Acid fallout in Northwestern Siberia: regional and local aspects

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The data on the ion composition of atmospheric aerosol, snow, and surface water are presented along with the data on the content and speciation of heavy metals in river and lake water at the territory of the Pur and Krasnosel'kup regions of the Yamalo-Nenetsk Okrug (Northwestern Siberia, Russia). The data were obtained in 1997–1998. It is shown that the natural and climatic factors are favorable for acid fallout on the regional scale. At the local level, their effect is weaker due to the growing contribution from the processes of thawing water interaction with the surface.

Acid fallout is one of the global ecological problems caused by growing technogenic emissions of gaseous acid-forming substances, which can be transported to long distances by air masses. Apart from the direct effect on forests, soil, and water, the negative consequences of acid fallout include distortion of biogeochemical cycles of elements in local ecosystems, in particular, elevated migration of some toxic metals Me (Refs. 1–4). Thus, the problem of acid fallout is a complex problem including analysis of sources and processes of formation of ion composition of atmospheric aerosols, wet precipitations, and surface water, as well as the total content and state of Me in water bodies. This problem became a subject of extensive studies in some regions of the world, including the northern European part of Russia,[5,6] but, unfortunately, Northern Siberia has been studied very poorly.

The aim of this paper is the combined study of the ion composition of atmospheric aerosol, wet precipitations, and surface water, as well as the content of Cu, Cd, Pb, and Hg in the surface water of tundra and forest-tundra in Northwestern Siberia (Pur and Krasnosel'kup regions of the Yamalo-Nenetsk Okrug). The observations were made in different seasons of 1997–1999.

The distinguishing climatic and geographical features of the region, which are important for the problem under consideration, are the long periods of snow isolation of ground surface (up to 8 months) and plain relief of the terrain. This determines the seasonal inhomogeneity in formation of aerosols of erosive origin. The same features give rise to a great number of shallow lakes filled with thawing water in the flood-time. These natural factors being the same for Pur and Krasnosel'kup regions can be characterized as regional. At the local level, some differences manifest themselves in influence of subsurface water on the surface water composition; they are caused by inhomogeneity of terrain and geochemical conditions.[7] On the whole, this influence is minimum for water bodies of the Pur region (basin of the River Pur) due to close position of the permafrost layer, and it is more significant for water bodies of the Krasnosel'kup region (basin of the River Taz), where the “warm,” rarely frozen lakes are situated.

Measurement technique

The atmospheric aerosol was daily sampled on AFA–KhA filters in the series of continuous observations up to 30 days long in the Pur region at site 1 (near Samburg village), site 2 (near Tarko-Sale village), and site 3 (Krasnosel'kup village) at different seasons. The pH, concentration of ions $[NH_4^+]$, $[Na^+]$, $[K^+]$, $[F^- + HCOO^-]$, $[Cl^-]$, $[NO_3^-]$, $[SO_4^{2-}]$ (method of ion chromatography), $[HCO_3^-]$ and $[Ca^{2+} + Mg^{2+}]$ (conductimetric titration) were determined in the water extract.[8] The results of analysis were related to the content of ions in the unit (1 m^3) air volume.

Wet precipitation sampling was made late in winter seasons of 1997–1999 at different points of the Pur and Krasnosel'kup regions. The ion composition of snow fallouts was determined by the same methods after filtration of the thawing water.

The surface water was sampled in both winter and summer periods from the rivers Pur and Taz, as well as from lakes of different depth. The ion composition of the filtered (0.45 μm) samples was analyzed by the same methods with the only difference that the total Alk and carbonate Alk_{carb} alkalinity were determined separately; their difference was related to the humus alkalinity Alk_{hum}. The total concentration of dissolved

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and suspended Hg, Cd, Cu, and Pb in the filtrate and on the filters was analyzed by the method of atomic absorption.

Regional factors of formation of the ion composition of atmospheric aerosol

The mean concentrations of ions in the water-soluble fraction of atmospheric aerosol (ng-equ/m^3 of air) and their total mass concentration Σ (μg/m^3) for the observation sites 1–3 are given in Table 1. The total concentration of ions in the atmospheric aerosol only slightly depends on the season and the observation site. At the same time, it should be noted that in winter period the portion of the water-soluble fraction in the total mass of aerosol particles achieves 47%, whereas in summer it drops down to 3.7%. The significant increase of mass concentration of aerosol in the period of open ground surface (not isolated by the snow cover) is likely caused by the income of difficultly soluble products of wind erosion to the atmosphere.

Sulfate is the main anion in the composition of the atmospheric aerosol. The equivalent ratio $[NH_4^+]/[SO_4^{2-}]$ is less than 0.5 in all cases. This fact indicates that for efficient neutralization of sulfate and other anions, the water-soluble fraction of atmospheric aerosol must contain significant amount of lithophile cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), which have not volatile species and are to be carried out of the land surface or come with marine aerosol.

The equivalent ratio $[Na^+]/[Cl^-] \gg 1$ in all observations. So, it can be concluded that only a part of sodium ions comes to the atmospheric aerosol from the marine source, whereas another part comes from the erosive source. However, at the excess acidity of aerosol particles as the result of the reactions

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl, \quad (1)$$

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3, \quad (2)$$

chloride and nitrate depletion of these particles can occur due to volatility of HCl and HNO_3. Therefore, the low concentration of chlorides in the aerosol composition is not indicative of insignificant contribution of the marine source to formation of atmospheric aerosol in the region under study.

The statistical (factor) analysis of variability of different ions concentration in each observation series allows the contributions from different sources to be revealed. These data are given in Table 2. In some situations, the combination (NH_4^+, SO_4^{2-}, H^+), which represents the action of the acid factor, stands out; in some series this combination is complemented with lithophile cations – the products of neutralization of the excess acidity of calcium, magnesium, sodium, and potassium salts. In eight of 12 series, the marine source (combination of Na^+ and Cl^-) stands out as independent or in combination with other ions; in the rest of the series the correlation between sodium and chloride breaks down likely due to more complete realization of the reactions (1) and (2). The absence of correlation between ($Ca^{2+} + Mg^{2+}$) and Na^+ in most observation series indicates that the products of soil erosion are not the main source of sodium in the atmospheric aerosol. On the whole, the gas-phase processes play the leading part in formation of the ion composition of the water-soluble fraction of atmospheric aerosol (these processes determine the excess acidity of aerosol). The smaller contribution of the marine and soil-erosion sources proves to be insufficient for complete neutralization of products of the gas-phase reactions.

It should be noted that in time dynamics of sulfate and nitrate concentrations the periods of their growth and decrease, dependent on the wind direction, are distinguished. The mean mass concentration of sulfates (1.2–2.9 μg/m^3) and nitrates (0.05–0.31 μg/m^3) in all observation series are characteristic of geochemically clean regions (0.5–5 and 0.05–4 μg/m^3, respectively).[2] The five to seven times increase of the sulfate content in the atmospheric aerosol correlating with the increase of the concentration of Cu, Ni, Pb, and some other Me was noticed in the periods of air mass income from the Norilsk region.[9] So, we can conclude that the effect of far atmospheric transport of acid-forming components together with metals takes place in the region of observations, which aggravates the action of local natural and technogenic factors.

Table 1. Mean concentrations of ions and their mass concentration in water-soluble fraction of atmospheric aerosol at sites 1–3

Site, period	NH_4^+	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	H^+	HCO_3^-	$F^- + HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	Σ
1, 10–11.1997	15.4	9.1	13.9	2.0	8.7	3.0	1.1	5.2	3.6	34.7	3.1
1, 4–5.1998	14.1	11.9	12.1	3.6	8.1	6.4	4.3	2.3	1.4	39.9	3.5
1, 7.1998	18.0	10.2	7.3	3.9	7.9	3.5	2.5	2.0	0.8	49.0	3.6
1, 9–10.1998	5.1	8.3	11.6	1.2	9.6	4.6	3.1	4.3	1.2	25.1	2.3
2, 12.1997	14.8	11.8	7.5	3.3	13.3	0	1.1	0.8	4.2	37.2	2.9
2, 5–6.1998	16.8	25.5	8.4	2.3	0.1	18.2	1.6	2.5	1.8	30.3	3.8
2, 7–8.1998	9.0	24.7	6.0	2.4	0.1	19.7	2.4	2.4	2.0	25.3	3.5
2, 9–10.1998	12.6	11.3	12.5	2.1	2.7	10.1	3.5	3.5	2.1	28.8	3.1
2, 1.1999	24.1	12.5	7.6	4.1	0.1	10.4	2.9	3.3	1.9	46.2	4.1
2, 4.1999	27.6	15.4	16.1	4.8	0.1	13.2	1.6	3.6	5.0	60	5.0
3, 5.1999	39.7	13.6	9.0	1.4	12.0	9.8	3.8	2.9	1.3	68.6	5.4
3, 7.1999	13.1	11.9	4.7	2.1	4.7	11.7	2.8	1.5	0.9	23.3	2.6

Table 2. Data on factor analysis of ion concentration variability in atmospheric aerosol

Site, period	Factor 1	Factor 2	Factor 3
1, 11.1997	NH_4^+, H^+, SO_4^{2-}, $F^- + HCOO^-$	$Ca^{2+} + Mg^{2+}$, Na^+, Cl^-, NO_3^-	K^+
1, 4–5.1998	$Ca^{2+} + Mg^{2+}$, Na^+, NO_3^-	NH_4^+, H^+, SO_4^{2-}	K^+, Cl^-, F^-
1, 7.1998	NH_4^+, H^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, Na^+	K^+, NO_3^-, $F^- + HCOO^-$	–
1, 9–10.1998	H^+, HCO_3^-, SO_4^{2-},	Na^+, Cl^-	NH_4^+
2, 12.1997	$Ca^{2+} + Mg^{2+}$, Na^+, NO_3^-, F^-	NH_4^+, K^+, SO_4^{2-}	H^+, Cl^-
2, 5–6.1998	$Ca^{2+} + Mg^{2+}$, H^+, HCO_3^-,	NH_4^+, SO_4^{2-}	Na^+, Cl^-
2, 7–8.1998	NH_4^+, K^+, SO_4^{2-}	Na^+, HCO_3^-	Cl^-, F^-
2, 9–10.1998	Na^+, Cl^-, NO_3^-	NH_4^+, H^+, SO_4^{2-}	$Ca^{2+} + Mg^{2+}$, HCO_3^-
2, 1.1999	NH_4^+, $Ca^{2+} + Mg^{2+}$, HCO_3^-, SO_4^{2-}, NO_3^-	K^+	Na^+, Cl^-
2, 4.1999	Na^+, Cl^-, HCO_3^-	K^+, SO_4^{2-}	F^-, NO_3^-
3, 5.1999	NH_4^+, SO_4^{2-}	Na^+, Cl^-	HCO_3^-, NO_3^-
3, 7.1999	NH_4^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, K^+	Na^+, Cl^-, NO_3^-	H^+, HCO_3^-

Ion composition of snow fallouts and surface water

The mean values of pH, ion concentration (μg-equ/l) and total mass concentration of ions Σ (mg/l) for snow fallout (15–17 samples in every series) and surface water (6–12 samples in winter and summer periods) sampled at the territory of the Pur and Krasnosel'kup regions in 1997–1999 are given in Table 3. As compared to the aerosol, the portion of lithophile cations among other cations increased in snow. Sulfate does not play the dominating role among anions due to significantly increasing contribution of chloride and nitrate. In contrast to the atmospheric aerosol (see Table 1), in snow fallout the ratios $[Na^+]/[Cl^-]$, $[Ca^{2+} + Mg^{2+}]/[SO_4^{2-}]$, and $[NH_4^+ + K^+]/[NO_3^-]$ are close to unity, i.e., the ion compositions of snow fallout and the atmospheric aerosol differ significantly.

These general regularities keep also for individual snow samples from different sites, although the amount of collected snow and the ion concentration vary. The variability of these parameters is apparently caused by different terrain conditions and possible influence of local pollution sources. The difference between the mean composition of the snow samples taken at the territory of the Pur region in different seasons should be mentioned. At low mineralization of snow in winter 1997/98, the deficit of lithophile cations manifested itself, and that resulted in the elevated acidity of snow. In winter 1998/99, the mean concentration of basic acid-forming anions (sulfate and nitrate) was almost unchanged, but increase of concentration of cations Na^+, K^+, $(Ca^{2+} + Mg^{2+})$ governed the increase of pH up to the "normal" level [the calculated value of pH for the equilibrium of water with the atmospheric air at background content of CO_2, SO_2, and NH_3 is equal to 5.8 (Ref. 10)]. The mineralization, pH, and concentration of individual ions in snow at the territory of the Pur and Krasnosel'kup regions in the season of 1998/99 were close, as well as the amount of the collected snow (216 and 187 kg/m^2, respectively). This indicates that the same factors contribute to formation of ion composition of atmospheric aerosol and precipitation all over the region of observations.

As is shown in Table 3, the ion composition of the surface water differs from that of the thawing water. The stoechiometric relations of ions, as well as the data of the correlation analysis given in Table 4, suggest the cause of this difference. The increase of the role of $[HCO_3^-]$, $[Ca^{2+} + Mg^{2+}]$, $[Na^+]$ and close correlation between them in the surface water, absent in snow, are caused by leaching of carbonate salts. Another process, forming the composition of the surface water, as follows from the absence of correlation between Alk_{hum} and the above-listed ions, is a formation of humus substances – the products of biotic processes. In some water bodies of the Pur region, the portion of the humus alkalinity achieves 55% of the sum of equivalent anions.

The efficiency of these processes, transforming the composition of the thawing water in water bodies of the Pur region, is relatively low: the value of Σ for the surface water in the summer period, once water bodies are filled with the thawing water, is only three times higher, whereas pH is a little higher than that for snow. In the winter period, the value of Σ increases, nevertheless the mineralization of water remains low. The mineralization of the surface water in the Krasnosel'kup region is far higher mostly due to HCO_3^-, $Ca^{2+} + Mg^{2+}$, and Na^+, i.e., ions leached from soil and surface rock. The drastic change of surface water composition as compared to that of snow leads to the growth of pH (the mean of 7.03) and the buffer capacity to the action of acid fallout. Thus, just the local differences in the efficiency of the processes of surface interaction with different types of atmospheric precipitation of close composition determine variations of the ion composition and acidity of the surface water.

Table 3. Ion composition of snow fallout and surface water in the region of observations

Characteristic	Σ	pH	NH_4^+	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	H^+	Alk_{hum}	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}
Pur region													
Snow*	4.6	4.73	8.3	25	19	8	43	–	18	3	15	14	25
Snow**	9.3	5.67	6.6	44	79	24	4	–	20	25	48	17	26
Surface water, summer	15	5.44	2	127	57	7	4	46	135	5	10	5	10
Surface water, winter	40	6.16	77	539	102	42	0.7	228	437	2	19	1.6	14
Krasnosel'kup region													
Snow*	8.0	5.66	15.4	37	50	20	3	–	22	28	37	17	21
Surface water, winter	244	7.03	7.9	3050	490	75	0	410	2940	10	39	1	21

* 1997/98

** 1998/99

Table 4. Correlation coefficients of ions in snow fallout and surface water

Snow fallout (N = 29)

Characteristic	Σ	pH	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}
Σ	1								
pH	0.54	1							
$Ca^{2+} + Mg^{2+}$	0.37	0.02	1						
Na^+	**0.77**	0.57	0.04	1					
K^+	0.67	0.69	– 0.21	**0.82**	1				
HCO_3^-	0.60	**0.84**	0.14	0.64	**0.76**	1			
Cl^-	– 0.10	0.38	0.07	**0.77**	0.63	0.39	1		
NO_3^-	0.22	0.12	– 0.36	0.13	0.18	– 0.02	0.23	1	
SO_4^{2-}	0.27	– 0.44	0.50	– 0.04	– 0.26	– 0.48	0.03	– 0.08	1

Surface water (N = 18)

Characteristic	Σ	pH	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	Alk_{hum}	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}
Σ	1									
pH	0.59	1								
$Ca^{2+} + Mg^{2+}$	**0.96**	0.57	1							
Na^+	**0.85**	0.57	**0.90**	1						
K^+	**0.88**	0.46	**0.92**	**0.80**	1					
Alk_{hum}	**0.73**	0.59	**0.79**	0.68	**0.84**	1				
HCO_3^-	**0.95**	0.58	**0.98**	**0.92**	**0.86**	0.69	1			
Cl^-	– 0.20	– 0.20	– 0.12	0.07	– 0.08	– 0.02	– 0.15	1		
NO_3^-	– 0.03	0.23	– 0.02	0.00	– 0.08	– 0.13	– 0.02	0.15	1	
SO_4^{2-}	0.03	0.10	0.03	0.10	0.13	0.05	– 0.01	0.56	0.49	1

Content and speciation of metals in river and lake water

The mean data on the total content (sum of dissolved and suspended species) of some metals in the surface water of the Pur and Krasnosel'kup regions are given in Table 5. For comparison, this table also gives the data from Ref. 11 for the middle River Ob. The comparison shows that the concentration of metals in the regions of study, which are free of technogenic load, is higher than in the River Ob receiving polluted waste waters from industrial centers. This is indicative of high water migration of metals in the surface water in Northwestern Siberia and insufficient efficiency of their deposition in bottom sediments. As was noted above, the additional source of Me in the local water bodies can be the atmospheric fallout due to far transport of atmospheric aerosol, in particular, from the Norilsk region.

Table 5. Mean concentrations of metals (μg/l) in surface water of the Pur and Krasnosel'kup regions and in the River Ob (middle Ob)

Water bodies	Cu	Cd	Pb	Hg
Pur region (N = 11)	6.6	0.18	4.0	0.40
Krasnosel'kup region (N = 6)	4.2	0.33	5.3	0.26
River Ob (Ref. 11)	2.3	0.24	0.8	0.02

Regardless of the source of Me in the river and lake water, the content of metals in water depends on the processes of their transformation under specific physical-chemical conditions in some water body. Thus, in Ref. 6 it was shown that the total concentration of Me in water bodies of the Kola Peninsula episodically increases in spring floods at temporary decrease of the water pH due to income of the thawing water. As this takes place, the part of most toxic metal species, aquaions Me^{2+}, increases, what is connected not only with their oxidation but also with the low content of dissolved organic matter (DOM).[6]

The water bodies of interest in this paper are characterized by the low pH and the elevated DOM content (as is implicitly indicated by Alk_{hum}) not only in spring floods, but also in winter and summer samples (see Table 3). We have experimentally determined the parameters of coupling the copper, lead, and cadmium with DOM for different water bodies at the territory of the Pur region and have chemically-thermodynamically simulated the state of these Me.[12] The averaged simulation data are given in Table 6 as a fractional distribution of species at different pH values. This table also gives the similar data (italicized) for some typical fresh-water body in Southwestern Siberia – Novosibirsk reservoir – for the mean value pH = 8.0. These data are indicative of the significant difference in the species distribution of copper and lead between the low-mineralized weakly acidic surface water in Northwestern Siberia and more mineralized weakly alkaline water bodies in Southwestern Siberia. The dominating species in the former are aquaions Me^{2+} and complexes MeL with DOM, whereas inorganic hydroxo- and carbonate complexes play a significant role in the latter. This difference for cadmium is less pronounced. It is important to note that the portion of most toxic species Me^{2+}_{aq} increases significantly, whereas the portion of less toxic species $MeCO_3^0$ and $Me(OH)_2^0$ decreases with decreasing pH. This means that not only the elevated total concentration of metals, but the degree of their danger for water organisms as well, is connected with the peculiarities of distribution of metal species in water bodies of Northwestern Siberia.

Table 6. Fractional distribution (%) of basic species of copper, lead, and cadmium in lake water at different pH

Characteristic	Cu				Pb				Cd			
pH	5.0	6.0	7.0	*8.0*	5.0	6.0	7.0	*8.0*	5.0	6.0	7.0	*8.0*
Me^{2+}	33.9	14.2	4.7	*0.9*	38.5	16.7	5.6	*1.4*	81.3	58.4	31.3	*52.3*
$MeOH^+$	0	0.2	0.7	*1.3*	0	0.2	0.6	*1.5*	0	0	0.3	*4.8*
$Me(OH)_2^0$	0	0	1.4	*26.0*	0	0	0	*0.7*	0	0	0.1	*0.01*
$MeCO_3^0$	0	0.4	3.8	*29.0*	0	0.9	7.7	*79.8*	0	0	0	*7.0*
MeL	66.1	85.2	89.4	*42.8*	61.5	82.2	86.1	*16.5*	18.7	41.5	68.3	*36.0*

Conclusions

The natural and climatic conditions of Northwestern Siberia determine the low content of the basic ions in the atmospheric aerosol, what is typical of geochemically clean regions. Erosion contributes insignificantly in formation of the ion composition of the aerosol. This results in the deficit of lithophile ions capable to neutralize the excess acidity in products of gas-phase reactions of aerosol formation. Apart from natural factors, the effect of remote technogenic sources (in particular, Norilsk Plant) of sulfate and some metals in the composition of aerosol shows itself in the region of study.

The ion composition of snow differs from that of the atmospheric aerosol, but the deficit of lithophile cations in snow remains, and the thawing water has a weak acid reaction. At predominant role of snow feeding in formation of composition of surface waters they are characterized by low mineralization, elevated acidity, and low buffer capacity. This implies the elevated total level of toxic metal species and increase of their fraction in water bodies. At the local level, the effect of these unfavorable factors depends on the processes of thawing water interaction with the surface and biotic processes inside water bodies. The increasing role of these processes leads to the growth of mineralization and buffer capacity, increase of pH, and decrease of the portion of most toxic metal species in the lake and river water. From this point of view, the ecological situation for water bodies at the territory of the Pur region proves to be more unfavorable than that in the Krasnosel'kup region of the Yamalo-Nenetsk Okrug.

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References

1. C.J. Brandt, ed., *Acidic Precipitations. Formation and Impact on Terrestrial Ecosystems* (VDI-Kommission, Düsseldorf, 1987).
2. Yu.A. Izrael', N.M. Nazarov, A.Ya. Pressman, F.Ya. Rovinskii, and A.G. Ryaboshapko, *Acid Rains* (Gidrometeoizdat, Leningrad, 1989).
3. *Acid Precipitation. Long-term Tendencies* [Russian translation] (Gidrometeoizdat, Leningrad, 1990).
4. G.E. Zaikov, S.A. Maslov, and V.L. Rubailo, *Acid Rains and the Environment* (Khimiya, Moscow, 1991).
5. T.I. Moiseenko, Vodnye Resursy **25**, No. 1, 16–23 (1998).
6. T.I. Moiseenko, V.A. Dauvalter, and I.V. Rodyushkin, Vodnye Resursy **25**, No. 2, 231–243 (1998).
7. L.K. Karpov, E.P. Sorokina, and N.L. Dmitrieva, in: *Abstracts of Reports at the International Meeting on Geochemistry of the Biosphere*, Novorossiisk (1999), pp. 71–73.
8. B.S. Smolyakov, L.A. Pavlyuk, A.M. Nemirovskii, K.P. Koutsenogii, and V.I. Makarov, Atmos. Oceanic Opt. **9**, No. 6, 489–492 (1996).
9. V.F. Raputa, A.I. Smirnova, K.P. Koutsenogii, B.S. Smolyakov, and T.V. Yaroslavtseva, Atmos. Oceanic Opt. **13**, No. 6, ???–??? (2000).
10. P. Brimblekombe, *Air Composition and Chemistry* (Cambridge University Press, New York, 1986).
11. S.S. Shvartsev, O.G. Savichev, G.G. Vertman, et al., Vodnye Resursy **23**, No. 6, 723–728 (1996).
12. B.S. Smolyakov, V.I. Belevantsev, A.P. Ryzhikh, Zh.O. Badmaeva, M.V. Zhigula, and A.A. Bobko, Khimiya v Interesakh Ustoichivogo Razvitiya **7**, No. 5, 575–584 (1999).