PAPER

www.rsc.org/jem

Correlations in the chemical composition of rural background atmospheric aerosol in the UK determined in real time using time-of-flight mass spectrometry

David C. S. Beddows,[a,b]† Robert J. Donovan,[a] Roy M. Harrison,[b] Mathew R. Heal,[a] Robert P. Kinnersley,[b] Martin D. King,*[a]‡ David H. Nicholson[a] and Katherine C. Thompson[a]§

[a]*School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b]*Division of Environmental Health and Risk Management, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*

Received 15th September 2003, Accepted 21st November 2003
First published as an Advance Article on the web 21st January 2004

An aerosol time-of-flight mass spectrometer (ATOFMS) was used to determine, in real time, the size and chemical composition of individual particles in the atmosphere at the remote inland site of Eskdalemuir, Scotland. A total of 51 980 particles, in the size range 0.3–7.4 μm, were detected between the 25th and 30th June 2001. Rapid changes in the number density, size and chemical composition of the atmospheric aerosol were observed. These changes are attributed to two distinct types of air mass; a polluted air mass that had passed over the British mainland before reaching Eskdalemuir, interposed between two cleaner air masses that had arrived directly from the sea. Such changes in the background aerosol could clearly be very important to studies of urban aerosols and attempts at source apportionment. The results of an objective method of data analysis are presented. Correlations were sought between the occurrence of: lithium, potassium, rubidium, caesium, beryllium, strontium, barium, ammonium, amines, nitrate, nitrite, boron, mercury, sulfate, phosphate, fluorine, chlorine, bromine, iodine and carbon (both elemental and organic hydrocarbon) in both fine ($d <$ 2.5 μm) and coarse ($d >$ 2.5 μm) particle fractions. Several previously unreported correlations were observed, for instance between the elements lithium, beryllium and boron. The results suggest that about 2 in 3 of all fine particles (by number rather than by mass), and 1 in 2 of all coarse particles containing carbon, consisted of elemental carbon rather than organic hydrocarbon (although a bias in the sensitivity of the ATOFMS could have affected these numbers). The ratio of the number of coarse particles containing nitrate anions to the number of particles containing chloride anions exceeded unity when the air mass had travelled over the British mainland. The analysis also illustrates that an air mass of marine origin that had travelled slowly over agricultural land can accumulate amines and ammonium.

1. Introduction

A detailed knowledge of the chemical composition of particles present in the atmosphere, alongside a knowledge of their size and concentration, is crucial to determining the sources of particulate matter in the atmosphere, assessing the health problems associated with airborne particles, and to understanding the influence of particles on atmospheric chemistry and *vice versa*. The atmospheric particle burden is extremely diverse and influenced by a multitude of sources and transformation processes. While much progress has been made in understanding and quantifying the atmospheric particulate system,[1] more needs to be resolved. Much of the uncertainty stems from a lack of measurement techniques with sufficient time resolution. Traditional chemical speciation is dependent on accumulation of sufficient material (often over days) on traps or filters and subsequent off-line analyses. These methods do not allow the chemical composition of individual particles to be ascertained.

Over the past few years there has been considerable development of instrumentation capable of sizing and chemically characterising airborne particles in real time.[2–9] The considerably enhanced time resolution provided by these instruments permits investigation of correlations in chemical composition of particles, and of the role of meteorology and chemistry in the evolution of the particle burden in the atmosphere.

In this work we describe the deployment of an aerosol time-of-flight mass spectrometer (ATOFMS)[2] to study the rural background aerosol. In contrast to some other single-particle instrumentation, the ATOFMS yields, simultaneously, size and chemical composition data for each particle analysed, together with information on changes in number density with time. The ATOFMS was sited at Eskdalemuir (55.3° N, 3.2° W; elevation, 250 m), a remote location in the Southern Uplands of Scotland approximately 80 km south of Edinburgh and 100 km south east of Glasgow. The site is surrounded by animal pasture, unimproved moorland and coniferous forest plantations. Sampling was undertaken continuously between 20:00 on 25th June and 09:00 on 30th June 2001 (Julian Days 176 to 181). This study is a prelude to a series of studies on urban aerosols which will be reported in due course.

During the campaign the mass spectra of 51 980 individual particles were recorded. The emphasis in this study was on the

---

† Present address: Department of Physics, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, UK.

‡ Present address: Department of Geology, Royal Holloway University of London, Egham, Surrey, TW20 0EX, UK. E-mail: m.king@gl.rhul.ac.uk; Fax: +44 (0)1784 471780; Tel: +44 (0)1784 414038.

§ Present address: School of Biological and Chemical Sciences, Birkbeck College, University of London, Malet Street, Bloomsbury, London, WC1E 7HX, UK.

DOI: 10.1039/b311209h

elemental composition of the aerosol particles and the data were analysed in a manner that assumed no prior knowledge or preconceived idea as to the origin or chemical nature of the particles. The method of analysis does not group the particles into broad categories such as sea salt, nitrate, elemental carbon *etc.*; rather, correlations were determined between a suite of species (both elemental and molecular) present in individual size-fractionated particles. The correlations were related to changes in air mass source region during sampling. The enormous versatility of the ATOFMS instrument in elucidating the composition of particles in the atmosphere is demonstrated.

2. Experimental

2.1 Description of the ATOFMS

The main features of the aerosol time-of-flight mass spectrometer (ATOFMS) instrument used here (TSI, Model 3800) have been described previously,[2] and only an overview is presented here. Air is sampled from the atmosphere through a differentially pumped aerodynamic nozzle to produce a collimated beam containing the particles which then passes two orthogonal laser beams (532 nm, diode-pumped solid state lasers) separated by a known distance. Scattered light from a particle actuates a timing circuit and the transit time yields the aerodynamic diameter of the particle. The particles pass through to a mass spectrometer section where material is ablated and ionised in the focus of a pulsed UV laser light at 266 nm (frequency quadrupled Nd-YAG laser). The desorption-ionisation laser is triggered by the same timing circuit used to size the particles. The mass-to-charge ratios of both the positive and the negative ions produced are determined simultaneously in two time-of-flight reflectron mass spectrometers. Only the 400 ions giving rise to the largest signal were considered in the analysis of each spectrum, with the limitation that the smallest signal to noise ratio used was $\sim$2:1.

Although, in principle, particles with aerodynamic diameter 0.3 μm to 10 μm can be detected and sized, size-sampling efficiency is not uniform. For a similar ATOFMS instrument, Allen *et al.*[10] showed that particle detection efficiency obeyed a power law on diameter in the range 0.32–1.8 μm, decreasing by two orders of magnitude over this range. Since sizing efficiency must be determined for each instrument individually and, since for this work, only a division between fine and coarse particles was required, no attempt was made to "correct" for sizing efficiency. The minimum and maximum particle diameters detected in this work were 0.36 and 7.4 μm, respectively.

The ablation and ionisation process used in this work has been studied by a number of groups.[11] A limitation of the time-of-flight mass spectrometer is its inability to yield direct quantitative information on the amount of each chemical species in each particle. However, the work presented sought only to correlate chemical species present in rural aerosol, not to quantify the amounts. There are relatively few published attempts to quantify the response of ATOFMS instruments to particles of known composition. Bhave *et al.*[12] demonstrated that the detection efficiency of their ATOFMS to NH_4^+ and NO_3^- was reduced as the particle diameter decreased from 1.8 to 0.32 μm, as compared with collocated impactor measurements. Gross *et al.*[13] determined relative sensitivity factors of 0.14, 5.1, 6.0, 7.9 and 0.014 for detection of the ions Li^+, K^+, Rb^+, Cs^+ and NH_4^+, respectively, relative to Na^+. The trend of increased detection efficiency with atomic number for these ions correlated with lattice energies and ionisation potentials for the precursor salts and elements respectively. The authors tested the machine in the laboratory before committing it to the field. Using artificial aerosol generated in the laboratory we investigated the typical response of expected chemical constituents of common aerosols in the laboratory.

2.2 Mass calibration

A reliable method of mass calibration for the time-of-flight signal was the obvious series of peaks separated by 12 Da provided when elemental carbon particles were detected. Mass calibration was undertaken every hour throughout the field campaign by sampling particles produced from nebulisation of a calibration solution containing an aqueous solution of the ions Na^+, Fe^{3+}, Zn^{2+}, Pb^{2+}, Cl^-, SO_4^{2-}, and NO_3^-. It should be noted that when identifying ions from their mass spectra it is possible that other species present may have the same mass and thus cause interference. All likely interferences of this kind were considered and the conclusions presented in the text for each relevant species. However, the possibility of interference caused by the presence of an unsuspected species cannot be completely ruled out.

2.3 Aerosol sampling and meteorological data

The ATOFMS was housed in a static van throughout the campaign. Outside air was sampled into the inlet of the instrument from approximately 2 m height above the ground through a 2 m length of 2.5 cm (OD) clean copper tubing. A portable meteorological station (Campbell) was positioned within 50 m of the vehicle and recorded wind speed and direction, relative humidity (at 1.4 m height), air temperature and visible irradiance as 5 min averages.

2.4 Air mass back trajectories

Back trajectories were calculated for 00:00, 06:00, 12:00 and 18:00 h on Julian days (JD) 176.5–181.5 of the campaign using the models available from the British Atmospheric Data Centre. Parcel pressures of 900, 950 and 1000 mbar and potential temperatures of 300, 320 and 340 K were used for vertical advection and isentropic models, respectively. Both models gave similar results. Clusters of trajectories arriving at a 10 km radius of the field site were also similar, indicating that the air mass source regions were well-characterised.

3. Results and discussion

3.1 Air mass source region and local meteorology

The back trajectories, which were obtained after the field campaign, revealed a major switch in air mass source region during sampling. From JD 176.5 to JD 177.5, and again from JD 179.0 to JD 181.5, air masses followed an almost entirely marine path over the Atlantic Ocean and Irish Sea before reaching Eskdalemuir. In contrast, back trajectories in the period JD 177.5 to JD 178.75 travelled over mainland Britain from a southerly direction. Examples of these "clean/marine" and "dirty/continental" air masses are illustrated in Fig. 1.

During the campaign, local winds remained light ($<$1–6 m s^{-1}), relative humidity was high (80–$\sim$100%), and there was little diurnal temperature variation (11–16 °C). A large (for the United Kingdom) thunderstorm impacted the site between JD 177.75 and 178.0 and was the only precipitation event. The local meteorological variables did not correlate with the size or chemical composition of the particles. This confirms the absence of a local point source of particles, which is not surprising given the remoteness of the sampling site.

3.2 Variation of particle size fractions

The size, and positive and negative ion mass spectra of all 51 980 particles recorded during the campaign were grouped into 1 h time intervals. Although the ATOFMS provided a quasi-continuum of size classification, particles were re-classified as either fine ($<$2.5 μm) or coarse ($>$2.5 μm) in order to expedite analysis of this large dataset. This yielded 30 949 fine and 21 031 coarse particles. The maximum number of fine and coarse particles detected were 1379 h^{-1}, at around 06:00 on day 178, and

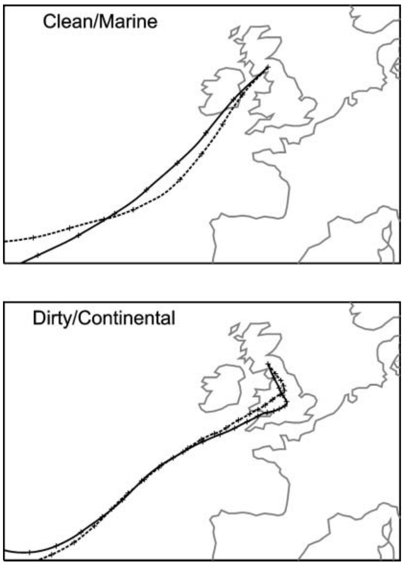

Fig. 1 Back trajectories illustrating the two types of air mass experienced during the measurement campaign. Solid and dashed lines are trajectories arriving at 900 and 950 mbar, respectively. Markers are at 6 h intervals. The upper pane is for JD 180.5 and shows ~2 days of an example "clean/marine" air mass trajectory. The lower pane is for JD 177.5 and shows ~6 days of an example "dirty" air mass trajectory.

$1126\ \mathrm{h}^{-1}$, at around 20:00 on day 178, respectively. The time series of hourly particle numbers is shown in Fig. 2. The elevated total number of particles in the air mass that passed over the mainland UK is striking, as is the significant increase in the ratio of fine particles relative to coarse particles in this dirty air mass.

3.3 Correlations between particle chemical composition

Each time-of-flight mass spectrum was converted into a conventional stick mass spectrum using calibration values described in Section 2.2. The stick mass spectra, and the associated size data for the particles, were placed in Microsoft Access databases from which it was possible to query the number of occurrences of a species of x Da in each hourly period. Tables 1 and 2 summarise the percentage of the total number of coarse and fine particles that contained each chemical species considered, and the maximum number of occurrences of particles containing the species that were detected in any one hour period.

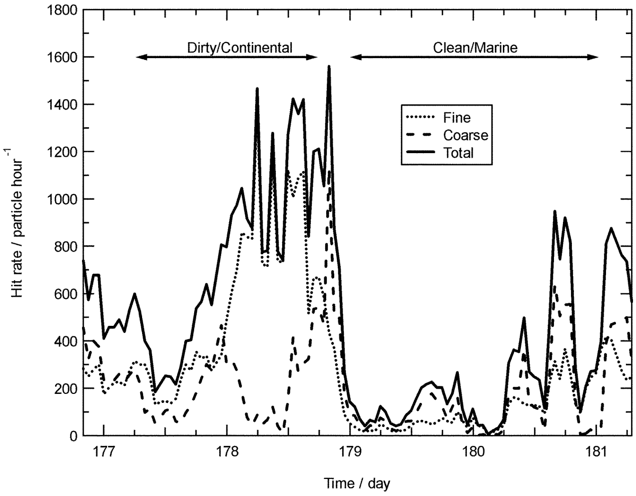

Fig. 2 The number of coarse and fine particles detected per hour. The periods corresponding to "dirty" or "clean" air mass were determined by 6 hourly back trajectories.

Tables 3 and 4 list, for fine and coarse particles respectively, the correlation matrices (crosses indicate $r^2 > 0.5$) for the hourly number of occurrences of pairs of species of x and y Da, for those species examined. It should be noted that the chemical analyses performed were not mutually exclusive: a particle found to contain potassium and sodium would not be classified as solely sodium or solely potassium, but classified as containing sodium and classified as containing potassium.

The databases could also be interrogated using basic logic commands. For example, searching for m/z = 200 AND 202 Da (*i.e.* both common isotopes) yielded more confidence for the presence of mercury in a particle.

3.3.1 Positive ions.

Lithium. The ATOFMS is particularly useful for detecting lithium since the X-ray techniques often used to

Table 1 A summary of species detected in the positive ion time-of-flight mass spectra of single particles at Eskdalemuir, June 2001

Element or ion: Daltons	Fine[a]	Coarse[a]	Maximum number, fine[b]	Maximum number, coarse[b]
Lithium: 7	2.0%	2.7%	22 (12.8%, 178.12)	26 (6.3%, 178.54)
Sodium: 23	50.1%	96.4%	456 (68.2%, 178.75)	1111 (98.7%, 178.83)
Potassium: 39 AND 41	44.3%	87.4%	412 (61.7%, 178.75)	1039 (92.3%, 178.83)
Rubidium: 85 AND 87 NOT 86	3.0%	1.9%	32 (10.5%, 177.29)	16 (3.9%, 178.54)
Caesium: 133	3.2%	2.2%	40 (2.9%, 178.25)	24 (5.8%, 178.54)
Caesium: 133 NOT 132	1.1%	1.2%	16 (1.2%, 178.25)	10 (2.7%, 176.92)
Beryllium: 9	0.4%	0.8%	7 (3.4%,177.12)	9 (7.3%, 177.71)
Strontium: 88	2.4%	3.8%	28 (8.8%, 177.25)	32 (7.1%, 176.83)
Barium: 138	1.6%	1.9%	18 (6.3%, 177.29)	20 (3.7%, 178.70)
Mercury: 200	0.7%	0.6%	10 (1.2%, 178.12)	8 (1.7%, 178.00)
Mercury: 200 AND 202	0.4%	0.2%	7 (3.9%, 177.50)	4 (4.1%, 177.33)
Boron: 11	0.4%	0.5%	7 (2.5%, 177.71)	5 (3.9%, 177.71)
C: 12	58.2%	12.3%	1208 (87.6%, 178.25)	155 (37.3%, 178.54)
C_3: 36	65.1%	18.2%	1284 (93.1%, 178.25)	237 (57.1%, 178.54)
C, C_3, C_7: 12, 36, 84	10.7%	3.2%	223 (16.2%, 178.25)	51 (12.3%, 178.54)
C, CH, CH_2: 12, 13, 14	0.5%	0.2%	19 (38.2%, 179.75)	7 (7.6%, 179.00)
C_3, C_3H, C_3H_2: 36, 37, 38	23.6%	7.0%	454 (32.9%, 178.25)	106 (19.8%, 178.70)
NH_4NO_3: 80	3.5%	9.3%	41 (6.1%, 178.75)	72 (6.4%, 178.83)
NH_4 (or H_2O): 18	20.6%	9.7%	419 (30.4%, 178.25)	109 (35.9%, 178.62)
$NH_3.NH_4$: 35	22.7%	4.5%	463 (40.1%. 178.37)	70 (16.9%, 178.54)
CH_4N (or NO^+): 30	20.8%	30.0%	362 (26.3%, 178.25)	300 (26.6%, 178.83)
C_3H_8N: 58	12.7%	19.5%	202 (17.5%, 178.37)	170 (15.1%, 178.83)
$C_5H_{12}N$: 86	7.5%	5.4%	105 (14.3%, 178.45)	44 (10.6%, 178.54)
Amines: 30 AND 58 AND 86	2.7%	2.3%	39 (12.3%, 177.25)	22 (4.7%, 177.95)

[a] Percentage of all fine (<2.5 μm) or all coarse ($d > 2.5$ μm) particles which contain the species. [b] The maximum number of fine or coarse particles which contain the species in any one hour period. The numbers in parentheses are the percentage of particles in that hour period that contained the species, and the Julian day fraction at which this hour period occurred.

Table 2 A summary of species detected in the negative ion time-of-flight mass spectra of single particles at Eskdalemuir, June 2001

Element or ion: Daltons	Fine[a]	Coarse[a]	Maximum number, fine[b]	Maximum number, coarse[b]
Fluorine: 19	0.3%	0.3%	7 (2.6%, 177.21)	4 (1.1%, 176.96)
Chlorine: 35	6.1%	20.4%	80 (19.7%, 181.12)	351 (20.4%, 176.83)
Bromine: 79 AND 81	4.5%	6.6%	79 (28.8%, 177.17)	97 (34.3%, 177.25)
Iodine: 127	0.7%	1.2%	15 (1.4%, 178.58)	18 (6.9%, 177.12)
NO_2^-: 46	15.9%	38.3%	182 (16.3%, 178.62)	401 (87.9%, 176.83)
NO_3^-: 62	17.7%	35.7%	259 (23.2%, 178.62)	387 (84.9%, 176.83)
NO_3^-: 62 NOT 60	13.2%	29.5%	222 (19.9%, 178.62)	315 (58.9%, 178.70)
SO_3^-: 80	7.5%	10.7%	96 (8.8%, 178.58)	157 (34.4%, 176.83)
HSO_3^-: 81	4.7%	3.1%	78 (5.7%, 178.25)	46 (17.6%, 177.12)
HSO_3^-: 81 NOT 79	2.9%	1.1%	73 (6.3%, 178.37)	20 (16.4%, 178.37)
SO_4^-: 96	10.6%	11.8%	121 (49.0%, 177.38)	220 (48.2%, 176.83)
SO_4^-: 96 NOT 84	8.8%	9.2%	102 (32.3%, 177.25)	205 (45.0%, 176.83)
HSO_4^-: 97	13.3%	9.2%	239 (20.7%, 178.37)	132 (28.9%, 176.83)
PO_2^-: 63	6.4%	9.5%	150 (10.9%, 178.25)	116 (41.0%, 177.25)
PO_4^-: 95	5.1%	9.7%	68 (27.5%, 177.38)	229 (50.2%, 176.83)
O^-: 16	13.9%	24.6%	259 (82.0%, 177.25)	421 (92.3%, 176.83)
OH^-: 17	8.8%	20.5%	121 (42.6%, 176.83)	390 (85.5%, 176.83)

[a] Percentage of all fine (<2.5 μm) or all coarse ($d > 2.5$ μm) particles which contain the species. [b] The maximum number of fine or coarse particles which contain the species in any one hour period. The numbers in parentheses are the percentage of particles in that hour period that contained the species, and the Julian day fraction at which this hour period occurred.

detect metals in bulk particle samples are not sensitive to lithium.[4] During this campaign, 2.0% and 2.7%, respectively, of fine and coarse particles contained lithium (m/z = 7 Da). The temporal behaviour of coarse and fine particulate lithium was similar. Lithium occurs naturally in crustal rocks (18 ppm by mass globally) and has been detected by ATOFMS in Californian soil dust.[14] In a measurement campaign with a single particle mass spectrometer at Idaho Hill in the US, 9% of particles analysed were found to contain lithium, and these particles correlated positively with those containing potassium and sodium.[4] No such correlation was observed in this study (Tables 3 and 4). However, fine particle lithium was correlated with fine particle barium which is probably indicative of an automotive source, since barium is associated with automobile emissions.[13] One anthropogenic source of Li includes high temperature automobile greases, alongside fluxes for porcelain enamels and aluminium brazing.[16]

Sodium. Sodium, and other alkali metals, are readily detected by the ATOFMS because of the low ionisation energies. It was found that nearly all coarse particles and half of all fine particles contained sodium (m/z = 23 Da). This reflects the prevailing maritime meteorology at Eskdalemuir, with sea-salt contributing particularly to the coarse mode. The temporal trend, shown in Fig. 3, in numbers of fine particles containing sodium closely tracked that of coarse particles containing sodium. Murphy and Thompson[4] observed that even at Idaho Hill in Colorado, over 50% of particles contained sodium.

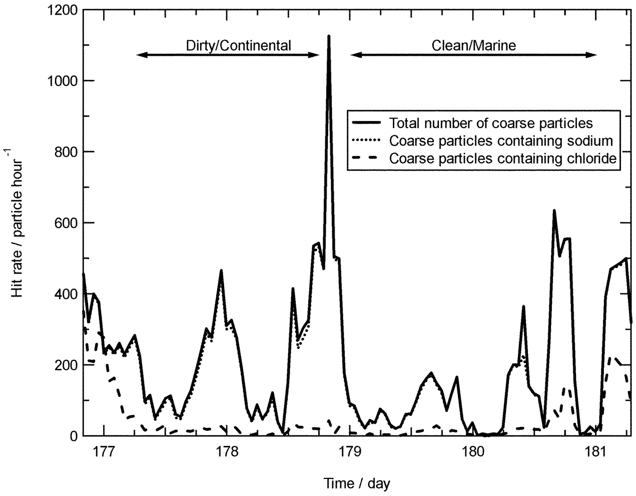

Fig. 3 The number of coarse particles detected per hour containing sodium or chloride. The figure demonstrates the depletion of particles containing chloride, especially the particles that have travelled overland, taken to indicate displacement reaction by nitrate.

Potassium. Over 44% and 87% of fine and coarse particles, respectively, contained potassium (identified using m/z = 39 AND 41 Da). The numbers of particles containing potassium and sodium were very strongly correlated. This can indicate a sea-salt origin, but potassium is also both a crustal component and a major trace element for plant growth. The widespread occurrence of potassium is therefore not surprising. An ATOFMS study of biomass burning in California noted that >90% of particles contained potassium,[17] while another ATOFMS study detected potassium in California soil dust.[14] Potassium has been reported as a biogenic component in the coarse fraction of particles collected in the Amazon.[18] At Eskdalemuir the potassium signal was correlated with sodium and nitrate and, in the coarse component only, to the ions CH_4N^+ and $C_2H_8N^+$, which are indicative of amines. This latter association has not been previously reported.

Rubidium. The isotopes of Rb^+ at 85 AND 87 Da are coincident with the organic ions C_7H^+ and $C_7H_3^+$ Since these latter two ions should also occur with the $C_7H_2^+$ ion (86 Da), particles containing rubidium were identified using m/z = 85 AND 87 NOT 86 Da. However, this may still not unequivocally distinguish between rubidium and organic hydrocarbon. Rubidium characterised in this way was present in 3.0% and 1.9% of fine and coarse particles, respectively, and correlated with, amongst others, lithium and caesium, cations thought to derive from the amines, and, particularly for fine particles, anions containing sulfur. Previous literature data on particulate rubidium is scarce. Rubidium has been detected as a component of aerosols associated with biomass burning.[18] The correlation between rubidium and lithium noted in this work could be indicative of a common, soil-related source.

Caesium. The caesium cation has m/z = 133 Da. This value may also correspond to the organic ion $C_{11}H^+$, so if it is assumed that the C_{11}^+ ion occurs concurrently with $C_{11}H^+$, caesium may be identified by m/z = 133 NOT 132 Da. Particles containing caesium were 1.1% and 1.2% of all fine and coarse particles, respectively. The temporal trend of caesium in coarse particles was similar to the trend in total coarse particle number, suggesting marine origin. The trend in fine particulate

Table 3 Observed correlations between the number of fine ($d < 2.5$ μm) particles per hour containing the specified pairs of ions. A filled square indicates $r^2 \geqslant 0.5$

	Sodium, Na^+	Potassium, K^+	Rubidium, Rb^+	Caesium, Cs^+	Beryllium, Be^+	Strontium, Sr^+	Barium, Ba^+	NH_4^+	CH_4N^+	$NH_3NH_4^+$	$C_2H_8N^+$	$C_5H_{12}N^+$	CH_4N^+ AND $C_2H_8N^+$ AND $C_5H_{12}N^+$	$NH_4NO_3^+$	NO_2^-	NO_3^-	Total Carbon, C_3^+	Hydrocarbon, C_3^+ AND C_3H^+ and $C_3H_2^+$	Boron, B^+	Mercury ,Hg^+	SO_3^-	HSO_3^-	SO_4^-	HSO_4^-	SO_3^- and SO_4^-	PO_2^-	PO_4^-	O^-	OH^-	Fluoride, F^-	Chloride, Cl^-	Bromide, Br^-	Iodide, I^-
Lithium,Li^+			X	X	X	X	X					X	X						X		X		X									X	
Sodium, Na^+		X																															
Potassium, K^+																X																	
Rubidium, Rb^+				X		X	X	X	X	X	X	X	X		X					X	X	X	X	X	X	X						X	
Caesium, Cs^+						X	X	X	X	X	X	X	X				X	X			X	X	X	X	X	X							
Beryllium, Be^+																			X														
Strontium, Sr^+									X		X	X	X	X							X		X		X							X	
Barium, Ba^+								X				X	X								X				X								
NH_4^+									X	X	X	X	X				X	X			X	X		X		X							
CH_4N^+										X	X	X			X	X	X	X			X	X	X	X	X	X							
$NH_3NH_4^+$											X	X					X	X				X		X		X							
$C_2H_8N^+$												X	X		X	X	X	X			X	X	X	X	X	X							
$C_5H_{12}N^+$													X		X	X	X	X			X	X	X	X	X	X							
CH_4N^+ AND $C_2H_8N^+$ AND $C_5H_{12}N^+$															X	X					X	X	X	X	X	X						X	
$NH_4NO_3^+$															X	X																	
NO_2^-																X					X	X	X	X	X	X	X	X	X		X	X	X
NO_3^-																					X	X	X	X	X				X				
Total Carbon, C_3^+																		X				X		X		X							
Hydrocarbon, C_3^+ AND C_3H^+ AND $C_3H_2^+$																					X	X		X		X							
Boron, B^+																																	
Mercury ,Hg^+																																	
SO_3^-																						X	X	X	X	X			X				X
HSO_3^-																							X	X	X	X							
SO_4^-																								X	X	X	X		X			X	
HSO_4^-																									X	X							
SO_3^- and SO_4^-																										X			X			X	X
PO_2^-																																	
PO_4^-																												X	X		X	X	
O^-																													X		X		
OH^-																															X		
Fluoride, F^-																																X	
Chloride, Cl^-																																	
Bromide, Br^-																																	

caesium signal correlated with fine organic carbon. As with rubidium, particles containing caesium correlated with lithium, amine-derived cations and anions containing sulfur.

Beryllium. Particles containing beryllium ($m/z = 9$ Da) were very infrequent ($<1\%$) and did not show any temporal trend. The only chemical species associated with beryllium in both fine and coarse particles were lithium and boron.

Magnesium and calcium. It was not possible reliably to distinguish peaks at $m/z = 24$, 25 and 26 Da arising from isotopes of magnesium from those from the common molecular ions C_2^+, C_2H^+ and $C_2H_2^+$. Therefore no data for magnesium can be presented. Likewise, the Ca^+ ion ($m/z = 40$ Da) coincides with the $NaOH^+$ and $C_3H_4^+$ ions. Although, $C_3H_4^+$ is not a common ion from hydrocarbons, the $NaOH^+$ ion is always observed in mass spectra of particles containing Na. During this campaign nearly all coarse particles contained Na so attempts to determine calcium *via* $m/z = 40$ NOT 36 (C_3^+) NOT 23 (Na^+) Da were unsuccessful.

Strontium. Strontium ($m/z = 88$ Da) was present in 2.4% and 3.8% of fine and coarse particles, respectively. Sea-salt particles play a role in the global distribution of strontium, and the strontium is often associated with calcium sulfate.[19] In this study fine and coarse particles containing strontium did indeed correlate with particles yielding the sulfur containing ions SO_3^-, SO_4^-, HSO_3^-, and HSO_4^-, and strontium correlated with chloride in coarse particles. Artaxo and Hansson[18] noted that strontium was associated with particles classed as biogenic

Table 4 Observed correlations between the number of coarse ($d > 2.5$ µm) particles per hour containing the specified pairs of ions. A filled square indicates $r^2 \geqslant 0.5$

	Sodium, Na$^+$	Potassium, K$^+$	Rubidium, Rb$^+$	Caesium, Cs$^+$	Beryllium, Be$^+$	Strontium, Sr$^+$	Barium, Ba$^+$	NH_4^+	CH_4N^+	$NH_3NH_4^+$	$C_2H_8N^+$	$C_5H_{12}N^+$	CH_4N^+ AND $C_2H_8N^+$ AND $C_5H_{12}N^+$	$NH_4NO_3^+$	NO_2^-	NO_3^-	Total Carbon, C_3^+	Hydrocarbon,C_3^+ AND C_3H^+ and $C_3H_2^+$	Boron, B$^+$	Mercury ,Hg$^+$	SO_3^-	HSO_3^-	SO_4^-	HSO_4^-	SO_3^- and SO_4^-	PO_2^-	PO_4^-	O^-	OH^-	Fluoride, F$^-$	Chloride, Cl$^-$	Bromide, Br$^-$	Iodide, I$^-$
Lithium,Li$^+$			×	×	×			×				×	×																				
Sodium, Na$^+$		×							×		×																						
Potassium, K$^+$									×		×					×																	
Rubidium, Rb$^+$				×				×				×	×					×															
Caesium, Cs$^+$								×	×		×	×					×	×															
Beryllium, Be$^+$																			×														
Strontium, Sr$^+$									×						×	×					×		×	×	×		×		×		×		
Barium, Ba$^+$												×	×																				
NH_4^+									×	×	×	×	×				×	×															
CH_4N^+											×	×			×	×	×																
$NH_3NH_4^+$																×	×																
$C_2H_8N^+$												×				×	×	×															
$C_5H_{12}N^+$													×				×	×															
CH_4N^+ AND $C_2H_8N^+$ AND $C_5H_{12}N^+$															×	×	×																
$NH_4NO_3^+$															×																		
NO_2^-																×					×		×	×	×		×	×	×		×		
NO_3^-																					×		×	×	×		×	×	×		×		
Total Carbon, C_3^+																		×															
Hydrocarbon, C_3^+ AND C_3H^+ AND $C_3H_2^+$																																	
Boron, B$^+$																																	
Mercury ,Hg$^+$																																	
SO_3^-																							×	×	×		×	×	×		×		×
HSO_3^-																										×							
SO_4^-																								×	×		×	×	×		×		×
HSO_4^-																									×		×	×	×		×		×
SO_3^- and SO_4^-																											×	×	×		×		×
PO_2^-																																×	
PO_4^-																												×	×		×		
O^-																													×		×		×
OH^-																															×		
Fluoride, F$^-$																																	
Chloride, Cl$^-$																																	
Bromide, Br$^-$																																	

and containing the elements phosphorus and potassium. In this study, coarse strontium containing particles correlated with the PO_4^- ion, but not with potassium.

Barium. Coarse and fine particles containing barium (m/z = 138 Da) were more prevalent when the site was impacted mainly by a dirty air mass. This is expected since the main source of barium in particles is crustal or vehicle emissions. Barium has been detected in Californian soil dust[14] and particles from the automobile emissions of light and heavy duty vehicles.[15] The latter was attributed mainly to vehicle, or more specifically, brake-wear.

Mercury. Particulate mercury was determined using m/z = 200 AND 202 Da and was detected in 0.4% and 0.2% of total fine and coarse particles, respectively. Although traditional filter sampling techniques have shown mercury containing particles at ground level, the occurrence of mercury in atmospheric particles detected at ground level was not reported by Murphy and Thomson[4] who also used a single-particle mass-spectrometer. In general, particles containing Hg did not correlate with any other species studied.

Boron. Particles containing boron (m/z = 11 Da) were rare and distributed evenly between fine and coarse particles (0.4% and 0.5%, respectively). Correlations existed between boron, lithium and beryllium in fine particles and between boron and beryllium in coarse particles. The source of the boron or the correlation is not known. Fogg and Duce[20] have suggested that sea-salt aerosol is a major source of atmospheric boron, however, the absence of a correlation between the occurrence of boron and sodium in coarse particles detected in this work does not support this. Murphy and Thomson[4] detected boron in 5% of the particles they analysed by a single particle mass spectrometer at Idaho hill, Colorado. The authors report that the presence of boron was always accompanied by a signal for the C^+ ion but was negatively correlated to elemental carbon, and uncorrelated with the signals for potassium and iron. It was not known whether the origin of the C^+ peak was organic or inorganic carbon.

Carbon containing particles. When Eskdalemuir was impacted with polluted air masses, a large proportion of the particles contained carbon. Particles containing elemental or organic carbon yielded characteristic positive mass spectra with progressions of C_n^+ and $C_nH_m^+$ ions, respectively. Values of n and m were typically 1–10 and 1–3, respectively. Similar, but weaker, progressions of ions were observed in the negative ion mode. The following combinations were tried as markers for total carbon: C^+ only, C_3^+ only, C^+ AND C_3^+ AND C_7^+. The marker C_3^+ proved most useful. The combinations: C^+ AND CH^+ AND CH_2^+, and C_3^+ AND C_3H^+ AND $C_3H_2^+$ were tried as markers for organic carbon, the C_3^+ AND C_3H^+ AND $C_3H_2^+$ series was found to be the most useful.

Fig. 4 shows the temporal variation of fine particles containing total carbon (defined using $m/z = C_3^+$) and hydrocarbon (defined using $m/z = C_3^+$ AND C_3H^+ AND $C_3H_2^+$). It is clear that when Eskdalemuir was subjected to a dirty continental air mass, characterised by a large increase in numbers of fine particles, the majority of the fine particles contained carbon. Noteworthy from Fig. 4 is the almost constant factor between the number of particles yielding C_3^+ and (C_3^+ AND C_3H^+ AND $C_3H_2^+$), reflected in the large correlation coefficients of $r^2 = 0.98$ (Fig. 5) and $r^2 = 0.82$ in fine and coarse particles, respectively. The difference in the number of particles containing C_3^+ and (C_3^+ AND C_3H^+ AND $C_3H_2^+$) is an indicator of the number of particles containing elemental carbon. The slope of Fig. 5 indicates that, on average, 37 ± 3% of carbon containing fine particles were organic carbon during the sampling period at Eskdalemuir. For coarse particles the proportion was 52 ± 8% (data not shown). Errors are 95% confidence intervals. These proportions correspond to EC/OC number ratios of 1.7 and 0.9 for fine and coarse particles, respectively. For comparison, Finlayson-Pitts and Pitts[21] quote EC/OC ratios of around unity, while Castro *et al.*[22] report EC/OC ratios for particles collected on quartz-fibre filters for urban and rural sites in the UK, Ireland and Portugal. Their maximum EC/OC value of 0.9 corresponded to conditions of low photochemical activity.

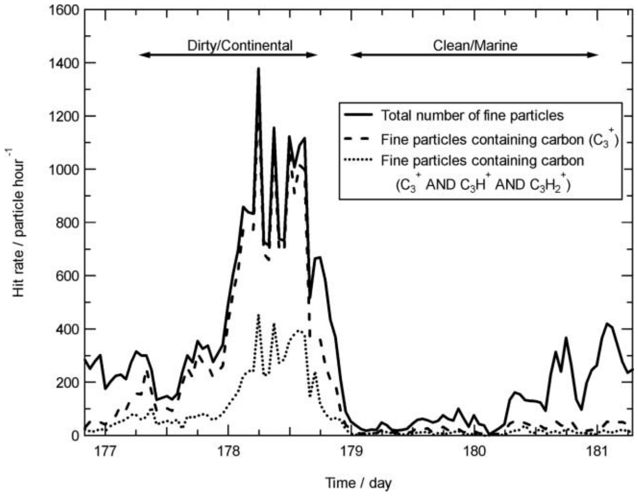

Fig. 4 The number of fine particles detected per hour containing total carbon (C_3^+) and organic carbon (C_3^+ and C_3H^+ and $C_3H_2^+$). The majority of fine particles during the dirty episode contained carbon.

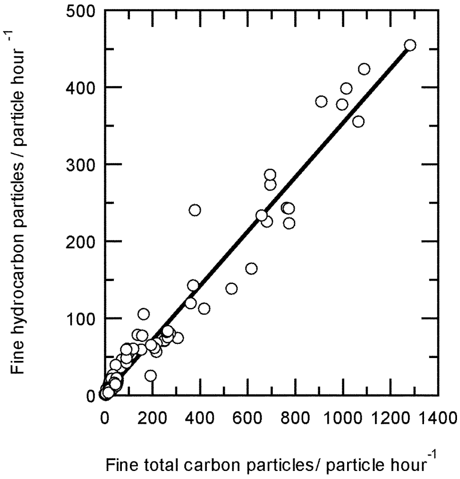

Fig. 5 A scatter plot of number of fine particles per hour containing total carbon (C_3^+) and organic carbon (C_3^+ AND C_3H^+ AND $C_3H_2^+$). $r^2 = 0.98$.

EC/OC ratios of 1.0 and 1.35 have been reported for the Los Angeles basin[23] and an urban area in Japan,[24] respectively. The value of EC/OC is generally lower during photochemical activity, and after long-range transport, due to increased gas to particle conversion from the oxidation of volatile organic compounds. The higher EC/OC ratio at Eskdalemuir for fine particles indicates atmospheric conditions not conducive to secondary organic aerosol formation. However the EC/OC ratios reported by the ATOFMS are number ratios, *i.e.* $\frac{n(\mathrm{EC})}{n(\mathrm{OC})}$, where n(EC) and n(OC) are the number of particles in an hourly period containing just elemental carbon or hydrocarbon respectively. Literature values of EC/OC ratios are often reported as a mass ratio recorded over periods from 24 h to 7 days, *i.e.* $\frac{m(\mathrm{EC})}{m(\mathrm{OC})}$ where m(EC) and m(OC) are the mass of elemental and organic carbon respectively. The ATOFMS data are, at present, subject to a size sampling bias. Nevertheless, the above analysis demonstrates the usefulness of the single-particle technique in distinguishing changes in EC/OC ratios with particle size in real time. The interesting question of the response of the ATOFMS to particles containing both organic and elemental carbon particles, say formed from the condensation of organic particles onto an elemental carbon core, would make an interesting future study.

The fine and coarse particles containing carbon correlated with nearly all the ammonium and amine species measured as well as the sulfur containing anions. A time-series plot for fine particles is shown in Fig. 6.

Ammonium nitrate. The proportions of fine and coarse particles containing NH_4NO_3 (m/z = 80 Da) were 3.5% and 9.3%, respectively. The number of fine particles yielding $NH_4NO_3^+$ increased during the period when air masses had passed over the UK. Tables 3 and 4 show that particles yielding $NH_4NO_3^+$ correlated with few other chemical components.

Ammonium. Ammonium ion was defined by m/z = 18 Da. Although this may also correspond to H_2O^+, mass spectra obtained by Thomson and Murphy[4] for wet salt particles generated in laboratory studies yielded little or no ions at 18 Da, so it is assumed that 18 Da observed in the field is primarily due to NH_4^+. This is corroborated by the strong correlation between the presence of m/z = 18 and m/z values corresponding to $NH_3NH_4^+$, CH_4N^+, and $C_5H_{12}N^+$ (Tables 3 and 4). Both Hughes *et al.*[25] and Whiteaker *et al.*[26] detected NH_4^+ in particles using ATOFMS instruments and found that the species was more prevalent in air that had passed over sources of ammonia in the Los Angles Basin and had stagnated. Carson *et al.*[27] showed that NH_4^+ is readily detected by mass

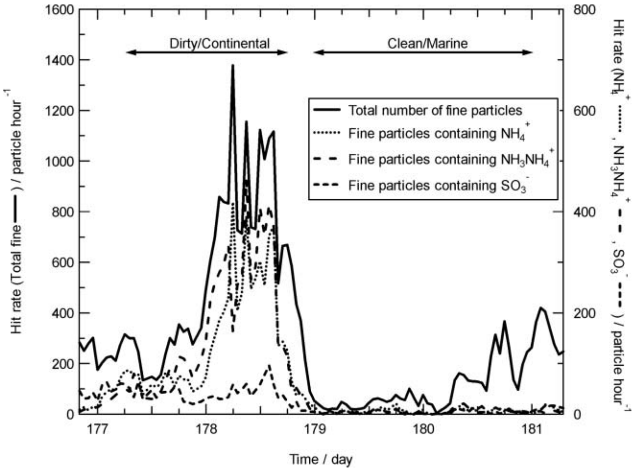

Fig. 6 The number of hourly occurrences of NH_4^+, $NH_3NH_4^+$ and SO_3^- ions in fine particles relative to hourly occurrence of total fine particles.

spectrometry when ammonium nitrate, deposited on the surface of particulate matter, is subject to laser-ablation. Fig. 6 demonstrates that the air mass which impacted on Eskdalemuir on day 178 and had travelled over the UK had acquired considerable ammonium on its journey en route. The source of ammonia could be agricultural and/or road traffic.

Amines. The *m*/*z* values of 58 and 86 Da were assigned to $C_3H_8N^+$ and $C_5H_{12}N^+$ ions, respectively. The occurrence of *m*/*z* = 30 Da was also considered, although this may be due to CH_4N^+ or to NO^+ ions, so the criterion *m*/*z* = 30 AND 58 AND 86 Da was taken to represent a signal for amines in general. The temporal profile of particles containing CH_4N^+ (or NO^+), $C_3H_8N^+$, $C_5H_{12}N^+$ was similar. Particles containing these ions would be expected to also give a signal for organic carbon and so the strong correlation of the amine signal with the organic carbon signal is expected.

Following their campaign at Idaho Hill, Murphy and Thomson[4] noted that the amine signals, reported as peaks in the positive ion mass spectrum at 18, 30, 58 and 88 Da, correlated with a wind direction that passed "over vegetated terrain from Denver urban areas and the large feedlots in eastern Colorado." Studies by Angelino *et al.*[28] and Silva and Prather[29] demonstrated that peaks at 86 Da arise from secondary and tertiary amines. The work by Angelino *et al.*[28] also demonstrated that strong amine signals arise from automotive exhausts from a busy freeway. Measurements of amines in the atmosphere have also been reported from agricultural[30] and marine[31] sources.[32] The data presented here are consistent with background coarse aerosol containing amines from a marine and/or agricultural origin.

3.3.2 Negative ions. *Fluorine.* Only 0.3% of particles contained fluorine (identified by *m*/*z* = −19). This is broadly in agreement with Murphy *et al.*[33] who report that only 1% of particles contained fluorine at a coastal site (Cape Grim, Tasmania). No data on the occurrence of fluorine are reported by Murphy and Thompson[34] in their inland study at Idaho Hill, Colorado. The fluoride at Eskdalemuir did not correlate with any other chemical component studied, making it difficult to suggest a source, although it is probably marine. Murphy *et al.*,[33] report that fluoride in particles at Cape Grim was correlated with O^- and OH^- ions but this was not observed here. Sources of fluorine in particulate matter have also been reported as coal burning,[35,36] brazing and welding,[37] and volcanoes.[38] The source at Eskdalemuir is not known.

Chlorine. Chlorine was determined using *m*/*z* = −35 Da, but NOT *m*/*z* = −37 Da because of ambiguity of the latter with C_3H^-. Chloride was present in 6.1% and 20.4% of fine and coarse particles analysed.

Murphy and Thomson[34] observed chloride in approximately 20% of all particles detected at Idaho hill, Colorado, in broad agreement with the Eskdalemuir data. An anti-correlation of chloride with nitrate is evidence of the reaction of HNO_3 with NaCl,[39]

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \qquad (1)$$

In this dataset, Cl^- in coarse particles correlated positively with NO_3^- (and with SO_4^-). However, Fig. 7 shows a plot of the ratio of the numbers of coarse particles containing NO_3^- and Cl^- with time, and indicates that, for the particles detected during the period when Eskdalemuir was impacted by dirty air, the chloride originally present in the particles had been exchanged, presumably by reaction (1), for nitrate. This is in agreement with studies using filters[40] and a single particle mass spectrometer.[41]

Bromine. The temporal trends of fine and coarse particles containing bromine (defined by *m*/*z* = −79 AND −81 Da) were similar, peaking in the mornings of day 177 and 181, and the evenings of days 178 and 179. Bromine was not detected at Idaho Hill, Colorado,[34] but was detected at a coastal site at Cape Grim, Tasmania.[33] Murphy *et al.*[33] suggested that bromide was not detected at Idaho Hill because it had been displaced from the particles by sulfate ions. These workers showed that, for particles at Cape Grim, a decrease in bromine signal corresponded to an increase in sulfate signal. Plotting the ratio of NO_3^- to Br^- and SO_4^- to Br^- *versus* time for the data here does suggest a high ratio of nitrate to bromide during the dirty air period and a low ratio of nitrate to bromide during the clean air periods, although the ratio of SO_4^- to Br^- does not demonstrate any trend. Reactions between nitrogen oxides and acids with NaBr and Br^- in sea water particles have been studied in the laboratory and are suggested to occur in the atmosphere.[21]

Iodine. Iodine (*m*/*z* = −127) was detected in only 0.7% and 1.2%, respectively, of fine and coarse particles analysed. Previous single particle studies of costal marine air have suggested that, in the presence of low sulfate, the amount of iodide in marine particles correlated with the organic content.[33,42] Anti-correlations between sulfate and iodide,

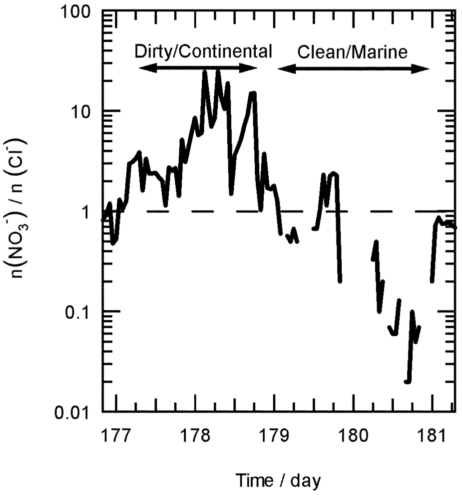

Fig. 7 The temporal trend in the ratio $\frac{n(NO_3^-)}{n(Cl^-)}$ of the number of coarse particles per hour containing nitrate and chloride. The ratio is greater than unity during the dirty period and less than unity during the clean period.

bromide and chloride have also been observed.[31] From an analysis of 5 years of aerosol data collected at Mace head, Ireland, Huang *et al.*[43] have suggested an additional source of iodine in particulate matter other than sea salt, while O'Dowd *et al.*[44] demonstrated that particle formation was possible from volatile organoiodine compounds of marine origin. In this work, the ratio of the number of coarse particles containing iodine to the number containing NO_3^- was unchanged throughout the campaign and the occurrence of iodine correlated with the occurrence of sulfate.

Nitrate (and nitrite). The NO_2^- ion ($m/z = -46$ Da) strongly correlates with the NO_3^- ($m/z = -62$ Da), although the ratio of number of particles with signals at −62 to −46 was not unity (Table 5) because of interference at $m/z = -62$ Da from the $C_5H_2^-$ ion. Using the criterion $m/z = -62$ NOT −60 considerably improved the −62 to −46 ratio (Table 5). In laboratory trials, nebulised solutions containing NO_3^- ions always yielded a strong signal at −46 as well as −62 Da. It is proposed that NO_2^- may be formed in the ablation process from NO_3^- anion in the aerosol and is indicative of NO_3^-. During the campaign a signal for nitrite was not observed without a signal for NO_3^-. Thus the signal at −46 Da appears to be a good marker for NO_3^-

Particles containing nitrate correlated strongly with particles containing sulfate.

Sulfur containing anions. The following sulfur containing anions were monitored: SO_3^- ($m/z = -80$ Da), HSO_3^- ($m/z = -81$ Da), SO_4^- ($m/z = -96$ Da) and HSO_4^- ($m/z = -97$ Da). The signal at $m/z = -80$ Da is almost certainly SO_3^-, but signals at −81, −96 and −97 Da may be Br^-, C_8^- and C_8H^-, respectively. Thus HSO_3^- was characterised in two ways, using −81 Da alone or −81 NOT −79 Da. The anion C_8^- (−96 Da) was not usually observed without C_7^- (−84 Da), so the presence of SO_4^- was inferred by comparing signals at −96 Da and −96 NOT −84 Da. However, the occurrence of the C_8^- ion was rare, so the difference between the two methods was negligible. Since the occurrence of the C_8H^- ion was likewise very rare, the signal at −97 Da was taken to indicate the presence of HSO_4^-.

SO_3^- and HSO_3^-. Fine particles containing SO_3^- and HSO_3^- were more prevalent during the first half of the measurement period. The number of particles giving a signal for SO_3^- and HSO_3^- increased markedly during the pollution event on day 178 (Fig. 6), and was not correlated with the signal from fine particles containing organic species.

SO_4^- and HSO_4^-. Fine particles containing SO_4^- were more numerous during the first half of the campaign and peaked during the polluted air mass on day 178. The number of fine particles containing HSO_4^- increased significantly during the polluted air mass influence, increasing from below 50 h^{-1} to over 200 h^{-1} during this period. In contrast, coarse particles containing SO_4^- and HSO_4^- peaked during the first few hours of the campaign and decreased throughout the remaining time.

Table 5 The ratio of the number of occurrences of $m/z = -62$ Da or $m/z = -62$ NOT −60 to $m/z = -46$ Da, for fine and coarse particles. A signal at $m/z = -46$ is assumed to indicate NO_2^-. A peak at $m/z = -62$ may indicate NO_3^- or $C_5H_2^-$. The latter can be accounted for using $m/z = -60$ (C_5^-)

m/z query used to detect presence of NO_3^-	Fine	Coarse
−62	0.78 ± 0.04	0.91 ± 0.07
−62 NOT −60	0.90 ± 0.06	1.00 ± 0.06

Phosphorus containing anions: PO_2^- and PO_4^-. The phosphorus containing anions PO_2^- and PO_4^- were monitored using $m/z = -63$ and −95 Da, respectively. The latter is believed to be free from interference but PO_2^- may have interference from $C_5H_3^-$. However, carbonaceous particles did not usually yield extensive negative ion mass spectra so the C_5^- ion was considerably less common then the C_5^+ ion and monitoring particles containing PO_2^- using −63 Da alone, or −63 NOT −60 Da gave very similar results. Attempts to monitor the PO_3^- anion at $m/z = -79$ Da were unsuccessful due to interferences from Br^-.

Phosphates have been detected in Californian soil dust,[14] and have also been attributed to industrial sources.[45,46] However, Artaxo and Hansson[18] apportioned phosphorus to a biogenic source in a forested area. Particulate lipid phosphorus is found in coastal waters[47] and could be transferred to the atmosphere by wave motion and bubble bursting. In this study, fine and coarse particles giving rise to PO_4^- ions had different temporal patterns to those giving rise to PO_2^- ions. The trends in the occurrence of PO_2^- and PO_4^- seem to indicate that either the two species have different sources or that one of the signals is better representing a separate, unidentified species.

O^- and OH^-. Peaks at $m/z = -16$ and −17 Da were assigned to O^- and OH^- ions respectively. The peaks commonly (but not always) appeared in conjunction with oxy-anions such as sulfate. Fine and coarse particles giving rise to O^- and OH^- ions tended to peak in number at the same times.

4. Conclusions

The deployment of the aerosol time of flight mass spectrometer at the remote inland site of Eskdalemuir, southern Scotland, has yielded unprecedented time-resolution of the chemical composition of the UK remote background aerosol under two distinct air mass regimes: marine, and air masses that had passed slowly over the UK. The number of fine particles was very considerably elevated during the latter air mass type. Allowing for any sensitivity bias, one in three of all fine particles containing carbon consisted of organic carbon (hydrocarbon). The proportion for coarse particles containing carbon was one in two.

Analysis of these single-particle data shows that an air mass with marine origin that passes slowly over UK agricultural land accumulated amines and ammonium, when compared with air masses that had not. In addition, the ratio between the numbers of coarse particles containing nitrate or chloride anions was shown to be greater than unity for an air mass that travelled over the UK and less than unity for direct marine air masses, providing evidence for chloride displacement from sea-salt particles by acidic gases. Similar ratios for bromide and iodide to nitrate suggested similar but less conclusive behaviour to chloride.

The ATOFMS has particular advantage in detecting the lighter elements lithium, beryllium and boron which are not usually detected by conventional analytical methods in filter pack sampling. Although rare, these elements, when detected using the ATOFMS in these UK air masses, were generally correlated, perhaps suggesting an unusual source not previously recognised.

Acknowledgements

The EPSRC provided financial support for this project. We are grateful to J. Riddick, E. Scott and D. Kerridge of the British Geological Survey for access and assistance at the Eskdalemuir site. We also acknowledge use of the British Atmospheric Data

Centre (BADC) and the data supplied to it by the European Centre for Medium range Weather Forecasts (ECMWF).

References

1 Airborne Particles Expert Group (APEG), Source apportionment of particulate matter in the United Kingdom, DETR, HMSO, London, 1999.
2 C. A Noble and K. A. Prather, *Environ. Sci. Technol.*, 1996, **30**, 2667.
3 C. A. Noble and K. A. Prather, *Geophys. Res. Lett.*, 1997, **24**, 2753.
4 D. M. Murphy and D. S. Thomson, *J. Geophys. Res.*, 1997, **102**, 6341.
5 A. Trimborn, K. P. Hinz and B. Spengler, *Aerosol Sci. Tech.*, 2000, **33**, 191.
6 J. T. Jayne, D. C. Leard, X. F. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb and D. R. Worsnop, *Aerosol Sci. Tech.*, 2000, **33**, 49.
7 R. V. Mallina, A. S. Wexler, K. P. Rhoads and M. V. Johnston, *Aerosol Sci. Tech.*, 2000, **33**, 87.
8 M. J. Coggiola, Z. Shi and S. E. Young, *Aerosol Sci. Tech.*, 2000, **33**, 20.
9 W. D. Reents and M. J. Schabel, *Anal. Chem.*, 2001, **73**, 5403.
10 J. O. Allen, D. P. Fergenson, E. E. Gard, L. S. Hughes, B. D. Morrical, M. J. Kleeman, D. S. Gross, M. E. Galli, K. A. Prather and G. R. Cass, *Environ. Sci. Technol.*, 2000, **34**, 211.
11 K. R. Neubauer, M. V. Johnston and A. S. Wexler, *Int. J. Mass Spectrom.*, 1995, **151**, 77; K. R. Neubauer, M. V. Johnston and A. S. Wexler, *Atmos. Environ.*, 1998, **32**, 2521; D. S. Thomson and D. M. Murphy, *Appl. Optics*, 1993, **32**, 6818; P. G. Carson, M. V. Johnston and A. S. Wexler, *Rapid. Commum. Mass. Spectrom.*, **11**, 993; A. C. Lazar, P. T. A. Reilly, W. B. Whitten and J. M. Ramsey, *Anal. Chem.*, 2000, **72**, 2142; B. A. Mansoori, M. V. Johnston and A. S. Wexler, *Anal. Chem.*, 1994, **66**, 3681; B. A. Mansoori, M. V. Johnston and A. S. Wexler, *Anal. Chem.*, 1996, **68**, 3595.
12 P. V. Bhave, M. J. Kleeman, J. O. Allen and L. S. Hughes, *Environ. Sci. Technol.*, 2002, **36**, 2154.
13 D. S. Gross, M. E. Galli, P. J. Silva and K. A. Prather, *Anal. Chem.*, 2000, **72**, 416.
14 P. J. Silva, R. A. Carlin and K. A. Prather, *Atmos. Environ.*, 2000, **34**, 1811.
15 D. S. Gross, M. E. Galli, P. J. Silva, S. H. Wood, D. Y. Liu and K. A. Prather, *Aerosol Sci. Tech.*, 2000, **32**, 152; R. M. Harrison, R. Tilling, M. S. Callén Romero, S. Harrad and K. Jarvis, *Atmos. Environ.*, 2003, **37**, 2391.
16 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1989.
17 P. J. Silva, D. Y. Liu, C. A. Noble and K. A. Prather, *Environ. Sci. Technol.*, 1999, **33**, 3068.
18 P. Artaxo and H. C. Hansson, *Atmos. Environ.*, 1995, **29**, 393.
19 C. E. Whipkey, R. C. Capo, O. A. Chadwick and B. W. Stewart, *Chem. Geol.*, 2000, **168**, 37.
20 T. R. Fogg and R. A. Duce, *J. Geophys. Res.*, 1985, **90**, 3781.
21 B. J. Finlayson-Pitts and J.N. Jr. Pitts, *Chemistry of the upper and lower atmosphere: theory, experiments and applications*, Academic Press, 2000.
22 L. M. Castro, C. A. Pio, R. M. Harrison and D. J. T. Smith, *Atmos. Environ.*, 1999, **33**, 2771.
23 B. J. Turpin and J. J. Huntzicker, *Atmos. Environ.*, 1995, **29**, 3527.
24 S. Kadowaki, *Environ. Sci. Technol.*, 1990, **24**, 741.
25 L. S. Hughes, J. O. Allen, P. Bhave, M. J. Kleeman, G. R. Cass, D. Y. Liu, D. F. Fergenson, B. D. Morrical and K. A. Prather, *Environ. Sci. Technol.*, 2000, **34**, 3058.
26 J. R. Whiteaker, D. T. Suess and K. A. Prather, *Environ. Sci. Technol.*, 2002, **36**, 2345.
27 P. G. Carson, M. V. Johnston and A. S. Wexler, *Aerosol Sci. Tech.*, 1997, **26**, 291.
28 S. Angelino, D. T. Suess and K. A. Prather, *Environ. Sci. Technol.*, 2001, **35**, 3130.
29 P. J. Silva and K. A. Prather, *Anal. Chem.*, 2000, **72**, 3553.
30 G. W. Schade and P. J. Crutzen, *J. Atmos. Chem.*, 1995, **22**, 319.
31 A. van Neste, R. A. Duce and C. Lee, *Geophys. Res. Lett.*, 1987, **14**, 711.
32 K. Gorzelska and J. N. Galloway, *Global Biogeochemical Cycles.*, 1990, **4**, 309.
33 D. M. Murphy, D. S Thomson and A. M. Middlebrook, *Geophys. Res. Lett.*, 1997, **24**, 3197.
34 D. M. Murphy and D. S. Thomson, *J. Geophys. Res.*, 1997, **102**, 6353.
35 M. Ando, M. Tadano, S. Yamamoto, K. Tamura, S. Asanuma, T. Watanabe, T. Kondo, S. Sakurai, R. D. Ji, C. Liang, X. Q. Chen, Z. Hong and S. Cao, *Sci. Total Environ.*, 2001, **271**, 107.
36 Y. Zhang and S. R. Cao, *Fluoride*, 1996, **29**, 207.
37 A. T. Zimmer and P. Biswas, *Am. Ind. Hyg. Assoc. J.*, 2000, **61**, 351.
38 A. G. Allen, P. J. Baxter and C. J. Ottley, *Bull. Volcanol.*, 2000, **62**, 8.
39 R. Vogt, P. J. Crutzen and R. Sander, *Nature*, 1996, **383**, 327.
40 L. M. McInnes, D. S. Covert, P. K. Quinn and M. S. Germani, *J. Geophys. Res.*, 1994, **99**, 8257.
41 E. E. Gard, M. J. Kleeman, D. S. Gross, L. S. Hughes, J. O. Allen, B. D. Morrical, D. P. Fergenson, T. Dienes, M. E. Galli, R. J. Johnson, G. R. Cass and K. A. Prather, *Science*, 1998, **279**, 1184.
42 A. M. Middlebrook, D. M. Murphy and D. S. Thomson, *J. Geophys. Res.*, 1998, **103**, 16475.
43 S. Huang, R. Arimoto and K. A. Rahn, *Atmos. Environ.*, 2001, **35**, 1421.
44 C. D. O'Dowd, J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hameri, L. Pirjola, M. Kulmala, S. G. Jennings and T. Hoffmann, *Nature*, 2002, **417**, 632.
45 C. Migon, V. Sandroni and J. P. Bethoux, *Mar. Environ. Res.*, 2001, **52**, 413.
46 E. Ganor, Z. Levin and R. Van Grieken, *Atmos. Environ.*, 1998, **32**, 1631.
47 M. Suzumura and E. D. Ingall, *Mar. Chem.*, 2001, **75**, 141.