

Comparison of analytical results for chloride, sulfate and nitrate obtained from adjacent ice core samples by two ion chromatographic methods

T. Kekonen,^{*a,b} P. Perämäki^b and J. C. Moore^a

^aArctic Centre, University of Lapland, P.O. Box 122, FIN-96101 Rovaniemi, Finland.

E-mail: teija.kekonen@oulu.fi; Fax: +358-8-5531603

^bDepartment of Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 Oulu, Finland

Received 10th June 2003, Accepted 6th November 2003

First published as an Advance Article on the web 15th December 2003

The anions chloride, sulfate and nitrate in nearly 500 pairs of ice core samples from the same depth were determined in a 121 m long ice core from Svalbard. The analyses were performed separately using an ion chromatograph with Dionex AS9 and AS15 columns with Na₂CO₃ and NaOH eluents. Results showed a small (5–6 µg l⁻¹) but statistically significant difference in mean concentrations for chloride and sulfate but not for nitrate. 2% of the data indicate real differences in concentrations across the ice core. Despite these differences ion information in ice core layers are comparable for ice core paleoclimate and environmental studies even though analyses are made using two different procedures.

1. Introduction

The layers of an ice core contain a unique record of the chemical composition of the past atmosphere. Ice core data are widely used to understand environmental and climate processes in the past.¹ Ionic species especially give valuable information as they have many different sources. Water soluble ions have both natural and anthropogenic origins, and are mainly derived from marine, terrestrial, biogenic and gaseous sources. In many Arctic ice cores, anion analysis has shown a clear anthropogenic input from the middle of the 20th century.^{2–4}

Ion chromatography exhibits high sensitivity and is well suited for the analysis of low concentrations of soluble ions in ice core samples without pretreatment.^{5–8} Various ion chromatographic techniques using different columns, eluents and methods (gradient, isocratic, suppressed, non-suppressed) have been used in glaciochemical analyses,^{9–11} and recently a continuous flow injection system has been used in ion determinations.¹² To get reasonable detection limits for all ions using a continuous melting device, separations and detections must be achieved using ion chromatographs.

Adjacent samples from an ice core at the same depth (Fig. 1) are generally assumed to give the same information even though the concentrations of ions are extremely low, and the effects of snow accumulation, snow drifting and partial melting are known to vary over lengths comparable to the diameter of an ice core (~10 cm). Differences in individual samples are important for understanding ice physical chemistry, but longer term trends are the most essential for paleoclimate studies. To achieve a good ice core time-scale and to enable a determination of other parameters from the same ice core with comparable resolution, only small sample volumes are available for ion analyses. Therefore duplicate ion analyses from samples at the same depth are not normally done. Inter-laboratory comparisons of only a few meters of ice core samples have been reported,¹³ and show no significant differences between individual samples. No results from a relatively long ice core comparison have been published earlier.

In this paper we compare the results obtained for a large number ($n = 493$) of adjacent ice core samples of the lowest 60 m of the 121 m long ice core (Fig. 1). The aim of this paper is to clarify whether there are any significant differences in the results from the adjacent samples when the analyses are made

using different procedures. After cleaning the surface of the ice core determinations of adjacent ice core, samples were performed separately using different columns and eluents. Both analyses were carried out using a single isocratic elution with the suppressed technique.

2. Experimental

2.1 Reagents and standards

All standard solutions, control samples and eluents were made in ultra pure water prepared daily with a Millipore Milli-Q water purification system. Sodium carbonate (Na₂CO₃, Merck Pro Analyti) was used for the preparation of the 9 mM sodium carbonate eluent. Sodium hydroxide (NaOH, Merck Pro Analyti) from Merck was used to prepare 38 mM eluent solution. Eluents were degassed using an ultrasonic bath (Fritsch) for 15 min and kept under nitrogen gas pressure during analysis. Six anion calibration standard solutions were prepared by diluting 1000 mg l⁻¹ commercial stock standard solutions (Merck). Mixed control solutions (combined five anion standard, Dionex, 37157) were diluted daily to obtain concentrations near real sample concentrations. All the calibration standard and control solutions were prepared in a clean room under a laminar flow hood (Kojair). Concentration levels of standard solutions and control samples were chosen to be similar to those in the upper part of the core. Finnipette Variabels were used to deliver all the solutions.

2.2 Sample collection and preparation before analyses

The 121 m long ice core was drilled on Lomonosovfonna in Svalbard,¹⁴ in spring 1997 by a multinational drilling team. All samples were transported in a frozen state from Svalbard and stored in a cold room (-22 °C) at Norwegian Polar Institute in Tromsø and then transported to the Rovaniemi Research Station of the Finnish Forest Research Institute. Artificial cores were also made by freezing ultra pure water and processed in the same manner as the real ice core. Ice core sampling and cleaning was done in a cold room under a laminar flow hood (Kojair) with strict contamination control as described elsewhere.¹⁵

All the sample vials and caps (Dionex), bottles and other

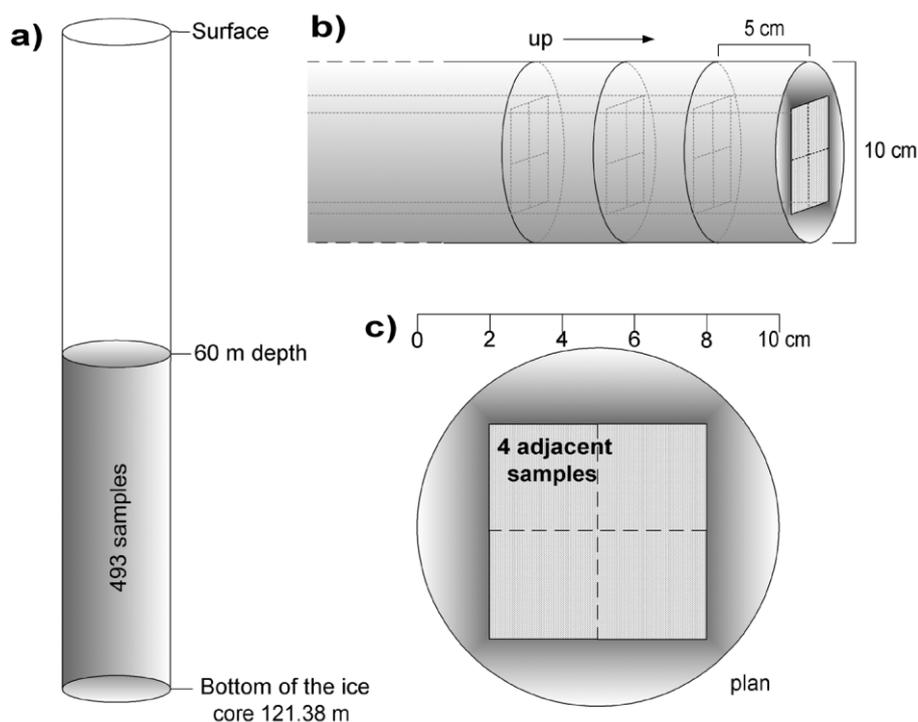


Fig. 1 (a) The whole ice core. Samples discussed here were taken between 60 m depth and the bottom of the core. (b) The 10 cm diameter ice core was first cut into 5 cm long pieces. (c) The outer part of the core was then removed and the inner part cut into 4 adjacent samples.

containers were cleaned using ultra pure water (Millipore Milli-Q water). All the equipment was rinsed twice with ultra pure water and left to soak over 24 h. Then the equipment was placed in an ultrasonic bath (Fritsch) for 15 min and rinsed three times with ultra pure water. Prior to use all the equipment was rinsed once again and dried under the laminar flow hood. The ice core was first cut into 5 cm sections along its length, then the outer (possibly contaminated part) removed and the inner part then subsampled into 4 pieces (Fig. 1). The pairs of samples discussed here were randomly selected from the four spanning the same depth range. Melted sample volume was about 5–10 ml. Samples were melted, standard solutions and control samples were prepared and placed in the auto sampler under the laminar flow hood just before analyses to prevent contamination. Clean suits, masks and plastic gloves were worn in the cold and clean rooms at all times during sampling and preparation of the samples and standard solutions. During the analysis the clean laboratory was kept unoccupied.

2.3 Instrumentation and sample analysis

Ion determinations were made using a Dionex Dx-120 ion chromatograph with conductivity detector housed in a clean laboratory under a laminar flow hood. Three major anions (Cl^- , NO_3^- , SO_4^{2-}) in the ice core samples were analysed by direct injection and isocratic elution as described below:

In the first part of the study one half of paired samples was analysed in random depth order using a Dionex IonPac AG9-HC (4×50 mm) guard column and a Dionex IonPac AS9-HC (4×250 mm) separator column with 20 min runs. The sample loop volume was 500 μl and 9 mM sodium carbonate (Na_2CO_3) eluent was used. The flow rate of the eluent was 1.2 ml min^{-1} . Anions were analysed *via* suppressed ion chromatography. The suppression was performed by a Dionex Anion Self-Regenerating Suppressor (ASRS-ULTRA). The current output level of the suppressor was 50 mA.

In the second part of the study major anions in the other half of the paired samples were analysed in random depth order *via* suppressed chromatography with a Dionex IonPac AG15 (4×50 mm) and AS15 (4×250 mm) columns with 15 min runs.

The 2 ml sample loop and 38 mM sodium hydroxide (NaOH) eluent was used. The flow rate of the eluent was 1.6 ml min^{-1} . The current output level of the suppressor was 300 mA. An external room temperature water flow was also used through the suppressor to get ultra low detector electronic noise. The anions were eluted in the same run in a reasonable time without gradient elution.

Samples were introduced into the instrument *via* AS40 Automated Samplers, using 5 ml Poly Vials with plain caps. Instrument control was performed and all the chromatograms were collected and elaborated by a personal computer and Dionex PeakNet chromatography software. Correlation coefficients above 0.999 were obtained for all anions with the linear calibration equations based on peak area.

3. Result and discussion

3.1 Comparison of different methods on adjacent samples

The first run sequence was made using the AS9 column that separated anions in the order: chloride, nitrate and sulfate (Fig. 2a). The AS15 column separated anions in the different order: chloride, sulfate and nitrate (Fig. 2b). Separation between all the measured peaks was good. Even a very high sulfate peak at the depth of 66.8 m (the Icelandic volcanic eruption Laki 1783) did not disturb the determination of other anions. The detector electronic noise conductivities were 0.009 μS and 0.002 μS for the methods employing columns AS9 and AS15, respectively. With the AS15 column the noise conductivity was lower and the sensitivity was better (Fig. 2a and 2b). Therefore the AS15 column has a better detection limit than the AS9 column (Table 1). Anion concentrations measured for artificial core samples were zero or negligible with both the columns used. Analyses of control samples showed good agreement with certified values for all the anions.

Theoretically ion chromatography results are expected to be heteroscedastic, lognormally distributed at high concentrations. However, in this paper we examine concentration differences, a plot of the concentrations found by the two methods plotted against each other shows that errors are not

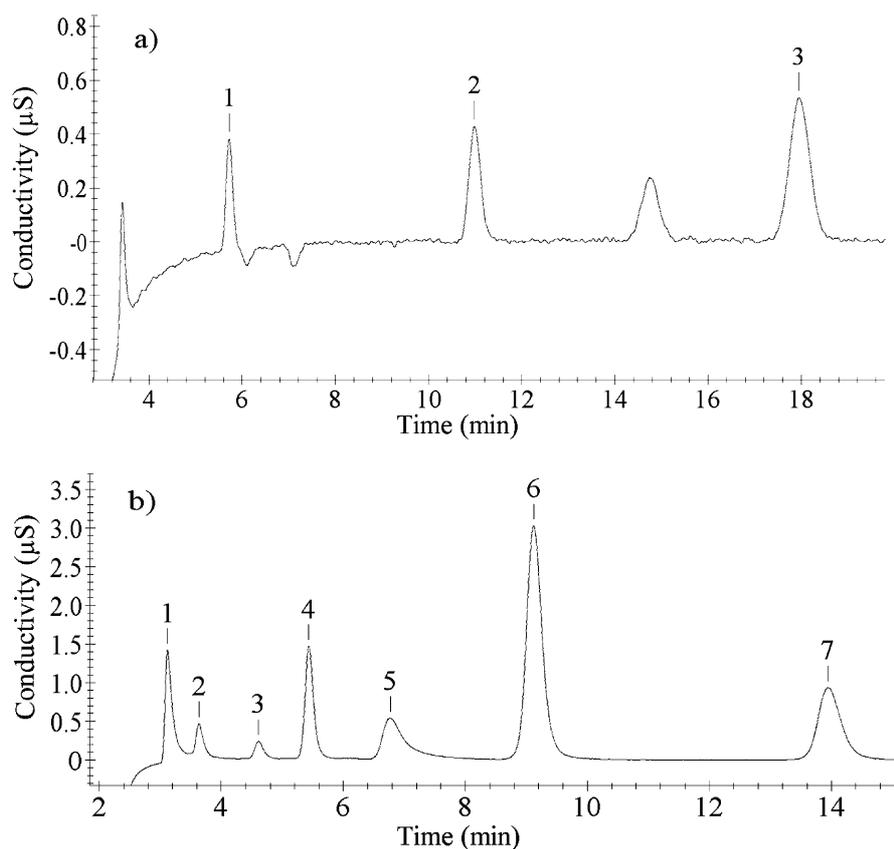


Fig. 2 (a) An example anion chromatogram of a control sample using the AS9 column and a 500 µl sample loop. Spiked concentrations of chloride (1), nitrate (2) and sulfate (3) anions were 30 µg l⁻¹, 100 µg l⁻¹ and 150 µg l⁻¹, respectively. (b) An example anion chromatogram of a control sample using the AS15 column and a 2 ml sample loop. Spiked concentrations of chloride (4), sulfate (6) and nitrate (7) anions were 30 µg l⁻¹, 150 µg l⁻¹ and 100 µg l⁻¹, respectively. Detailed experimental conditions are given in the experimental section.

Table 1 Descriptive statistics of the deepest half (60 m) of the 121 m long ice core for the three selected anions and columns

	Cl ⁻ /µg l ⁻¹		SO ₄ ²⁻ /µg l ⁻¹		NO ₃ ⁻ /µg l ⁻¹	
Column	AS15	AS9	AS15	AS9	AS15	AS9
Number of samples	493	493	491	491	493	493
Mean concentration	272.8	266.4	109.9	115.3	38.45	38.95
Median concentration	259.1	248.5	87.52	97.88	35.38	35.07
Minimum concentration ^a	35.23	32.40	14.29	9.29	6.92	8.67
Maximum concentration ^b	795.9	881.6	800.4	786.8	157.8	138.9
Detection limit ^c	0.10	1.65	0.01	7.83	0.58	6.37

^a Minimum value is the smallest detectable value. ^b Sulfate concentrations exclude two samples at the Laki peak. ^c Detection limit is a concentration corresponding of signal to noise ratio equal to three. All concentrations are given in µg l⁻¹.

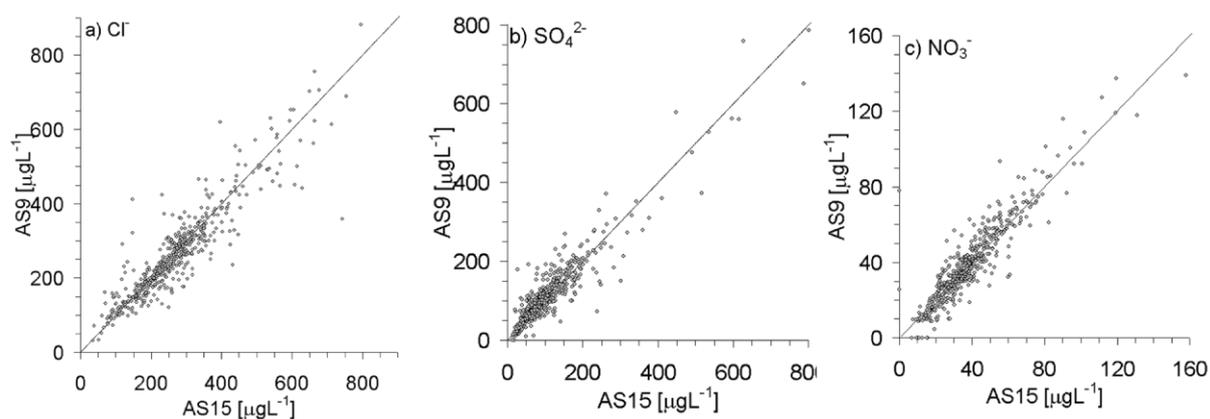


Fig. 3 AS9 versus AS15 concentrations with a line of equality for (a) chloride, (b) sulfate and (c) nitrate. Sulfate concentrations exclude two samples at the Laki peak.

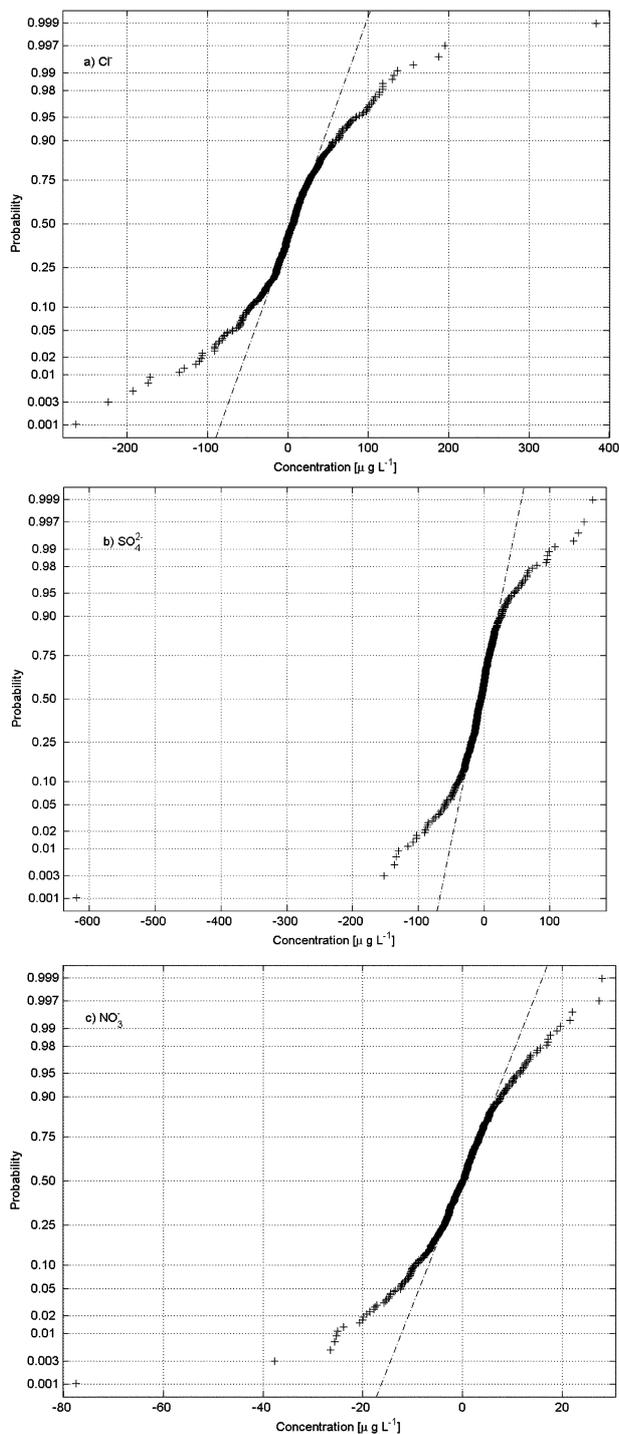


Fig. 4 Normal probability plots of (a) chloride, (b) sulfate and (c) nitrate concentration differences obtained for adjacent samples with the AS15 and AS9 columns, the straight dashed line shows the line joining the first and third quartiles extrapolated to the ends of data. Normally distributed data will lie on a straight line. Detailed statistics are shown in Table 2.

heteroscedastic to a reasonable approximation (Fig. 3). Therefore in this study we use raw data instead of logarithmic transformed data. We also did a full analysis of log transformed data but as the results were very similar they are not presented here.

Descriptive statistics are presented in Table 1, Kolmogorov–Smirnov testing of the two methods shows no significant difference between the results found by the two methods, despite the different detection limits. The Normal probability plots (Fig. 4) and statistics in Table 2 show that the concentration difference probability distributions are not Normal. However this is largely a result of a few sample pairs having

Table 2 Statistics for adjacent ice core samples of the whole data set (a) and for the subset of samples excluding those with more than three standard deviations (3σ) differences in concentrations (b). Differences are AS15–AS9

	Cl ⁻		SO ₄ ^{2-d}		NO ₃ ⁻	
	a	b	a	b	a	b
Number of samples	493	484	491	478	493	485
Mean difference ^a	6.4	6.7	-5.4	-5.0	-0.50	-0.17
Standard deviation ^b	51	41	34	27	8.3	6.8
Paired <i>t</i> -test	2.8	3.6	-3.4	-4.2	-1.4	-0.76
Kurtosis ^c	9.4	1.4	5.6	2.4	16	1.1
Skewness	0.31	0.020	0.29	-0.25	1.9	-0.064

^a Mean difference is shown per sample. ^b Standard deviation is calculated for adjacent sample differences. ^c A kurtosis of one is expected for a normal distribution. ^d Sulfate concentrations exclude two samples at the Laki peak. All concentrations are given in µg l⁻¹.

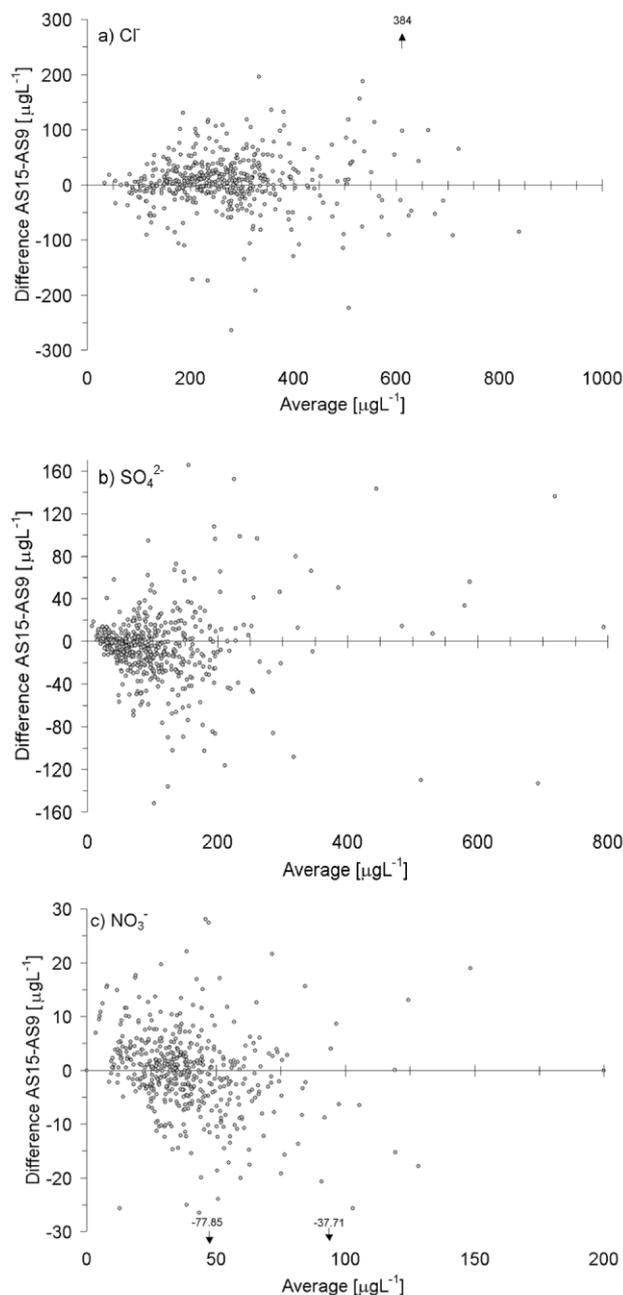


Fig. 5 Concentration differences between two methods for (a) chloride, (b) sulfate and (c) nitrate plotted against the mean concentration found by both methods. Sulfate concentrations exclude two samples at the Laki peak.

very large differences in concentrations leading to large kurtosis in the distributions (Table 2). It is possible that reporting errors or mislabeling samples may contribute to some of these outliers, however, as mentioned earlier there are glaciological reasons why concentrations may be actually different in samples from the same depths. For the purposes of comparing the two methods we assume that sample pairs with differences greater than 3σ are not due to random errors in the analysis (which we could expect to occur only 4–5 times in all the 1477 analyses (0.3%) if errors were Normally distributed). Using this criterion we remove 9 samples from chloride data, 13 from sulfate and 8 from nitrate, in total 2% of analyses. These samples are discussed later. The statistics for the remaining samples shown in Table 2 columns b are close to Normally distributed.

Comparison of the results of the adjacent samples in the same depth was carried out using a paired t -test (Table 2) of the mean concentrations. The null hypothesis being that there is no

difference between adjacent samples. The calculated t -values are significant at the 1% level for both sulfate and chloride. Null hypothesis can be accepted only for nitrate and it can be concluded that concentrations for adjacent samples do not differ. For chloride and sulfate the null hypothesis is not acceptable.

To investigate the differences in the methods further, we show differences between two methods against their average (Fig. 5). Both positive and negative differences were found over the full range of concentrations, concentration differences do not increase with average concentration, and the distribution of the large concentration differences appear random. Fig. 5 shows that there is no great difference between the methods in terms of determining ion concentrations over a wide range of concentrations, despite the small but significant difference in mean concentrations measured.

Anion profiles along the ice core of adjacent sample pairs obtained with the two different analytical procedures show

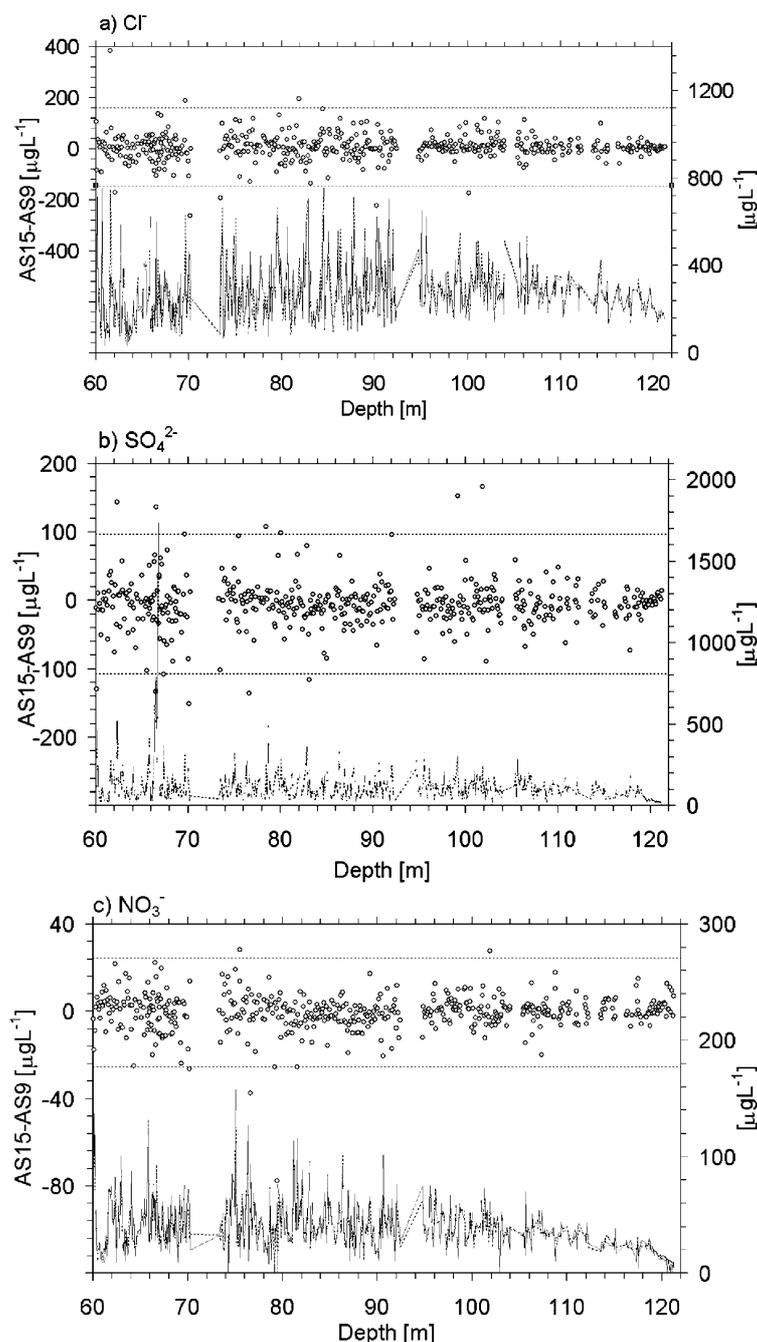


Fig. 6 (a) Chloride, (b) sulfate and (c) nitrate concentrations using the AS9 column (solid line) and AS15 column (dotted line), right hand axis. Concentration differences between columns (circles), left hand axis, horizontal lines indicate 3σ levels.

excellent agreement (Fig. 6) despite their different detection limits. Changes in concentrations happen at exactly the same depth even though the concentrations in adjacent samples are not exactly equal.

3.2 Samples with large concentration difference

The 2% of samples having high concentration differences ($>3\sigma$) between the adjacent samples could be a result of real glaciological effects, or simply due to errors in recording or contamination. The methodology we use should make recording errors very unlikely as all 4 samples were kept in the same container from cutting until immediately prior to analysis. As a check on the statistics of mislabeling analysis vials we can compare the known error rate of 1 in 273 (0.4%) found for labeling the original drilled ice cores. From our experience in ice core analyses this seems a plausible error rate, certainly much less than the 2% of samples we observe with high concentration differences. As samples were analyzed in depth-random order, we would expect accidental sample contamination to be reflected in random distribution of outliers with depth.

The depth distributions of the high concentration differences are not random (Fig. 6). No high concentration differences in any anions were found in the lowest one third (20 m) of the core. Half of the high sulfate concentration differences were between 60 and 70 m. All except two of the high nitrate concentration differences were in samples between 70 and 80 m. Chloride concentration differences appear random over the interval 60–100 m. Only one sample at 70 m had high concentration differences in all anions. Therefore we must look for glaciological reasons for the large concentration differences. Small concentration differences in the lowest parts of the core indicate that anions are better mixed as may be expected as they have had the longest time for diffusion processes to act. The most striking single event recorded in the core is the large volcanic eruption signature of Laki (Iceland, 1783) seen as the high sulfate peak at 66.8 m depth (Fig. 6). It is tempting to attribute the eruption as the cause of the large number of sulfate outliers between 60 and 70 m depth, though the detailed mechanism can only be speculated upon at present. The eruption seems to have had no impact on chloride or nitrate concentrations. Nitrate is known to be preferentially co-located with particles in ice cores,² and as particles are highly inhomogeneously distributed within ice,^{1,16} it is not unreasonable that a few nitrate samples show very high differences in concentration between adjacent samples.

4. Conclusion

The results clearly prove that despite differences between ion chromatographic methods and some real differences in adjacent samples, long-term ion profiles with two methods give comparable information. Single adjacent samples do not store exactly the same concentration but still provide reasonably comparable results for time series analyses and can be used to detect chemical composition of the atmosphere in the past. Our results show that nitrate in general has the closest

correspondence between two samples from the same depth. This may be expected as nitrate is known to be rather mobile both within the ice and also while near the snow surface due to post-depositional processes.¹⁶ Our results show that there is a statistically significant difference in mean concentrations between two different columns for chloride and sulfate ($5\text{--}6\ \mu\text{g l}^{-1}$). The AS9 column also has a much higher detection limit than the AS15 column and therefore we recommend using the AS15 for isocratic ice core work. Only 2% of the data show such large differences in concentration that must be accounted for by concentrations variations in the ice core. These large concentration gradients across the ice core may be due to chemical species being adsorbed onto particle surfaces. This confirms that despite differences in sensitivity and small-scale inhomogeneity in chemistry the information in ice core layers are comparable even though analyses are made using two different procedures.

Acknowledgements

The comments of referees and editors improved the manuscript considerably. We gratefully thank the Lomonosovfonna ice core 1997 field group and all the people involved in this project. The Finnish Forest Research Institute Research Station in Rovaniemi is gratefully acknowledged for cold and clean room facilities. The Finnish Academy Figare project provided financial support.

References

- 1 M. Legrand and P. Mayewski, *Rev. Geophys.*, 1997, **35**, 219.
- 2 T. Kekonen, J. Moore, R. Mulvaney, E. Isaksson, V. Pohjola and R. S. W. van de Wal, *Ann. Glaciol.*, 2002, **35**, 261.
- 3 R. M. Koerner, D. A. Fisher and K. Goto-Azuma, *Atmos. Environ.*, 1999, **33**, 347.
- 4 K. Goto-Azuma and R. M. Koerner, *J. Geophys. Res.*, 2001, **106**, 4959.
- 5 J. P. Ivey and D. M. Davies, *Anal. Chim. Acta.*, 1987, **194**, 281.
- 6 J. Ivask and J. Pentchuk, *J. Chromatogr.*, 1997, **A 770**, 125.
- 7 M. Legrand, M. DeAngelis and R. J. Delmas, *Anal. Chim. Acta.*, 1984, **156**, 181.
- 8 M. R. Legrand and R. J. Delmas, *NATO ASI Ser. C*, 1987, **211**, 225.
- 9 R. Udisti, S. Bellandi and G. Piccardi, *Fresenius' J. Anal. Chem.*, 1994, **349**, 289.
- 10 C. F. Buck, P. A. Mayewski, M. J. Spencer, S. Whitlow, M. S. Twickler and D. Barrett, *J. Chromatogr.*, 1992, **594**, 225.
- 11 J. Ivask and M. Kaljurand, *J. Chromatogr.*, *A*, 1999, **844**, 419.
- 12 T. M. Huber, M. Schwikowski and H. W. Gäggeler, *J. Chromatogr.*, *A*, 2001, **920**, 193.
- 13 M. A. J. Curran and A. S. Palmer, *J. Chromatogr.*, *A*, 2001, **919**, 107.
- 14 E. Isaksson, V. Pohjola, T. Jauhiainen, J. Moore, J. F. Pinglot, R. Vaikmäe, R. S. W. van de Wal, J. O. Hagen, J. Ivask, L. Karlöf, T. Martma, H. A. J. Meijer, R. Mulvaney, M. Thomassen and M. van den Broeke, *J. Glaciol.*, 2001, **47**, 335.
- 15 T. Jauhiainen, J. Moore, P. Perämäki, J. Derome and K. Derome, *Anal. Chim. Acta.*, 1999, **389**, 21.
- 16 R. Röthlisberger, M. A. Hutterli, S. Sommer, E. W. Wolff and R. Mulvaney, *J. Geophys. Res.*, 2000, **105**, 20565.