

SNOW COVER AND GLACIERS

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**FEATURES OF LAYERED VARIABILITY
OF INTEGRATED PHYSICO-CHEMICAL PARAMETERS IN THE SNOW COVER
IN THE MIDDLE TAIGA ZONE IN THE NORTH-EAST OF THE EUROPEAN PLAIN****M.P. Tentyukov***Institute of Natural Sciences, Pitirim Sorokin Syktyvkar State University,
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The results of testing the upgraded device for layer-by-layer snow sampling have been used to determine changes in the integrated physical-chemical parameters of snow (pH value, ox-red potential, electrical conductivity and density of the snow) in the snow mass during its formation in the mid-taiga zone in the northeast of the European Plain. The value of these parameters for monitoring aerosol pollution of the snow cover has been estimated.

Geochemistry of snow, monitoring, oxidation-reduction potential, electrical conductivity, layer-by-layer snow sampler, snow cover

INTRODUCTION

As early as in 1871, the Russian scientist A.I. Voeykov emphasized the important role the snow cover played in the natural processes [Voeykov, 1949]. In his work, the scientist first indicated the main areas for the study of snow cover, which are traditionally being developed now [Kotlyakov, 2002]. However, it should be pointed out that in the most part of the scientific studies devoted to snow, snow is regarded as a depositing medium, in which substances coming to the Earth's surface from the atmosphere are accumulated and preserved [Skripalshchikova et al., 2002; Yunker and Macdonald, 2003; Lokoshchenko, 2005; Meyera and Wania, 2008; AMAP Assessment..., 2009; Pavlov et al., 2011; Rempillo et al., 2011].

The continuing studies of variability in the composition of snow in the framework of the territorial distribution of the snow cover characteristics accounted for formation of an area of science related to the geochemical studies of the snow cover. Its start in 1936 was indicated by two studies, in which the snow cover was considered as an embedding substrate for natural [Vlodavets, 1936] and anthropogenic dust [Vashkov et al., 1936]. As an independent object of geochemical testing, snow cover was first used in the study of dispersion halos of ore deposits [Kolotov et al., 1965] and in detection of aerial anthropogenic contamination [Elpatyevsky, 1976].

Geochemical studies of the snow cover proved to be informative in relation to anthropogenic contamination of landscapes [Glazovsky et al., 1983; Beloertseva, 1999; Walker et al., 2003], assessment of transborder transport of sulfates [Vasilenko et al., 1985] and

remote atmospheric transport of aerosols [Welch et al., 1991; Ganzey and Raszhigaeva, 2006; Shevchenko et al., 2015], as well as pollution of surface waters [Breslav et al., 1985] and of townscapes [Kasimov, 1995].

It is to be noted that these studies relating to the geochemical subject are united by one feature: all of them somehow or other characterize changes in the qualitative and quantitative parameters of the geochemical composition of snow in the snow mass. In accordance with the existing concepts, the snow cover is a kind of sedimentary porous matter consisting of two-component (air–water) medium, in which ice crystals, which form the structure and the texture of the snow mass, form pore walls. Due to the continuous processes of sublimation, the snow pores, unlike the pores of other porous media, are always saturated with water vapor. Its condensation leads to emergence of subcooled film liquid. In large pores, water covers their inner surface, and in narrow pores, it forms capillary liquid. The possibility of forming subcooled film liquid on the surface of ice crystals was theoretically proven by B.P. Veinberg [1940] and experimentally tested by V.I. Kvilikhidze et al. [1970]. It is supposed that gradient (thermoforetic) movement of film liquid on the surface of certain facets of ice crystals under conditions of saturation of the interporous space with water vapor may boost cryochemical reactions in the snow mass between the subcooled film liquid and the accumulated aerosol substance. Little is known about the geochemical effects of these reactions, despite the accumulated results of the snow cover studies.

SETTING THE PROBLEM

It is considered [Kotlyakov, 1968] that the activity of sublimation metamorphism is manifested in structural transformations of snow layers (changes in snow granularity, formation of dense/loose zones in the snow mass). Hence, layer-by-layer diagenetic transformations in the snow layers may affect the vertical variation of geochemical and physical parameters (pH value, ox-red potential, conductivity and snow density), controlling chemical transformation of aerosol substance accumulated in the snow mass. However, analysis of layer-by-layer changes in the indicated parameters is rarely applied; perhaps, this occurs because the use of cylindrical snow samplers for sampling snow layers (see, for example, [Kuzmin, 1957; Gray and Male, 1981]) leads to not exactly correct results, as the round-shaped cross-section of the sampler sampling snow horizontally does not fit into the geometry of the snow layers constituting the snow mass.

The objective of this study was to reveal the characteristics of layer-by-layer variation of integrated physico-chemical parameters (pH value, ox-red potential, conductivity and snow density) occurring during formation of the snow cover and to assess the informative value of the results obtained in order to monitor aerosol contamination of the snow cover.

DESCRIPTION OF SNOW ACCUMULATION IN THE REGION UNDER STUDY

Snow observations were conducted in the area under study, within the green zone 4 km west of Syktyvkar. The territory under study is situated in the watershed region in the near-palin part of the Sysol River and refers to the Mezen-Vychegodskaya plain, the surface of which has a wavy relief and banks of snow. The primary vegetation is represented by middle-taiga pleurocarpous moss forests with blackberry spots, which in boggy interfluves are replaced by hair-cap-moss spruce forests with participating birches and pine-trees. In cut areas, secondary small-leaved deciduous forests replacing the primary forests, with inclusions of ploughed plots, are found: the latter are usually covered by meadow vegetation.

Characteristics of snow accumulation. In the winter season of 2009/10, snow cover was formed in a non-uniform way. The first snow fell at the end of October, and by the beginning of the November thaw (the first decade), its depth in the key area was 18–23 cm. By the end of the thaw, the thickness of the snow cover decreased to 4–6 cm, and ice crust was formed on its surface (up to 3–5 mm), which stayed in the snow mass till the end of winter. On the last five days of December and in the first half of January, severe snowfalls were observed, with snow increment being 10–20 cm within ten days. From January 13 to February 24, the anticyclone weather set in with rare

snowfalls and low air temperatures. In the snowless period, which lasted on January 13–25, radiation crust was formed on the snow surface from transparent ice 2–3 mm thick, which preserved in the snow mass till the beginning of snow melting. The average weekly increment of the snow cover depth on the key site in this period of little snow reached 3–5 cm. The regime of snow accumulation changed by the end of winter, caused by severe snowfalls at the end of February and at the beginning of March. In this period, the snow mass increment was 10–12 cm. However, the highest increment of the snow cover was recorded from March 9 to March 27. By the end of this period, the thickness of the snow cover increased to 81 cm, but beginning with March 27, warm weather set in, and intense snow melting started. Already by April 5, the thickness of the snow cover decreased to 42 cm. Snow melted completely from the key site on April 22.

THE TECHNIQUE OF OPERATING THE MODIFIED LAYER-BY-LAYER SNOW SAMPLER

The layer-by-layer snow sampler with rectangular cross section expands the range of the equipment applied to the studies of the snow cover. The concept of a layer-by-layer snow sampler and the operation principles have already been previously described by the author [Tentyukov, 2014], and the sampler's design has been protected with a patent [Tentyukov, 2011b]. Shown below are the results of testing the modified device "Tentyukov's Snow Sampler".

The modification consists in the presence of an additional assembly, including a frame with roller rails and a knife-box. The improved design of the layer-by-layer snow sampler is protected with a patent [Tentyukov, 2013]. The new snow sampler enables scientists to obtain samples of snow of equal volume, when the snow mass has complex stratigraphy, consisting of horizons with interlayers, differing by their density and the number of glaciated inclusions, not homogeneous throughout the volume. The frame with roller bearing rails installed inside casing 1 has two pairs of longitudinal 2 and transverse 3 stiffening ribs (Fig. 1, *a*). The longitudinal ribs are made as roller bearing rails, and transverse ribs are made as metal plates. To fixate the frame at the required depth, the internal transverse plate 3 has stationary projecting fixers 4, and the external one has mobile fixers 5. Their mobility is ensured by reciprocal motion of the fixing rods 5 in the bearing cylinders 6, stiffly fixated at the ends of the transverse plate 7 (Fig. 1, *a*). Restriction of the reciprocal motion and of the projection of the fixing rods is regulated with the spring mechanism 8, located on the frontal transverse plate. To install the frame at the required depth, installation holes 9 are drilled in the three square plates with a

fixed step. To sample snow slabs of equal volume, the device has a knife-box 10, made as a rectangular box without the back side and with a knife-like front side. On the sidewalls of the knife-box, there are bearing rails 11, which move along the roller rails of the frame (Fig. 1, *a*). The height of the walls of the knife-box is greater than the fixed testing step. The error of the parallel layer-by-layer measurements of snow density with snow thickness being up to 50 cm is 6–8 %.

The procedure of snow sampling is shown in Fig. 1, *b–f*. The prism of the snow sampler (Fig. 1, *b*) is immersed vertically with constant downward force applied (Fig. 1, *c*). After the prism is immersed, a snow pit is dug before its front wall (Fig. 1, *d*). Then the front wall was removed, and the frame is installed fitting the installation holes over the snow surface (Fig. 1, *e*). The distance as far as the frame should be less than the height of the knife-box walls. Then the knife-box is installed into the roller rail (Fig. 1, *f*), which is moved into the snow core by translator movement. A snow slab (sized $2 \times 27 \times 36$ cm) from the knife-box is placed into a plastic bag to be weighed and for the snow density to be evaluated. Then, using a spring mechanism, the front fixers are released, the

frame is moved out of the installation holes of the back plate, removed lower by one fixed interval and fixated in the installation holes, after which the operation of sampling a new snow cake is repeated.

To be operated in deep and loose snow, the device is equipped with three composite legs 0.8 mm in diameter, each 1.5 m long (Fig. 1, *g*). The legs are inserted into special loop eyes mounted on the walls of the snow sample prism. As fiberglass plastic has a low heat exchange index, snow does not stick to the snow sampler walls, and the device can easily move in the snow mass along the bearing legs. The prism is fixed in the snow mass at the required depth with stopper screws. To allow easy deepening of the snow sampler prism into the snow mass, in which there are interlayers consisting of ice crust and/or snow slabs, the device is equipped with a metal ruler (1 m), one end of which is pointed, allowing penetration of the snow slabs and ice crust in the prism perimeter without crushing the snow layers.

Sample preparation for analysis on the sampling day consisted in weighing the sample on an electron balance having the accuracy of 0.1 g and in calculating snow density (ρ). After that snow was melted at



Fig. 1. A device for layer-by-layer snow sampling (*a*) a series of photos demonstrating its use (*b–g*).

1 – the casing of the snow sampler; 2 – longitudinal stiffening ribs; 3 – transverse stiffening ribs; 4 – immovable projecting fixers; 5 – movable fixing rods; 6 – bearing cylinders for movable fixator rods; 7 – the front transverse plate with movable fixating rods; 8 – the spring mechanism ensuring the reciprocal movement of movable fixating rods; 9 – the installation holes for the frame with roller bearing rails; 10 – a knife-box for making layer-by-layer snow samples; 11 – roller rails for moving the knife-box.

room temperature. In snow water, the pH values were determined using the potentiometric method with a glass and a flow silver-chloride electrode, the device HI 8519N, while electrical conductivity (EC) was measured with the conductometric method*. Deviation of the estimated values from the measured ones was on average: for electrical conductivity – 12 %, for pH – 17 %. In measuring the oxidation-reduction (ox-red) potential (Eh), a platinized glass electrode HI 3220 was used, which before the beginning of the work was tested by measuring the ox-red potential of $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ (ferricyanide – ferrocyanide) of equal concentrations $3 \cdot 10^{-3}$ M in 0.1 M potassium chloride solution. For the given system, $E_h = 430$ mV at 25°C . The platinized glass electrode was verified on a testing sample of snow water (10 aliquots were taken from one sample, which constituted the control sample). The testing showed that the equilibrium condition between thawed water and the electrode was reached after 4–5 minutes; the Eh records were stable with mean square deviation being $\sigma \pm 8.4$ mV, while the variation in the control sample was 350–370 mV.

RESULTS AND DISCUSSION

The structure of the snow mass. By the beginning of the observations (25.01.2010), the depth of the snow cover at the snow gauging station was 54 cm. In the snow mass, three horizons are identified, consisting of fine-, medium- and large-grained snow. The upper layer up to 25 cm deep is formed by loose matte white fine-grained snow, which in the lower part increases gradually, to form a layer (10–15 cm) of non-transparent grains of medium size. Beginning with the depth from 35 to 54 cm, the relative size of the ice crystals of snow increases even more – a layer of in-depth hoarfrost is formed. There are two layers in it, the texture of which differs. The upper layer is represented by loose snow of in-depth hoarfrost consisting of large-grained snow (the size of the ice crystals is 3–5 mm) with distinct Forel's lines on the sides, whereas the lower layer is formed by aggregates (6–10 mm) from large-grained firn-like snow. Between them, there is an ice interlayer as crust formed during the November thaw. Such three-layer structure of the snow mass was stable throughout the entire observation period and began to become quickly destroyed as snow began to melt (March 27). In general during the period of observation (25.01–05.04.2010), 11 snow sections were described, in each of which snow samples were taken from the layers, with the snow sampling schematic shown for each profile in Fig. 2).

Observation over the layer-to-layer variation of snow density showed a trend for the increase of snow density as the depth of the snow mass increased

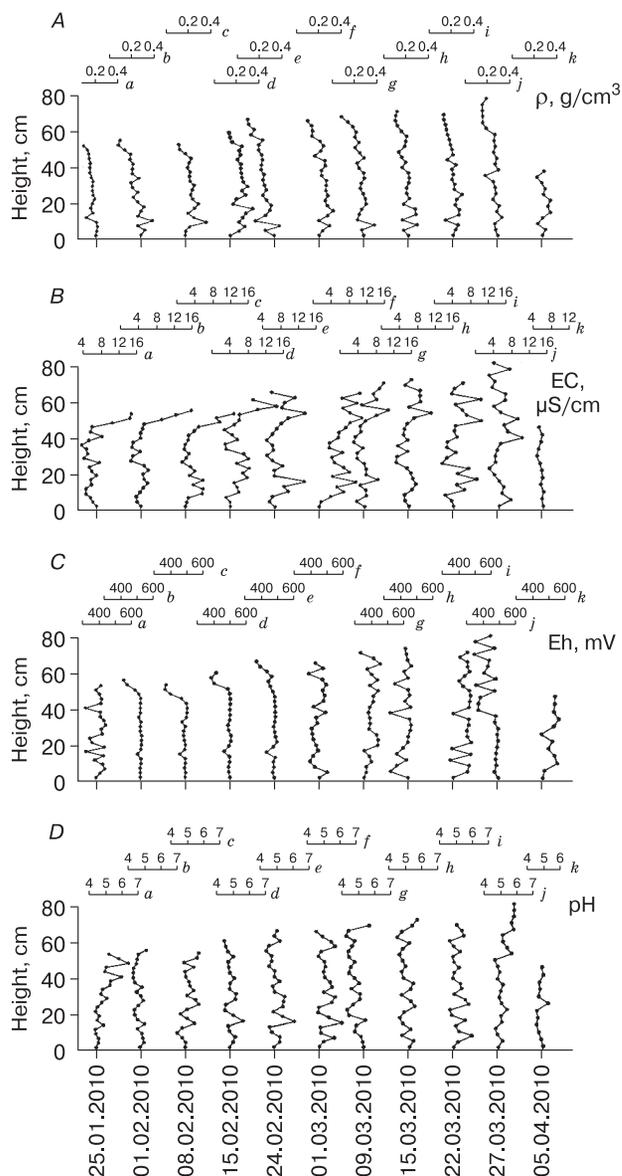


Fig. 2. Layer-by-layer variation of the integrated parameters of snow mass:

A – snow density (ρ); B – electrical conductivity (EC); C – the oxidation-reduction potential (Eh); D – the pH value (pH). The letters to indicate the order and the time of snow sampling: a – 25.01.2010; b – 01.02.2010; c – 08.02.2010; d – 15.02.2010; e – 24.02.2010; f – 01.03.2010; g – 09.03.2010; h – 15.03.2010; i – 22.03.2010; j – 27.03.2010; k – 05.04.2010.

Fig. 2, A), which preserved till the beginning of snow melting. By the end of the period of snow accumulation, the layer-by-layer changes in the snow mass density became more distinct. For example, while in February snow density variations in the middle part

* The integrated physical and chemical parameters of the snow water were determined in the ecoanalytical laboratory of the Institute of Biology, Komi Scientific Center, Ural Branch of the Russian Academy of Sciences (leading chemist V.V. Sitnikova and senior laboratory technician N.A. Trofimova, to whom the author expresses his thanks).

of the snow mass were in the range of 0.20–0.25 g/cm³ (profiles 08.02–24.02), in March the variation increased – 0.20–0.35 g/cm³ (profiles 01.03–27.03). In the last decade of March, penetration of relatively warm and moist air was accompanied by stronger winds. That caused solidification of snow from the snow surface, too – from 0.09 to 0.22 g/cm³ (profiles 09.03–22.03). However, already a week after, the density of the snow layers changed. In profile 27.03, under the upper solidified layer (0.20 g/cm³), a layer of medium-grained dry snow up to 10 cm deep and 0.13–0.15 g/cm³ was formed from fine-grained snow. As the snow height increased, the variation of snow density in the lower part of the snow mass decreased.

It should be generally pointed out that in the period of the snow cover increment, the density of newly fallen snow in the profiles amounted to 0.07–0.11 g/cm³, while that of snow in the deep layers was 0.29–0.40 g/cm³. At the same time, the data on the mean snow density varied little among the profiles – from 0.22 to 0.24 g/cm³, which agrees with the long-term mean values. In other words, in the snow profile vertical changes (variations between layers) were more contrasting and dynamic than the mean density values between the profiles.

Electrical conductivity (EC) was measured by a conductometric method. Conductometry is related to electrochemical methods of analysis, and it is based on measuring electric conductivity of dilute solutions*, which is proportional to concentration of electrolyte in the solution [Grilikhes and Filanovsky, 1980]. Observations over the behavior of electrical conductivity of snow in the period between snowfalls showed that from 25.01 to 01.02 its value in the top layer gradually increased from 12.0 to 16.2 μS/cm (Fig. 2, B). Electrical conductivity in the sample of newly fallen snow always proved to be lower than in settled snow taken from the snow surface in the period between snowfalls approximately by a factor of 1.5–4 (from 4.1–12.0 to 16.2–18.1 μS/cm). We assume that this is caused by sedimentation of sulfates, which are part of the ice hoar crystals [Tentyukov, 2007, 2011a].

The mechanism of sulfur dioxide oxidation forming ion-containing sulfates under conditions of low air temperatures is well elucidated in scientific literature [Gershenson et al., 1990; Gershenson and Purnal, 1990; Ermakov et al., 2003]. It is known that sulfate complexes of iron are formed in the atmosphere, which, subsiding on the surface, become hydrolyzed. Their mineral form in the snow mass under conditions of reducing environment is possible as copperas. Such are water sulfates with bivalent iron, which are often complemented by isomorphic admixture of Cu,

Mg, Zn, or Mn. All of these are formed exclusively as seasonal and anthropogenic minerals as they are frozen out of solutions [Miroshnikov and Shcheglova, 1959; Amichba, 1983]. As a result, the fraction of soluble compounds grows in the upper snow layer. Their electrolytic dissociation results in the growth of ion concentration and in the increase of electrical conductivity of snow in this part of the snow profile.

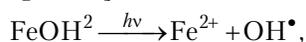
The oxidation-reduction potential. The temporal and layer-by-layer variation in the distribution of the ox-red potential Eh in the snow cover is shown in Fig. 2, C. The mean values of the parameter in the period of snow cover growth changed from 404 to 512 mV, and in the period of snow melting, from 347 to 399 mV. The variation coefficient for the first and second periods were 64 and 28 %, respectively. As a rule, the layer of newly fallen snow was characterized by a lower value of Eh (331–380 mV) than the lower layers – 400–460 mV. It is to be noted that in the first phase of the observations (25.01–24.02), the oxidation-reduction processes in the upper snow layer (10–12 cm from the surface) were more intensive. The mean values of Eh from five profile pits (from 25.01 to 24.02) M were (420.0 ± 61.5) mV with extreme values 370–521 mV, while in the lower mass of snow – M = (513.0 ± 18.4) mV, with the variation range from 502 to 527 mV (without considering fluctuations of Eh in pit 25.01). In the second phase of observations (from 01.03 to 22.03), which was characterized by increased cyclonic activity, frequent snowfalls and inflows of relatively warm air masses, the contrast of the ox-red processes increased throughout the entire snow profile, the mean values of Eh for four profile pits (from 01.03 to 22.03) proved to be lower: M = (410.5 ± 58.4) mV with the variation range from 331 to 480 mV. The third phase of the observations coincided with the beginning of intense snow melting (from 27.03 to 05.04). In this interval, the mean values of Eh were (391.7 ± 46.4) mV with the parameter varying from 338 to 479 mV.

Analysis of the distribution of Eh values in the cuts made in 25.01 and 01.02 profiles revealed the common behavior of the distribution curves for the ox-red potential (Fig. 2, C). It is assumed that such behavior of the curves in the upper part of the snow profile is related to photoelectrocatalytic oxidation of the aerosol substance accumulated in the snow cover. To a large extent, this is caused by “ultraviolet (UV) transparency” of the snow cover. It is known that sunlight may penetrate snow mass to the depth of 60 cm [Kuzmin, 1957]. At the same time, active areas on the surface of aerosol particles may influence capillary condensation and emergence of nanofilms with electrolytic and light sensitizing properties. The

* Molar electrical conductivity of solution (μ) is known to be equal to electrical conductivity of the volume of solution containing 1 mole of substance and contained between electrodes which are at the distance of 1 cm from each other. Its measurement unit is Siemens (S), a unit which is inverse to Ohm.

latter quality contributes to decrease of the width of the prohibited zone of UV-radiation, which makes it possible for reactions of photo-electrocatalytic oxidation of aerosol substance to take place when exposed to daylight and at rather low temperatures [Cort and Scot, 2001]. In elucidating the peculiar features of the reactions of photo-electrocatalytic oxidation of aerosol substance when exposed to daylight, a schematic is often applied, in which two submicron aerosol particles held on the surface of a large one due to adhesion exercised by capillary forces of the condensed liquid form an electrochemical cell, in which one particle performs the functions of a cathode, while the other one, those of an anode. The electrodes close in an external circuit, and photo electrolysis proceeds due to generation of photo current when the capillary liquid capable of photo sensitization is radiated. It is assumed that sunlight initiates formation of primary short-living radicals, which later participate in irreversible reactions of interaction, which end by forming stable products of the photo reaction.

The following schematic of photolysis of inorganic ions forming short-living radicals (OH^\bullet) is known [Wolling, 1960]:



where ν is the light oscillation rate; h is the Plank constant.

When a solution is radiated, a metal ion moves to the cation to become reduced, resulting in the change in the ox-red potential in the upper layers. Downwards in the snow profile, the activity of ox-red processes with participating short-living radicals is controlled by inter-layer differences of the ox-red potential, which play an important role in redistribution of the products of chemical transformation of the aerosol substance. As this redistribution occurs due to the electromotive force of the oxidation-reduction reactions in the wide pH range, the greater the intra-layer diffusion rate of the substance is, the greater is the potential difference between the snow layers or horizons. Such inter-layer variance in E_h in the snow mass creates prerequisites for boosting radial migration of elements with variable valence (Cr^{2+} , V^{2+} , Mo^{3+} , Ni^{2+} , Co^{2+}). As in all the studied snow cross sections the potential difference between individual layers reaches hundreds of millivolts and higher, it is clear that oxidation-reduction activity proceeds in the snow mass.

The pH value. Analysis of the behavior of the pH value in snow water has shown that at the beginning of the observation it varied in the range from 4.3 to 6.5 (Fig. 2, D). Later the distribution of pH was recorded within the range of 4.6–5.5 and remained such till the beginning of melting of the snow cover (March 27). In the period from March 27 to April 05, variations of the pH value somewhat decreased. Its

mean pH values by profile pits varied from 5.3 to 5.5, while layer-by-layer variance of the unit values of acidity in the snow mass proved to be more contrasting: the difference between minimum and maximum values of pH was 1.1–1.6. It should be noted that the observed behavior of changes in the pH reflects the integrated characteristic of the entire set of the acidic-basic interactions in the snow cover. Therefore, given the high extent of dust contamination of the snow cover, analysis of the behavior of vertical pH distribution provides little information [Kondratenok et al., 1995].

CONCLUSION

A modified layer-by-layer snow sampler has been tested, allowing to make samples of snow of equal volume when the snow mass has complex stratigraphy, consisting of horizons with interlayers, differing by their density and the number of glaciated inclusions, not sustained by the strike. The results obtained indicate that the new device will complement the list of equipment applied to the study of the snow cover.

The results of testing the upgraded device for layer-by-layer snow sampling have been used to determine changes in the integrated physical-chemical parameters of snow (pH value, ox-red potential, electrical conductivity and density of the snow) in the snow cover. It has been shown that electrical conductivity in the sample of newly fallen snow is always lower than in settled snow taken from the snow surface in the period between snowfalls approximately by a factor of 1.5–4. It has been demonstrated that layer-to-layer variation of distribution of the oxidation-reduction potential in the snow mass is higher in the period of the snow cover growth than in the period of snow melting (from 404 to 512 mV and from 347 to 399 mV, respectively). It is reasonably assumed that the layer-to-layer differences in the ox-red potential play an important role in redistribution of the products of chemical transformation of the aerosol substance accumulated in the snow mass. It has been shown that the greater the intra-layer diffusion rate of the substance is, the greater is the potential difference between the snow layers or horizons. It has been ascertained that the mean pH values by profile pits varied little (from 5.3 to 5.5, while layer-by-layer variance of the unit values of acidity in the snow mass proved to be more contrasting: the difference between minimum and maximum values of pH was 1.1–1.6).

According to the results obtained, it can be concluded that active physical and chemical transformations of the aerosol substance take place in the snow mass. This should be taken into consideration when interpreting the results of geochemical monitoring of the aerial anthropogenic contamination of the snow cover.

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