Conditions for formation of chemical composition of atmospheric aerosols and precipitations over the Baikal nature territory

E.V. Chipanina-Molozhnikova,[1] L.P. Golobokova,[1] E.V. Kuchmenko,[2] O.G. Netsvetaeva,[1] and T.V. Khodzher[1]

[1]*Limnological Institute,*
Siberian Branch of the Russian Academy of Sciences, Irkutsk
[2]*L.A. Melent'ev Institute of Power Systems,*
Siberian Branch of the Russian Academy of Sciences, Irkutsk

Received February 12, 2007

The data on chemical composition of atmospheric aerosols (AA) and atmospheric precipitation (AP) were analyzed to identify the sources of aerosol coming to the Baikal nature territory. Irkutsk is supposed to be a typical industrial center of Eastern Siberia, the station Mondy is taken as a background site, and the station Listvyanka represents a rural settlement influenced by a large industrial center. The factor analysis of the AA and AP composition was used to identify the main sources (factors) of atmospheric pollutants. Four main factors were distinguished for the points under consideration: soil, gas-phase, anthropogenic, and local. The role and composition of the factors vary for aerosols and precipitation. Using the statistic methods (STATISTICA software package) cyclic (seasonal) components of observational series were determined and interrelations between chemical composition of aerosols and precipitation at the point of observation were estimated. The role of advective (circulation) factor was assessed taking into account four geographical groups of air mass transfer trajectories that were identified before. The anthropogenic sources were studied in sum. Further it is planned to reveal the contributions of mobile sources (vehicles), energy, and other industrial enterprises.

Introduction

The problem of long-range transfer of anthropogenic pollutants is of high interest due to regional and global pollution of the atmosphere. The determination of the dependence of chemical composition of atmospheric precipitation (AP) and atmospheric aerosols (AA) at observational points (points-receptors) on the direction of motion of air masses for the Baikal natural territory (BNT) is the goal of this paper. The following stations are taken as points-receptors:

– Irkutsk city, a large industrial center of Eastern Siberia;

– Listvyanka settlement, located on the northwest coast of South Baikal and exposed to the effect of air transfer from Irkutsk (60 km in the direction of prevailing winds).

– Mondy is a high-mountain background station (2000 m above the sea level) in the south of Vostochnyi Sayan.[1]

Material and methods of research

Traditionally, to identify the sources of pollutant arrival in the region-receptor with AP and AA, methods of the path and factor analysis are used.[2,3] In this paper, we assess the pollutant arrival to the considered area with the long-range transfer of air masses (AM) based on special investigations, including:

a) chemical analysis of the composition of atmospheric precipitation falling at the monitoring station of the Baikal natural territory for the period 1998–2004;

b) chemical analysis of the composition of soluble fraction of atmospheric aerosols arrived to the monitoring stations of the BNT for the period from 1998–2004;

c) factor analysis of data on chemical composition of AP and AA (method of principal components: factor rotation by VARIMAX method);

d) identification of aerosol formation sources (regional, long-range transfer), with the use of the model of long-range transfer HYSPLIT.[4]

Procedure of construction of back trajectories

To construct back trajectories of air masses (AM) motion, we used the model HYSPLIT.[4] Based on the archives of meteorological data for every day, the back trajectories were built for different seasons (1998–2004). We have recognized 12 commonly occurring types of trajectories for air masses at heights of 1500 and 3000 m, including local circulations, corresponding to weak wind velocities. It was

0235-6880/07/10 822-05 $02.00

supported in the course of investigations that the west, northwest and southwest transfers prevail in the south of Eastern Siberia; air masses from the east arrive more rarely, they consist between 1 and 13% (taking into account the southeast and northeast directions).

When developing the classification procedure of AM trajectories (four sectors),[5] the authors have used the commonly accepted concepts that the AM are characterized by the region of formation and the geographic classification.[6] According to Ref. 5, the most air transparency is characteristic of arctic AM, and the greatest turbidity is typical for tropical AM. Besides, the position of main industrial centers of the region and the occurrence of different trajectories are also taken into account. Thus, the *first sector* (Fig. 1) corresponds to the transfer of arctic and moderate-latitude AM formed above the North Atlantic Ocean and transformed when moving over Europe and Western Siberia. Just these AM are transported over the industrial regions of Western and Eastern Siberia.

The *second sector* includes the west-south-west, south-west, and south-south-west directions. From this sector, the moderate AM arrives to the territory of Eastern Siberia; and in summer the tropical AM arrives as well, which first was formed in the region of the Atlantic Ocean and transformed over subtropical regions of Europe and Middle Asia. Large anthropogenic sources of pollution in this sector are situated far from the region-receptor.

The *third sector* consists of trajectories of the south, south-south-east, south-east, east-south-east and east types. Based on our data, their occurrence at Irkutsk and Listvyanka does not exceed 4%. At Mondy the occurrence of the south-east types increases up to 12%. This is connected with the influence of the mountain ridges Khamar-Daban and Vostochnye Sayany, shielding Irkutsk from arrival of south-east air masses.

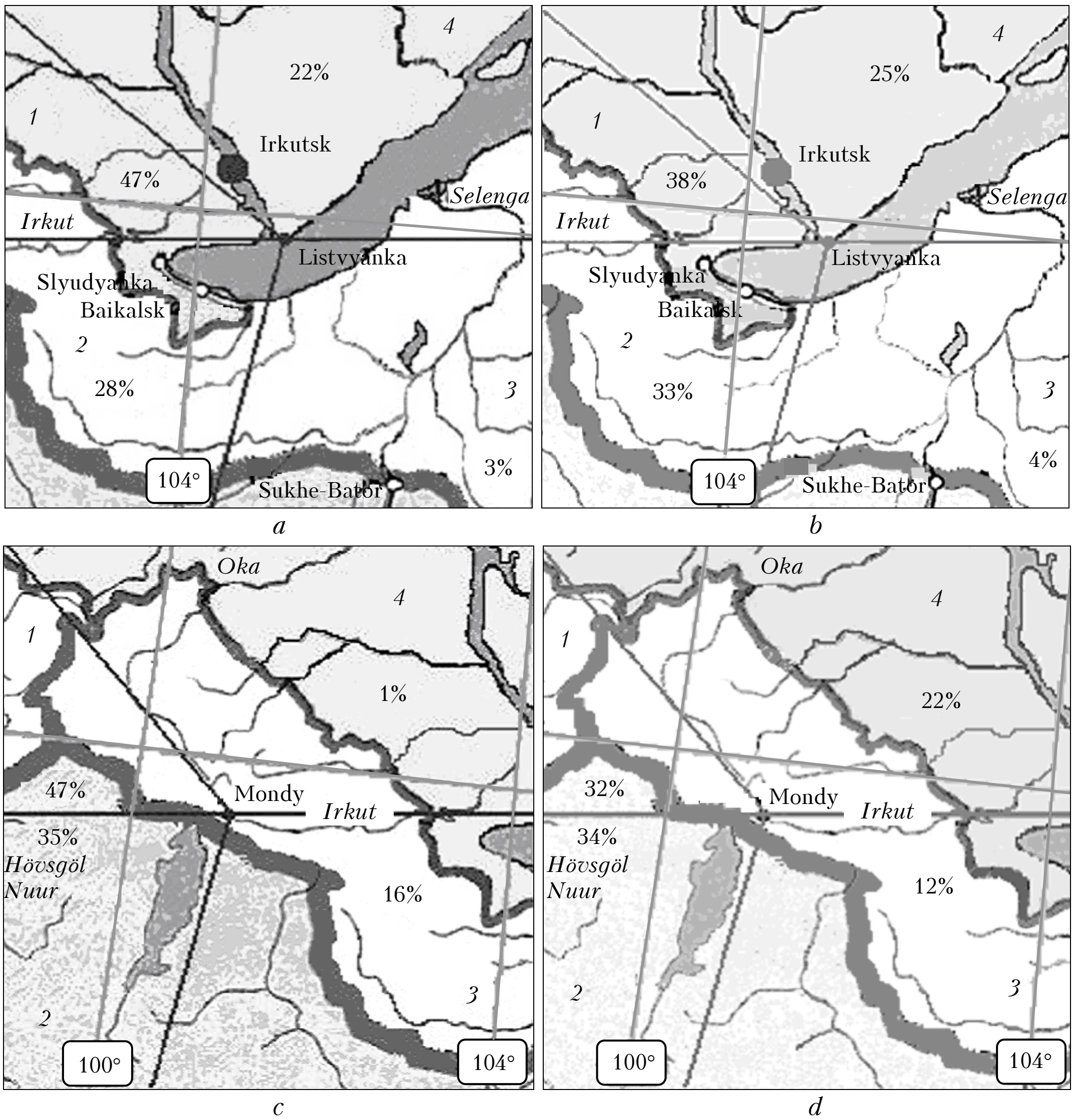

Fig. 1. Geographic zoning for classification of trajectories of air masses: *1* – NW, W-NW, W; *2* – W-SW, SW; *3* – S, S-SE, SE, E-SE, E, LC; *4* – E-NE, NE, N-NE, N, N-NE. Irkutsk, days with precipitation (*a*); Irkutsk (*b*); Mondy, days with precipitation (*c*); Mondy (*d*).

The *fourth sector* includes trajectories, typical for "diving" cyclones, which carry the cold arctic air formed over the Arctic Ocean to the Baikal natural territory; as well as the north-east trajectories, which occur when developing great anticyclonic formations over the territory of Eastern Siberia in winter.

Analysis is carried out for all available data for the investigation period, including about 2500 cases (Figs. 1*b* and *d*). Besides, the trajectories for days with precipitation (about 750 cases) are analyzed separately.

It is evident that during days with precipitation the occurrence of north-west trajectories typical for the back part of cyclones is much higher than for the total amount of trajectories. The motion of air masses during cloudless period in this case was not considered. It is known that cloudless weather is typical for anticyclones and often is accompanied by south-east winds or by reduced transfer of air masses, which in the accepted classification is characterized as local circulations (LC).[7,8] Analysis of the mass of back trajectories for days with precipitation has shown that the air mass transfer from the west and north-west directions (the first sector) reaches 47% and in the general case – 38%. When air mass transferring from this sector, the chemical composition of aerosols and atmospheric precipitation is formed under the action of anthropogenic emissions from the south of Krasnoyarsk Kray and the Irkutsk – Cheremkhovo industrial region (Fig. 1). Another prevailing direction is south-west, which occurrence is 28% and 35% (the second sector).

Factor analysis

Identification of sources of the atmosphere pollution for a given point-receptor according to the results of analysis of chemical composition of AP and AA received the name "receptor simulation".[9] The receptor simulation is based on the present-day statistical methods, such as dispersion and factor analysis.[10–12] The principal problems of the factor analysis are: 1) the reduction of the number of variables (data reduction) and 2) the determination of structural relations between the variables (classification of variables). The factors are distinguished sequentially and contain less and less general variance (variability), that is, the first factor is commonly the determining. At the first stage of investigations, we used for the factor analysis a standard program package for statistical data processing for Microsoft Windows *Statistica for Windows* (99th Edition).

Based on data on chemical composition of AP and AA from three stations of BNT four factors (sources) were determined. The *first* factor correlates significantly with concentrations of ions SO_4^{2-}, NO_3^-, NH_4^+. The *second* factor is determined by the ions Ca^{2+}, Mg^{2+}, and HCO_3^- and only in some cases the interconnection with Na^+, K^+ is noted. The *third* factor is connected with the concentrations of ions NO_3^-, Na^+, K^+, Cl^-, and the *fourth* factor, as the first one, is connected with SO_4^{2-}, NO_3^-, NH_4^+. In investigations by different authors[2,13] the first factor, as a rule, is connected with the influence of anthropogenic sources, the second factor is connected with the arrival of soil components in the atmosphere. The third factor, separated out using the observational data, characterizes the influence of local pollution sources. The fourth factor is determined only at the station Mondy, resulting, probably, from gas-phase transformations in the clear atmosphere (Tables 1–3).

Table 1. Factor loads obtained using the method of principal components for AA (station Mondy)

Ions	Factor		
	soil	gas-phase	local
SO_4^{2-}	**0.62**	**0.66**	0.18
NO_3^-	–0.03	**0.76**	–0.06
Cl^-	0.09	0.14	**0.95**
NH_4^+	0.20	**0.80**	**0.43**
Na^+	**0.88**	0.01	–0.09
K^+	**0.78**	–0.09	**0.37**
Mg^{2+}	**0.92**	0.19	0.06
Ca^{2+}	**0.86**	0.28	0.14

Table 2. Factor loads and generalities obtained by the method of principal components for cold period (atmospheric precipitation)

Ions	Factor 1		Factor 2		Factor 3	Factor 4	Generalities		
	anthropogenic		soil		local	gas-phase			
	1*	2**	2**	3***	2**	3***	1*	2**	3***
HCO_3^-	**0.84**	0.25	**0.79**	**0.93**	–0.22	–0.01	0.81	0.86	0.94
SO_4^{2-}	**0.91**	**0.84**	0.30	0.44	0.20	**0.77**	0.97	0.94	0.92
NO_3^-	**0.92**	0.00	0.62	0.26	**0.49**	**0.85**	0.89	0.89	0.77
Cl^-	**0.80**	**0.65**	0.01	0.23	0.03	**0.75**	0.96	0.40	0.66
Na^+	**0.85**	0.07	0.51	**0.75**	**0.88**	0.34	0.97	0.53	083
K^+	**0.74**	0.01	0.08	0.70	**0.84**	0.41	0.74	0.47	0.80
Ca^{2+}	**0.91**	0.12	**0.95**	**0.91**	0.20	0.23	0.96	0.95	0.96
Mg^{2+}	**0.93**	0.21	0.66	**0.76**	0.50	0.47	0.95	0.82	0.78
NH_4^+	**0.80**	**0.92**	–0.02	0.09	–0.06	**0.93**	0.80	0.91	0.89

N o t e . * Irkutsk, ** Listvyanka, *** Mondy.

Table 3. Factor loads and generalities obtained by the method of principal components for warm period (atmospheric precipitation)

Ions	Factor 1 anthropogenic		Factor 2 soil			Generalities		
	1*	2**	1*	2**	3***	1*	2**	3***
HCO_3^-	–0.04	–0.16	**0.95**	**0.94**	**0.81**	0.95	0.99	0.96
SO_4^{2-}	**0.78**	**0.82**	0.44	0.51	0.63	0.94	0.98	0.93
NO_3^-	**0.76**	**0.92**	0.54	–0.13	0.67	0.90	0.86	0.79
Cl^-	**0.90**	0.59	0.17	0.55	0.61	0.96	0.88	0.58
Na^+	0.47	0.62	**0.78**	0.54	**0.81**	0.87	0.78	0.84
K^+	0.69	0.24	0.58	**0.84**	0.63	0.89	0.80	0.76
Ca^{2+}	0.64	0.50	**0.74**	**0.81**	**0.90**	0.99	0.99	0.91
Mg^{2+}	0.48	0.34	**0.85**	**0.85**	**0.87**	0.96	0.95	0.79
NH_4^+	**0.88**	0.44	0.08	0.59	0.76	0.93	0.95	0.96

Note. * Irkutsk, ** Listvyanka, *** Mondy.

Results of investigation

Analysis of factors (sources) of atmospheric precipitations at the station Mondy

Based on the results of the factor analysis of atmospheric aerosol at the station Mondy three factors (sources) are distinguished (Tables 1, 4, and 5). The soil factor is decisive in formation of chemical composition of atmospheric precipitation in this region. The second (gas-phase) factor is connected with processes of gas-phase transformations and generation of the atmospheric secondary aerosol (*in situ*) at long-range transfer from the second or first sector (see Table 1).

The third (local) factor is clearly defined, including ions Cl^-, NH_4^+, and K^+. The maximum of these components is connected with the north-east direction of air masses.

Analysis of trajectories of air mass transport with accounting for the defined factors (see Fig. 1) has shown that the soil factor prevails in transporting air masses from the second sector (south-west regions of Asia) and their arriving from the third sector (south-east regions of Asia). The total occurrence of these types of trajectories is 46%. Air masses arriving from

Table 4. Factor loads and generalities obtained by the method of principal components for cold period (atmospheric aerosol)

Ions	Factor 1 anthropogenic		Factor 2 soil	Factor 3 local		Generalities	
	1*	2**	2**	1*	2**	1*	2**
HCO_3^-		0.04	**0.91**		0.17		0.87
SO_4^{2-}	**0.95**	**0.82**	0.03		0.31	**0.90**	0.77
NO_3^-	**0.95**	**0.83**	–0.10		–0.17	**0.90**	0.73
Cl^-	0.75	0.20	0.15		**0.68**	**0.57**	0.81
Na^+	0.78	0.01	0.04		**0.99**	**0.61**	0.97
K^+	0.52	–0.03	0.07		**0.99**	0.27	0.98
Ca^{2+}	**0.87**	**0.59**	**0.27**		–0.11	**0.75**	0.43
Mg^{2+}	**0.89**	0.44	0.19		0.13	**0.79**	0.25
NH_4^+	**0.93**	**0.58**	**0.63**		–0.06	**0.87**	0.74

Note. * Irkutsk, ** Listvyanka.

Table 5. Factor loads and generalities obtained by the method of principal components for warm period (atmospheric aerosol)

Ions	Factor 1 anthropogenic		Factor 2 soil		Factor 3 local		Generalities	
	1*	2**	1*	2**	1*	2**	1*	2**
HCO_3^-	–0.04	**0.83**	0.25	–0.02	**0.86**	0.09	0.81	0.70
SO_4^{2-}	**0.87**	**0.67**	0.21	0.36	0.09	–0.47	0.82	0.79
NO_3^-	**0.66**	**0.93**	0.36	0.18	–0.17	–0.15	0.58	0.92
Cl^-	**0.85**	0.10	–0.20	0.16	–0.05	**0.96**	0.76	0.96
Na^+	–0.13	0.04	**0.59**	**0.83**	0.44	**0.24**	0.55	0.75
K^+	0.03	0.38	0.13	**0.82**	**0.87**	–0.12	0.77	0.83
Ca^{2+}	0.33	0.51	**0.88**	**0.67**	0.07	0.02	0.88	0.70
Mg^{2+}	0.13	–0.06	**0.89**	**0.58**	0.37	0.01	0.93	0.33
NH_4^+	**0.96**	**0.90**	0.15	0.11	0.03	**0.36**	0.94	0.94

Note. * Irkutsk, ** Listvyanka.

the first sector (32%) carry AA formed over the industrial regions of the south of Eastern Siberia (gas-phase factor). The origin of salts in AA connected with a local factor is due to air masses arriving from the fourth sector (22%).

Based on the results of the factor analysis of chemical composition of atmospheric precipitation at the station Mondy two factors were clearly defined. One of them is typical both for cold and warm periods (a soil factor). Another one is mainly observed during cold period and is a result of gas-phase transformations in the atmosphere. The gas-phase factor, as a rule, is determined by the long-range transfer from territories of the second or first sectors (see Tables 2 and 3).

Analysis of factors (sources) of atmospheric precipitation in Irkutsk

The statistical analysis of the AA and AP chemical composition in the vicinity of Irkutsk has shown the local anthropogenic sources of emissions to be the determining factor of their generation both in cold and warm seasons. However, during warm season the second (soil) factor can be clearly defined (see Tables 3 and 5). The decrease in intensity of the fuel-power complex, snow cover melting, strengthening of turbulence and processes of convection in the atmosphere favor the growth of emission of powder-like terrigenous materials in the atmosphere. When analyzing chemical composition of AP close to the industrial center, the influence of air mass transport from the Kazakhstan territory (south-west trajectory) on formation of rain water composition is observed.

Analysis of factors (sources) of atmospheric precipitation at the station Listvyanka

The atmosphere at the station Listvyanka is exposed to the influence both of emissions of neighboring industrial complexes and the large water basin. During cold period one of main factors forming the chemical composition of aerosols and atmospheric precipitation, is anthropogenic (see Tables 2 and 4). This is evidenced by significant values of factor loads for concentrations of SO_4^{2-}, NO_3^-, NH_4^+, and Ca^+. The soil factor is also important. During warm period, the influence of the soil factor is much stronger than of anthropogenic one.

In the area of this station a local factor is also clearly distinguished. Significant values were determined for concentrations of such ions as Na^+, K^+, NO_3^-, and Cl^- (see Tables 2, 4, and 5) both in winter and in summer periods. In winter the local factor is, possibly, connected with air masses arriving from sector 3 (Fig. 1) and the sources located there. Components of anthropogenic origin form the composition of AP from the territory of the first sector, and components of soil origin – from the territory of the fourth sector.

Conclusion

Thus, the analysis of the dependence of chemical composition of AP and AA on the air mass transport direction at the observational points (Irkutsk, Listvyanka, Mondy) has made it possible to assess the role of natural and anthropogenic sources in formation of the atmospheric impurity composition at the Baikal natural territory. In Irkutsk the dominating sources of atmospheric impurities are the local anthropogenic emissions; the contribution of terrigenous sources increases during warm period. A key role in formation of anthropogenic impurities is played by the fuel-power complex. This is manifested by the values of factor loads of the sulfate-ion concentration in the industrial center during all seasons.

At the Lake Baikal coast (Listvyanka) which is located in the area influenced by industrial emissions, the anthropogenic factor is the most significant during the stove-heating season at the north-west trajectories of air masses. The soil factor becomes a determining in the chemical composition of aerosols and precipitation both in warm and cold periods, predominantly, at the southern direction of air mass transfer. In the vicinity of Listvyanka, a significant contribution of the local factor is clearly seen, for which chloride-ion serves as the chemical tracer.

Chemical composition of atmospheric aerosols and precipitation in the vicinity of the background station Mondy is mainly determined by natural factors including both local sources and the impurities formed in the atmosphere as a result of a long-range transfer.

Acknowledgments

This work was financially supported by Russian Foundation of Basic Research (project No. 05–05–097233r_baikal_a).

References

1. T.V. Khodzher, L.P. Golobokova, V.A. Obolkin, V.L. Potemkin, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **10**, No. 6, 403–406 (1997).
2. H. Plaisance, J.C. Galloo, and R. Guillermo, Sci. Total Environ. **206**, 79–93 (1997).
3. Y. Zeng and P.K. Hopke, Sci. Total Environ. **143**, 245–260 (1994).
4. R.R. Draxler, J. Appl. Meteorol. **29**, 240–248 (1990).
5. T.V. Khodzher, *"Investigation of the composition of atmospheric precipitation and their impact on ecological systems of the Baikal natural territory,"* Author's Abstract of Doct. Geogr. Sci. Dissert. (Moscow, 2005), 42 pp.
6. L.T. Matveev, *Manual of General Meteorology. Atmospheric Physics* (Gidrometeoizdat, Leningrad, 1984), 751 pp.
7. N.A. Myachkova, *Climate of the USSR* (Moscow University Press, Moscow, 1983), 193 pp.
8. A.S. Zverev, *Synoptic Meteorology* (Gidrometeoizdat, Leningrad, 1977), 711 pp.
9. G.E. Gordon, Environ. Sci. Technol. **22**, No. 10, 1132–1142 (1988).
10. Y. Qin and K. Oduyemi, Atmos. Environ. **37**, 1799–1809 (2003).
11. J.G. Watson, J.C. Chow, and E.M. Fujita, Atmos. Environ. **35**, 1567–1584 (2001).
12. S. Huang, K.A. Rahn, and R. Arimoto, Atmos. Environ. **33**, 2169–2185 (1999).
13. B.S. Smolyakov and M.P. Shinkorenko, Atmos. Oceanic Opt. **15**, Nos. 5–6, 397–400 (2002).