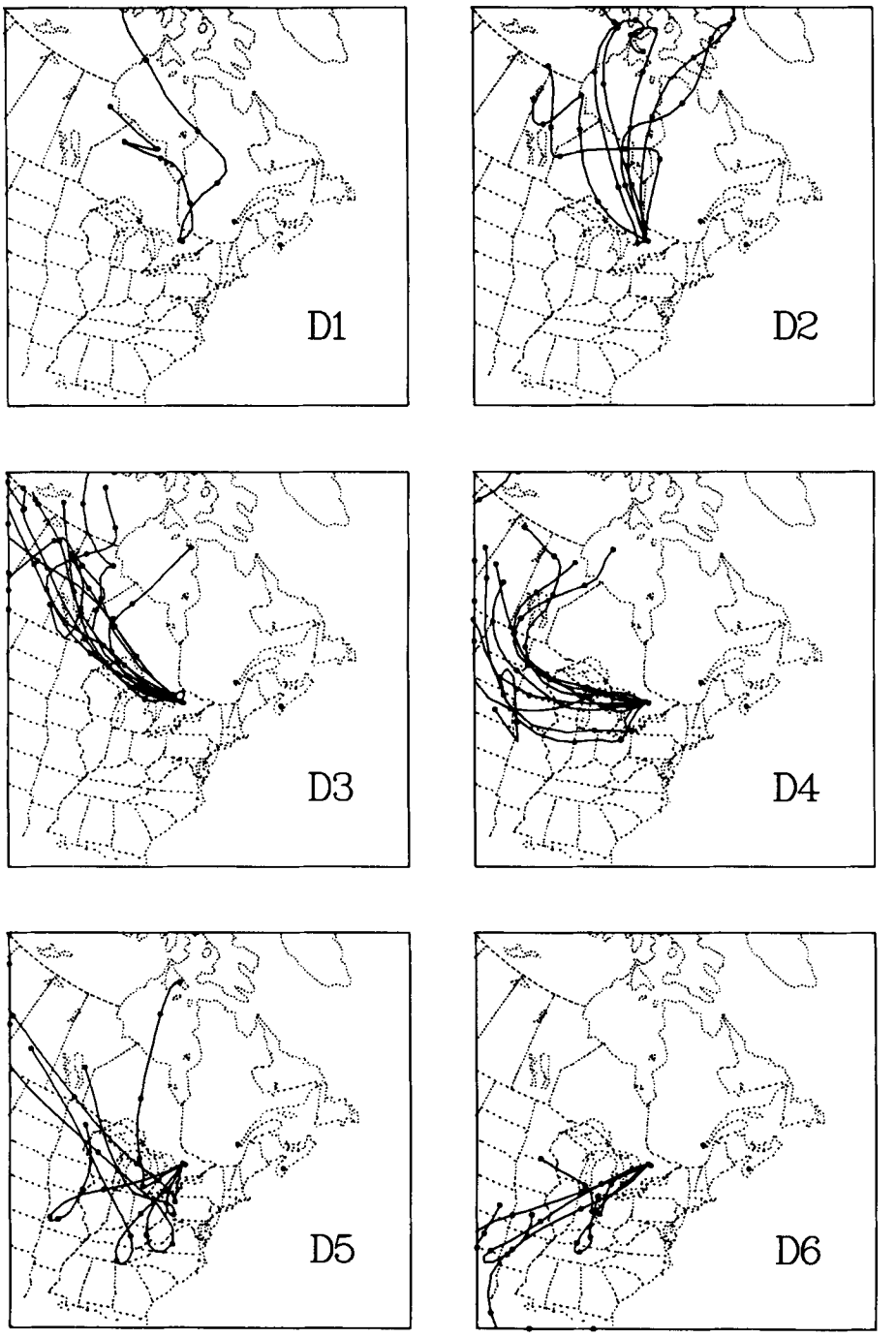
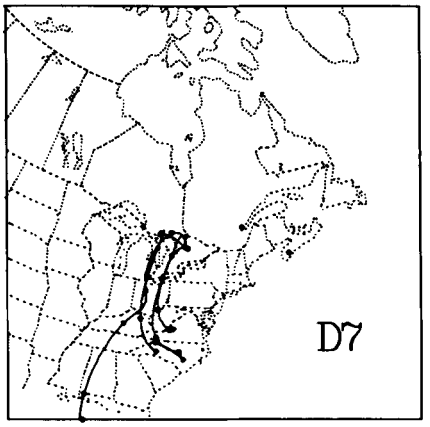
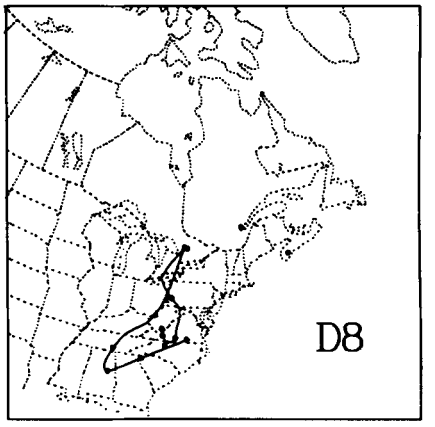
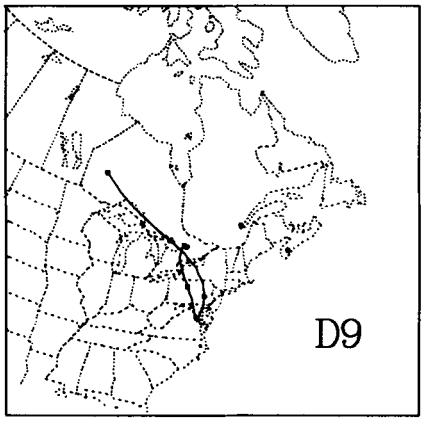
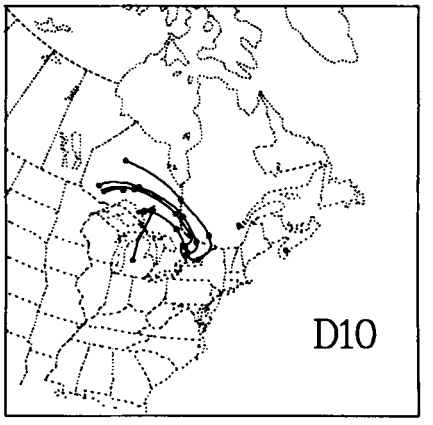


Fig. 1. Back-trajectory groupings (92.5 kPa, 5-days) at Dorset from 1 October to 9 December 1984. The trajectory calculations began at 00-GMT, approximately the middle of the sampling period for each aerosol sample. 18 of the possible 64 trajectories were not classified (see Tables 6 and 8 for aerosol trace element concentrations for each group).









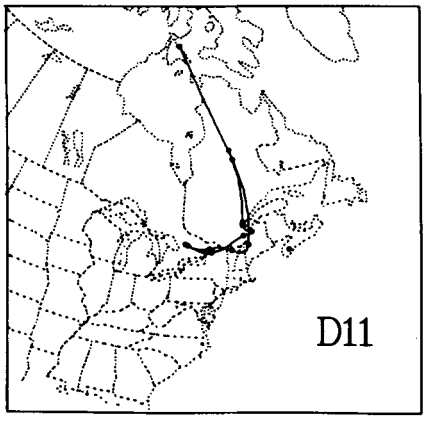


Fig. 1 (cont.)

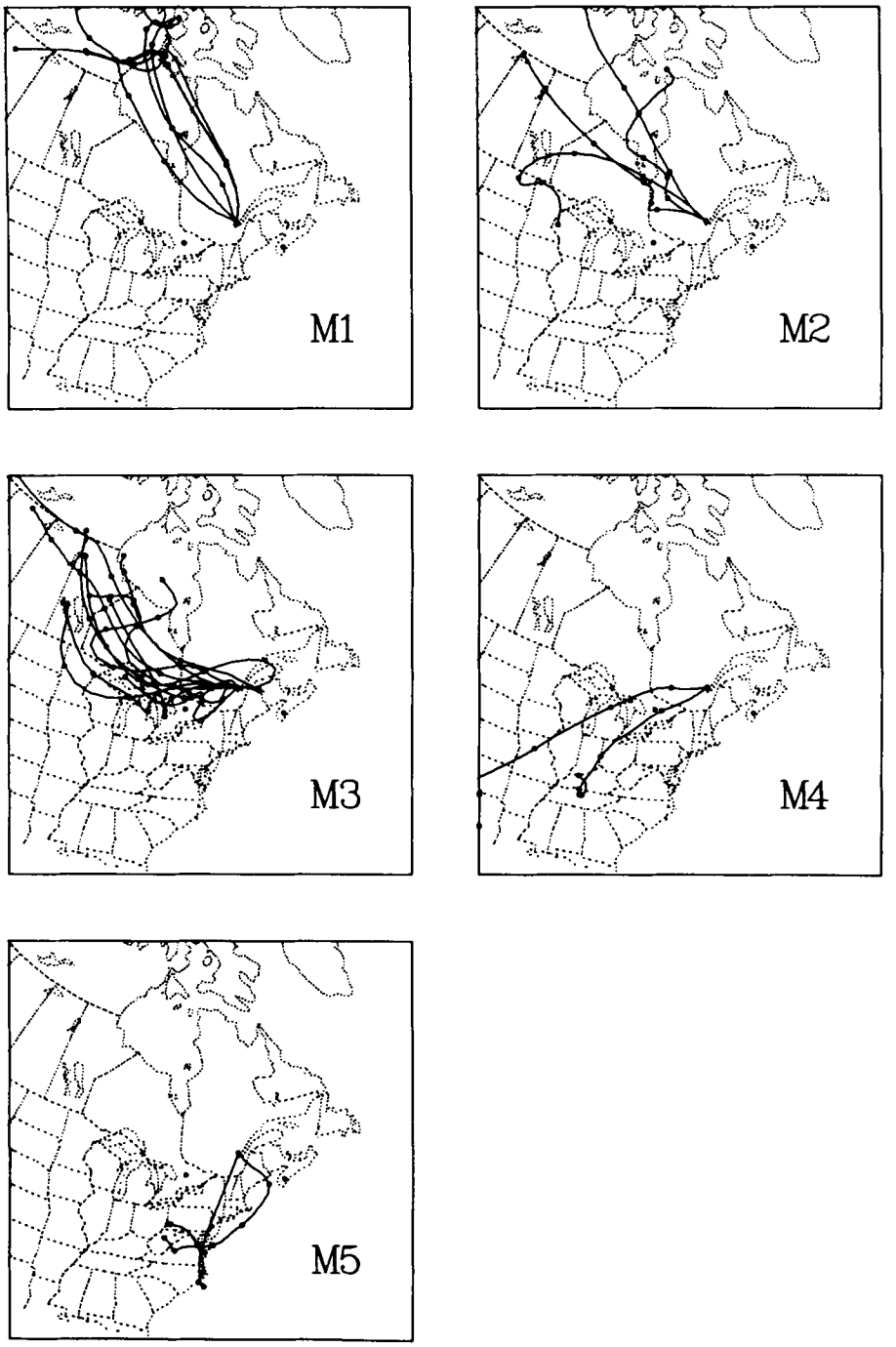


Fig. 2. Back-trajectory groupings (92.5 kPa, 5-days) at Forêt Montmorency from 1 to 15 October 1984, and from 26 November to 9 December 1984. The trajectory calculations began at 00-GMT, approximately the middle of the sampling period for each aerosol sample. 3 of the possible 28 trajectories were not classified (see Tables 6 and 8 for aerosol trace element concentrations for each group).

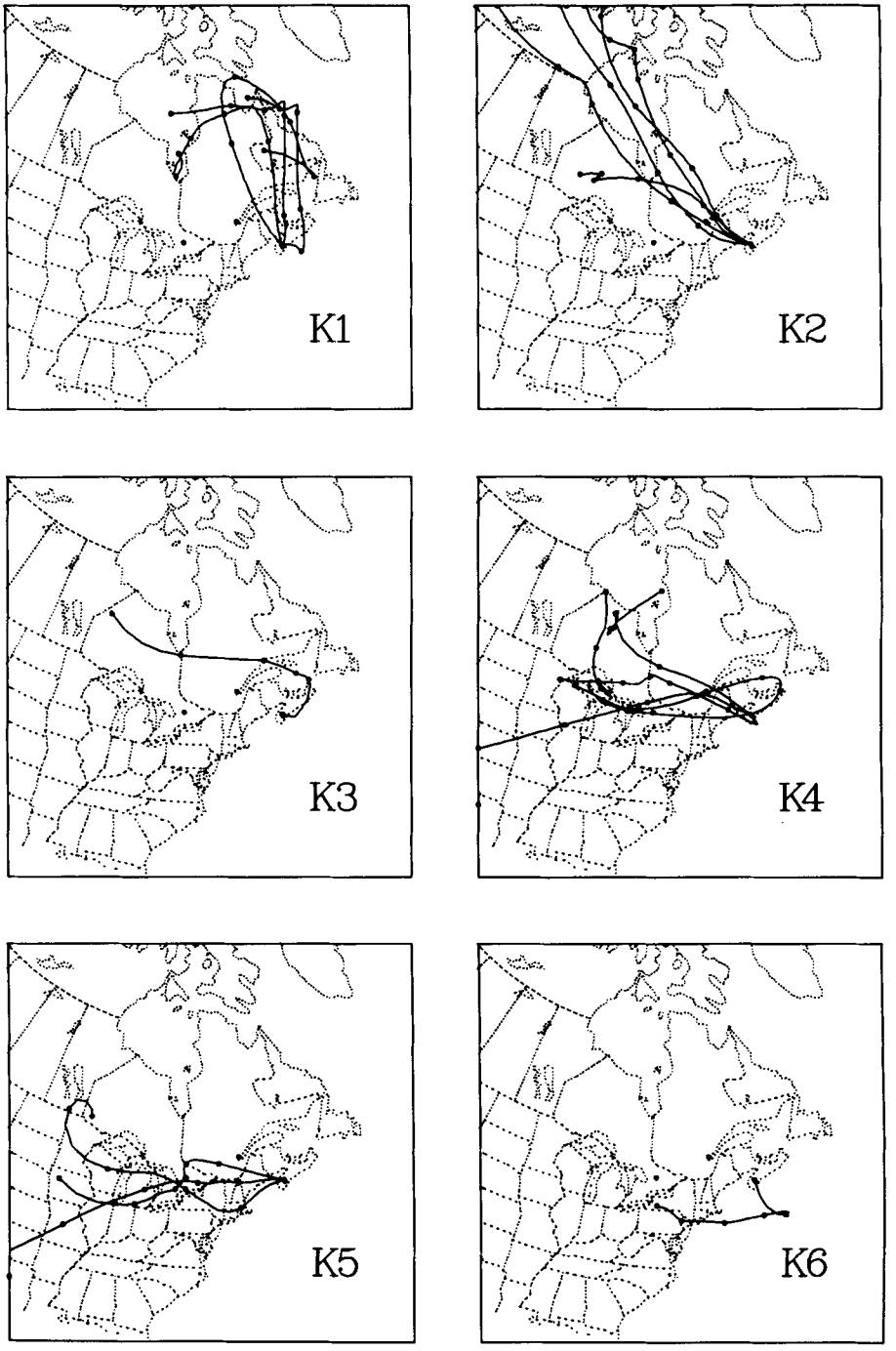


Fig. 3. Back-trajectory groupings (92.5 kPa, 5-days) at Kejimkujik from 1 to 15 October 1984, and from 26 November to 9 December 1984. The trajectory calculations began at 00-GMT, approximately the middle of the sampling period for each aerosol sample. 10 of the possible 28 trajectories were not classified.

Table 7. *Mean concentrations (ng m^{-3}) in samples from trajectory groups identified as background at Dorset, Forêt Montmorency, and Kejimkujik, compared to the mean concentrations in weekly samples collected at Alert*

Location/group	No. of samples	Ti	Br	Mn	Na	V	Al	Ca	Cu	Pb	Mg	Zn	Ba
Dorset (D3)	10	2.9	2.2	1.1	32	0.22	84	50	5.0	5.2	9.7	24	0.75
Forêt Montmorency (M1)	6	7.6	2.8	1.7	74	2.7	140	50	4.0	8.6	*	*	*
Kejimkujik (K1)	4	5.0	3.6	2.0	568	4.4	81	53	3.2	3.1	*	*	*
Alert (Oct.–Dec. 1984)	9	0.6	<0.3	0.4	162	0.09	61	92	1.1	<0.5	48	4.5	<0.13
Alert (July–Aug. 1984)	9	<0.1	0.2	0.3	38	0.05	42	57	0.6	<0.5	14	0.9	<0.13

* Data not available.

coastal land areas. While both groups produce aerosol samples with high Na concentrations, their chemical composition is significantly different because concentrations of anthropogenic elements such as Br, Se, Cu and Pb are increased in K6 by advection of aerosols from urban areas. By contrast, these elements reach their lowest concentrations in the modified polar air masses reaching Kejimkujik, as exemplified by group K1.

The importance of the composition of the "background" aerosol at sites in northeastern North America can be seen from the high frequency of air flow from areas without major industrial or urban sources of anthropogenic aerosols. As used in this paper, the term "background aerosol" refers to aerosols in air masses flowing into eastern North America. It is a function of air mass origin and meteorological characteristics. On the basis of the 5-day Lagrangian back-trajectory groupings and the associated concentrations of all elements, groups D3 and M1 can be taken to represent background continental air masses. Group K1 might also be considered of similar origin, with some maritime influence. These groups form 20%–25% of the classified samples at each of the monitoring sites. This is a minimum estimate of the frequency of the background aerosol, since many samples may be influenced by identifiable sources (such as the on-ferrous smelter groups at Dorset and Forêt Montmorency) affecting a few select elements, while the majority of the elements remain at their background concentrations.

In Table 7, the mean concentrations of elements from samples in the trajectory groups identified as background in this study, are compared to the mean concentrations observed in weekly samples collected at Alert during the same time period. The Alert concentrations show the influence of the composition of local soil which has a Ca/Al ratio of 1.44, versus a ratio of 0.45 based on the mean crustal abundances of these two elements (Mason, 1966). Na and Mg are also higher in concentration at Alert than in background samples at Dorset and Forêt Montmorency. This is probably due to long-range transport of sea salt from lower latitudes (Barrie and Hoff, 1985) and exposed local soil at Alert, respectively.

Concentrations of metals in the Alert samples may be influenced by Arctic haze, which begins to appear late in the year (Barrie, 1986). Table 7 also contains mean concentrations at Alert from weekly samples collected in July and August, 1984, when Arctic aerosol concentrations are at their lowest.

5. Lead concentrations and lead isotope ratios

Sturges and Barrie (1987) found a significant difference in the isotopic composition of atmos-

pheric lead from various sources in North America in the period 1984–1986. Because most aerosol Pb originates from automobiles, the Pb-206/207 ratio in aerosols reflects the ratio found in the ore bodies from which the lead additives were originally extracted. Canadian and American fuel producers utilize ores with different Pb-206/207 ratios, so that the fraction of aerosol Pb from Canadian and from US automobile sources can be estimated.

In addition, Sturges and Barrie (1987) found that Pb-206/207 ratios in aerosols associated with emissions from non-ferrous smelters were much lower than those in auto exhaust aerosols. Using their estimates of the Pb-206/207 ratios for each of these sources, and some simplifying assumptions, the atmospheric Pb in the Dorset, Forêt Montmorency, and Kejimkujik samples can be apportioned between these three sources.

Table 8. *Mean Pb concentrations, Pb-206/207 ratios, and their standard deviations, observed in the aerosol samples after stratification into the same trajectory groupings of Figs. 4–6*

Group no.	No. of samples	Pb ng m^{-3}	Pb-206/207
		Dorset	
D1	2	5.7 ± 7	1.089 ± 0.112
D2	7	7.3 ± 6	1.127 ± 0.030
D3	10	5.2 ± 5	1.166 ± 0.017
D4	9	18 ± 23	1.182 ± 0.016
D5	6	29 ± 13	1.187 ± 0.008
D6	5	50 ± 23	1.182 ± 0.015
D7	4	22 ± 13	1.167 ± 0.012
D8	2	41 ± 36	1.196 ± 0.006
D9	1	20	1.174
D10	4	22 ± 4	1.164 ± 0.009
D11	2	25 ± 4	1.151 ± 0.004
		Forêt Montmorency	
M1	6	8.6 ± 11	1.155 ± 0.007
M2	4	6.9 ± 7	1.129 ± 0.019
M3	11	7 ± 5	1.153 ± 0.031
M4	2	21 ± 8	1.195 ± 0.006
M5	2	12 ± 11	1.214 ± 0.025
		Kejimkujik	
K1	4	3.1 ± 2	1.156 ± 0.005
K2	5	7.6 ± 7	1.152 ± 0.012
K3	1	5.5	1.164
K4	5	13 ± 17	1.136 ± 0.061
K5	3	27 ± 26	1.141 ± 0.078
K6	1	20	1.190

Table 8 summarizes Pb concentrations and Pb-206/207 ratios for the trajectory groups. The Dorset samples were used in the earlier study by Sturges and Barrie (1987), and their presentation here does not constitute additional proof. However, the Forêt Montmorency and Kejimkujik Pb-206/207 data are new results. They are consistent with the Dorset analyses by Sturges and Barrie (1987) in that high Pb-206/207 ratios are found in groups of trajectories originating in the United States, while trajectories exclusively over Canada have lower lead isotope ratios. In addition, a few very low Pb-206/207 ratios were observed at Forêt Montmorency and Kejimkujik, associated with trajectories which were most likely to have passed near Sudbury or Noranda-Val d/Or.

Time series of the lead concentrations and Pb-206/207 ratios are compared in Figs. 4–5 (samples with Pb concentration less than twice the standard deviation of that of field blanks have been deleted). During the last week of November, the data are highly correlated between stations as a result of a slow moving anti-cyclone which advected aerosols from the southern Great Lakes states across New England and the Maritime provinces. The air flow reaching Kejimkujik during this period was southerly or southwesterly, according to the 92.5 kPa back-trajectories, which eliminates the possibility of a strong influence from non-ferrous smelters in Sudbury and Noranda-Val d'Or. The high Pb-206/207 ratios observed in these samples further support a predominantly American automobile source of Pb.

Sturges and Barrie (1987) suggested Pb-206/207 ratios for US automotive sources of 1.213 ± 0.008 in 1984 and 1.221 ± 0.009 in 1986, and mean values of around 1.15 for Canadian sources. By further assuming that the parent ore bodies being processed in the Sudbury and Noranda-Val d'Or smelters have a ratio of 1.01 (the lowest Pb-206/207 ratio observed at Dorset), the observed Pb-206/207 ratios can be used to distribute the atmospheric lead between these three source types.

A concentration-weighted apportionment scheme was used. This is advantageous for assessing environmental impacts because the depo-

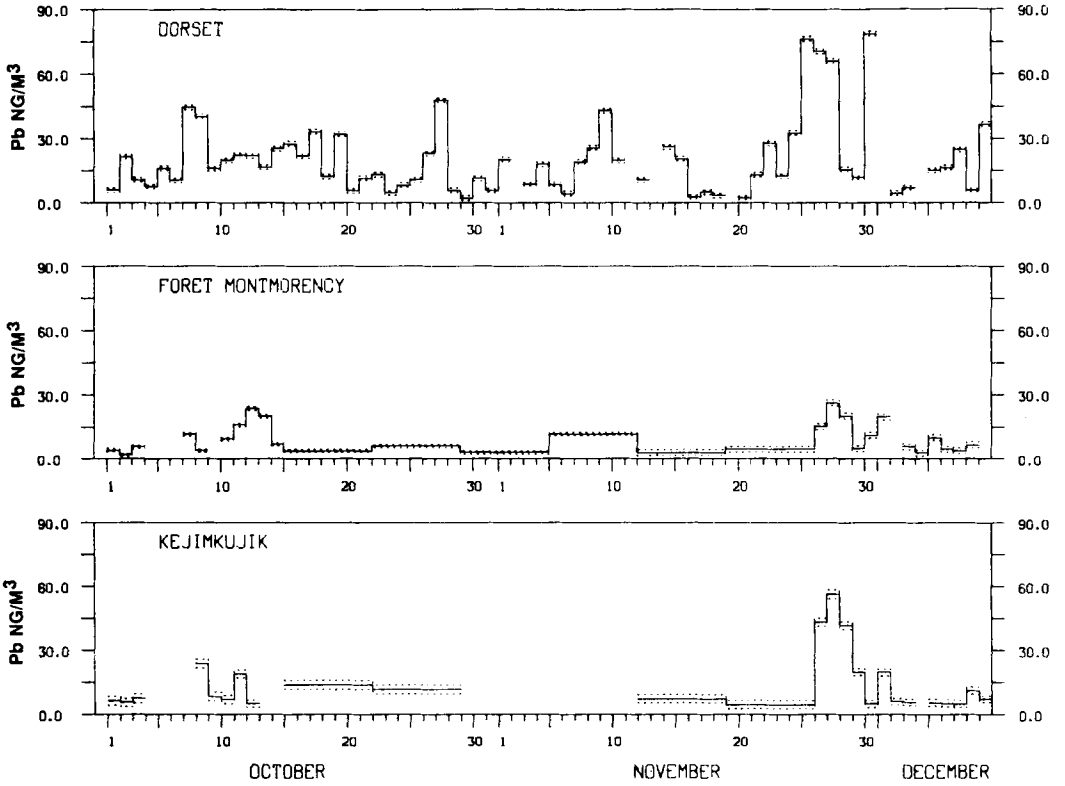


Fig. 4. Time series of aerosol Pb concentrations measured at the three sites. Concentrations from weekly samples at Forêt Montmorency and Kejimkujik have also been included. Samples were deleted if the Pb concentration was less than twice the standard deviation of the Pb concentrations in field blanks. The dotted lines indicate the approximate uncertainty in the concentrations.

sition of atmospheric Pb is approximately proportional to concentration. The mass loading m_{ij} of Pb from each source j was calculated in each sample i using $m_{ij} = C_i f_{ij}$ where C_i is the observed Pb concentration in sample i. The mass fractions were then summed to obtain the portions from each source type during the study period. A necessary assumption for the model was that on any given day only two sources could contribute to the sample.

In order to assess the effects of uncertainties in the assumed source ratios and in the observations, a Monte Carlo method of error propagation was employed. For each station, 100 apportionments were calculated with random errors added to each source ratio, observed concentration, and observed ratio. All random errors were assumed to be normally distributed. The standard deviations of the assumed source ratios were taken to be ± 0.01, while the random error added to the observed concentrations and ratios were equivalent to RSD errors of 10% and 1%, respectively. The mean and standard deviation of the fraction of atmospheric Pb from each source type were then calculated from the results of the 100 runs.

Results of the apportionment are shown in Table 9 for ratios of 1.01, 1.15, and 1.22 from smelters, Canadian automotive exhaust, and US sources respectively. Small differences (well within the standard deviation of apportionment estimates) between the estimates of Sturges and Barrie (1987) and those in Table 9 are due to differences in methodology of apportionment.

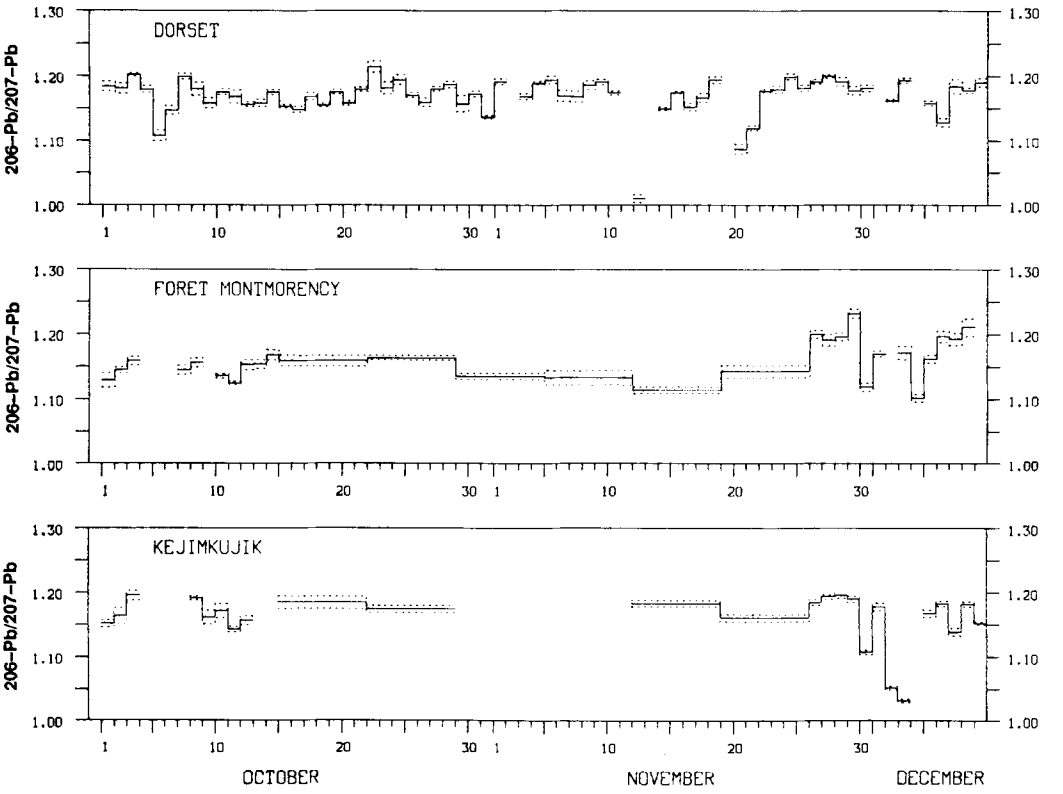


Fig. 5. Time series of the Pb-206/207 ratio in the aerosol samples collected at the three sites. Concentrations from weekly samples at Forêt Montmorency and Kejimkujik have also been included. Samples were deleted if the Pb concentration was less than twice the standard deviation of the Pb concentration in field blanks. The dotted lines indicate the standard deviation of 5 replicate measurements of the isotope ratio.

Table 9. *Results of a concentration-weighted apportionment of atmospheric Pb using the Pb-206/207 ratio observed in the aerosol samples. The results are the mean and standard deviation of 100 runs which added normally-distributed errors (approximately equivalent to the observational uncertainties) to the assumed source ratios, observed concentrations, and observed ratios. The number of samples with Pb concentration above detection limits is also indicated*

Site	Canadian auto	US auto	Canadian smelter
Dorset ($n = 64$ of 70)	51.6% ± 8.5%	46.1% ± 9.1%	2.3% ± 0.8%
Forêt Montmorency ($n = 23$ of 28)	67.5% ± 4.7%	28.2% ± 6.0%	4.3% ± 1.7%
Kejimkujik ($n = 21$ of 28)	51.0% ± 7.5%	44.1% ± 8.2%	*4.9% ± 1.1%

* Based on isotope signatures of smelters in central Canada. The validity of the source signature is questionable at this site.

We used the mean of the distribution of 100 runs in the Monte Carlo method while Sturges and Barrie used a simple arithmetic division. The results are consistent with the locations of the aerosol monitoring sites. Canadian automotive sources are much more significant at Forêt Montmorency than at Dorset or Kejimkujik. At these two sites, US automotive sources contribute almost as much as Canadian automotive sources. The non-ferrous smelters of central Ontario and southwestern Quebec appear to have similar impact at Forêt Montmorency and Kejimkujik despite the longer distance from the smelter areas to the coastal area. The higher In concentrations observed in the Kejimkujik trajectories which had passed near the smelters are further proof of the long-range influence of smelter emissions.

The roughly equal impact of smelter emissions at Forêt Montmorency and Kejimkujik is most likely the result of using the same source Pb-206/207 ratios at each site. There is evidence that this may be inappropriate for both smelter and automotive emissions. For instance, Sturges and Barrie (1987) noted that aerosol samples from Rhode Island had a lower ratio (1.196 ± 0.007) than that used in this apportionment (1.22), and suggested that automotive Pb from the US east coast may be better represented by this lower value. Another simulation with a US ratio of 1.19 did not substantially change the size of the smelter contribution at Kejimkujik, although the estimated fractions of US and Canadian automotive Pb changed from $44.1\% \pm 8.2\%$ and $51.0\% \pm 7.5\%$, to $55.0\% \pm 7.5\%$ and $41.0\% \pm 7.0\%$, respectively.

An uncertainty affecting the "smelter" contribution at Kejimkujik, is the effect of emissions from lead processing operations in the neighbouring province of New Brunswick. While automobiles are the largest source of atmospheric Pb in Canada, estimated at 63% of the national total emissions in 1978 (EPS, 1983), it is incorrect to ignore industrial Pb emissions. In particular, lead production (mining, milling, smelting, refining) in Canada is concentrated in a handful of locations.

In 1978, the ratio of emissions from Pb production to automotive Pb emissions in this region was approximately 0.36, instead of the national average of 0.11 (calculated from EPS, 1983).

There is no hard evidence that New Brunswick smelters are a significant source of Pb in the Kejimkujik samples. Trajectory group K1 might be expected to show this smelter influence most strongly, but this is the group with the lowest mean Pb concentration and, in other respects, appears to represent the background aerosol at Kejimkujik. Neither In nor As have significantly higher mean concentrations in this group, although it is possible that they are not appropriate tracers for aerosol emissions from this particular smelter. It is unlikely that atmospheric Pb from this source could be identified by the Pb-206/207 ratio because lead ores in the New Brunswick area have a ratio close to the ratio for Canadian auto exhaust. If this source is indeed significant, the aerosols from these production facilities would appear as Canadian automobile emissions, and the apportionment based on Pb-206/207 ratios would underestimate the smelter contribution.

6. Conclusions

Analysis of daily aerosol samples from three sites in eastern Canada in autumn 1984 revealed groups of elements with a crustal (Ti, Mn, Al, Ca), marine (Na, Cl), and anthropogenic (Br, V, Se, Sb, Cu, Pb) origin. Additionally, In was a good source-specific tracer for aerosol emissions from non-ferrous smelters in Quebec and Ontario. Arsenic was similarly associated with this source type, but also originated from regions in the mid-west US known to be prominent coal-burning areas. Na and V concentrations were much higher at Kejimkujik than at the inland sites, Na because of the coastal location and V because of the predominance of oil combustion as an energy source along the east coast of North America.

Lagrangian back-trajectories were useful for stratifying the aerosol samples into groups of similar origin. The frequency of samples with a "background" aerosol composition was 20% to 25% at each site. Comparison of the "background" aerosol at Dorset, Forêt Montmorency, Kejimkujik, and Alert revealed differences due to local effects and to long-range transport of aerosols.

A concentrated-weighted apportionment

scheme based on the Pb-206/207 ratio showed that most of the atmospheric Pb at each site originated from Canadian automotive emissions (51%–68%). American automotive emissions had slightly less impact (28%–46%), while the contribution from Canadian on-ferrous smelters was 2%–5%. Both low lead 206/207 isotope ratios and high In concentrations were sensitive indicators of non-ferrous smelter emissions, and were capable of detecting aerosols from this source over distances approaching 1000 km.

The data set from this study, although relatively small, is sufficiently useful when combined with trajectory analysis to warrant generation of a larger data set of one to two year duration at selected locations across eastern Canada. More sophisticated trajectory analyses such as Quantitative Transport Bias Analysis of Keeler and Samson (1987) isolate source regions of aerosol trace elements by what essentially amounts to a "triangulation" technique.

7. Acknowledgements

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