VARIABILITY OF A CHEMICAL COMPOSITION OF THE SNOW COVERS IN A BACKGROUND AREAS OF SIKHOTE-ALIN AS AN INDEX OF THE TRANS-BOUNDARY TRANSFERE OF CONTAMINATION

KACHUR A.N. AND KONDRATYEV I.I.
Pacific Institute of Geography, Far Eastern Branch of Russian Academy of Sciences

Primorskii Krai located at the boundary of the Eurasian continent and Pacific Ocean is under the influence of both continental air masses and oceanic ones which should determine the macro- and microelement composition of aerosol delivered by air currents. Along with the developed territories and relatively great industrial centers, there are in Primorye areas quite distant from the settlements which could be considered as the background ones. The “natural”, not distorted by the anthropogenic impact composition of the atmospheric fallings could be only determined in the background areas, i.e., within areas distant from the local emission sources (settlements, roads and industrial centers). Data of the background composition of the atmospheric fallings is objective information that can be used for both evaluation of the extent of anthropogenic effect on the environment in the urbanized zones of the region and for control of the regional background of the trans-boundary transportation of pollutants.

The authors of the paper make the attempt to fill gaps in information of the composition of atmospheric fallings in winter within the background areas of Sikhote-Alin, to estimate the effect of the mountain system and to determine regional sources of delivery of the aerosol matter.

The assumption of the deciding role of air currents in the formation of the composition of atmospheric fallings within the background areas has determined a necessity to obtain the quantitative characteristics of the ratio of continental and oceanic transportation of air masses to Sikhote-Alin. The climatological studies and everyday observations suppose that, at least, in winter, a predominance of the northern and western directions of winds is characteristic of Primorye. However, the quantitative estimates of the contribution of one or another direction of transport based on the retrospective analysis of trajectories of air masses movement for the area under study were earlier not obtained. They were obtained by authors from analysis of the prehistories of movement of air masses using the baric topography maps for a level of 850 mb.

As the source material for this work, the results of studying the chemical composition of the snow cover carried out in 1985-1989 jointly by the Far-Eastern Research Hydrometeorological Institute of GOSKOMGIDROMET and Pacific Institute of Geography, Far-Eastern Branch of Russian Academy of Sciences were used.

The investigations of the chemical composition of the snow cover have been carried out both within the background areas of the middle Sikhote-Alin and in the settlements and close to roads (Fig. 1). In the paper, the results of studies within the background areas, i.e. data obtained on the reserve territory or in the locations distant from settlements and roads are only analyzed. On the skeleton map, the points of sampling are shown by transparent circles. The area of background studies is zones of the Ussuriisk mountain taiga difficult of access, therefore, the helicopter was usually used to convey a place of study.

Fig.1. Sampling of snow in Primorsky Krai in 1985-1991.

The snow samples were taken using the plastic tube of 120 mm in diameter and were storage in the polyethylene packs. In the each point of background zones, three samples which were simultaneously analyzed were taken which allowed to exclude the probability of accidental errors. The snow samples were melted at the room temperature in the glass-ware. The volume of melted snow reached 3-4 liters. In the water from melted snow, pH and basic ions: Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, $SO_4^=$ were determined, then it was forcedly filtered through the membrane filters of "Synpor" mark with pore size of 0.3-0.4 μm [1]. The filters, after decomposition, were used to determine the insoluble form of microelements.

In the suspended and soluble fractions, microelements Mn, Fe, Cu, Zn, Ni, Pb, Cd were determined. The microelements were determined using a chemical method, with ending of the analysis on the atomic absorptive spectrometer "Hitachi" 180/70" [2]. From the results of analyses of three snow samples taken at one point, the aggregate error which includes errors of sampling, preparation and analysis of sample was calculated. It was determined as the coefficient of variation with the assumption that the obtained values of concentrations of macro- and microelements at the sampling point are normally distributed. The aggregate error determined includes also the natural variability of concentrations of the determined elements in the snow cover. The aggregate error of pH determination was 2-3% while that of basic ions – 10-15%, microelements – 30% on the average and, for cadmium and lead, the aggregate error of determination reached 50% in individual samples. In those cases, when the error exceeded the criteria of data reliability, the results of analysis were rejected and the sample was excluded from the further analysis.

For a period of study, about 500 snow samples were taken. About 3500 maps of baric topography were processed based on which trajectories for 896 days were constructed.

The particles suspended in the atmosphere move along with air currents and the latter determine the ways of their transportation beyond the bounds of the generation zones. Settling on the surface of land, seas and oceans, the aerosol matter takes part in the formation of soil layer and bottom sediments. The distances for which aerosol is transported can reach several thousands kilometers. So, the dust of the Central-Asian deserts is recorded in Hawaii and Line Islands in the Pacific Ocean [3, 4]. It has long been known of the transportation of dust from the Asian continent to the Japanese Islands [5].

It is known that of the vertical structure of the wind directions and speeds in the area under study for all seasons, the predominance of the western0eastern transport at heights of 3 to 12 km is characteristic. And only within the surface layer, the seasonal variability of wind directions is observed [6]. In summer, the southern directions prevail while in winter – northern and north-western ones.

With the north and west winds, the continental air masses enriched with the terrigenous elements come to Primorye while the summer monsoon (south and east winds) deliver the oceanic air masses to Primorye.

As for the area under study located on the boundary of the ocean and continent, the frequency of arrival of air masses of one or another origin determines, to a large extent, the composition of the aerosol matter in the atmosphere and fallings. The major part of aerosol moves in the surface atmosphere layer, therefore, this layer is of the most interest of analysis

[7]. The surface layers of atmosphere exchange intensively by the matter with the underlying surface enriching from the natural and anthropogenic sources. The contribution of the transport directions has been analyzed using the maps of reverse trajectories of moving air masses. As the point to which the trajectories were reduced, the settlement Terney was taken as in 1980s close to it, the station of the background monitoring was located and, on the territory of the Sikhote-Alin biospheric reserve (SABR), the major number of investigations has been carried out. Trajectories were constructed using maps of baric topography AT^{850} for every day for a period of 1986 to 1988. The basic idea of this method is described in work [8]. The reverse trajectories were constructed with the retrospective of two days (Fig. 2). The frequency of passing trajectories was estimated for 8 sectors. If a trajectory passed through one sector then it was given a weight equal to 1 for the day at which the coming of air masses to the SABR falls. If a trajectory passed through two sectors in a given day then it was given a weight equal to 0.5 etc. For the sake of simplicity, it was considered that trajectories pass the same route sections within each sector. Then, values assigned to trajectories were summed up by sectors and their contributions in percentage for a month and year were determined.

The results of the analysis carried out showed that the continental directions of transportation (sectors I, II, III, IV) were predominant for all seasons. July 1986 proved to be the only exception for the whole period of observations when, at the side of ocean (sectors V, VI, VII, VIII), more than a half (55.6%) of all trajectories have fallen [9, 10, 16]. The general tendency of distribution of trajectories over sectors has remained over the whole period of observations (Table 1, Fig. 3).

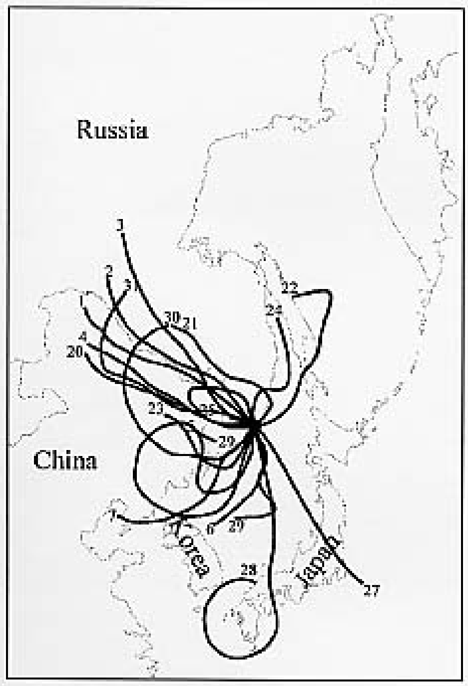

Fig. 2. Two-day isobaric 850 mb back trajectories of movements of atmosphere mass in Sikhote-Alin reserve.
(2,......31 days of arrival of air mass in Sikhote-Alin reserve territory).

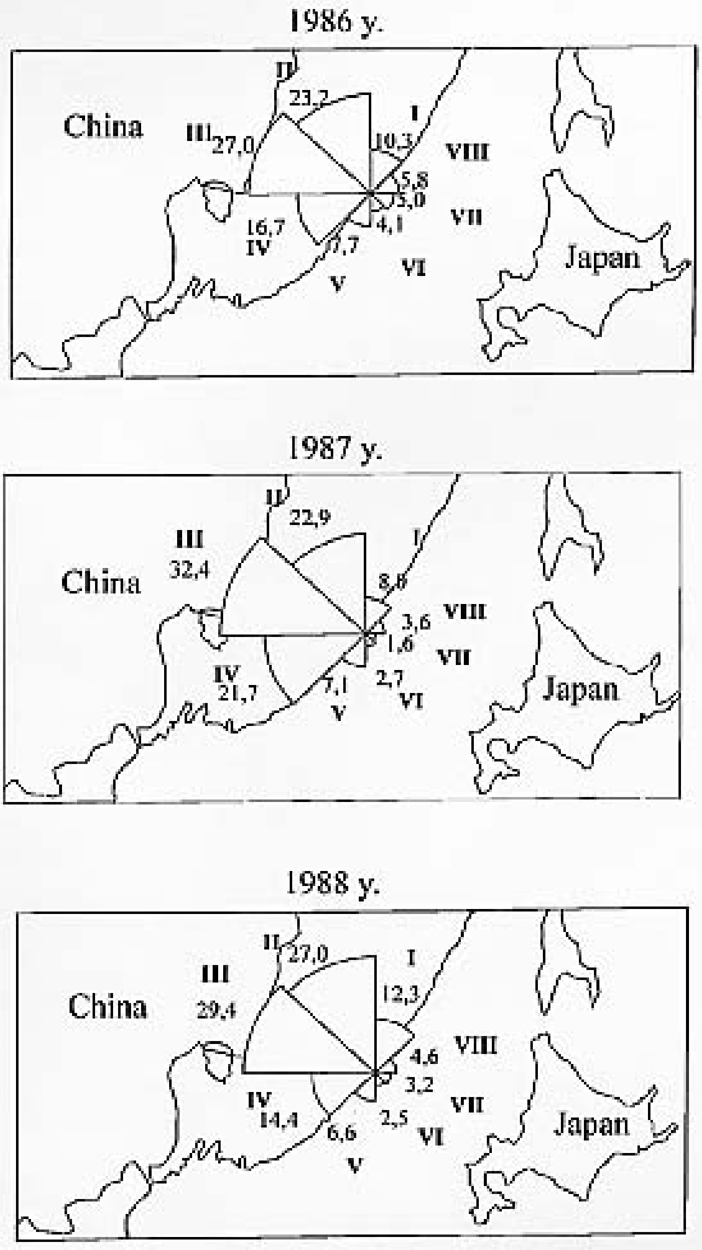

Fig. 3. Contributions (in %) of the number of back trajectories by sectors averaged for a year, for the background area

Table 1 Contributions (in %) of the number of reverse trajectories by sectors averaged for a year, for the background area

Sector / Year	I	II	III	IV	V	VI	VII	VIII	Contribution of oceanic directions
1986	10.3	23.2	27.0	16.7	7.7	4.1	5.0	5.8	22.6%
1987	8.0	22.9	32.4	21/7	7.1	2.7	1.6	3.6	15.0%
1988*	12.3	27.0	29.4	14.4	6.6	2.5	3.2	4.6	16.9%

* data of January-June

The relative contribution of the transportation directions by sectors can be lined up as follows: III > II > IV > I > V > VIII > VII > VI.

In the winter months, the contributions of the continental transportation increase (Table 2). From Table follows that during winters of 1986-1988, a tendency to increase in the number of trajectories coming on the side of continent was observed that supposes the intensification of the effect of continental air masses.

Table 2 Contributions of the continental directions of transportation of air masses to SABRduring winter seasons

Months	Contributions of continental directions
January (86) + February (86)	88.4%
December (86) + January (87) + February (87)	91.1%
December (87) + January (88) + February (88)	98.0%

The spatial variability of the atmospheric fallings has been studied using the integral samples of snow cover which were taken at the end of winter period. Taking into account a predominance of the western and northern directions of transportation of air masses as well as the meridional location of the Sikhote-Alin ridges, one could suppose that there are differences in the composition of fallings on the west and east slopes of this mountain country.

The spatial distribution of the concentrations of ion Cl, pH of snow cover and densities of fallings of the suspended matter over the Krai territory are given in Fig. 4, 5, 6. Of the distribution of the concentrations of ion Cl in the snow cover, a sharp growth in the concentration gradient on the east slope and its relatively smooth decrease on the west one are characteristic. So, in the Ussuriisk reserve (most west background point), concentrations of Cl reached 0.34, close to Snezhnaya hill 0.27 while in the middle reaches of Avvakumovka River 1.13 mg/l. The same pattern is also traced within the SABR. On the west slope, in the Kolumbe river valley, concentration of Cl is 0.21 while on the east one it is 0.61.

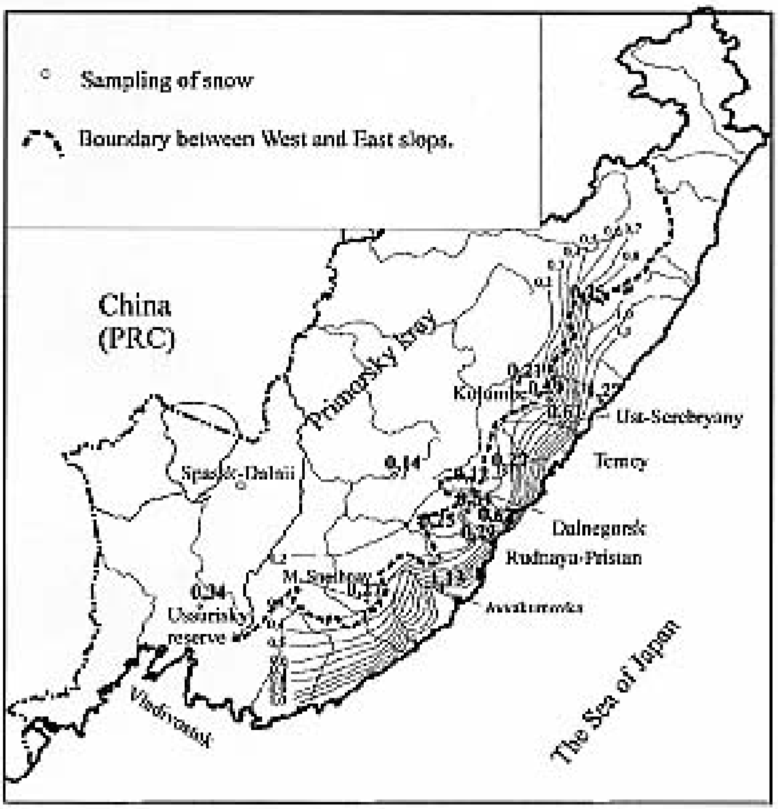

Fig. 4. Chloride content (mg/l) in snow in 1986.

Fig. 5. PH of snow in 1986.

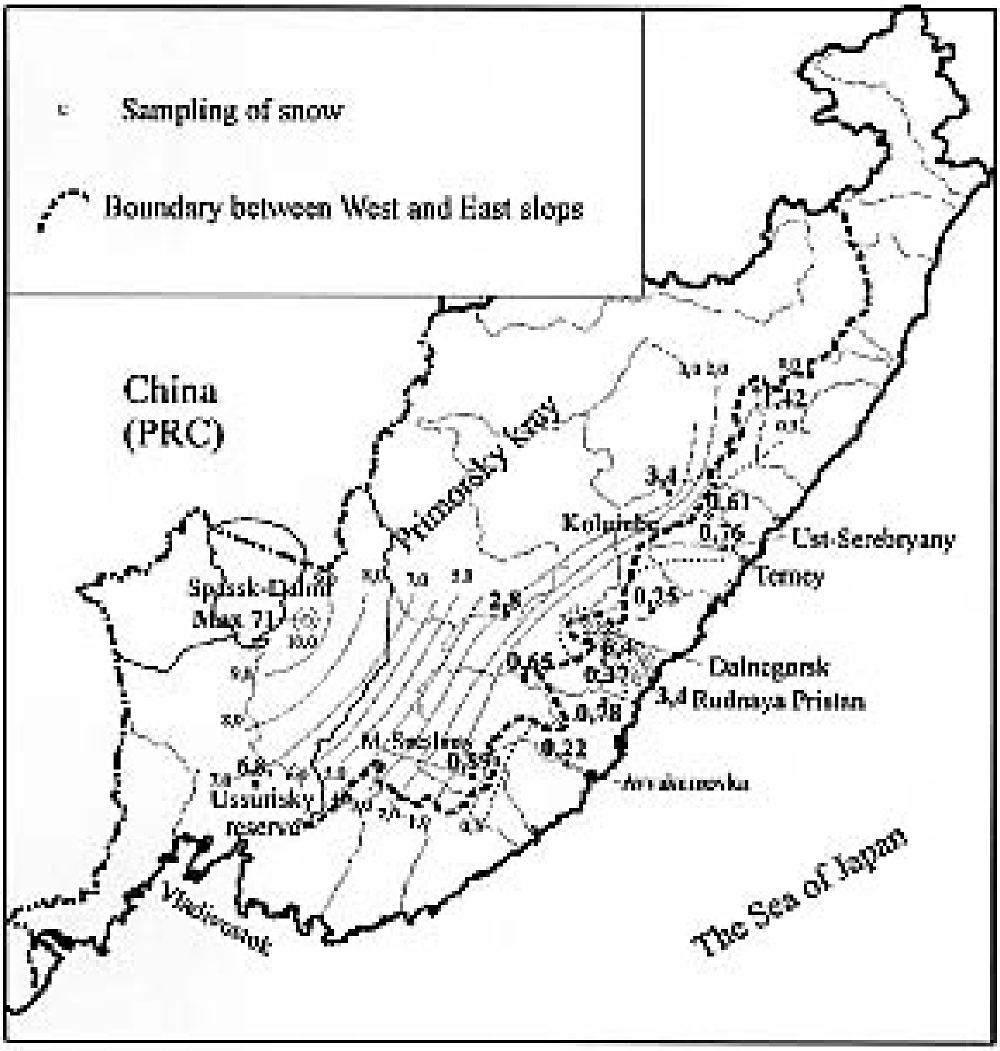

Fig. 6. Input of dust (mg/m² a day) in winter (snow) in 1985.

In the spatial distribution of pH of snow cover, its decrease in a direction from the west to the east and sharp growth in the anthropogenic areas are observed. So, pH gradient of snow cover within the section of Ussuriisk reserve – Avvakumovka is 0.95 pH units per 100 km. Within the SABR, it is even higher and, in the section between Kolumbe and Ust-Serebryanny reaches 1/94 units of p\pH per 100 km. It should be noted that in 1986, quite low values of pH of snow cover were observed in the background areas on the east slope of the middle and southern Sikhote-Alin. So, in the middle reaches of Avvakumovka river, pH reached 4.22 while in Ust-Serebryanny – 4.38.

Of the distribution of the suspended matter in the snow cover, a smooth reduction in the density of fallings from the west to the east and sharp fall of dust content in the snow on the east slope are characteristic. The sharp increase in the falling density in the anthropogenic areas is noted. It should be noted than isolines in Figures were constructed from data obtained in the background areas and only in two anthropogenic zones (Rudnaya river valley and

Spassk-dalny). The remaining towns and settlements are not presented in these Figures in view of non-availability of data for a period of observations. It is natural that if these data were presented then the fallings distribution pattern would be more complex.

Even such superficial analysis of the spatial distribution of fallings over the Krai territory does not allow to have doubts about that the flows of aerial matter are not equal on the west and east slopes of Sikhote-Alin. Obe could assume that the system of mountain ridges can effect on the intensity of the flows of aerial matter from atmosphere to the underlying surface.

The mountain system itself, due to its relatively moderate height is not an obstacle for transportation of aerosol in the upper layers of troposphere but most saturated with the suspended particles surface 1-km layer changes the turbulence parameters as a result of interaction with the underlying surface which, in turn, affects the intensity of aerial fallings. Moreover, a direct interaction of the surface air layer with the forest vegetation increases the rate of aerosol removal 2-16 times as compared with that for the open spaces (9).

In order to obtain the quantitative values of the parameters under study, data for the east and west slopes were properly averaged. In addition, two control points were chosen in the deliberately background area – on the Sikhote-Alin biospheric reserve territory: in the upper reaches of Kolumbe river – on the west slope and “cordon” of Ust-Serebryany – on the east one. For these points, there was most complete series of data [10, 11, 12]. The interface is the watershed of Ussuri river and Japan Sea basins. The results of analyses averaged over the whole period of observations are given in Table 3.

Table 3 Averaged over the whole period of observations (1985-1989) concentrations of basic ions and metals (in soluble form) in the snow cover within the background territories of the Sikhote-Alin region

Area	pH	Na^+	K^+	Cl^-	$SO_4^{=}$	Ca^{++}	Mg^{++}
mg/l							
East slope	4.99	1.39	0.34	1.12	1.57	0.9	0.23
West slope	5.38	0.99	0.35	0.35	1.66	1.23	0.24
Average over area	5.21	1.19	0.34	0.76	1.62	1.06	0.24
Average value for the west coast of Japan*	4.86	3.27	0.3	6.52	3.65 2.8	0.74 0.69	0.45

Area	Fe	Mn	Zn	Cu	Ni	Cr	Pb	Cd
μg/l soluble fraction (its contribution (in %) into total concentration)								
East slope	7.7 26%	9.0 78%	13.9 88%	1.0 58%	1.2 43%	0.38 26%	4.9 49%	0.33 84%
West slope	9.2 1.4%	9.6 61%	10.9 70%	0.98 48%	1.7 34%	0.49 17%	4.3 34%	0.28 82%
Average over area	8.4 1.8%	9.4 68%	12.2 78%	1.0 52%	1.4 36%	0.45 20%	4.7 41%	0.32 82%

* a numerator is total concentration while a denominator is a continental contribution

From Table follows that, for the whole period of observations (except 1985), pH of snow cover on the west slope is higher that that on the east one. Correspondingly, concentration of ion Cl on the east slope is three times higher than that on the west one. In addition, the contribution of the insoluble fraction of microelements into their total concentration on the west slope is more than that on the east one (Table 4). In Table, only data of Mn are given as there is the most complete series of data for this element.

Table 4 Temporal variability of pH, contribution of soluble fraction of manganese and ratios of basic ions in the snow cover within the background area

Year	Area	pH	Contribution of soluble fraction of MN, in %	SO_4/Cl	Ca/Na	Ca/Mg
1985	Average value	4.99	86	0.95	0.78	2.2
	East slope	5.07	84	0.74	0.59	1.91
	West slope	4.85	87	2.5	2.0	3.0
1986	Average value	4.8	60	2.4	1.36	3.59
	East slope	4.46	80	1.85	1.26	2.36
	West slope	5.19	48	6.99	1.82	4.18
1988	Average value	5.35	63	5.67	0.73	4.3
	East slope	5.15	70	4.57	0.59	4.6
	West slope	5.52	62	8.04	0.95	4.0
1989	Average value	5.71	62	1.26	1.0	14.8
	East slope	5.29	78	0.69	0.72	11.8
	West slope	5.98	47	2.48	0.96	17.9

It is not difficult to note that, year by year, pH of snow cover increases and, correspondingly, the contribution of insoluble component rises too. The change of the composition of the atmospheric fallings for a period of observations is most noticeable from a dynamics of a ratio of ions Ca and Mg. The former is an element of mainly continental origin while the latter of oceanic one. Accordingly, this rate for the west slope is higher than that for theeast one. On the average, over the background area, this ratio increased from 2.2 in 1986 to 14.8 in 1989. It increased still more for the point in Kolumbe river (from 1.6 to 21).

In spite of a predominance of continental directions of transfer of air masses, their intensity is unsteady in time. In 1986-1988, their intensification, especially in winter, was observed. This tendency is also traced from results of studying the ion and microelement composition of the snow cover.

The tendency to a growth of pH index has been revealed from 1986 and remained to the end of studies in 1989. In 1985, pH of snow cover on the east slope was higher than that on the west one and, accordingly, the contribution of soluble component of manganese was lower. The same tendency is also characteristic of other elements.

In opinion of authors, the general pattern of forming the composition of the atmospheric fallings in winter has the following appearance. Natural – background – precipitation coming with the oceanic air masses could be sufficiently “acid”, i.e. has an average pH equal to 4.5 and even lower [13]. The aerial matter of terrigenous origin contains compounds of calcium, aluminum, silicon. Falling on the snow, it alkalifies it, i.e. in snow and, later, in melted water, a partial dilution of these macroelements takes place. In this case, a reaction proceeds in which the free ions of hydrogen are bonded which, accordingly, increases pH of snow. In Table 3, concentrations of basic ions and microelements are given. This supposes that we deal with the ultra-fresh waters which are not saturated with practically all of elements and they can not drop out as salts [14]. Therefore, compounds of iron and other microelements can be in both soluble and insoluble forms at sufficiently large variations of pH index. But a ratio of these forms depends on the acid-base indicator of the water environment which we observe in the samples of snow cover.

The aerosol is more efficiently removed on the west slope of Sikhote-Alin. The west slope is windward for the prevalent air flow. The continental air masses, facing the obstacles in the form of mountain ridges, change the flow turbulence parameters which cause more intense removal of aerosol. Because a significant part of the aerial matter drops out in the continental areas and on the west slope of Sikhote-Alin, air masses relatively depleted of the terrigenous aerosol come to the east slope. This determines the lower levels of dropping-out of suspended matter on the east slope and the lower values of pH of snow cover remain there. However, the picture contrast is underlined by the orientation of the east slope towards ocean and proximity of the Japan Sea. To a certain degree, mountains are also a barrier for oceanic air masses. Accordingly, a considerable part of the oceanic aerosol drops out on the east slope of Sikhote-Alin.

Transformation of the aerosol composition of continental air masses continues as they are moving over the Japan Sea. It is natural that, in this case, the contribution of components of marine origin in these masses increases as compared with the Sikhote-Alin biospreric region. In Fig. 7, the averaged for 1983-1988 data of the ionic composition of fallings over the station network along the western coast of Hokkaido and Honshu as well as throughout Japan [15,16]. Average values of pH on the western Japan coast are lower than within the background areas of Primorye which is apparently explained by the relative depletion of lithophile elements of air masses which drop out as masses move over the Japan Sea. One can suppose that, without continuous arrival of continental air masses which are sufficiently “pure” and enriched in the lithophile elements, more “acidic” precipitation would fell in the Japanese Islands.

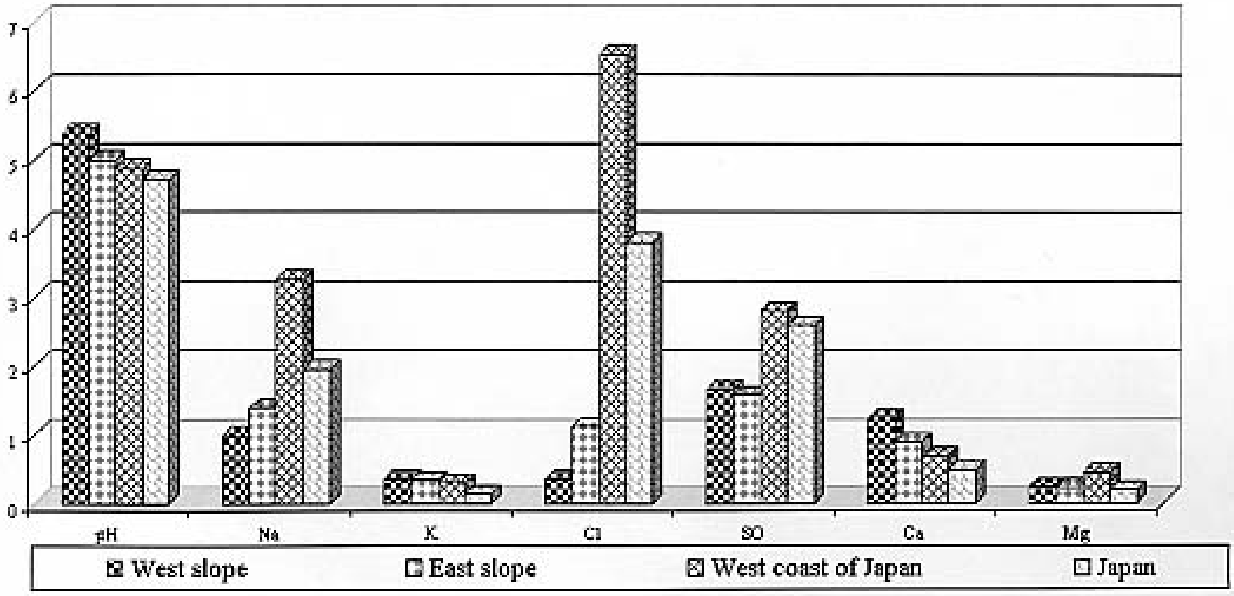

Fig. 7. pH and concentrations of main ions (mg/l) in atmospheric presipitation of Japan-Sea region.

The concentrations of ions of Na, Mg, SO_4 and especially Cl of marine origin on the western Japan coast are noticeably higher than in the SABR. The concentrations of Ca ion are somewhat lower than those in the area under study. In addition, the concentrations of Ca ion in the precipitation for Japan on the average are even lower that those on the western coast.

This information supplements the general pattern of aerial matter transfer in the Japan sea region. The air currents transporting the continental aerosol lose its considerable part on the western, windward macro-slope of Sikhote-Alin. As air masses are moving over the Japan Sea, they continue to lose continental aerial matter and get rich in aerosol of marine origin. With such changed composition of aerial matter, air masses reach the coasts of Japanese Islands and this is sufficiently clearly illustrated by the above data.

The analysis of data obtained for a period of study of the chemical composition of the snow cover in the background areas of the middle Sikhote-Alin in the latter half of the 1980s allows to formulate the obtained results in the generalized form.

1. The background concentrations of basic ions (Na, Cl, K, Ca, SO_4, Mg), microelements (Mn, Fe, Ni, Cu, Zn, Cd, Pb) in the suspended and soluble forms in the snow cover as well as its pH indices were determined. The found values of these parameters allowed to define an idea of actual background concentrations of macro- and microelements in the snow cover of the Russian Far East more exactly. The data obtained are an objective criterion for evaluation of the degree of the anthropogenic effect on the environment in the urbanized zones of the region.

2. It was shown that the composition of background atmospheric fallings depends directly on the atmospheric circulation variability in the region and the major factor is intensity of the continental or oceanic transfers of air masses.
3. It was established that continental air masses at the height of 1.5 km enter the Sikhote-Alin biospheric region on the average four times a year more often than oceanic ones.
4. The tendency to the intensification of continental transfer of air masses to the area of the middle Sikhote-Alin in the latter half of the 1980s was traced which was observed on the basis of increase in the number of trajectories of movement of air masses coming on the side of continent and change in the composition of atmospheric fallings.
5. It was stated that the Sikhote-Alin mountain system has a pronounced effect on the formation of the aerial matter flows to the underlying surface which becomes apparent in the relatively greater contribution of the continental component in the atmospheric fallings on the western macro-slope and oceanic one on the eastern slope.

References

Uniform methods of analysis of the USSR waters. Issue 1. – Leningrad: Gidromeoizdat. 1978. 144 p.

Yeremenko V.Ya. Spectrographic determination of microelements (heavy metals) in natural waters. - Leningrad: Gidromeoizdat. 1982. 109 p.

Duce R.A., Unni C.K. Ray B.J. et al. Long-range atmospheric transport of soil dust from Asia to Tropical North Pacific: temporal variability. // Science, vol. 209. 1980. P. 1522-1524.

Umatsu M., Duce R.A., Prospero J.M. Transport of mineral aerosol from Asia over the North Pacific Ocean. // Geophys. Res., vol. 88, No. 9C. 1983. P. 5343-5352.

Inoue K., Naruse T. Physical, chemical and mineralogical characteristics of modern colain dust in Japan and rate of dust deposition. // Soil Sci. Plamt Nutrition. Vol. 33. 1987. P. 327-345.

Verle E.K., Starichenko L.A. Basic features of the free atmosphere climate over Vladivostok. // Trudy DVNIGMI, Issue 44. - Leningrad: Gidromeoizdat. 1974. 220 p.

Yunge H. Chemical composition and radioactivity of atmosphere. – Moscow: Mir, 1965. 424 p.

Pacuna J.M., Semb A., Hanssen E. Emission and long-range transport of trace elements in Europe. // Tellus, Vol. 36B. 1984. P. 163-178.

Okita T. Behavior of aerosols since origin to break-up. “Sange kogai” No. 16, issue 10. – Japan. 1980. P. 995-1007. Translation No. D-37712.

Kachur A.N., Kondratyev I.I., Perepelyatnikov L.V. Ecologo-geochemical problems of the land and coastal-marine landscapes of the coastal zone of the Russian part of the Japan Sea basin. // Vestnik DVO RAN. Issue 5(99). – Vladivostok. Publ. House of the Far-Eastern Brach of Russian Academy of Sciences. 2001. P. 53-71.

Kondratyev I.I. Studies of the aerial matter flows in the southern Far-Eastern region of Russia. // Deposited in VINITI, No. 2265-V99, 1999. 18 p.

Kondratyev I.I., Svinukhov V.G. Interpretation of results of investigating the snow cover in the Sikhote-Alin biospheric reserve. // Deposited in IC VNIIGMI MCD No. 908-GM88. 1988. 10 p.

Miller J.M., Yoshinaga A.M. The pH of Hawaiian precipitation. A Preliminary Report. // Geophys. Res. Lett., Vol. 8, No. 7, P. 779-782.

Perelman A.I., Kasimov N.S. Geochemistry of landscape. – Moscow: “Astreya-2000”, 1999. 763 p.

Hirjshi Hara. Acid Deposition Chemistry in Japan. Strategy for air pollution control in East asia. – Japan, 1996, P. 7-17.

Seas at the Millennium: An Environmental Evaluation (Edited by C. Sheppard). Kachur A. N., Tkalin A.V. Sea of Japan. // Chapter 83. 2000. P. 467-480.

INFORMATION ABOUT AUTHORS

Kachur Anatoly Nikolaevich, PhD (Geography)

7, Radio street, Vladivostok, Russia 690041, Pacific Institute of Geography,

Far-Eastern Branch of Russian Academy of Sciences.

Tel: 31-30-71. E-mail: Kachur@tig.dvo.ru ;

Ap. 108, 101, Kirova street, Vladivostok 690022

Kondratyev Igor Ivanovich, PhD (Geography)

7, Radio street, Vladivostok, Russia 690041, Pacific Institute of Geography,

Far-Eastern Branch of Russian Academy of Sciences.

Tel: 31-28-33. E-mail: Igor@tig.dvo.ru ;

Ap. 45, 12, Vilkova street, Vladivostok 690077