

**Spatial-temporal
dynamics of chemical
composition of
surface snow**

T. V. Khodzher et al.

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

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

collected along the 350 km transect from the shelf glacier edge (Dronning Maud Land) decreased with the increase of distance from the coast by about 64 %/100 km (Kärkäs et al., 2005). There are numerous factors affecting chemical composition of the Antarctic snow: width, distance from the coast, relief, seasonal variability, etc. (Legrand et al., 1988; Cincinelli et al., 2001; Bertle et al., 2005; Udisti et al., 2005). Compounds may penetrate further inland together with fine-dispersed aerosols and acid forming gases. Fine aerosol fraction prevails among other size fractions contributing 86 % of the ionic budget. High content of sulphate and elevated acidity are recorded in this fraction (Piccardi et al., 1996; Udisti et al., 1999; Cincinelli et al., 2001; Udisti et al., 2005). The most probable sources of sulphate (SO_4^{2-}) are continental or stratospheric (Delmas et al., 1982; Legrand et al., 1988; Zielinski et al., 1997). Elevated concentrations of non-sea-salt sulphate (nss- SO_4^{2-}) are registered in the snow layers with buried signals of volcano eruptions (Legrand et al., 1988; Zielinski et al., 1997). Studies performed on James Ross Island revealed frequent formation of hydrochloric acid in the atmosphere (Aristarain and Delmas, 2002).

Parker et al. (1982) gave detailed description of sources and mechanisms explaining fluctuations of NO_3^- concentrations in the Antarctic snow. Cyclicality was determined in the variations of this ion content with the same periodicity (11, 22, and 66 yr) which is characteristic of variability in solar activity and intensity of aurora polaris (Olson, 1980).

Studies on chemical composition of the snow cover performed at different distances from the continent margin allow the researchers to analyse factors affecting the formation of snow cover in Antarctica and to specify rates of snow accumulation. The analysis of vertical profiles of snow thickness makes it possible to trace variability of these factors within time scales. The first detailed studies of the snow samples (up to 150 cm of the snow core) collected along the track traverse (TT) from Station Progress to Station Vostok showed spatial and temporal distribution of the major chemical components in snow and contribution of different sources to their formation in one of the regions of East Antarctica.

2 Materials and methods

Snow was sampled into special polypropylene containers (Corning Inc., USA) from the cores drilled at 55.3, 253, 337, 369, 403, 441, 480, 519, 560, 618, 911, and 1276 km from Station Progress with the resolution of 10 cm up to a depth of 100–150 cm (Table 1). The samples were frozen and transported to the Scientific Expedition Vessel Academician Fedorov, and then in thermo-insulating boxes by plain to Limnological Institute of the Siberian Branch of the Russian Academy of Sciences (LIN SB RAS), Irkutsk, Russia.

The samples delivered to the laboratory were melted in a laminar box at room temperature. Solutions were filtered through acetate-cellulose filters of 0.2 μm . Anions (NO_3^- and SO_4^{2-}) were analysed using a high-performance liquid chromatograph Milichrom A-02 (Russia), cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) and aluminium (Al) using a mass-spectrometer with induced coupled plasma ICP-MS (Agilent 7500 ce, USA) (Khodzher et al., 2011).

Laboratory inter-comparison of snow samples from East Antarctica was performed at two laboratories: Laboratory of Glaciology and Environmental Geophysics (LGGE, Grenoble, France) and Laboratory of Hydrochemistry and Atmospheric Chemistry (LIN SB RAS, Irkutsk, Russia). In total, both laboratories analysed 94 samples of snow water for major ions using ion chromatography. Concentrations of anions SO_4^{2-} , NO_3^- , Cl^- and cations Na^+ , K^+ , Ca^{2+} , Mg^{2+} were measured at LIN SB RAS on an ICS-3000 (Dionex, USA) using analytical columns IonPac CS12A and IonPac AS19. Six Cation Standard II and Seven Anion Standard II (Dionex, USA) were used as reference elements. The volume of injected material for cations was 500 μL , for anions – 3000 μL , and the rate of eluent ejection was 250 $\mu\text{L min}^{-1}$ (Weiss, 2005). Analyses performed at two laboratories showed identical dynamics in concentration changes from sample to sample and one order of magnitude measured (Fig. 1). About 75 % of sulphate-ion measurements obtained at the laboratories revealed the 30 % discrepancy, among them 32 % measurements differed by less than 10 %. Taking into account low concentrations of the

TCD

7, 2007–2028, 2013

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

components determined (for SO_4^{2-} about 70–150 ppb and for Na^+ less than 40 ppb), one can conclude that the analysis results of the same samples carried out by two independent laboratories were consistent.

3 Results

3.1 Spatial distribution of chemical components in the surface (0–10 cm) snow layer

An important characteristic of chemical composition of the surface Antarctic snow is total concentration of dissolved components – ions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} . Arithmetical mean value of concentrations (210 ppb) was used for comparison of these dissolved components in the 0–100 cm snow layer of the cores under study. For example, in the 0–10 cm layer, the total concentration of dissolved components was higher than the mean value at 55.3, 337, 560, and 1276 km from Station Progress. Maximal ionic concentrations (about 260 ppb) were recorded in the snow near the coast and at 560 km from the coast. Further inland from site 55.3 km to site 519 km, ionic concentrations decreased in the surface snow layer by approximately 30%/70 km along the tractor transect. Minimal ionic concentrations (95 ppb) were registered at 519 km from the coast (Fig. 2). It was almost 2 times lower than that of dissolved components in the surface snow at approximately the same distances from the coast in Dronning Maud Land (Kärkäs et al., 2005). The rise of ionic concentration was observed at a distance of 560 km from the ice edge, remaining higher (210 ppb) than the mean value further inland (Fig. 2).

3.2 Vertical distribution of chemical components in the 10–100 cm snow layer

Elevated concentrations of total ions compared to the mean value were recorded more frequently in the 50–100 cm snow layers. Sometimes they exceeded 300 ppb within the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

were higher than at the neighbouring sites (819 and 911 km). In the snow cores drilled at 253, 560, and 1276 km (examined up to 1.5 m), high sulphate concentrations were registered in the 130–150 cm layer. The maximal value of sulphate ion (511 ppb) was recorded at 253 km.

4 Discussion

As stated above, components in the Antarctic snow are emitted with aerosols from the atmosphere (sea salt, continental dust, and products of volcano eruptions) or they are generated by photochemical reactions involving gases (Olson, 1980; Delmas et al., 1982; Parker et al., 1982; Legrand et al., 1988). Sea surface is a powerful source for aerosol input into the atmosphere. It is noteworthy that there is a microlayer of less than 150 μm in which the concentrations of dissolved components are much higher than in the lower layers due to surfactants (Shevchenko, 2006). Marine aerosols formed as a result of bubble destruction at the “water-air” interface cause the emergence of particles of a submicron fraction with a diameter of less than 0.3 μm which can be transferred at hundreds or thousands of kilometres from the source. Those aerosols formed as a result of evaporation of water drops are much larger in diameter, and their sizes correspond to those of a coarse-dispersion fraction. These particles are accumulated close to the source (Ivlev and Dvogyuk, 1999). Taking into account this fact, aerosols formed both as a result of bubble destruction and evaporation of sea water could be a source of elevated concentrations of Na^+ in the snow at a distance of 55.3 km from Station Progress. Multiple decrease of Na^+ content in the snow core drilled at 253 km, compared to that in the snow core at 55.3 km, attests to the reduction of contribution of marine aerosols to chemical composition of snow further in land. Our data on the decrease of the sea factor effect are consistent with the results of other studies (Bertle et al., 2005; Prodi et al., 2008).

Components of the Antarctic marine-derived snow are easily dissolved in the snow water. Hardly soluble components, however, may be present in the water,

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



e.g. aluminosilicates coming with the continental dust the solubility of which increases in weak-acid solutions of snow (Sklyarov, 2001; Glinka, 2002). The pH value of snow water ranged from 4.2 to 5.2 in all cores studied.

The content of aluminium in the majority of snow samples equalled analytic zero. However, in some of the samples, particularly in the snow core drilled at 618 km from Station Progress with low pH (4.2–4.6), the Al content reached up to 10 ppb (Fig. 5). An attempt was made to determine possible continental sources of components from this element and from high concentrations of calcium and magnesium in snow samples.

The input of continental dust to the Antarctic continent is more likely to be attributed to the air mass transfer during cyclonic processes. It is known that cyclones bringing air masses to Antarctica are generated more often on the south-eastern coast of South America, South Africa, and Australia. Further inland, they reach 60–65° S where they usually regenerate. Deep north-western cyclones become high and nonmobile between 80 and 95° E and can cover vast territories of the continent. Their shift along the meridian is 5–8° (Pogosyan, 1972). Wind speed increases in the frontal zones causing the penetration of air masses further inland. This fact probably explains the rise of component concentrations in the snow cores drilled at 560 and 618 km from Station Progress located between 73°58′–74°23′ S and 82°50′–84°02′ E.

The origin of sulphate in the Antarctic snow is attributed to both sea salt and gas phase modifications in the atmosphere (Glinka, 2002; Zielinski et al., 1997). Volcanic sulphate emission may be also referred to the potentially substantial source of continental sulphate (Ivlev and Dovgalyuk, 1999).

The concentration of sea-salt ($ss\text{-SO}_4^{2-}$) and non-sea-salt ($nss\text{-SO}_4^{2-}$) sulphate were calculated using the known formulae:

$$[ss - \text{SO}_4^{2-}] = [\text{SO}_4^{2-}] - [nss - \text{SO}_4^{2-}]; \quad (1)$$

$$[nss - \text{SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.06028[\text{Na}^+], \quad (2)$$

**Spatial-temporal
dynamics of chemical
composition of
surface snow**

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



where $[\text{SO}_4^{2-}]$ is SO_4^{2-} concentration in snow; $[\text{Na}^+]$ is Na^+ concentration in snow (the initial concentrations are given in $\mu\text{Eq/l}$) (EMEP, 1996).

Figure 4 shows variations of sea-salt and non-sea-salt sulphate in the Antarctic snow along the Progress-Vostok transect. The highest concentrations of sea-salt sulphate were recorded in the snow at 55.3 km from Station Progress. Further inland, the concentrations of sea-salt sulphate decreased in the snow water. Elevated concentrations of non-sea-salt sulphate were registered within the 130–150 cm layer in the snow core collected to the 150 cm depth. Maximal nss- SO_4^{2-} concentrations were observed at a depth of 140–150 cm at 253 km from Station Progress. At 560 km from this station the peak of its concentration was recorded in the 130–140 cm layer, whereas at 1276 km – within 120–130 cm. Areas with high concentrations of nss- SO_4^{2-} are marked in grey in Fig. 4. Maximal sulphate concentrations fixed within these deep intervals are most likely evident of buried signals of the Pinatubo eruption in June of 1991 on the Philippines with the volcanic explosivity index (VEI) 6 (Newhall and Self, 1982).

5 Conclusions

Detailed chemical analysis of the Antarctic snow composition was performed for the first time at the transect Station Progress-Station Vostok at a distance from 55.3 to 1276 km from the ice edge. Marine-derived components are the main contributors to chemical snow composition near the coast and at a distance of up to 400 km further inland. They affect spatial and time variations of snow composition at the profile under study. However, their influence diminishes at a distance of 519 km from the coast. Further inland, additional sources of component input in the snow cover appear in East Antarctica, which cause a threefold rise of total concentrations of dissolved components at 560–618 km from the ice edge. The elevated content of components in the atmosphere in this area may be attributed to prevailing paths of cyclonic air masses coming from other continents of the Southern Hemisphere. The appearance of aluminium in the snow at 618 km from the ice edge is likely to be an indirect evidence

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of this supposition. The signals of the Pinatubo volcanic eruption (1991), judging by elevated concentrations of non-sea-salt sulphate (nss-SO_4^{2-}) in the snow cores up to a depth of 150 cm, can serve as a time marker.

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TCO

7, 2007–2028, 2013

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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TCD

7, 2007–2028, 2013

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2018



TCD

7, 2007–2028, 2013

Spatial-temporal
dynamics of chemical
composition of
surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Coordinates of snow sampling along the first tractor transect from Station Progress to Station Vostok (East Antarctica), February of 2008.

Distance from Station Progress km	Coordinates of sampling	
	Southern latitude	Eastern longitude
55.3	69°52′17″	76°35′29″
253	71 36 39	77 44 97
337	72 17 25	78 49 12
369	72 32 34	79 21 01
403	72 48 16	79 56 04
441	73 05 27	80 37 13
480	73 23 06	81 20 00
519	73 40 18	82 04 10
560	73 58 33	82 50 14
618	74 23 50	84 02 32
819	75 46 59	88 34 42
911	76 23 08	90 58 07
1276	78 12 14	103 39 11

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. Concentrations of Na⁺ in snow water along the tractor transect from Station Progress to Station Vostok, February of 2008, ppb.

Distance km	Snow layer cm									
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100
55.3	126	187	169	123	171	193	222			
253	22	12	25	12	11	24	36	7	13	24
337	72	37	37	57	74	24	35	21	66	25
369	53	31	34	65	88	58	41	33	8	82
403	45	46	28	22	31	28	29	35	41	51
441	20	15	34	31	28	23	18	12	10	26
480	16	18	16	11	16	8	8	9	6	25
519	5	5	6	13	7	4	11	11	15	15
560	15	15	21	43	37	27	31	17	22	13
618		12	40		29	40	41	53	32	47
819		5	37	22	7	7	14	8	3	9
911	16	27	16	18	27	18	14	10	11	38
1276	13	10	12	15	17	26	22	19	10	23

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 3. Concentrations of Mg^{2+} in snow water along the tractor transect from Station Progress to Station Vostok, February of 2008, ppb.

Distance km	Snow layer cm									
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100
55.3	6.2	8.4	6.9	6.1	8.4	1.2	1.7			
253	2.8	1.9	3.7	2.2	1.3	2.5	3.3	1.3	1.6	3.3
337	2.3	1.1	0.9	2.0	1.7	1.2	2.1	1.9	2.3	1.7
369	2.1	0.9	1.3	2.4	3.4	1.2	1.0	0.6	0.0	2.3
403	1.6	1.1	0.3	0.4	0.9	0.5	0.4	0.9	1.2	1.6
441	2.3	2.6	1.7	3.2	2.9	2.5	2.0	4.2	3.3	2.5
480	1.8	2.4	1.8	1.4	1.6	1.3	1.7	0.6	1.1	2.5
519	1.0	0.8	1.4	1.6	1.2	1.2	1.4	1.8	1.7	2.5
560	2.5	2.1	1.7	1.6	2.3	2.4	3.0	2.4	2.3	1.5
618		6.3	7.4		6.3	1.1	3.3	8.1	5.6	4.9
819		0.5	1.6	1.2	0.7	3.6	1.1	1.3	3.8	0.9
911	1.6	3.5	1.4	3.4	3.1	2.2	1.9	1.3	1.9	2.7
1276	2.1	2.0	3.2	2.4	2.8	3.5	3.1	2.6	1.8	1.4

TCD

7, 2007–2028, 2013

Spatial-temporal
dynamics of chemical
composition of
surface snow

T. V. Khodzher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 5. Concentrations of Ca^{2+} in snow water along the tractor transect from Station Progress to Station Vostok, February of 2008, ppb.

Distance km	Snow layer cm									
	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100
55.3	7	28	12	17	21	16	26			
253	28	11	23	11	19	20	13	24	29	16
337	11	9	8	14	24	12	12	3	29	13
369	12	7	24	6	11	10	3	2	0	20
403	1	4	2	6	2	9	7	2	9	9
441	8	6	27	2	10	12	2	16	15	17
480	16	11	10	9	31	27	37	18	10	16
519	11	2	16	17	14	17	17	19	14	26
560	34	31	21	43	37	38	30	40	26	22
618		23	13		16	38	26	22	28	22
819		8	10	8	7	7	5	0	9	14
911	6	12	3	16	20	12	12	5	8	10
1276	12	15	13	15	17	9	8	7	32	21

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

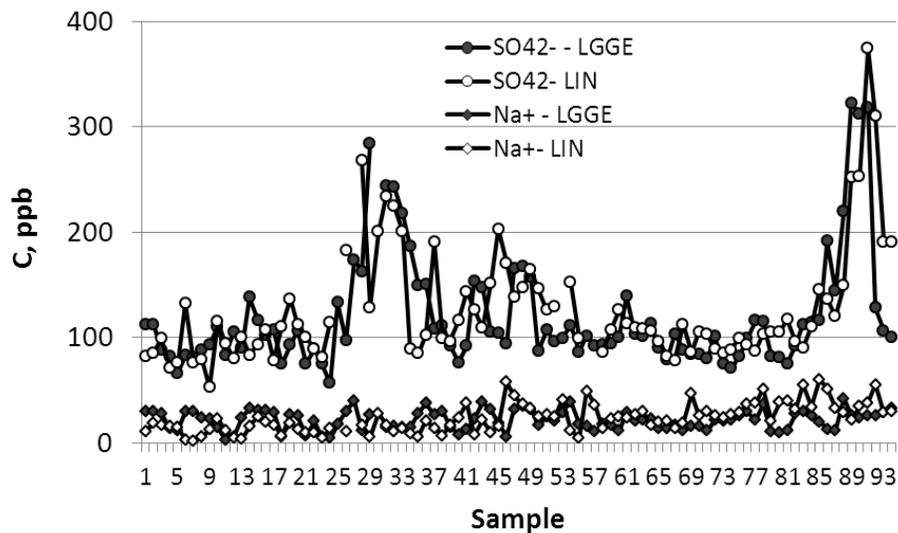


Fig. 1. Laboratory inter-comparison of the results on concentrations of SO_4^{2-} and Na^+ in snow water in East Antarctica.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

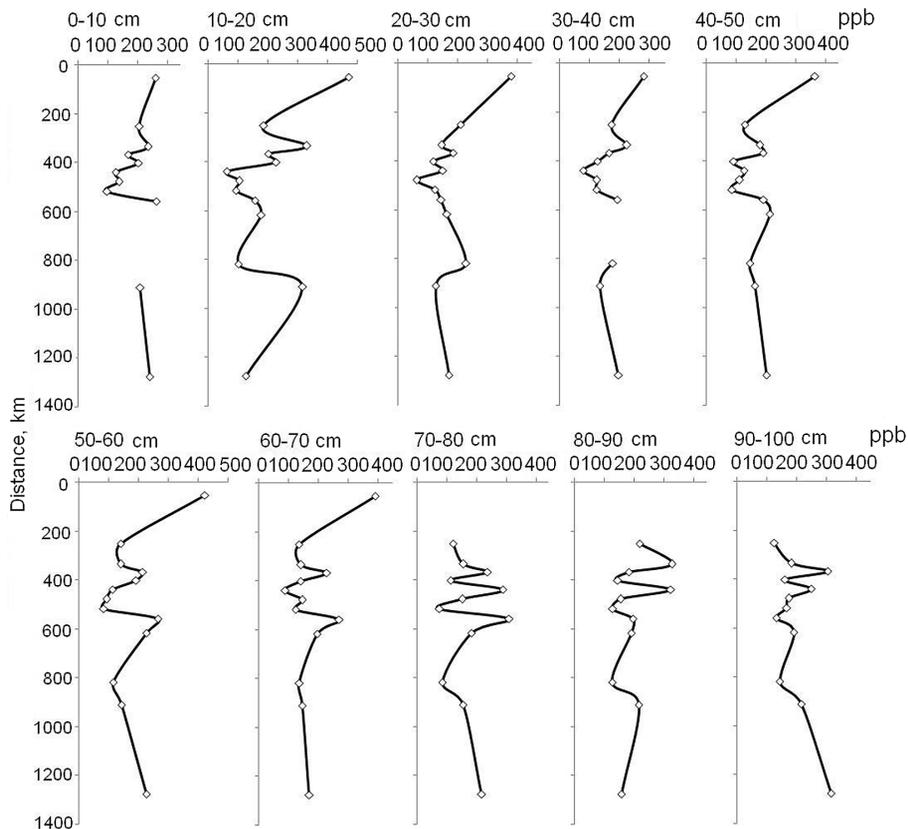


Fig. 2. Dynamics of total ion concentrations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-}) in snow along the tractor transect from Station Progress to Station Vostok, February of 2008.

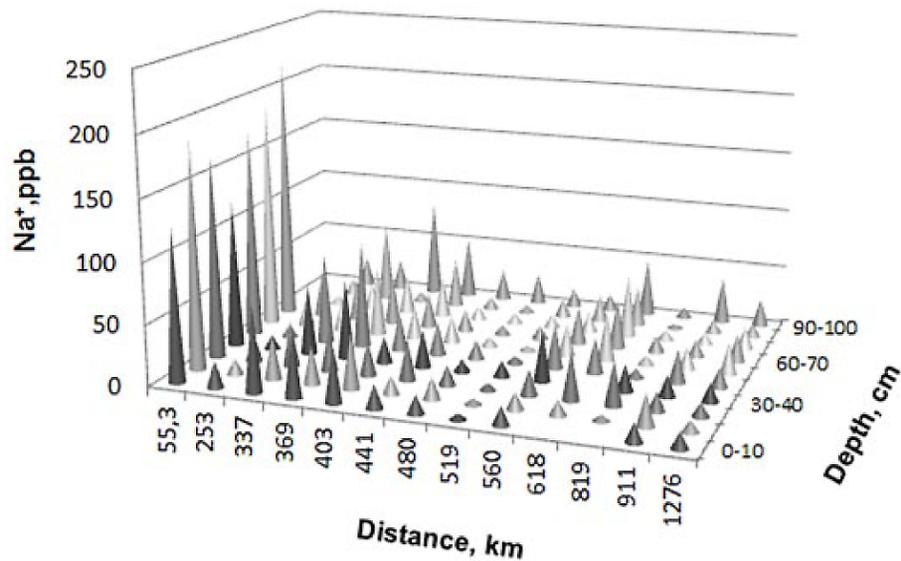


Fig. 3. Matrix diagram of Na^+ concentrations in snow at the Progress-Vostok transect (February of 2008).

Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
⏪	⏩
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

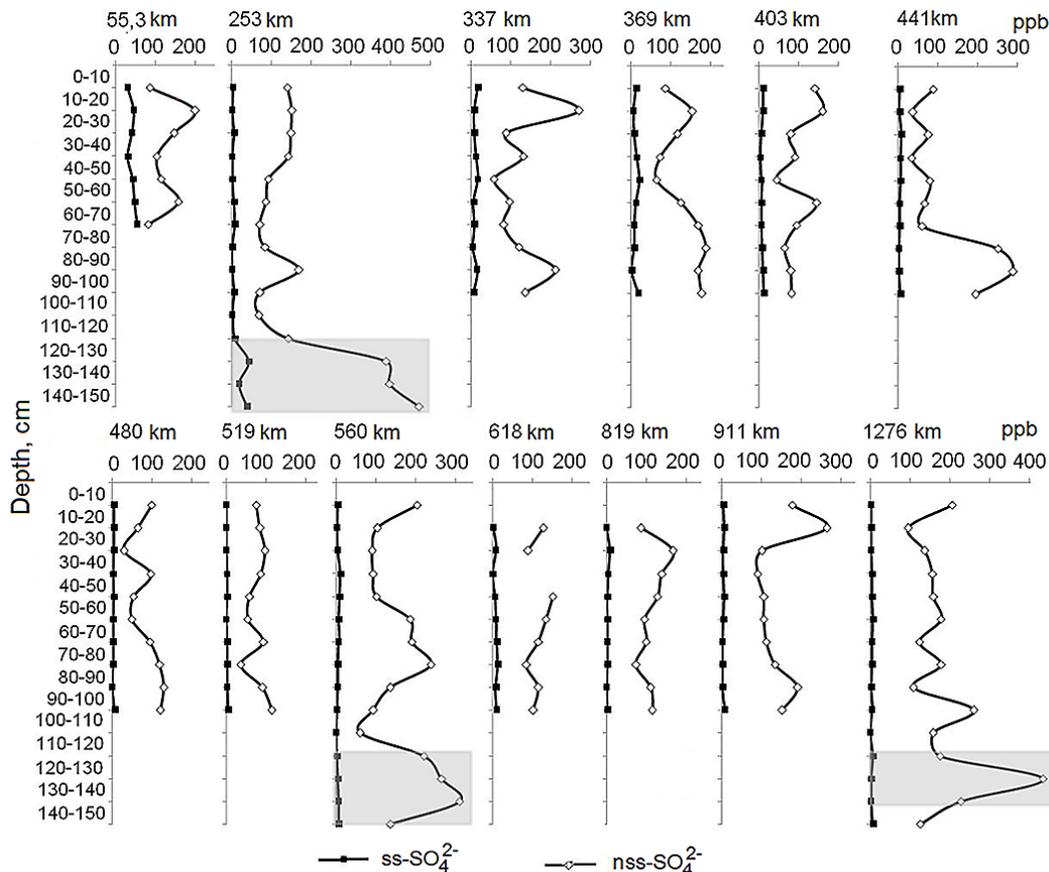


Fig. 4. Sea-salt (ss) and non-sea-salt (nss) sulphate in snow at the Progress-Vostok transect. Intervals of possible buried signals of the Pinatubo volcano eruption are marked in grey.

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Spatial-temporal dynamics of chemical composition of surface snow

T. V. Khodzher et al.

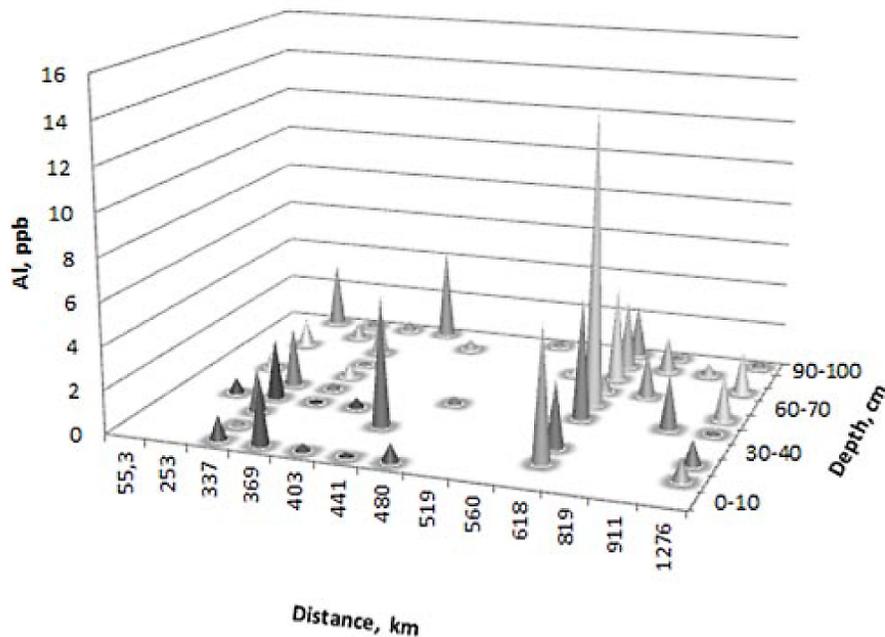


Fig. 5. Matrix diagram of Al concentrations in snow water at the Progress-Vostok transect

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

