The Cryosphere, 8, 931–939, 2014 www.the-cryosphere.net/8/931/2014/ doi:10.5194/tc-8-931-2014 © Author(s) 2014. CC Attribution 3.0 License.





Spatial-temporal dynamics of chemical composition of surface snow in East Antarctica along the Progress station-Vostok station transect

T. V. Khodzher¹, L. P. Golobokova¹, E. Yu. Osipov¹, Yu. A. Shibaev², V. Ya. Lipenkov², O. P. Osipova³, and J. R. Petit⁴

Correspondence to: T. V. Khodzher (khodzher_@lin.irk.ru)

Received: 27 February 2013 – Published in The Cryosphere Discuss.: 15 May 2013 Revised: 16 January 2014 – Accepted: 30 January 2014 – Published: 19 May 2014

Abstract. In January of 2008, during the 53rd Russian Antarctic Expedition, surface snow samples were taken from 13 shallow (0.7 to 1.5 m depth) snow pits along the first tractor traverse from Progress to Vostok stations, East Antarctica. Sub-surface snow/firn layers are dated from 2.1 to 18 yr. The total length of the coast to inland traverse is more than 1280 km. Here we analysed spatial variability of concentrations of sulphate ions and elements and their fluxes in the snow deposited within the 2006–2008 time interval. Anions were analysed by high-performance liquid chromatography (HPLC), and the determination of selected metals, including Na, K, Mg, Ca and Al, was carried out by mass spectroscopy with atomization by induced coupled plasma (ICP-MS). Surface snow concentration records were examined for trends versus distance inland, elevation, accumulation rate and slope gradient. Na shows a significant positive correlation with accumulation rate, which decreases as distance from the sea and altitude increase. K, Ca and Mg concentrations do not show any significant relationship either with distance inland or with elevation. Maximal concentrations of these elements with a prominent Al peak are revealed in the middle part of the traverse (500-600 km from the coast). Analysis of element correlations and atmospheric circulation patterns allow us to suggest their terrestrial origin (e.g. aluminosilicates carried as a continental dust) from the Antarctic nunatak areas. Sulphate concentrations show no significant relationship with distance inland, elevation, slope gradient and accumulation rate. Non-sea salt secondary sulphate is the most important contribution to the total sulphate budget

along the traverse. Sulphate of volcanic origin attributed to the Pinatubo eruption (1991) was revealed in the snow pit at 1276 km (depth 120–130 cm).

1 Introduction

Polar ice cores are good archives for the reconstruction of climatic conditions of the past. In particular, analysis of chemical components allows the reconstruction of mechanisms of atmospheric circulation over long time periods, including sources, travel pathways and deposition patterns of chemical compounds at a coring site (Legrand et al., 1988). However, for reliable paleoatmospheric interpretations of individual glaciochemical records we need to understand modern conditions and mechanisms of snow chemistry in different areas of Antarctica as well as possible. As new information on the modern snow chemical composition is available, we can build better models for elucidation of glaciochemical records.

The Antarctic surface snow chemistry was previously studied along the traverses from coast to inland (Legrand and Delmas, 1985; Kreutz and Mayewsky, 1999; Becagli et al., 2004; Bertler et al., 2005; Kärkäs et al., 2005; Dixon et al., 2013). In particular, concentrations of dissolved snow components (major ions) were studied versus such physical parameters as distance, elevation and accumulation rate along the traverses (Cincinelli et al., 2001; Udisti et al., 2004; Bertler et al., 2005). A negative correlation between sea salt

¹Limnological Institute SB RAS, Irkutsk, Russia

²Arctic Antarctic Research Institute, St. Petersburg, Russia

³V.B. Sochava Institute of Geography SB RAS, Irkutsk, Russia

⁴Laboratory of Glaciology and Environmental Geophysics, Grenoble, France

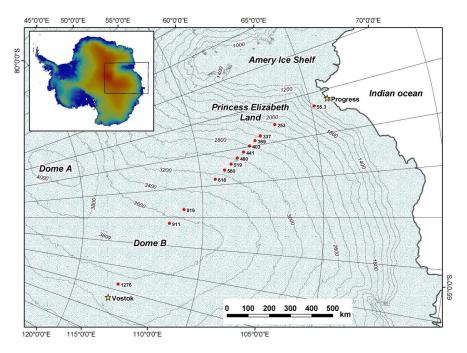


Fig. 1. A map of sampling sites (red circles with labelled distances in km) along the traverse between the Progress and Vostok stations (yellow stars). Topographic contours of > 1000 m a.s.l. are shown.

ion concentration and the distance from the sea was established (Legrand and Delmas, 1985; Kreutz and Mayewsky, 1999; Kärkäs et al., 2005). Ratios of snow ion concentrations to their concentration in the bulk sea water were used to determine sea or non-sea sources of aerosols (Aristarain and Delmas, 2002). It is also known that long-range continental transport of aerosols competes with the transfer of coastal air masses enriched, for example, with sodium ions. This suggests that the effect of the specific meteorological conditions on the snow chemistry in different parts of the continent is very important for the reconstruction of atmospheric circulation from ice core records.

In this paper, we present new snow chemistry data from the Princess Elizabeth Land sector, East Antarctica, obtained during the 53rd Russian Antarctic Expedition (RAE) in 2008 along the first tractor traverse from the Progress station to the Vostok station, one of few traverses extending for more than 1000 km from the coast further inland of Antarctica.

2 Materials and methods

2.1 Sampling procedures

Samples were collected in January of 2008 from shallow snow pits (down to 70–150 cm in depth) along the Progress–Vostok traverse at 55, 253, 337, 369, 403, 441, 480, 519, 560, 618, 819, 911, and 1276 km from Progress station with a resolution of 10 cm (Fig. 1, Table 1). Snow/firn was cut out from the pit walls in the form of 10 cm rectangular blocks with

a trowel and clean palette knife without any pre-treatment. The researchers wore a standard field uniform and new heatinsulated leather gloves. These gloves were kept in a clean plastic sleeve and used only for snow sampling. Then the snow blocks were sealed in the plastic sleeve. The samples were kept and transported frozen in thermo-insulating boxes to the Laboratory of Hydrochemistry and Atmospheric Chemistry of Limnological Institute of SB RAS, Irkutsk, Russia.

2.2 Measurements

The samples delivered to the laboratory were melted under a laminar hood at room temperature. Solutions were filtered through acetate-cellulose filters of 0.2 µm. Anions (NO₃ and SO_4^{2-}) were analysed using a Milichrom A-02 highperformance liquid chromatograph with UV detection (Russia). The sample injection was automatic. Specific modified columns were used for analysis of a sample without preliminary injection of reagents (Baram et al., 1999). Na, K, Mg, Ca, and Al were analysed on an Agilent 7500 ce, USA, by means of mass spectroscopy with atomisation by ICP-MS induced coupled plasma (Khodzher et al., 2011). Prior to analysis, the samples were acidified with 3 % nitric acid. The samples were automatically introduced into the argon flow using a concentric nebuliser. Biogenic compounds in the Antarctic snow such as methanesulfonic acid (MSA) were not analysed in this study.

Site (distance from Progress in km)	Latitude (°S)	Longitude (°E)	Altitude (m a.s.l.)	Accumulation (g cm ⁻² yr ⁻¹)	Snow pit depth, m	Mean snow/firn density, g cm ⁻³	Covered time period (AD years)
55	-69.87139	76.59139	1200	12.4	0.7	0.43	2008–2006
253	-71.61083	77.76028	2243	10.6	1.5	0.47	2008-2001
337	-72.29028	78.82000	2555	15.2	1.0	0.47	2008-2005
369	-72.54278	79.35028	2695	11	1.0	0.47	2008-2004
403	-72.80444	79.93444	2797	7.7	1.0	0.46	2008-2002
441	-73.09083	80.62028	2897	10.5	1.0	0.45	2008-2004
480	-73.38500	81.33333	2971	10.3	1.0	0.45	2008-2004
519	-73.67167	82.06944	3067	7.8	1.0	0.44	2008-2002
560	-73.97583	82.83722	3156	11.3	1.5	0.43	2008-2002
618	-74.39722	84.04222	3283	9.2	1.0	0.42	2008-2004
819	-75.78306	88.57833	3551	7.4	1.0	0.40	2008-2003
911	-76.38556	90.96861	3651	4.4	1.0	0.39	2008-1999
1276	-78.20389	103.65306	3540	$2.0^a (3.0^b)$	1.5	0.38	2008–1980 ^a

Table 1. Description of sampling sites along the Progress–Vostok traverse, East Antarctica, January of 2008.

Inter-laboratory comparison of the same samples was performed to estimate the accuracy of analytical data on the chemical composition of the Antarctic snow. This analysis was carried out by two laboratories: the Laboratory of Glaciology and Environmental Geophysics (LGGE, Grenoble, France) and the Laboratory of Hydrochemistry and Atmospheric Chemistry (LIN SB RAS, Irkutsk, Russia). In total, in both laboratories 94 equal snow samples have been analysed for major ions using ion chromatography. Analyses performed at two laboratories showed identical trends in concentration changes from sample to sample and similarity in their values. The mean discrepancy between the samples analysed in the two laboratories was 13 % and 24 % for sulphate and sodium ions, respectively. According to the documents of WMO and EMEP, the permissible discrepancy range is 30 % at a concentration of less than $0.05 \,\mathrm{meg}\,\mathrm{L}^{-1}$ (EMEP, 1996). Taking into account low concentrations of the components determined (on average, $0.002 \,\mathrm{meq}\,\mathrm{L}^{-1}$ for SO_4^{2-} and 0.001 meq L⁻¹ for Na), one can conclude that the analysis results of the same samples carried out by two independent laboratories were consistent. These results are reliable, as the Laboratory of Hydrochemistry and Atmospheric Chemistry that is involved in chemical analyses of the Antarctic snow annually participates in four international inter-laboratory comparison analyses (QA/QC Programme) of major ions and trace elements in artificially prepared certified samples of atmospheric precipitation and surface waters. The testing results of certified samples performed at the laboratory are available at: http://qasac-americas.org/, http://www.acap.asia/~interlab/os/, http://www.nilu.no, and http://kvina.niva.no/intercomparison2.

The discrepancy between the results obtained in the laboratory and those of certified samples represented in the programmes on quality control (QA/QC Programme) does not exceed 10–15%. This attests to the reliable accuracy of the techniques used and the validity of the results obtained.

2.3 Sea salt and non-sea salt sulphates

The most relevant sources of sulphate in the Antarctic snow are sea spray (ss- SO_4^{2-}), biogenic emission produced by oxidation of the gas-phase precursor DMS (nss- SO_4^{2-}), emission of explosive volcanic eruptions, which are able to inject large quantities of SO_2 , and continental dust (Legrand and Delmas, 1984). The concentration of sea-salt (ss- SO_4^{2-}) and non-sea salt (nss- SO_4^{2-}) sulphate were calculated using the known formulae:

$$[ss-SO_4^{2-}] = [SO_4^{2-}] - [nss-SO_4^{2-}];$$

 $[nss-SO_4^{2-}] = [SO_4^{2-}] - 0.06028[Na^+],$

where $[SO_4^{2-}]$ is SO_4^{2-} concentration in snow; $[Na^+]$ is Na^+ concentration in snow (the initial concentrations are given in μ mol L^{-1}) (EMEP, 1996).

3 Snow accumulation and dating of snow pit sections

Snow accumulation was calculated (Table 1) at each profile site based on: (a) 2- to 4-year (2008–2010 and 2006–2010) snow-stake measurements; (b) density measurements from surface to 20 cm depth; (c) density depth measurements at some sites in January 2008; and (d) scarce data of snow layer stratigraphy. The average thickness of the annual snow layers varies from 5.3 to 32.4 cm (maximal value at 337 km), mean accumulation from 2.0 to 15.2 g cm⁻² yr⁻¹. The errors in determination of the accumulation rate can reach 50 % due to a lack of reliable stratigraphic and snow-stake data.

Using snow accumulation and density data (see above), the ages of sampled snow horizons were calculated from the snow surface (January 2008). In accordance with these data, sub-surface snow/firn layers were dated from 2.1 to 26.6 years. Taking into consideration the accuracy of snow

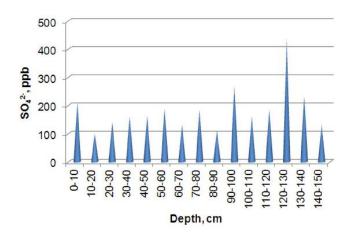


Fig. 2. The nss- SO_4^{2-} concentrations in the 1276 km snow pit.

accumulation calculations, the dating error can be as high as 50 %, but, in general, should be less at the sites more remote from the coast.

A sharp nss- SO_4^{2-} peak was recorded at 120–130 cm depth at the 1276 km site (up to 436 ppb, which is 2.4 times higher than the average concentration in the pit section). We assume that the peak was a signal of an explosive volcanic eruption with injection of SO₂ into the stratosphere (Fig. 2). According to the snow accumulation data, the sulphate enriched layer is dated by 1984, but no major eruptions are known at this time. The nearest in time stratospheric volcanic eruption recorded in the Antarctic snow at many sites is the Pinatubo eruption of June 1991, dated by 1992 in the snow (e.g. Cole-Dai et al., 1997, 2000). If our assumption is correct, the average snow accumulation rate between snow surface (January of 2008) and the Pinatubo layer (1992) should increase to $3.0 \,\mathrm{g}\,\mathrm{cm}^{-2}\,\mathrm{yr}^{-1}$. Hereinafter we used this value of snow accumulation for the 1276 km site (Table 1). Thus, the snow pits cover time intervals from 2 (2006-2008, at 55 km) to 18 (1989–2008, at 1276 km) years.

4 Results

4.1 Seasonality test

Na and SO_4^{2-} in the Antarctic snow are good markers of seasonal variability (Legrand and Delmas, 1984). Higher content of Na was observed in winter and spring due to intensification of atmospheric circulation, and of nss- SO_4^{2-} in summer due to enhanced marine biological productivity (Legrand and Mayewsky, 1997). It is believed that to resolve an annual layer, five to eight measurements were required for a seasonally changing parameter (Cole-Dai et al., 1997). However, taking into consideration the 10 cm resolution of snow sampling, we had data on only four measurements a year from the 337 km pit (site with maximal snow accumulation, Table 1). The mean Na concentration was 45 ± 21 ppb, and of

Table 2. Correlation coefficients between mean element concentrations (2006–2008) along the Progress–Vostok traverse. Significant correlations (p < 0.05, n = 13) are marked in bold.

	Na	K	Mg	Ca	SO ₄ ²⁻	nss-SO ₄ ²⁻	Al
Na	1.00	0.15	0.65	0.11	0.37	0.07	-0.07
K	0.15	1.00	0.50	0.67	0.13	0.09	0.43
Mg	0.65	0.50	1.00	0.47	0.32	0.13	0.53
Ca	0.11	0.67	0.47	1.00	0.07	0.04	0.27
SO_4^{2-} nss- SO_4^{2-}	0.37	0.13	0.32	0.07	1.00	0.95	0.02
nss-SO ₄ ²⁻	0.07	0.09	0.13	0.04	0.95	1.00	0.05
Al	-0.07	0.43	0.53	0.27	0.02	0.05	1.00

nss-SO₄²⁻ 134 \pm 64 ppb; the variation coefficients were 0.46 and 0.48, respectively. In both Na and nss-SO₄²⁻ profiles we observed four concentration peaks (1.1 and 1.4 peaks per accumulation year for Na and SO₄²⁻, respectively). However, no correlation between sodium and sulphate profiles was seen here (r=0.01). Thus, while the test suggests oscillations which could be conventionally attributed to seasonal patterns, the low sampling resolution does not allow the analysis of seasonal changes.

4.2 Spatial distribution of chemical components in snow

Measured concentrations of sulphate ion and elements in snow layers along the traverse are shown in Fig. 3. To investigate spatial differences in the chemical composition of snow, we compared the averaged concentrations in the sub-surface 20–80 cm snow layers spanning approximately 2006–2008. This time interval was present at all sites and was chosen to make the data more homogeneous for further comparison. Using snow accumulation data (see above) and measured ion concentrations, we calculated ion fluxes for this period. Spatial trends of concentrations of sulphate ion and elements and their fluxes along the traverse are shown in Fig. 4 and correlation coefficients between different species in Table 2. To evaluate the relative contribution of each factor (distance inland, elevation, accumulation rate, and slope) to variation in concentration we used linear regression analysis (Table 3).

Maximal concentrations of Na and Mg are observed at 55 km. With increasing distance from the coast their concentrations exponentially decrease. There is significant correlation between these species (r=0.65), suggesting that sea spray is their dominant source. The maximal reduction in content occurs between 55 and 253 km (by 150 and 3 ppb, respectively). However, unlike Na, Mg demonstrates a weaker negative relationship with inland distance due to its increased concentration at 618 km (up to 5.3 ppb). Strong negative relationships were revealed between Na concentration and altitude ($r^2=0.70$) and surface slope gradient ($r^2=0.67$).

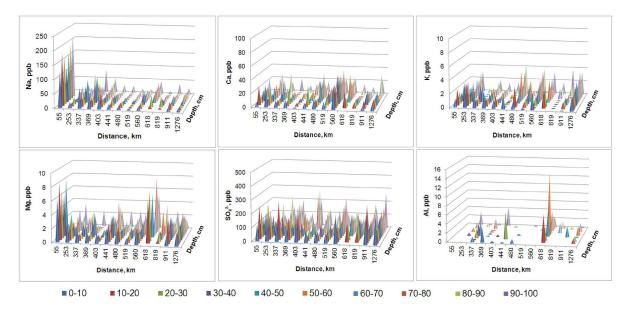


Fig. 3. Matrix diagram of measured ion concentrations in snow samples within the 0–100 cm snow layer along the traverse.

The pair of K and Ca demonstrates a similar significant relationship (the correlation coefficient is 0.67) between inland distance and concentration. However, in contrast to Na and Mg, the content of K and Ca slightly increases between 55 and 253 km due to a higher influence of continental sources of these elements. On the other hand, the concentrations of K, Ca and Mg increase (to 2, 33 and 5 ppb, respectively) in the middle section (between 403 and 618 km) of the traverse. In addition, we see an increase in K and Ca content from 911 km inland (by 1.6 and 6.5 ppb, respectively). Concentrations of these species do not show any significant correlations with distance from the coast, altitude and slope gradient.

Spatial distribution of nss- SO_4^{2-} also has some irregularities. While between 55 and 337 km the concentration is almost constant (125 ppb), from 337 to 480 km it demonstrates a two-fold decrease (to 65 ppb). Then it increases again to maximal value at 911 km (185 ppb). The nss- SO_4^{2-} demonstrates no significant relationship between concentration and altitude or slope gradient, although there is a weak positive relation with distance inland ($r^2 = 0.20$). The lowest portion of nss- SO_4^{2-} (75 % of the total SO_4^{2-} content) is at 55 km. At the inner stations (819–1276 km) it exceeds 95 %.

The content of aluminium in the majority of snow samples was below the detection limit. We observe a prominent concentration peak of Al (up to 7 ppb) at 618 km. Since Al demonstrates a moderate correlation with Mg and K (the correlation coefficients are 0.53 and 0.43, respectively), we assume the detected peak of Al is not rather its origin from continental aluminosilicates than a result of sample contamination. In addition, a slight increase in the Al content (up to 2 ppb) is observed at 337 km.

Calculated fluxes show strong positive correlation with concentrations (correlation coefficients are not less than 0.82) except for nss- SO_4^{2-} (r=0.40). The weaker relationship between non-sea salt sulphate concentration and its flux is due to the two-fold decrease in snow accumulation between 618 and 911 km (from 92 to 44 mm w. eq.).

5 Discussion

Different patterns of spatial concentration distribution of sulphate ion and elements in the surficial snow along the traverse reflect their various sources. Na and Mg concentrations are expected to demonstrate spatial distribution typical of sea-salt species, i.e. almost exponential decrease with inland distance and altitude. Similar trends were noted for the majority of coast to inland traverses (Kreutz and Mayewsky, 1999; Bertler et al., 2005; Kärkäs et al., 2005; Dixon et al., 2013). It should be noted that, unlike Na, Mg shows decreasing trend only at the beginning of the traverse (between 55) and 519 km or from 1200 to 3100 m a.s.l.). Of all species, only Na concentrations display significant relationships with altitude, slope gradient and distance inland (Table 3). The strongest association of Na occurs with altitude likely due to steep ice surface topography in this sector of East Antarctica. Also, steeper slopes are expected to facilitate snow redistribution by wind. For example, the increased Na concentrations influenced by the slope variations have been revealed by Mahalinganathan et al. (2012) in the coastal traverse at Princess Elizabeth Land, East Antarctica. As there is a statistically insignificant positive relationship between Na concentration and snow accumulation (Table 3), we assume that a dilution effect noted previously for sea-salt species (e.g.

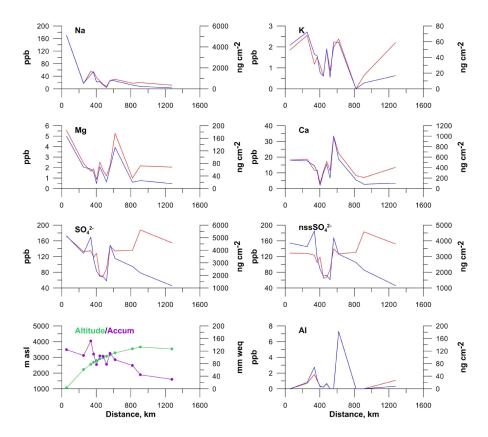


Fig. 4. Averaged (approximately for the 2006–2008 time interval) snow major ion concentrations (red) and fluxes (blue) versus distance for the Progress–Vostok transect. Distance is measured from the Progress station in km. Mean accumulation rates (purple) and elevation (green) are shown on separate diagram (lower left corner).

Table 3. Regression model explaining the relationships between mean element concentrations in surface snow (AD 2006–2008) and some physical characteristics of the Progress–Vostok traverse. Data reported are t values (t) and determination coefficients (t). Significant t values (t) values (t) are marked in bold.

	Distance		Altitude		Accumulation		Slope	
	t	r^2	t	r^2	t	r^2	t	r^2
Na	-2.32	0.33	-5.10	0.70	1.67	0.20	4.73	0.67
Mg	-0.99	0.08	-1.84	0.24	0.85	0.06	1.68	0.20
K	-0.48	0.02	-1.11	0.10	0.55	0.03	0.60	0.03
Ca	-0.50	0.02	-0.50	0.02	1.25	0.13	0.28	0.01
SO_4^{2-}	0.84	0.06	-0.23	0.00	-0.84	0.06	0.27	0.01
nss-SO ₄ ²⁻	1.68	0.20	0.67	0.04	-1.49	0.17	-0.60	0.03

Legrand, 1987; Udisti et al., 1999) is smoothed along the traverse. The moderate increase in Na concentrations at 337 and 369 km is likely attributed to local slope changes, wind distribution effects and snow deposition variability.

K and Ca concentrations do not show any significant relationship either with distance from the coast or with elevation. It is likely attributed to their terrestrial sources. It should be noted that there are decreasing trends of both element concentrations between 253 and 403 km. Taking into

consideration that the portion of non-sea salt components in this part of the traverse is 90-95 % (e.g. for calcium) of the total content, we assume that the change in concentration may be due to snow deposition variability here. On the other hand, these species demonstrate maximal concentrations in the middle part of the traverse (500–600 km from the coast). Also, there are increased Mg and Al concentrations at this route segment (at 618 km or 3300 m a.s.l.). Moderate (although not significant) correlations between K, Mg and Al (Table 2) may suggest their common origin from aluminosilicates carried as a continental dust. In order to assess the origins of the species in the surface snow, we used the enrichment factor (EF), which compares the relative element concentrations (Na, K, Mg, Ca, and S) in the Antarctic snow with those in the earth crust (Rahn, 1976). As a reference element we used aluminium:

$$EF = (X/Al)_{snow}/(X/Al)_{earth crust}$$

where X is an element concentration for which EF is calculated. The sulphur concentration was calculated from SO_4^{2-} content. EF values closest to unity were revealed at 618 km for K (EF = 1.0), Mg (EF = 2.6) and Ca (EF = 6.1), suggesting their terrestrial origin. EFs for other sites differ by 2–3

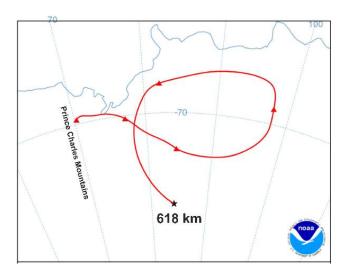


Fig. 5. Example of the 5-day back trajectory to the 5000 m level over the 618 km site (25 February 2007).

orders of magnitude, suggesting more complicated element sources.

Prevalence of marine and continental sources of the species is defined by differences in atmospheric circulation. To comprehend the circulation patterns over the studied area, we analysed the 5-day back trajectories of air masses coming to 5000 m over two sites of the traverse (618 km and 1276 km) and to 2000 m over the 55 km site using the HYS-PLIT model (Rolph, 2013; Draxler and Rolph, 2013). We used the NCEP/NCAR reanalysis data set as input for the trajectory model for the period of 2006–2008. The results suggest that while most (60%) of the trajectories coming to 55 km originated over the ocean, those coming to 618 km and 1276 km remained over Antarctica (65 % and 79 %, respectively). It should be noted that prevalence of continental trajectories occurs during the austral summers (30 % of all continental trajectories) when the snow cover was significantly reduced. Probably, the main dust sources in snow at 618 km are nunatak areas in East Antarctica (e.g. Prince Charles Mountains, Mac. Robertson Land) (Fig. 5).

In contrast to sea-salt species (Na and Mg), sulphate distribution in the Antarctic snow along the traverse is more complicated. There are no significant statistical relationships between SO_4^{2-} concentration and distance inland/elevation/slope/accumulation (Table 3). It is believed that the Antarctic sulphate is deposited both as primary and secondary aerosols (Legrand and Delmas, 1984). Primary sulphate, partly derived from sea spray input (ss- SO_4^{2-}), is expected to demonstrate an exponential decreasing trend with distance inland (similar to Na). The secondary aerosol (nss- SO_4^{2-}) source is H_2SO_4 , which may have a marine biogenic and/or volcanic origin and, hence, a more complicated spatial pattern. As the ratio of ss- SO_4^{2-} to total SO_4^{2-} varies from 25 % (near the coast) to 2 % (at the most remote

site), nss- SO_4^{2-} is the most important contribution to the total sulphate budget along the traverse. In general, a decreasing trend of nss- SO_4^{2-} at the beginning of the route (55–441 km, 1100–2900 m a.s.l.) is likely to reflect marine (low troposphere) influence. Further inland, nss- SO_4^{2-} demonstrates a secondary aerosol distribution pattern defined by middle/upper troposphere fine aerosol transfer, with predominant dry deposition in inland (low accumulation) areas of East Antarctica (Legrand and Delmas, 1984; Legrand, 1987).

As almost all sampled snow/firn pits span the time period which was quiet when referring to stratospheric nss- SO_4^{2-} content, we did not expect to reveal a significant disturbance of sulphate background by volcanic fall-outs. The only exception is a snow layer at a depth of 120–130 cm in the 1276 km pit. We attribute it to the stratospheric Pinatubo eruption in 1991, which had global concern (see above). It is possible that some volcanic events are reflected as nss- SO_4^{2-} peaks in the snow at 253 km (130–150 cm depth) and 560 km (130–140 cm).

6 Conclusions

Surficial snow was sampled in snow pits at 13 sites (55 to 1276 km from the coast) along the traverse from Progress to Vostok stations, East Antarctica (January of 2008 by the Russian Antarctic Expedition). The snow pits span time intervals from two (2006–2008, at 55 km) to 18 (1989–2008, at 1276 km) years.

Chemical analysis of snow samples was performed in the Laboratory of Hydrochemistry and Atmospheric Chemistry (LIN SB RAS, Irkutsk, Russia) using high-performance liquid chromatography (HPLC) and mass spectroscopy with atomization by induced coupled plasma (ICP-MS). Interlaboratory comparison with LGGE (Grenoble, France) has shown acceptable quality of measurements.

Analysis of spatial distribution reveals a significant positive relationship between Na concentration and accumulation (r = 0.45) and surface slope gradient (r = 0.82). Na and, partly, Mg concentrations demonstrate almost exponential decrease with inland distance and altitude, which is typical of sea-salt species.

K, Ca and Mg concentrations do not show any significant relationship either with distance from the coast or elevation. These species demonstrate maximal concentrations in the middle part of the traverse (500–600 km from the coast). Moreover, increased Mg and Al concentrations have been revealed at 618 km on the route (3300 m a.s.l.). Moderate correlation between K, Mg and Al suggests their common origin from aluminosilicates carried as a continental dust. Simple analysis of atmospheric circulation patterns using the HYS-PLIT model has shown that a probable source of the dust is nunatak areas in East Antarctica (e.g. Prince Charles Mountains, Mac. Robertson Land).

No significant statistical relationship was revealed between SO_4^{2-} concentration and distance inland, elevation, slope or accumulation. Primary sulphate, partly derived from the sea spray input, demonstrates exponential decreasing trend with distance inland (similar to Na). However, non-sea salt sulphate derived from marine biogenic sulphur emissions is the most important contribution to the total sulphate budget along the traverse. We assume that most sampled snow pits do not include sulphate of volcanic origin, as the sampled time period was quiet when referring to the stratospheric SO_4^{2-} record. The exception is the snow layer at a depth of $120-130\,\mathrm{cm}$ in the $1276\,\mathrm{km}$ snow pit. In terms of the prominent non-sea salt sulphate peak we attribute it to the Pinatubo eruption (1991).

Acknowledgements. We would like to thank two anonymous reviewers for providing useful comments and suggestions for the initial version of the manuscript. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication. This work was supported by Program of RAS No. 11.9 and RFBR Project No. 10-05-93109.

Edited by: M. Albert

References

- Aristarain, A. and Delmas, R.: Snow chemistry measurements on James Ross Island (Antarctic Peninsula) showing sea-salt aerosol modifications, Atmos. Environ., 36, 765–772, 2002.
- Baram, G. I., Vereshchagin, A. L., and Golobokova, L. P.: Microcolumn HPLC with UV Detection for the Determination of Anions in Environmental Materials, J. Anal. Chem., 54, 854–857, 1999.
- Becagli, S., Proposito, M., Benassai, S., Flora, O., Genoni, L., Gragnani, R., Largiuni, O., Pili, S. L., Severy, M., Stenni, B., Traversi, R., Udisti, R., and Frezzotti, M.: Chemical and isotopic snow variability in East Antarctica along the 2001/02 ITASE traverse, Ann. Glaciol., 39, 473–482, 2004.
- Bertler, N., Mayewski, P. A., Aristarain, A., Barrett, P., Becagli, S., Bernardo, R., Bo, S., Xiao, C., Curran, M., Qin, D., Dixon, D., Ferron, F., Fischer, H., Frey, M., Frezzotti, M.; Fundel, F., Genthon, C., Gragnani, R., Hamilton, G., Handley, M., Hong, S., Isaksson, E., Kang, J., Ren, J., Kamiyama, K., Kanamor, S., Kärkäs, E., Karlöf, L., Kaspari, S., Kreutz, K., Kurbatov, A., Meyerson, E., Ming, Y., Zhang, M., Motoyama, H., Mulvaney, R., Oerter, H., Osterberg, E., Proposito, M., Pyne, A., Ruth, U., Simões, J., Smith, B., Sneed, S., Teinilä, K., Traufetter, F., Udisti, R., Virkkula, A., Watanabe, O., Williamson, B., Winther, J. G., Li, Y., Wolff, E., Li, Z., and Zielinski, A.: Snow chemistry across Antarctica, Ann. Glaciol., 41, 167–179, 2005.
- Cincinelli, A., Desideri, P. G., Lepri, L., Checchini, L., Bubba, M. D., and Udisti, R.: Marine contribution to the chemical composition of coastal and inland Antarctic snow, Int. J. Environ. Anal. Chem., 79, 283–299, 2001.

- Cole-Dai, J., Mosley-Thompson, E., and Thompson, L. G.: Annually resolved southern 10 hemisphere volcanic history from two Antarctic ice cores, J. Geophys. Res., 102, 16761–16771, 1997.
- Cole-Dai, J., Mosley-Thompson, E., Wight, S. P., and Thompson, L. G.: A 4100-year 13 record of explosive volcanism from an East Antarctica ice core, J. Geophys. Res., 105, 24431–24441, 2000.
- Dixon, D. A., Mayewski, P. A., Korotkikh, E., Sneed, S. B., Handley, M. J., Introne, D. S., and Scambos, T. A.: Variations in snow and firn chemistry along US ITASE traverses and the effect of surface glazing, The Cryosphere, 7, 515–535, doi:10.5194/tc-7-515-2013, 2013.
- Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, available at: http://www.arl.noaa.gov/HYSPLIT.php (last access: 13 January 2014), NOAA Air Resources Laboratory, College Park, MD, 2013.
- EMEP: Manual for sampling and chemical analysis, EMEP Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe. NILU: EMEP/CCC-Report 1/95. Reference: 0-7726. EMEP, 176 pp., 1996.
- Kärkäs, E., Teinilä, K., Virkkula, A., and Aurela, M.: Spatial variations of surface snow chemistry during two austral summers in western Dronning Maud Land, Antarctica, Atmos. Environ., 39, 1405–1416, 2005.
- Khodzher, T. V., Golobokova, L. P., Osipov, E. Yu., Artemyeva, O. V., Maslennikova, M. M., Lipenkov, V. Ya., Shibaev, Yu. A., Belozerova, O. Yu., and Likhoshway, E. V.: Evidences of volcanic eruptions of Tambora and Krakatau (XIX) according to chemical and electron microscopy studies of snow-firn cores from Station Vostok (Antarctica), Ice and Snow, 1, 105–113, 2011.
- Kreutz, K. J. and Mayewski, P. A.: Spatial variability of Antarctic surface snow glaciochemistry: implications for palaeoatmospheric circulation reconstructions, Antarc. Sci., 11, 105–118, 1999.
- Legrand, M.: Chemistry of Antarctic snow and ice, Journal de Physique Colloques, 48, 77–86, 1987.
- Legrand, M. R. and Delmas, R. J.: The ionic balance of Antarctic snow: a 10-year 19 detailed record, Atmos. Environ., 18, 1867– 1874, 1984.
- Legrand, M. and Delmas, R. J.: Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica), Ann. Glaciol., 7, 20–25, 1985.
- Legrand, M. and Mayewski, P. A.: Glaciochemistry of polar ice cores: a review, Rev. Geophys., 35, 219–243, 1997.
- Legrand, M., Lorius, C., Barkov, N. I., and Petrov, V. N.: Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), Atmos. Environ., 22, 317–331, 1988.
- Mahalinganathan, K., Thamban, M., Laluraj, C. M., and Redkar, B. L.: Relation between surface topography and sea-salt snow chemistry from Princess Elizabeth Land, East Antarctica, The Cryosphere, 6, 505–515, doi:10.5194/tc-6-505-2012, 2012.
- Rahn, K. A.: The chemical composition of the atmospheric aerosol, Technical Report, Graduate School of Oceanography, University of Rhode Island, 265 pp., 1976.
- Rolph, G. D.: Real-time Environmental Applications and Display sYstem (READY) Website, available at: http://www.ready.noaa.

- gov (last access: 13 January 2014), NOAA Air Resources Laboratory, College Park, MD, 2013.
- Udisti, R., Becagli, S., Castellano, E., Travers, R., Vermigli, S., and Piccardi, G.: Sea spray and marine biogenic seasonal distribution to snow composition at Terra Nova Bay (Antarctica), Ann. Glaciol., 29, 77–83, 1999.
- Udisti, R., Becagli, S., Benassai, S., Castellano, E., Fattori, I., Massimo, I., Migliori, A., and Traversi, R.: Atmosphere-snow interaction by a comparison between aerosol and uppermost snow-layers composition at Dome C (East Antarctica), Ann. Glaciol., 39, 53–61, 2004.