Current estimate of dry surface deposition of chemical substances in different regions of Asian territory of Russia

L.P. Golobokova, T.A. Khodzher, and T.V. Khodzher

Limnological Institute,
Siberian Branch of the Russian Academy of Sciences, Irkutsk

Received February 6, 2007

Modern estimates are obtained for arrival of soluble substances with dry deposition (gas admixtures and aerosol) in different regions of Baikal natural territory (Irkutsk, Listvyanka, and Mondy stations) and Primorsky Krai (Primorskaya station). We demonstrate the seasonal and interannual dynamics of these substances, which depends not only on the physical-geographic conditions of the terrain and climate parameters, but also on the degree of the anthropogenic influence. A positive trend is noted for arrival of substances at the underlying surface at the region of Baikal natural territory in contrast to that observed in the 1980s. We studied Baikal aerosol using scanning electronic microscopy, and elucidated the main types of aerosol particles encountered in Baikal region.

Introduction

The intensity of dry deposition of chemical substances depends on the meteorological conditions (primarily, atmospheric turbulence), as well as on the physical and chemical properties of the underlying surface. *In situ* measurements of the dry deposition are highly complicated and, consequently, extremely rare. Moreover, they may be considered acceptable only for conditions and times of their acquisition. Earlier, on Baikal natural territory (BNT), such measurements were performed over water surface at a few stations in coastal Baikal regions.[1] This made it possible to estimate the interrelation of annual totals of wet and dry deposition on entire lake water area. In these cases, crude estimates were made using data on admixture concentrations in the atmosphere and on the known estimates of deposition rates of the corresponding admixtures. This method is widely employed in different mathematical models. Experimental estimates of dry deposition rates lie in quite wide range (from 0.1 to 2.0 cm/s for sulfates). The largest rates are usually characteristic for rough wet surfaces (such as wet forest), and the smallest are for flat, dry, or frozen surfaces.[2] Analogous *in situ* measurements of dry deposition intensity at BNS atmospheric monitoring stations (Mondy, Listvyanka, and Irkutsk) were not carried out.

Materials and methods of study

The calculation basis was the experimental material obtained for soluble fraction of dry depositions for 2000–2006 (atmospheric aerosols and gas admixtures). Samples were collected in different regions of the Baikal region at three ground based stations of continuous monitoring, reflecting diverse atmospheric conditions (global or regional background state, as well as anthropogenic influence on atmospheric composition).[3] To study the admixture transport by air flows from Siberian regions toward Pacific Ocean, the dry deposition was sampled at Primorskaya station in Primorsky Krai.

The Primorskaya, Listvyanka, and Mondy stations are located in forested regions where high rates of dry deposition of atmospheric admixtures are to be expected. Large roughness is characteristic for building-dense urban areas (Irkutsk station), also favoring the increase of the deposition rate.

For detailed systematization of individual aerosol particles, their shapes and sizes, we studied Baikal aerosol using the Philips SEM 505M scanning electronic microscope, which ensures large depth resolution, the high image contrast, and a wide magnification range (down to 10^{-9} m). For analysis of individual particles, the samples were deposited on Nuclepore filters ($d = 0.45$ μm, an average volume of pumped air $V = 0.225$ m^3). Samples of Baikal aerosol were studied under magnification of $3.12 \cdot 10^{-2}$ m for large biologic samples and of $1.41 \cdot 10^{-4}$ m for small carbon particles. Samples were photographed using specially developed software for IBM-PC computer, converting the signal from the scanning electronic microscope to the digital image. Direct connection (microscope – automated working place PC) made it possible to obtain quality high-resolution images; also, this reduced the total number of errors in the image transfer to PC. Using the computer, it is possible to determine the origin of aerosols, simplifying the solution of the problem of quantitative estimate of the contribution of individual sources in the aerosol substance composition.

Results and discussion

Deposition of individual elements from the atmosphere on the underlying surface can be determined as the product of the element concentration in the

0235-6880/07/06 470-04 $02.00

atmosphere by its deposition rate over observed interval of time. The element deposition rate is a quantity, which depends on the size and density of particles, in which the given element resides, on meteorological conditions, and the underlying surface character. Our calculations use the mean values of the element deposition rates, obtained for the territories of temperate zones of the former USSR, similar to physical-geographical conditions at the observation stations.

Arrival of substances from the atmosphere was calculated by the formula

$$D = CV\Delta t,$$

where D is the arrival of substances; C is the mean concentration for period Δt; V is the dry deposition rate taking into account the surface type and certain climatic conditions.[4] The calculations were based on the concentrations of substances (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-) in soluble aerosol fractions and minor gases (SO_2, HNO_{3gas}, HCl_{gas}, NH_3), sampled from the near-surface air layer at the monitoring stations. This made it possible to more correctly calculate the arrival of elements (S, N, Cl, C, H, Na, K, Ca, Mg) of soluble chemical compounds on the underlying surface with dry deposits.

Figure 1 shows typical aerosol particles observed in the atmosphere of the BNT. Study of the chemical composition of the soluble fraction of dry atmospheric fallouts has revealed both their similarity and drastic differences. In the present period, there is a tendency toward decrease of the mass of soluble chemical compounds in aerosol particles in the Baikal region atmosphere. During 2000–2006, in the near-ground atmosphere of stations Irkutsk and Listvyanka we observed, respectively, 25 and 36% reductions of the absolute mass of ions in aerosols in comparison with their mass in 1991–1999. The mass decrease is mainly due to the reduction of the concentration of ions NH_4^+, SO_4^{2-}, and HCO_3^-. The largest totals of ions in the chemical composition of soluble fraction of atmospheric aerosols in 2000–2006 (7.05 μg/m^3) were observed at the Irkutsk station (industrial center), and the smallest totals – at the background station Mondy (1.25 μg/m^3). Possibly, a considerable role in the change of qualitative and quantitative compositions of aerosol is played by climate warming, accompanied by the increase of the atmospheric precipitation amount.[5] As the amount of soluble ingredients in the aerosol substance in the BNT atmosphere decreases, we simultaneously observe the concentration growth of acid-producing gases, containing sulfur and nitrogen.

At the Primorskaya station, in contrast to the BNT monitoring stations, a gradual increase of the concentrations of soluble substances on the aerosol particles due to ions NH_4^+, Ca^{2+}, Na^+, and SO_4^{2-} (Fig. 2) took place in 2002–2006.

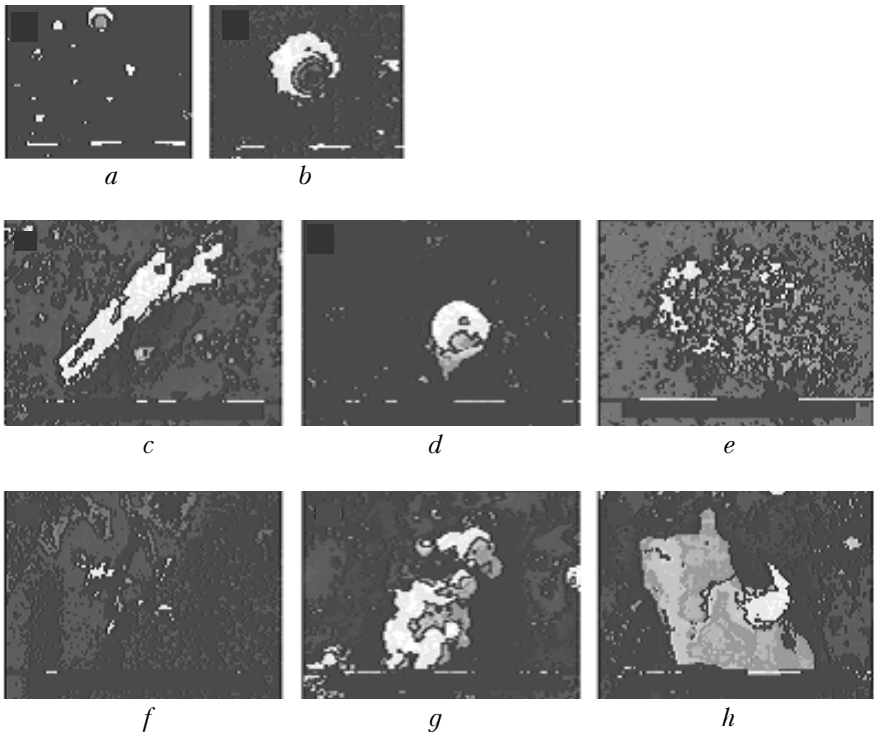

Fig. 1. Individual aerosol particles in the BNT atmosphere (the images are obtained using SEM): carbon particles formed of the coil combustion (Irkutsk) (*a*, *b*); aggregate of mineral particles (region of Middle Baikal) (*c*); biologic object (cyst) over water basin of Baikal Lake (*d*); conglomerate (residual cellulose) of emissions in the region of Baikal Pulp and Paper Plant (*e*); bioaerosol (*f*); agglomerate of mineral and carbon particles (region of South Baikal) (*g*); terrigenous particles (Mondy station) (*h*).

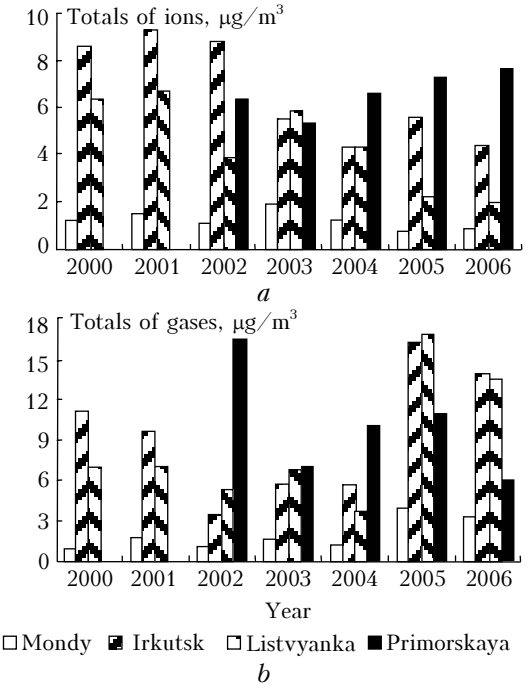

Fig. 2. Annually mean values of the total content of ions (*a*) and gas admixtures (NH_3, SO_2, HCl_{gas}, HNO_{3gas}) (*b*) at BNT monitoring stations and Primorskaya station.

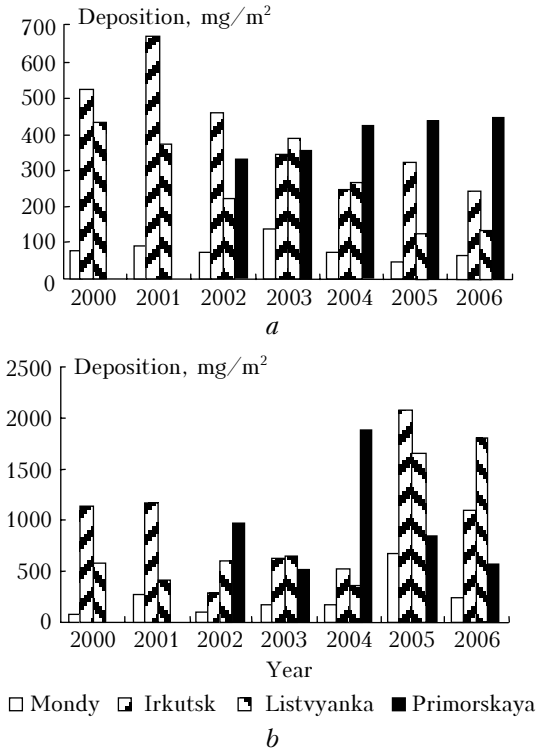

Fig. 3. Annually mean deposition of total content of ions (*a*) and gas admixtures (NH_3, SO_2, HCl_{gas}, HNO_{3gas}) (*b*) at BNT monitoring stations and the Primorskaya station.

As calculations show, the observed tendency in variations of quantitative characteristics of the chemical composition of soluble ingredients of atmospheric dry fallouts remain the same in the deposition of substances on the underlying surface.

Together with the soluble fraction of atmospheric aerosols, on average about 400 mg/m^2 of the total mass of ions is deposited yearly with a variability range from 670 mg/m^2 in 2001 to 240 mg/m^2 in 2006 in the region of Irkutsk, and on average 280 mg/m^2 with a variability range from 430 mg/m^2 in 2000 to 120 mg/m^2 in 2005 at the Listvyanka station (Fig. 3).

The smallest fluxes of ions were recorded in the region of the Mondy background station, where, for mean value of 81 mg/m^2 per year over the last six years, for period 2005–2006 their amount decreased to 46–61 mg/m^2 per year. Obviously, the decrease of deposition of soluble substances on the underlying surface was observed at BNT monitoring stations. At the Primoskaya station in period 2002–2006, about 400 mg/m^2 of soluble compounds arrived yearly with variability range from 330 mg/m^2 in 2002 to 450 mg/m^2 in 2006.

Total amount of elements, arriving on the surface in the studied regions together with soluble compounds in aerosol particles and gaseous components, is shown in the Table.

Amount of elements, deposited on the underlying surface together with soluble aerosol fraction, at all stations is about 30% of their total arrival with gas admixtures and aerosol substance.

The largest fraction in the total amount of deposited elements together with soluble substances falls on the oxidized forms of sulfur and nitrogen; their fluxes make more than 80% of the total number of soluble substance fluxes. Minimal monthly values of deposition of sulfur in the form of SO_4^{2-} were determined at the station Mondy: they ranged from 0.3 to 0.8 mg/m^2 in winter and from 0.8 to 3.1 mg/m^2 in summer (Fig. 4). Arrival of sulfur in the form of SO_2 at this station in the cold period was close to the sulfur fluxes, arriving with SO_4^{2-}, while in the warm period it increased from 1.8 to 8.4 mg/m^2.

Table. Annually mean amount of elements, arriving together with soluble substances during dry deposition at the monitoring stations (in mg/m^2) in 2000–2006

Station	*C*	S ($S{-}SO_4^{2-} + S{-}SO_2$)	N ($N{-}NO_3^- + N{-}HNO_{3gas}$)	Cl ($Cl{-}Cl^- + Cl{-}HCl_{gas}$)	Na + K + Mg + Ca	H	Total
Mondy	2.2	89	36	52	11	0.1	190
Irkutsk	13.6	455	113	103	56	0.2	741
Listvyanka	8.1	368	116	77	31	0.1	600
Primorskaya	5.4	368	222	122	54	0.3	772
Baikal[4]		290 ± 174	30 ± 18	–	–	–	–

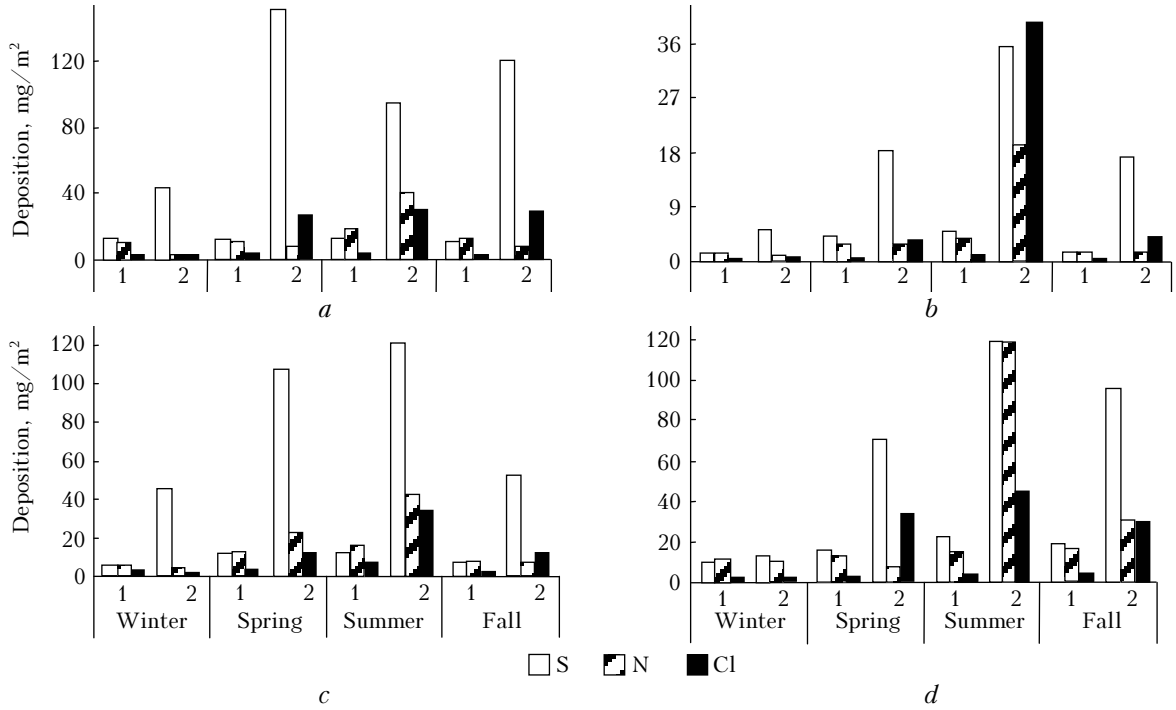

Fig. 4. Annually mean deposition of acidified components on the surface together with aerosol substance (*1*) and gas components (*2*) at the Irkutsk stations (*a*), Mondy (*b*), Listvyanka (*c*), and Primorskaya (*d*) for 2000–2006. (Data are summarized for 3 months of each climatic season).

At the Irkutsk, Listvyanka, and Primorskaya stations, the seasonal dynamics of sulfur fluxes is the same as at the background station; however, quantitatively, the sulfur fluxes are 3–4 times higher and, moreover, the deposition of sulfur in the form of SO_2 is also higher than in the form of SO_4^{2-}.

Like sulfur, arrivals of nitrogen fluxes are larger with gas admixtures (HNO_{3gas}) than with aerosol substance (NO_3^-) at the Irkutsk, Listvyanka, and Primorskaya stations, especially in warm period. At the Mondy station, deposition of nitrogen in the form of HNO_{3gas} is less than at other stations; however, its maximum is observed in the cold time of the year. High values of nitrogen fluxes in the form of NO_2 in summer period were also marked in Ref. 4 for west regions of the former USSR and for plains of Central Asia.

In comparison with the 1980s, the sulfur fluxes containing soluble substances, on the BNT surface have increased on the average by 20%, the nitrogen – by 70%.[4] Deposition of alkaline and alkali-earth metals varied between 5 and 8% and ions of hydrogen – in the range 0.05% of the total number of depositing elements with soluble substances.

Conclusion

Based on the large experimental material, obtained in different regions of Asian territory of Russia, we have estimated the deposition of elements of soluble substances with gaseous and aerosol admixtures on the underlying surface. We have revealed their seasonal and interannual dynamics, which depends both on the physical-geographical conditions of the territories and on the anthropogenic influence degree.

In the present period (2000–2006), as compared to the 1980s, fluxes of sulfur (up to 20%) and nitrogen (up to 70%) to the underlying surface of BNT are increased.

The performed calculations are important for determination of balance and turnover of matter in different water and land ecosystems.

Acknowledgements

This work is supported by the Research Fund of Ministry of Environment of Japan.

References

1. V.A. Obolkin and T.V. Khodzher, Meteorol. i Gidrol., No. 7, 71–76 (1990).
2. P.W. Summers, Water Quality Bulletin **8**, No. 2, 81–88 (1983).
3. T.V. Khodzher, *"Study of the Composition of Atmospheric Fallouts and Their Impacts on Ecosystems of Baikal Natural Territory,"* Author's Abstract of Doct. Geogr. Sci. Dissert., Moscow (2005), 44 pp.
4. S. Paramonov, A. Ryaboshapko, S. Gromov, L. Granat, and H. Rodhe, *Sulfur and Nitrogen Compounds in Air and Precipitation Over the Former Soviet Union in 1980–1995, Report CM-95* (International Meteorolodgical Institute, Stockgolm, 1999), 42 pp.
5. Yu.A. Izrael, ed., *State and Complex Monitoring of Environment and Climate. Measurement Limits* (Nauka, Moscow, 2002), 248 pp.