

Regional Pollution and Its Formation Mechanism over Greater Caucasus Glacier Taking into Account Atmospheric Dry Deposition

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Abstract—Atmospheric precipitation is an important factor in the self-purification of the atmosphere from trace impurities of both natural and anthropogenic origin. Microparticles in the atmosphere are effectively removed from it, both with precipitation and in the form of dry precipitation. Snow cover is a natural plate storage of pollutants falling out of the atmosphere in dry form and with precipitation. The study of the chemical composition of microimpurities in solid sediments in the zone of accumulation of glaciers opens up significant opportunities in the study of background monitoring of air pollution.

The microstructural analysis and chemical composition of the microparticles of the snow-ice stratum of high-mountain glaciers allows determining the composition of aerosols, the rate of their receipt, genesis, as well as the exact dating of the layers according to the historical time interval.

In the paper we present microparticle concentration falling on the glacier surface determined when obvious precipitation (dry fallout) has not been observed. Dry fallout monitoring has been conducted for different elevations of Elbrus Region including its bottom valley and upper level of 4000m a.s.l. The concentration of water-solid insoluble particles in snow samples has been determined using electron and optical microscopes. The results revealed a clear vertical volume and size distribution of microparticles (MP), as well as their modification during the summer and autumn months.

The heavy metal (HM) concentrations in snow have been determined using emission spectral analysis.

Keywords—*aerosol; glacier; impurity concentration; snow layer; precipitation; ascending currents*

I. INTRODUCTION

The state of the atmosphere and its changing over a long time is judged by condition of glaciers, natural collectors of atmospheric precipitations. Contaminated ice within glaciers is

accumulated due to leaching and dry aerosol deposition. Caucasian glacier sample analysis and aerosol size and mass distributions from spectral solar radiation contributed to identifying annual and seasonal snow layers, and to revealing the progress of impurity modification over a number of years. In addition, it has been found that in the seasonal, especially in the winter layers, there are more layers that, obviously, have been formed as a result of heavy snowfall and their metamorphism [1-5].

In our opinion, the formation mechanism of seasonal layers and the study of the transport and accumulation of impurities in them are of considerable interest. These studies are likely of certain value, if we consider that the Caucasus is situated in the mountain belt with the west-east transfer, and, as is known, the mountainous terrain plays a big part in air's self-cleaning capacity. The part of the “dry” fallout distributed in the form of aerosols from the western area, as well as the contribution of local pollution sources (weathering of rocks, rock falls, dust storms, avalanches, etc.) should, therefore, be measured. The evaluation of various sources contribution to the total content of impurities is also very important: leaching, “dry” precipitation and redistribution of impurities caused by snow sublimation. Apparently, such measurements can be made, at least, for the snow accumulated in winter, when mountain slopes are covered with snow and there are no powerful convective currents that raise the mass of aerosol particles of local origin to greater heights [4, 6-10].

To meet that challenge, a comprehensive approach is required:

1. To undertake researches and systematic observation at various heights over seasonal snow cover and its metamorphism, since a change in its properties is accompanied by impurities redistribution in the snowpack.

2. To investigate the content of impurities in the seasonal layers of glaciers (fine structure) and fresh precipitation at an altitude of 4000m and higher, tracing the air mass sources that led to precipitation.

3. To collect samples of "dry" fallout onto horizontal substrates and aerosol samples at various altitudes of the atmosphere near the Earth's surface [10].

A preliminary analysis of the experimental results indicates that the impurity concentration in an outer surface layer and inside differ, may be because of a substantive contribution made by "dry" fallout. It should also be noted that the impurities amount in the old snow is greater than in newly fallen one probably due to significant evaporation of snow, resulting in impurity redistribution within the snowpack. Moreover, the type of air masses that cause precipitation determines the nature and content of impurities and aerosols fall [7, 8, 10].

As already mentioned, sampling is performed at an altitude of 4000m above the sea level and more as atmospheric aerosol concentration at this elevation is close to the universal one and almost independent of the underlying surface (in a mild wind anticyclonic weather). But high in the mountains, even with a stable stratification and a small wind, a rather intensive convective mixing occurs as a result of mountain-valley circulation and turbulent exchange. Cumulus clouds continually emerging and a very slow decreasing tendency in the aerosol concentration (according to the data of aircraft soundings) point to this. Therefore, in mountainous regions, elevation has a significant impact on the concentration and spectral distribution of aerosols.

After precipitation events, the impurity concentration can increase significantly. The main role in this process belongs to the second source of accumulation of impurities in glaciers to atmospheric dry deposition. On days without precipitation there are two mechanisms for removing aerosols from the atmosphere: diffusion and gravitational sedimentation which simultaneously produce their effect as a rule. The aerosol removing intensity from the atmosphere largely depends on the aerosol particle dispersion [7].

II. MATERIALS AND METHODS

Dry deposition of aerosols is often estimated as follows. A shallow middle snow layer deposited during the last snowfall and a surface layer (1–2cm) samples are collected for several days without precipitations following snowfall. Since the surface of the snow cover can be considered as a natural collector of the dry deposition, a comparison of the impurity concentrations in the samples contributes to their evaluating. The microparticle concentration on the surface is 3–4 times, and sometimes an order of magnitude higher than in the middle layer. The longer the time between two snowfalls, the greater, due to dry fallout, the accumulation of aerosol particles. Study of snow pits containing the entire seasonal snow layers have also revealed that the middle part of each layer deposited during each snowfall is less polluted than the surface one. This applies both to the weight and number concentration, and to the average size of the micro-particles. Thus, samples of a snow pit near the hotel "Shelter 11" (firm

plateau) at an altitude of 4,000m have showed that the average particle concentration in the snow surface layers, deposited by three snowfalls, is 0.017 g/L, and in the middle of the same layers is 0.003 g/L. Accordingly, the number of particles in these samples are $35 \cdot 10^7$ L⁻¹ and $15 \cdot 10^7$ L⁻¹, and the mean sizes are 3.6 μm and 2.8 μm . The layers have been encountered with the surface contaminated more than the middle ones [7, 11].

On days free of precipitation, aerosols are removed from the atmosphere using three mechanisms: sedimentation, diffusion, and inertial deposition onto the surface of an object. As a rule, almost in all cases, three mechanisms operate simultaneously. However, the mechanisms that ensure the removal of aerosols from the atmosphere can vary greatly depending on the dispersion of aerosols.

III. RESULTS AND ITS DISCUSSION

Table I presents the study's results on snow contamination in the Elbrus region: a) near the village of Terskol - 2150 m; b) Cheget peak - 3000 m; c) a firm plateau on the southern slope of Elbrus in the area of the "Shelter of the Eleven" - 4000 m. The following parameters were determined: m – volume and n - particles concentration, d_3 - average size of insoluble micro-particles.

By Table I the mass and size distribution, and the mean aerodynamic diameter of microparticles in surface layer samples are larger than in the middle part of the layer. Moreover, this ratio is valid for all altitudes where the samples have been collected. The difference between micro-particles volume contained in the samples of surface layer and middle layers varies to a large extent. There are surface snow layers contaminated half an order of magnitude higher than the middle layers, for example, the third layer collected near Terskol area and even an order of magnitude higher, for example, the second layer collected at an altitude of 4000m a.s.l. In other samples, for example, collected at the elevation of 3000m a.s.l., we have observed that the micro-particle concentration at the surface layer is not significantly higher than in the middle one. Thus, such uneven distribution of impurities in the snow layer occurs due to the amount of time elapsing between two successive snowfalls. In particular, the maximum concentration of impurities in the third layer of the Terskol area can be explained by lengthy interval between two snowfalls (no significant precipitation for the month) and substantial anthropogenic air pollution on a valley floor.

Snow particle size spectra of collected snow samples (Table II) show that the maximum observed diameters of the particles under study are 0.5–4.0 μm , they make up 90–95 %.

TABLE I. MASS AND SIZE PARTICLES DISTRIBUTION, AERODYNAMIC DIAMETER OF MICROPARTICLES IN VERTICAL PROFILES OF BORES AT DIFFERENT HEIGHTS

Pollution parameters	Snow falling	Surface of the 2nd layer	The middle of the 2nd layer	Surface of the 3d layer	The middle of the 3d layer	The 4th layer
2100m						
m, g L ⁻¹	0,022	0,087	0,061	0,157	0,029	0,033
n, 10 ⁷ , L ⁻¹	34,43	110,06	92,06	182,59	55,29	124,67
d ₃ , MKM	3,96	4,10	3,98	4,64	3,66	2,92
Pollution parameters	Surface of the 1st layer	The middle of the 1st layer	The 2nd layer	The 3d layer	The 4th layer	The 5th layer
3000m						
m, g L ⁻¹	0,006	0,005	0,031	0,018	0,011	0,013
n, 10 ⁷ , L ⁻¹	8,79	31,54	77,49	55,31	28,98	20,04
d ₃ , μm	4,02	3,07	3,36	3,07	3,27	3,5
Pollution parameters	Surface of the 1st layer	The middle of the 1st layer	Surface of the 2nd layer	The middle of the 2nd layer	Surface of the 3d layer	The middle of the 3d layer
4000m						
m, g L ⁻¹	0,013	0,004	0,024	0,002	0,014	0,004
n, 10 ⁷ , L ⁻¹	39,54	28,80	39,87	10,14	25,55	6,60
d ₃ , μm	3,18	2,35	3,8	2,4	3,78	3,68

TABLE II. SPECTRAL PARTICLE SIZE AND MASS DISTRIBUTION AT DIFFERENT HEIGHTS

H, m	0,5 < d ≤ 4, μm		4 < d ≤ 10, μm		10 < d ≤ 20, μm		d > 20, μm	
	m,%	n,%	m,%	n,%	m,%	n,%	m,%	n,%
2100	25,45	89,77	34,33	9,56	17,78	0,57	22,44	0,06
3000	26,64	93,64	35,88	5,39	27,9	0,55	9,58	0,25
4000	37,35	95,26	34,88	4,74	26,27	0,48	-	-
5000	41,53	96,31	33,69	3,51	24,78	0,18	-	-

Particles size of more than 4 microns is an order of magnitude less, and larger particles sizes (d > 10–12 microns) are two orders of magnitude less. This is because the largest particles, d > 10 μm, have short atmospheric residence time and are removed near the particles sources through sedimentation. The particles counting with d > 10 μm in concentration of freshly fallen snow samples is about 0.5% of all particles, while the mass concentration of particles varies to a wider extent: 5–50%. Size-distribution of micro-particles in the glaciers winter layers has the same order. The mean particle aerodynamic diameter in freshly deposited sediments at altitudes of 2100, 3000 and 4000 m a.s.l. vary in the range from 2.92 μm to 4.64 μm; 3.07 μm - 4.02 μm and 2.38 μm - 3.80 μm, respectively, and on the Adyrsu and Ullukol Glaciers

- in the range from 2.80 μm - 4.53 μm and 2.50 μm – 2.90 μm, respectively. It is clear from the data presented here that particle size distribution in the newly fallen snow, as well as in seasonal snowpack and glaciers winter layers, is not significantly different. The differences are attributable primarily to the regional high-rise distribution of atmospheric aerosols. This additionally emphasizes our assumption that the enlargement of particles due to melt water infiltration in the areas where sampling have been collected does not take place, at least in winter layers [3]. Comparison between the surface and middle layers pollution as well as the micro-particles size distribution in glacier layers and seasonal snowpack, lead us to conclusion that a significant contribution to the complicated metamorphic processes of snow-ice transformation is made by dry fallout.

We have measured the soluble part of the impurities. The content of trace elements have been determining in the sample prior to filtration and in suspended solids. The analysis indicates that chemical concentrations of Cr, Ni, Ag in samples and suspensions that were processed before filtration are comparable, for some elements the spread is 30 - 40%. The concentration of Mn in suspensions is three to five times less than in the collected glacial water. This suggests that the compounds in which Mn is found are mainly soluble in water, whereas Cr, Ni, Ag compounds are sparingly soluble [2].

In addition, full spectrum characterization of aerosol numbers shows that although giant in size (d > 1 μm) and supergiant (d > 30 μm) particles make little contribution to total aerosol particle number concentration, they have a significant impact on the particle mass distribution. Since these particles make a great contribution to the aerosol mass during dry fallout, most attention has been paid to this part of the spectrum.

In winter, the particles transfer into the upper layers in the troposphere is difficult because of the surface inversion layers and snowy underlying surface. At the same time, giant and supergiant particles are very important in the mass distribution, and therefore, in the dry fallout. The above is well illustrated in Table III, which include mean, minimum and maximum particle number concentrations and particle mass concentrations for individual summer and autumn months.

TABLE III. MINIMUM, AVERAGE AND MAXIMUM PARTICLE CONCENTRATIONS FOR THE SUMMER AND AUTUMN MONTHS

month	n cm ⁻³			m 10 ⁻¹² g cm		
	n ^{min}	\bar{n}	n ^{max}	m ^{min}	\bar{m}	m ^{max}
July	130	210	270	0,9	34	90
August	80	202	310	1,4	27	92
September	85	105	250	0,5	6	23
October	80	111	210	0,2	0,9	5

From Table III it can be seen that the concentration in the autumn months is only two times lower compared to summer ones, while the particles mass is almost 40 times lower. On different dates, the particles concentration also varies greatly but less than the mass, the maximum value of which reaches two orders of magnitude. Thus, from the above results, it follows that in summer the mass of large and giant particles,

which are the dry deposition main components, is almost 1.5 times higher than in autumn.

Particle size spectra of fresh precipitation and air fall deposits at altitudes of 3,000–4,000 m and in glacial layers have revealed that the main reason for the divergences between the trace contaminants in seasonal layers of the glaciers and deposits brought by precipitation and dry deposition is due to the largest aerosol particles with a diameter of up to 20 μm . Particles of this size are mainly resulted from rock crushing.

It is known [9] that various aerosol fractions are closely related to their chemical composition. Medium and coarse aerosols mainly consist of a substance that is characteristic for soil particles. They represent such elements as aluminum, silicon, magnesium, manganese, nickel, titanium, iron. With this in mind, we have investigated the relationship between the concentration of a water-insoluble aerosol released from clouds and heavy metals concentration in the sub-cloud layer. The correlation between heavy metals and water-insoluble aerosols concentrations is non-linear in their size spectrum. The regression equation can be expressed in terms of Chebyshev orthogonal polynomials up to the fourth order. It has the form of:

$$Y = C_0 P_0(x) + C_1 P_1(x) + C_2 P_2(x) + \dots + C_3 P_3(x) + C_4 P_4(x), \quad (1)$$

where Y – heavy metal (HM) concentration, $P_i(x)$, $i=0, 1, 2, 3, 4$ – Chebyshev polynomials with respect to the water-insoluble particles concentration with a set of values x_1, x_2, \dots, x_n .

Table IV presents the HM concentration values in fresh snow samples, determined experimentally (C) and calculated (C_b) using this equation.

TABLE IV. EXPERIMENTAL AND CALCULATED VALUES FOR HM CONCENTRATION, MKG L⁻¹

Samples at the height b.s.l.	Cr		Ni		Mn	
	C	C _b	C	C _b	C	C _b
H = 3500 M	7,31	7,308	2,24	2,240	10,73	10,731
H = 3700 M	44,34	44,340	12,75	12,750	84,15	84,150
H = 4000 M	14,99	14,991	7,58	7,939	35,11	33,852
H = 4020 M	16,45	18,469	5,46	5,462	32,60	33,852
H = 4300 M	20,49	18,469	8,30	7,939	20,86	20,867

Table IV shows, for the indicated elements, the concentration is almost functionally related to the concentration of water-insoluble aerosol particles. The coefficient of determination for these elements, including zinc and lead, is higher than 0.98 [11].

IV. CONCLUSIONS AND RECOMMENDATIONS

1. Assessment of the relationship between HM concentration and water-insoluble particles indicate that the washed out heavy metals impurities are rather closely associated with both fractions of fine and coarse water-insoluble particles. Hydrometeors such as clouds and precipitations intensively absorb aerosol particles and resulted in chemical composition.

2. Large, giant and supergiant contaminants deposited from the atmosphere and carried by air currents, significantly change the radiation properties in the underlying surface. Therefore, studying them, estimating measurements of mass and volume will provide more accurately assess the radiation flux on the snowpack melt including glaciers.

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