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Research Activities of the "Environmental Geochemistry" European Associated Laboratory

B. Dupré[a], S. A. Lapitski[b], Yu. V. Alekhin[b], O. S. Pokrovskii[c], J. Viers[d], N. N. Akinfiev[e], A. V. Zotov[e], and A. V. Savenko[b]

[a] L'Observatoire Midi Pyrenees, Toulouse, France

[b] Faculty of Geology, Moscow State University,
Vorob'evy gory 1, Moscow, 119992 Russia
e-mail: lapitsky@geol.msu.ru

[c] Centre Nationale de la Recherche Scientifique, Toulouse, France

[d] Universite Paul Sabatier III, Toulouse, France

[e] Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,
Staromonetnyi per. 35, Moscow, 110017 Russia
e-mail: akinfiev@igrm.ru, azotov@igem.ru

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Abstract—The results of research activities of the Laboratoire Européenne Associé en Géochimie Environnementale (LEAGE) ("Environmental Geochemistry" European Associated Laboratory) devoted to study of fluids at low and high temperatures during the first year activity were presented.

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On December 12, 2005, in Moscow, the Russian Academy of Sciences, the Lomonosov Moscow State University, and the Russian Foundation for Basic Research (RFBR), from the Russian side, and Centre National de la Recherche Scientifique (CNRS), France, Universite Paul Sabatier III, Toulouse, and Institut de Recherche pour le Developpement, from the French side, signed an agreement on establishment of the "Environmental Geochemistry" European Associated Laboratory [Laboratoire Européenne Associé Géochimie Environnementale (LEAGE)].

The "Environmental Geochemistry" European Associated Laboratory carries out environmental geochemistry researches connected with low- and high-temperatures fluids. Basic regions of research encompass the vital problems of contemporary geochemistry, i.e., the influence of climate variations on the geochemical cycles of water, carbon, mercury, and other macro- and microelements (heavy metals) in the temperate and boreal zones and experimental and theoretical simulation, as well as nature and experimental work on the transfer of metals in the hydrothermal systems in connection with the formation of ore deposits.

The establishment of the Laboratory was an answer to the need in elucidating the mechanisms of interaction in the mineral–solution–organic substance–living matter system, aimed at geochemical simulation of the implications of the climate warming and changes in the global cycles of chemical elements on the Earth's surface under increasing anthropogenic loads on the continental biosphere.

The Laboratory carries out researches in the field of environmental geochemistry, including experimental physicochemical and comprehensive expedition work. The geochemical research program addresses the following current problems of water system geochemistry.

(1) Rock weathering and macroelement cycles, in particular, carbon cycle, in soils and surface streams in boreal and Arctic zones.

(2) The behavior of microelements, above all, heavy metal pollutants (Hg, Cd, Zn, Cu, Pb) and their isotopes in the continental biosphere.

(3) Forms of occurrence and migration of metals and metalloids in vapor hydrotherms.

At the present time, implementation of several joint Russian-French projects is under way at the Laboratory.

(1) “Acid-base and redox properties of hydrothermal fluids in equilibrium with the major natural ore associations in the Cu–Fe–Au–As–S–O–H system at 300–450°C and 10–100 MPa: direct experimental measurements and thermodynamic analysis” RFBR-CNRS project no. 07-05-72553; Project Leader A.V. Zotov (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences).

(2) “The behavior of ore elements in hydrothermal fluids of different densities: experiment and thermodynamic description;” Project Leader N.N. Akinfiev (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences).

(3) “Development of new field and experimental research methods for the major components of the geochemical mercury cycle” RFBR-CNRS project no. 06-05-72550; Project Leader Yu.V. Alekhin (Moscow State University).

(4) “Chemical transformation of the continental runoff on the river–sea geochemical barrier and its contribution to the environmental status of the aquatic environment in mouth areas” RFBR-CNRS project no. 05-05-66810; Project Leader A.V. Savenko (Moscow State University).

The Laboratory of Mechanisms and Transfer in Geology (Laboratoire de Mecanismes de Transfert en Geologie, Universite de Toulouse, France), in cooperation with Russian scientists, undertakes research activities on “Physicochemical examination of the migration forms of microelements and organic matter in Karelian region rivers”, supervised by O.S. Pokrovskii. The EC$_2$CO theme “Continental and nearshore environment” (supervised by J. Viers) is supported by the Institut National des Sciences de l’Universe (UNSU).

The boreal zones in Russian Arctic regions can be of fundamental importance for regulation of the flows of microelements and organic matter into the Arctic Ocean. High concentrations of dissolved organic matter and the colloid status of the most of microelements are specific for the matter transport in river systems of this region.

THE BEHAVIOR OF ORE ELEMENTS IN HYDROTHERMAL FLUIDS OF DIFFERENT DENSITIES: EXPERIMENT AND THERMODYNAMIC DESCRIPTION

In the recent two years we undertook systematic multidisciplinary researches into the forms of occurrence of microelements in river, lake, and bog systems in Russia’s Northwest. Up-to-date frontal filtration and ultrafiltration methods were applied immediately under field conditions via progressively decreasing the pore size of the filters [5 μm, 2.5 μm, 0.22 μm, 100 kDa, 10 kDa, and 1 kDa (1 kDa ~1 nm)], as well as dialysis through semipermeable 10-kDa and 1-kDa membranes. These experiments revealed two types of colloids, organic humic and fulvic acids and organoiron colloids. Based on behavior of the dissolved components in fractional separation and their association with a certain type of colloids, three groups of chemical elements can be identified. The first group includes elements forming particles that are not subject to filtration or ultrafiltration, as they occur as truly dissolved inorganic complexes (Ca, Mg, Li, Na, K, Cs, Si, B, Sc, Sb, Mo) or weak organic complexes (Ca, Mg, Rb, Sn). The second group comprises elements with particle size under 1–10 kDa, that tend to form inorganic or organic complexes (Ni, Zn, Cu, Cd, Ge, As, Ba, W, and, for some rivers, Cr and U). The third group integrates elements strongly bound to the colloid iron in all ultrafiltrates and dialysates, with 30–50% forming stable colloids having particle size over 10 kDa (Mn, Al, Ga, Re, Pb, V, Cr, Ti, Zr, Th, U, Co, Sr, Y, Nb, Hf, Ta, Bi).

Since recently, the attention of geochemists has been focused on transfer of ore elements in a low-density (gas) fluid, above all, in a water vapor. There exist extensive geological evidence of the transfer of ore elements from many deposits by low-density ($\rho < 0.5$ g cm^{-3}) supercritical fluids [1–9]. However, by contrast to dense phases for which the equilibrium can find a fairly reliable description [e.g., in terms of the Helgeson–Kirkham–Flowers (HKF) equation of state], low-density phases have not received a general approach to description of the thermodynamic properties of a dissolved component, taking into account its vapor hydration. Evidently, this type of hydration is responsible for a fairly high solubility of nonvolatile elements in low-density phases [10–14].

Getting key experimental data and development of a new approach to description of the thermodynamic properties of ionic associates over wide ranges of solvent (water) temperatures and densities are the focus of the joint projects “Behavior of ore elements in hydrothermal fluids of different densities: experiment and thermodynamic description” and “Acid-base and redox properties of hydrothermal fluids in equilibrium with the major natural ore associations in the Cu–Fe–Au–As–S–O–H system at 300–450°C and 10–100 MPa: direct experimental measurements and thermodynamic analysis”. This approach is underlain by the equation of state for dissolved volatiles, proposed by Akinfiev and Diamond [15, 16]. Special attention is given to the “intermediate” density range (0.05–0.4 g cm^{-3}) in which the currently existing equations of state are no more valid, while hydration is still fairly considerable.

Thermodynamic Properties of the $B(OH)_3$ Neutral Complex in Water at 400°C and 3–100 MPa

The solubility of takedaite $Ca_3(BO_3)_2$ in a supercritical water fluid was examined at 400°C, depending on the H_2O density (ρ = 0.01–0.7 g cm^{-3}). The experiments were run in autoclaves manufactured from VT8 alloy, at 400 ± 2°C and a pressure of (3–100) ± 0.5 MPa determined by the degree of filling of the autoclave with distilled water. As solid phase we used calcium trioxoborate [an artificial analog of takedaite $Ca_3(BO_3)_2$], prepared by dry synthesis from calcium hydroxide and boric acid at 400°C.

The equilibrium was attained within less than one day. After cold water “quenching” of the autoclaves the boron concentration was determined by spectrophotometry (at 30–100 MPa) and ICP-MS (up to 30 MPa). Figure 1 shows the experimental results. It is seen that, with decreasing pressure, the solubility of $Ca_3(BO_3)_2$ initially tends to smoothly (100–30 MPa) and further sharply (in the low-density area) decrease .

Dissolution of takedaite proceeds incongruently and can be represented as

$$Ca_3(BO_3)_{t,sol} + 6H_tO \rightarrow 3Ca(OH)_{2,sol} + 2B(OH)_{3,aq.} \qquad (1)$$

There exist fairly reliable data on the thermodynamic properties of $B(OH)_{3,aq}$ under standard conditions. Figure 1 shows that the widely used HKF equation of state adequately describes the thermodynamic properties of $B(OH)_{3,aq}$ in the dense fluid area (30–100 MPa). An appreciable disagreement between the model and experimental data in low-density solutions gets more pronounced with decreasing density of the solvent. This “weak point” of the electrostatic models, in particular, HKF, was repeatedly noted [16, 17]. At the same time, it is seen from Fig. 1 that, at low vapor pressures, the experimental results reasonably agree with the ideal gas model data, but at higher pressures this model is unsuitable.

For describing the thermodynamic properties of $B(OH)_{3,aq}$ throughout the solvent density range examined we used the recently suggested [16] equation of state:

$$\mu_{aq}(T, P) = \mu^0_{gas}(T) - RT\ln N_w + (1 - \xi)RT\ln f^0_{H2O}$$

$$+ \xi RT\ln\left(\frac{RT}{M_w}\rho^0_{H_2O}\right) + RT\rho^0_{H_2O}\left[a + b\left(\frac{10^3}{T}\right)^{0.5}\right]. \qquad (2)$$

Here $\mu_{aq}(T, P)$ and $\mu^0_{gas}(T)$ are the chemical potentials of $B(OH)_{3,aq}$ and $B(OH)_3$ ideal gas at given T and P, respectively; N_w = 55.51 mol; R, gas constant; f^0_{H2O} and ρ^0_{H2O}, volatility, Pa, and density, kg m^{-3}, of neat solvent (H_2O) at given T and P, respectively; and a, b, and ξ, empirical parameters estimated from the known thermodynamic properties of $B(OH)_{3,aq}$ under standard conditions ($\xi = -1.085$, $a = -3.543 \times 10^{-3}$ m^3 kg^{-1}, $b = 3.469 \times 10^{-3}$ m^3 kg^{-1}).

Equation of state (2) satisfactorily describes the experimental data throughout the solvent (water) density range examined, from nearly ideal gas (ρ ~0.01 g cm^{-3}) to a dense liquid (1 g cm^{-3}) (Fig. 1). The inconsistency between the experimental and model data at low fluid densities is evidently associated with an increase in the experimental error under these conditions.

Thermodynamic Properties of Neutral AgCl Complex in Water at 400–450°C and 5–100 MPa

The water solubility of chloroargyrite $AgCl_{cr}$ under supercritical conditions (400–450°C) was examined over a wide density range of the solvent (ρ_{H2O} = 0.01–0.7 g cm^{-3}). The experiments were carried out in an autoclave by a “quenching”-based technique and supplemented by internal sampling-based control experiments [18]. As the AgCl source we used pure-grade (99.8%) crystalline silver chloride pellets. The equilibrium was established within less than one day. The solubility was determined by atomic absorption and weight loss methods; the data obtained by these methods agreed within 7%. Figure 1 presents the

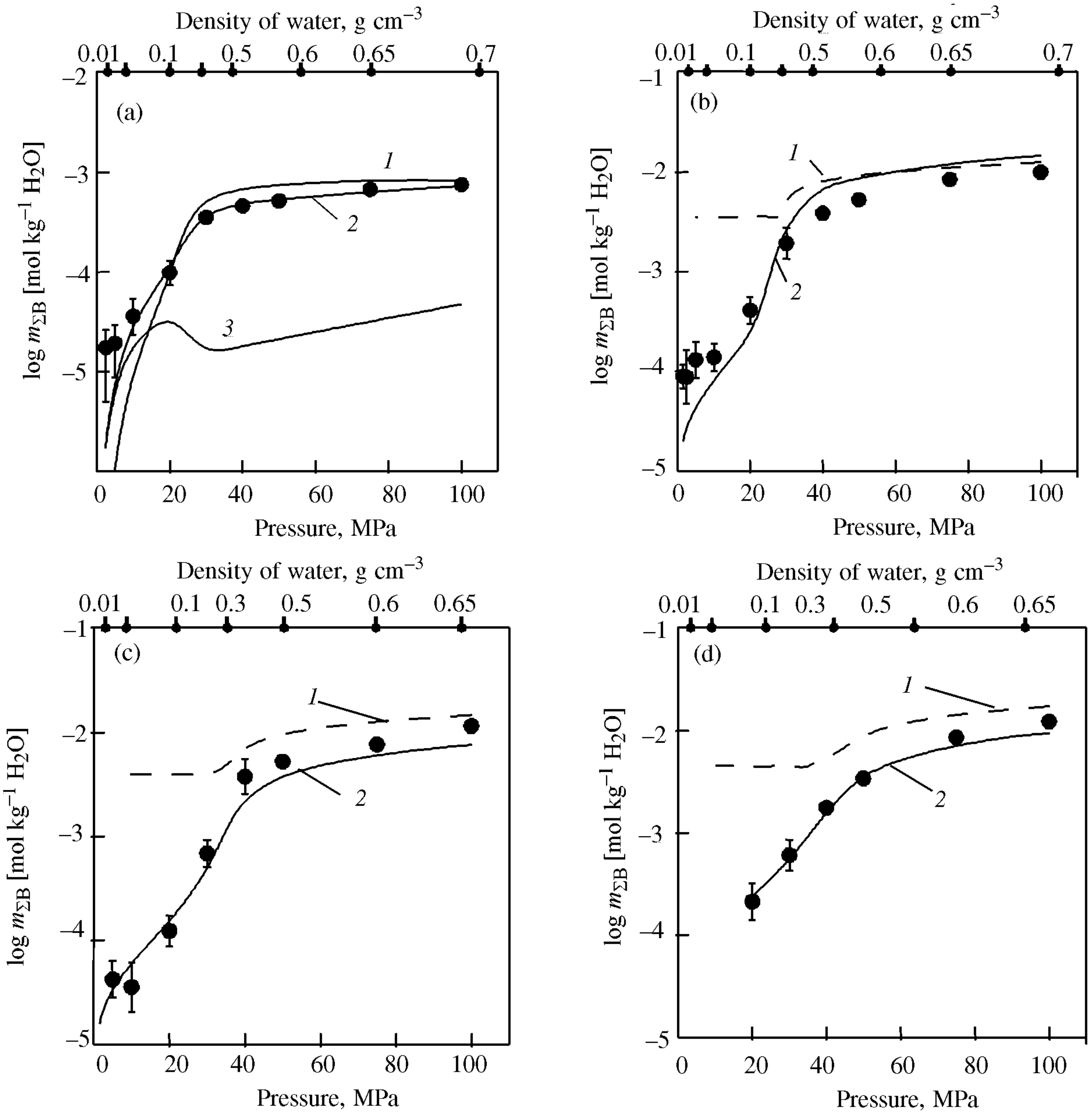

Fig. 1. Baric dependences of the solubility of (a) takedaite and (b–d) chloroargyrite: (●) experimental data and (*1–3*) calculation in terms of the (*1*) HKF (Helgeson–Kirkham–Flowers), (*2*) A–D (Akinfiev and Diamond), and (*3*) ideal gas model. Temperature, °C: (a, b) 400, (c) 425, and (d) 450.

results; it is seen that the solubility of $AgCl_{cr}$ smoothly decreases with decreasing pressure at 100–40 MPa and sharply decreases in the low-density area. At high pressures (100 MPa) the solubility of chloroargyrite is determined by the presence of Ag^+, $AgCl_{aq}$, and $AgCl_2^-$ making comparable contributions. With de-crease in pressure and the associated decrease in the solvent density, the association of ions is enhanced, and $AgCl_{aq}$ becomes the dominating species.

Attempts to describe the behavior of the $AgCl_{aq}$ ion pair in terms of equation of state (2), successfully approbated for a large number of dissolved volatile components, yield overestimated solubilities of AgCl in the low-density fluid area ($\rho_{H2O} < 0.1$ g cm^{-3}). Most likely, this is a hydrated species AgCl × $(H_2O)_{N,aq}$. Migdisov at al. [10] examined the solubility of chloroargyrite in a water vapor and arrived at identical conclusion.

Modification of equation of state (2) to fit the case of the hydrated component [19] yields expression (3) for the chemical potential of the "seemingly nonhydrated" $AgCl_{aq}$ ion pair at given temperature T and pressure P.

Here, $N_w = M_w^{-1} = 55.51$ mol kg^{-1}; $R = 8.314$ J mol^{-1} K^{-1}; R, universal gas constant, f^0_{H2O} and ρ^0_{H2O}, volatility, Pa, and density, kg m^{-3}, of neat solvent (H_2O) at given T and P, respectively; $\mu^0_{gas,h}$ and $\mu^0_{H2O,gas}$, chemical potentials of the hydrated ion pair $AgCl \cdot (H_2O)_N$ and H_2O in the ideal gas state (depend on temperature solely); and ξ, a, and b, empirical parameters of the model.

$$\mu_{aq}(T, P) = \mu^0_{gas,h}(T) - N\mu^0_{H2O,\ gas} - RT\ln N_w + (1 - \xi - N)RT\ln f^0_{H_2O} + \xi RT\ln\left(\frac{RT}{M_w}\rho^0_{H_2O}\right) + RT\rho^0_{H_2O}\left[a + b\left(\frac{10^3}{T}\right)^{0.5}\right]. \quad (3)$$

The baric (density) dependence of μ_{aq} is determined by a set of parameters, N, ξ, a, and b, while the temperature dependence of $\mu^0_{gas,h}(T)$ is governed by the nature of the gas particle. Unfortunately, by contrast to volatiles, for $AgCl \cdot (H_2O)_N$ this character-istic is unknown and is, essentially, a parameter of equation of state (3) as well. To estimate $\mu^0_{gas,h}(T)$, we used the μ_{aq} parameters for $AgCl_{aq}$ calculated in terms of the HKF model at temperatures within 0–360°C over the saturated H_2O vapor curve and at tempera-tures of 400 and 425°C and a pressure of 100 MPa. The parameters N, ξ, a, and b were chosen in such a way that the baric dependence of the experimental sol-ubility of $AgCl_{cr}$ be described most adequately (Fig. 1). This yielded the following values: $\mu^0_{gas,h}$(298 K, 1 bar) = –111255 cal mol^{-1}, $S^0_{gas,h}$(298 K, 1 bar) = 123 cal mol^{-1} K^{-1}, $N = 2.0$, $\xi = -2.0$, $a = 1.0 \times 10^{-2}$ m^3 kg^{-1}, $b = -7.48 \times 10^{-3}$ m^3 kg^{-1}.

It should be noted that these data are in poor agreement with the absolute values of the solubility of chloroargyrite reported in [10] for 300–360°C and pressures under P_{sat}, although the baric dependence of the solubility is reproduced correctly.

Thus, direct experimental data for the thermodynamic properties of aqua components $AgCl_{aq}$, $B(OH)_{3,aq}$ over a wide range of solvent densities were obtained for the first time. The limitation of the electrostatic (HKF) model in the low-density area of the fluid was confirmed. Much promise is offered by the universal equation of state we proposed, underlain to a significant extent by the "density" model. However, $AgCl_{aq}$ ionic associates should be described in the context of the possible formation of water-containing clusters of the $MA \cdot (H_2O)_n$ type, where MA is the "conventional" ionic associate, and n, number of the water molecules covalently bound to the associate.

GEOCHEMICAL MERCURY CYCLE RESEARCH

The emission of mercury and individual components of the natural global mercury cycle, as well as the technogenic contribution to contamination of the environment components is addressed by the project "Development of new field and experimental methods for the major components of the geochemical mercury cycle." A fundamental task in this context is to obtain reliable data on individual components to this cycle in the situation when only incomplete information on natural mercury emission sources is available [20].

The methods we suggested for independently assessing the partial pressures of mercury vapor [21] in litospheric rocks and in the atmosphere were applied to derive the first characteristics of the regional variability of the cold emission endogenic flows of mercury. Methods were developed for collecting the information about the partial pressures and chemical potentials of mercury in lithospheric rock sections, based on comparison of the initial mercury content with that in the adsorption-saturated samples. A large volume of methodically original nature work validated the novel conclusions concerning the considerable rates and the mechanism of gas emission of mercury from the lithosphere into the atmosphere, which allows elucidating the ratio of the natural to anthropogenic emission levels. Two new high-performance sorbents for mercury were synthesized that are suitable for reliable determination of the isotope composition [22]. The revealed regional variations of the composition and more detailed data on the partial pressures help assess the contributions from anthropogenic and natural emissions at the regional level to the global mercury balance in the environment.

For the first time, for a deep-lying thermal water source (Kamchatka, operating wells of the Mutnovsk geothermal power plant), the compositions of the coexisting vapor gas and liquid phases and those at temperatures within 180–200°C were determined, as well as the molal distribution coefficient for mercury in the vapor–liquid system. A technique was developed for estimating the contamination of the vapor gas phase condensate with phlegm, based on the liquid and dry vapor flow rates. It was found that the deep fluid samples (1600-m-deep wells) are dominated by elemental mercury which enriches the vapor gas phase in the vapor phase with a high distribution coefficient (8.17). Similar results were obtained for a large number of samples from other thermal sources under simultaneous sampling of the liquid phase and the vapor gas phase condensate. The data for mercury were compared with the distribution coefficients of other microelements. The project implementation was underlain by an integrated approach, which yielded a large body of analytical data for various regions of Russia using new field research methods and experimental simulation of the mass exchange. For the first time, special attention was devoted to the local mass-exchange processes and development of new methods to examine the inter-basin flows of mercury and other microelements.

HYDROCHEMICAL STUDIES OF THE CONTINENTAL RUNOFF MOUTH AREAS

The "Chemical transformation of the continental runoff on the river–sea geochemical barrier and its contribution to the environmental status of the aquatic environment in mouth areas" project is implemented in cooperation with the State Institute of Oceanology, Russian Academy of Sciences.

The hydrochemical studies of river mouth areas with their high economic value have been traditionally a focus of much attention. This concerns, above all, the hydrochemical regime of biogenic elements whose content strongly affects the biological productivity. Since the beginning of the 1970th, the highest priority has been assigned to environmental problems associated with rapidly growing contamination of the aquatic environment with heavy metals and radionuclides and with uncontrolled economic activities.

As known, the anthropogenic pollution of rivers in highly urbanized regions is approaching, or has already reached, the critical levels of water use standards in fisheries. The river mouth contamination presents even more pressing problem. The overwhelming majority of highly toxic pollutants, e.g., heavy metals and long-lived artificial radionuclides, exhibit very high sorption equilibrium coefficients K_{d} in low-mineralized river waters:

$$K_{\mathrm{d}} = m_i/C_i \approx 10^3–10^5, \quad (4)$$

where m_i and C_i are the respective concentrations of ith substance in the solid phase, mol g^{-1}, and in solution, mol ml^{-1}. Hence, 50–99% heavy metals and artificial radionuclides is transferred by rivers as part of slit. With increasing mineralization, the sorption equilibrium coefficients dramatically decrease and reach ~10–100 in seawater with normal salinity. This results in desorption and dissolution of pollutants and the ensuing significant deterioration of the environmental state of the aquatic medium. Importantly, the desorption mobilization maximum for pollutants can lie within a very narrow salinity range, which is responsible for emergence of local zones with extremely unfavorable environmental conditions. The situation is similar in the case when mobilization of pollutants is associated with dissolution or chemical transformation of solid phases which either are pollutants themselves or contain the latter as isomorphic impurities. This suggests that enhanced contamination of river waters is responsible for disproportionate growth of the potential risk of the critical deterioration of the environmental state of the aquatic environment in river–sea water mixing zones. This makes studying chemical transformation of the river runoff at river mouths an extremely important task.

Table 1 summarizes the trends in migration of dissolved substances in the mouth areas of Volga, Northern Dvina, and Onega rivers [23–25] under various physicogeographic and climatic conditions, also differing in the degree of anthropogenic impact. These data were obtained using a set of analytical methods: volumetric titration (Cl, Ca), colorimetry (P, Si), atomic absorption spectrophotometry (Fe, Sr), and ICP–MS (other microelements).

The nature work at the Volga mouth was carried out during the summer low-water (intermediate water level) period in August, 1996, and August, 2003–2006; at the Northern Dvina and Onega mouths, in different hydrological regime phases: in the lowest water winter period before the high-water time (March–April 1999, 2000, 2003), in early high-water period (May, 2006), in the high-water decay period (June–July 2000, 2002,

Table 1. Distribution of the dissolved microelements at the Volga mouth

Element *i*	Observation period[a]	Behavior	Parameters of Eq. (5)		Correlation coefficient, *r*	Number of samples, *n*
			a	*b*	*r*	
Li	2004, 2005	conservative	3.88	5.29×10^{-2}	0.996	35
Rb	2004—2006	—	1.12	1.54×10^{-3}	0.993	44
Cs	2004, 2005	—	0.0020	4.64×10^{-6}	0.942	30
Sr	1996	quasiconservative	excess (maximum 18% at Cl = 2.0 g l^{-1})			
	2003		0.39	2.34×10^{-3}	0.999	27
	2004		0.39	1.84×10^{-3}	0.998	17
	2005		0.30	2.11×10^{-3}	0.998	14
	2006		excess (maximum 8% at Cl = 2.0 g l^{-1})			
Ba	2004, 2005	nonconservative	excess (maximum 52% at Cl = 2.0 g l^{-1})			
B	2004—2006	conservative	0.015	6.30×10^{-4}	0.996	42
Al	2004	nonconservative	loss (maximum 59% at Cl = 0.2 g l^{-1})			
Ga	2004—2006	conservative	0.0083	7.07×10^{-6}	0.886	35
Sc	2004, 2006	The same	0.48	-1.08×10^{-4}	0.874	21
Y	The same	"	0.025	2.26×10^{-6}	0.406	22
Ti	The same	nonconservative	loss (maximum 88% at Cl = 0.2 g l^{-1})			
Mn	The same	The same	loss (maximum 91% at Cl = 0.3 g l^{-1})			
Fe	2004	"	loss (maximum 74% at Cl = 0.3 g l^{-1})			
Co	2004—2006	conservative	0.13	8.43×10^{-5}	0.920	38
Ni	2004, 2006	The same	1.72	6.88×10^{-4}	0.803	24
Cu	2004—2006	"	1.61	1.79×10^{-3}	0.881	40
Cd	2004, 2005	"	0.029	1.30×10^{-5}	0.725	30
Pb	The same	nonconservative	loss (maximum 87% at Cl = 0.2 g l^{-1})			
Ag	The same	conservative	0.0053	2.02×10^{-5}	0.861	34
V	2004, 2005	The same	2.35	7.59×10^{-3}	0.982	30
As	The same	"	1.97	6.04×10^{-3}	0.994	31
Sb	2004—2006	"	0.11	4.05×10^{-5}	0.928	41
Bi	The same	"	0.0018	8.63×10^{-7}	0.676	35
Br	2003	"	160	4.89×10^{-1}	0.982	25
I	2003	"	33.9	7.95×10^{-3}	0.780	24
Mo	2005, 2006	"	0.81	2.72×10^{-3}	0.992	27
W	2004, 2005	"	0.023	2.97×10^{-6}	0.459	34
U	2003—2006	"	0.58	9.13×10^{-4}	0.968	78

[a] For the results of surveys for the years 1996 and 2003, see [25] and [26], respectively.

Table 2. Distribution of the dissolved microelements at the Northern Dvina and Onega river mouths

Object	Observation period[a]	Parameters of Eq. (5)		Correlation coefficient, r	Number of samples, n
		a	b		
i = Sr					
Nortehrn Dvina mouth, Kuznechikha branch	03.1999, 03.2000	0.65	$2.99 \bullet 10^{-4}$	0.982	27
The same, Korabel'nyi branch	07.2000	0.35	$3.73 \bullet 10^{-4}$	0.998	5
The same, Maimaksa branch	06.2002	0.26	3.79×10^{-4}	0.999	15
Onega mouth	06.2002, 09.2002	0.21	3.68×10^{-4}	0.999	25
i = F					
Nortehrn Dvina mouth, Kuznechikha branch and Korabel'nyi branches	03.1999, 03.2000, 07.2000	0.175	4.82×10^{-5}	0.972	32
The same, Maimaksa branch	06.2002	0.086	5.57×10^{-5}	0.998	15
Onega mouth	06.2002, 09.2002	0.145	5.82×10^{-5}	0,998	24
i = B					
Nortehrn Dvina mouth	03.2000, 07.2000, 06.2002	0.050	1.61×10^{-4}	0.975	30
Onega mouth	06.2002, 09.2002	0.111	2.24×10^{-4}	0.997	25
i = Li					
Nortehrn Dvina mouth	06.2002	2.97×10^{-3}	9.07×10^{-6}	0.998	37
Onega mouth	06.2002, 09.2002				
i = Rb					
Nortehrn Dvina mouth	06.2002	8.20×10^{-4}	5.40×10^{-6}	0.999	37
Onega mouth	06.2002, 09.2002				
i = Cs					
Nortehrn Dvina mouth	06.2002	1.70×10^{-6}	1.24×10^{-8}	0.997	36
Onega mouth	06.2002, 09.2002				
i = As					
Nortehrn Dvina mouth	06.2002	4.57×10^{-4}	2.50×10^{-6}	0.998	37
Onega mouth	06.2002, 09.2002				
i = U					
Nortehrn Dvina mouth	06.2002	1.57×10^{-4}	1.42×10^{-7}	0.997	37
Onega mouth	06.2002, 09.2002				

[a] For the data on strontium, fluorine, and boron, see [25].

and 2003) and during the summer low-water period (August, 2003–2004).

At the Volga mouth and in the mouth areas of Northern Dvina and Onega, the majority of the examined microelements exhibit conservative behavior described with high correlation coefficients by a linear interdependence of the concentrations of ith element and chlorides (Tables 1, 2):

$$[i, \mu\text{g l}^{-1}] = a + b[\text{Cl, mg l}^{-1}], \qquad (5)$$

where *a* is a parameter closely corresponding to the concentration of *i*th element in river waters, μg l^{-1}, and *b*, slope.

Strontium exhibited a close to conservative behavior at the Volga mouth in 1996 and 2006, but its concentrations slightly exceeded those calculated by the conservative mixing equation (Fig. 2), 0.75 (18%) and 0.40 (8%) mg l^{-1}, respectively, at the chloride content of 2 g l^{-1}. This is evidently associated with different transformations of the waters in flowing and standing areas of the mixing zones due to evaporation and biological assimilation, with chemical processes making an insignificant contribution [26]. Also, a significant inter-annual variability of the strontium concentration at the marine side of the mixing zone can be due to the changes of the volumes of the river runoff and the evaporation intensity at the estuarine seaside.

The barium concentrations at the Volga mouth, 13.6 μ g l^{-1} at the chloride content of 1.2 g l^{-1}, more considerably (52%) exceeded those calculated by the conservative mixing equation. The nonconservative behavior of barium is presumably associated with its additional amount in the solution yielded by desorption from river suspensions, for which the composition of the exchange complex is strongly affected by the interaction with seawater. Notably, the plots of the barium concentration vs. chloride concentration for the years 2004 and 2005 exhibit virtually identical shapes and reasonably agree with the data reported by Brezgunov and Ferronskii [27] for the Northern Caspian Sea.

As for manganese, iron, and aluminum at the Volga mouth, their concentrations sharply decreased in the initial stage of mixing with seawater, whereupon their content remained virtually unchanged, at the level corresponding to their content in seawater (Fig. 3).

The maximal loss of these elements was estimated at 16.9, 12.6, and 5.4 μ g l^{-1} (91, 74, and 59%), respectively, at the chloride content of 0.2–0.3 g l^{-1}. The experimental and nature work [28] showed that the dissolved iron is actively removed with humic acids in the initial stages of salinization owing to flocculation of the colloids. Similar shapes of the curves suggest that migration of aluminum and manganese in the Volga–Caspian Sea water mixing zone is also controlled by flocculation. At the Northern Dvina mouth in May, 2006, a similar behavior was exhibited by iron and manganese (Fig. 4). Hence, the major biogeochemical processes in the river mouth areas proceed even in the period of the highest water in spring, when the current flow rates are at a maximum, though less intensively than in the summer period.

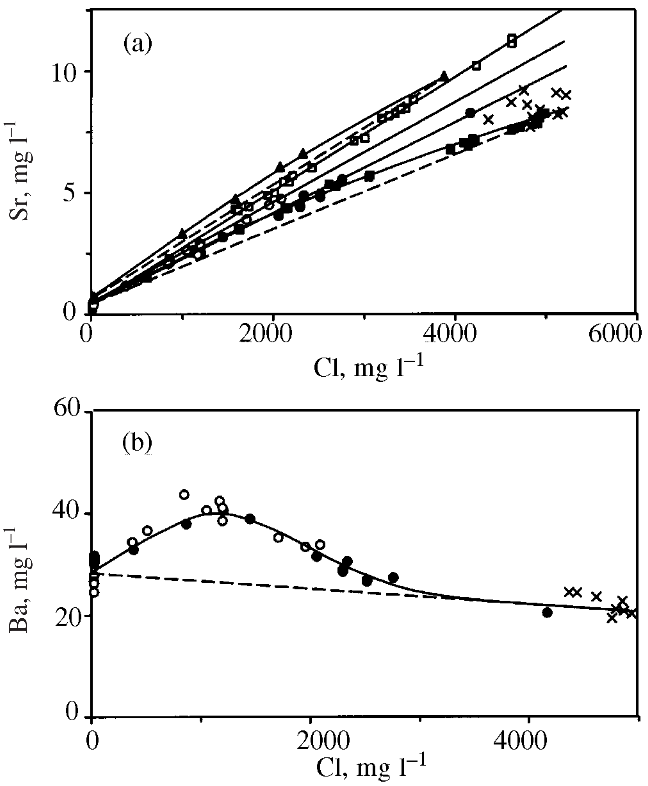

Fig. 2. Concentration of dissolved Sr and Ba vs. chloride content at the Volga mouth: (×) 1995, (■) 1996, (□) 2003, (○) 2004, (●) 2005, and (▲) 2006. The dashed lines correspond to the calculated data for conservative mixing; the same for Figs. 2–6.

The most complex patterns of variation with the chloride content at the Volga mouth is exhibited by titanium and lead (Fig. 5): With increasing salinity the concentrations of these elements initially decreased dramatically and further smoothly increased, with lead reaching the level corresponding to its content in the river water mass. The maximal titanium loss was estimated at 0.55 and 2.4 μ g l^{-1} (64 and 88%) for the chloride content of 0.2 g l^{-1} in 2004 and 2006, respectively, and the lead loss, at 0.37 and 0.40 μg l^{-1} (52 and 87%) for the chloride content of 0.6 and 0.2 g l^{-1} in 2004 and 2005, respectively. The factors responsible for these patterns are fairly difficult to identify because of scarce published data relevant to titanium and lead. It can only be noted in this connection that an increase in the concentrations of the dissolved microelements upon mixing with seawater

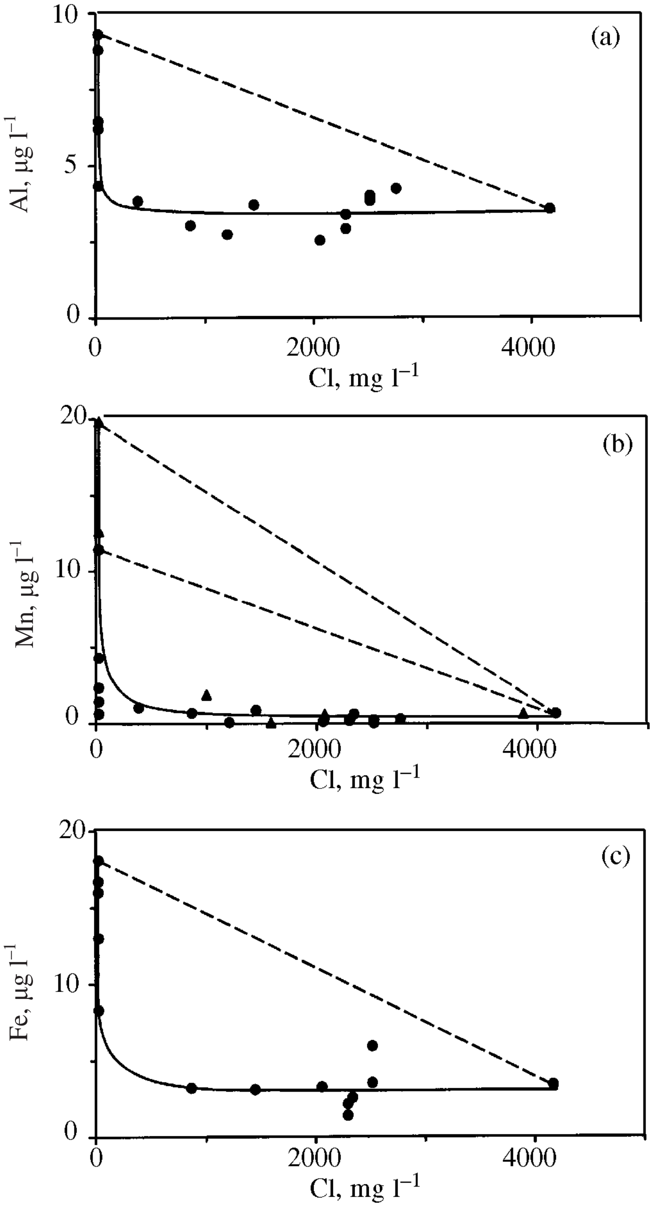

Fig. 3. Concentrations of dissolved (a) aluminum, (b) manganese, and (3) iron vs. chloride content at the Volga mouth: (●) 2004 and (▲) 2006.

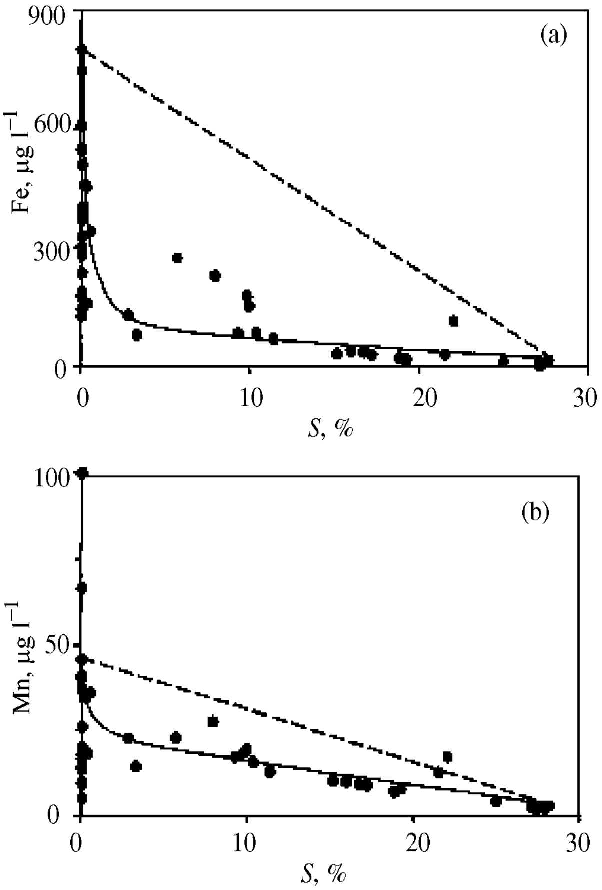

Fig. 4. Concentrations of dissolved (a) iron and (b) manganese vs. salinity at the Northern Dvina mouth in May 2006 (according to V.V. Gordeev and V.P. Shevchenko).

can be due to a decrease in the activity coefficients because of complexing with chlorides and sulfates and the associated decrease in the proportion of the sorbed species.

The biogenic elements exhibited strongly nonconservative behavior at the Volga mouth (Fig. 6). The intensity of removal of phosphates and silicon from solution exhibits regular features in different years: In 2003 and 2005 silicon displayed the most nonconservative behavior, while in 2004 and 2006 dissolved phosphates were virtually exhaustively removed. The maximal loss of mineral phosphorus was observed at the chloride content of 0.2 g l^{-1}, specifically, 0.022, 0.008, 0.054, and 0.009 mg l^{-1} (60, 63, 91, and 64%) in 2003, 2004, 2005, and 2006, respectively. The maximal silicon loss in 2003 and 2005, 2.32 and 3.33 mg l^{-1} (76 and 82%), respectively, corresponded to the chloride content of 0.2 mg l^{-1}. At the same time, in 2004 and 2006 the amount of removed silicon did not exceed 1.02 and 1.49 mg l^{-1}, or 46 and 62%, at the chloride content of 1.2 g l^{-1}. The inter-annual variation of the content of biogenic elements in the river water is determined, evidently, by variability of the runoff formation conditions in the catchment area, and the change of their concentrations on the marine side of the mixing zone is controlled

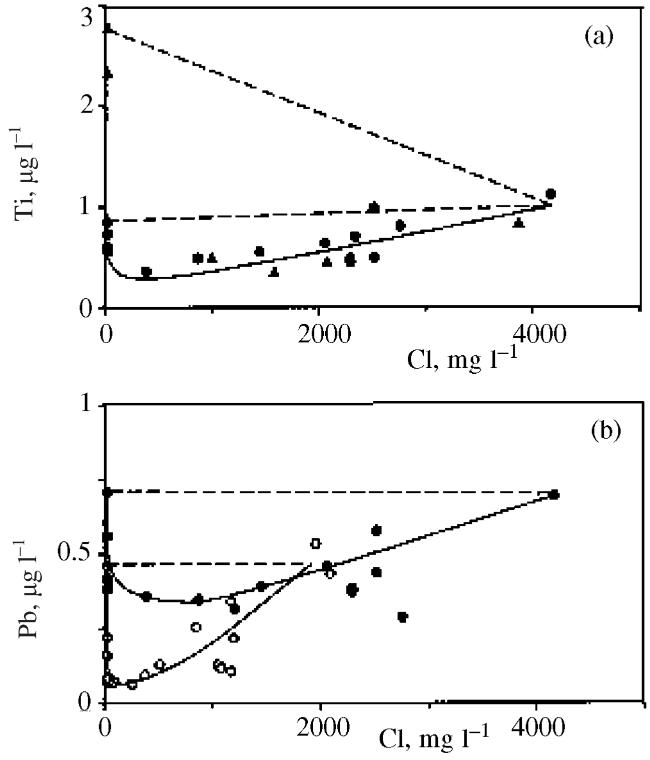

Fig. 5. Concentrations of dissolved (a) titanium and (b) lead vs. chloride content at the Volga mouth: (○) 2004, (●) 2005, and (▲) 2006.

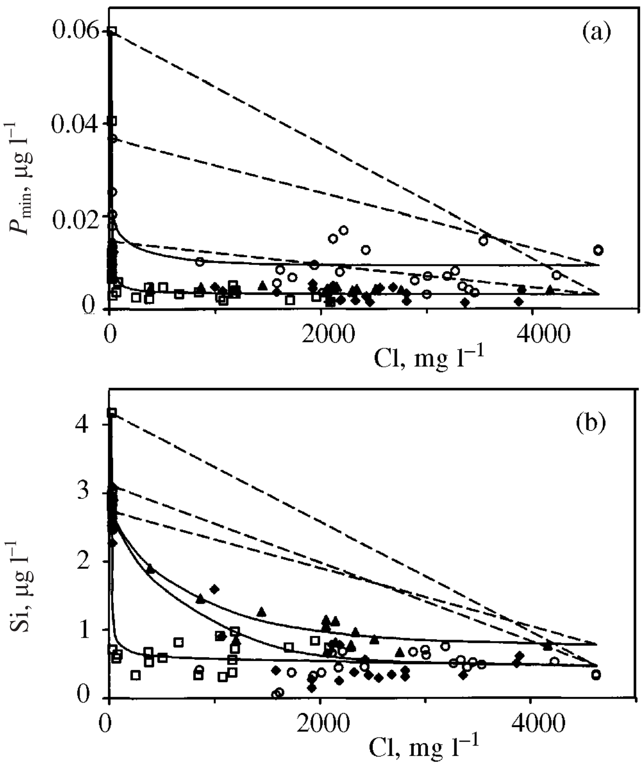

Fig. 6. Concentrations of dissolved (a) mineral phosphorus and (b) silicon vs. chloride content at the Volga mouth: (○) 2003, (▲) 2004, (□) 2005, and (♦) 2006.

mainly by the intensity of biological assimilation and regeneration in the estuarine seaside.

All the hydrological and hydrochemical surveys conducted at the Northern Dvina and Onega mouths revealed nonconservative distribution of mineral phosphorus and silicon (Fig. 7). In the vegetation period, from April till August, 2003, at the Northern Dvina mouth, the concentration of the examined elements both at the river and marine sides of the mixing zone gradually decreased, evidently, due to the fact that the intensity of the inflow of organic matter exceeded its degradation. The nonconservative behavior was the most pronounced in phosphates whose maximal removal in April and June, 2003, was estimated at 21 and 24%, respectively, of the content in the river water mass of 0.031 and 0.018 mg l^{-1}, while for silicon the same parameters were estimated at 3 and 10%, respectively, of its content in the river water (5.6 and 2.3 mg l^{-1}). At the Onega mouth in August, 2004, the mineral phosphorus and silicon exhibited lower concentrations virtually throughout the mixing zone.

The most probable reason for nonconservative behavior of biogenic elements is their removal by photosynthesizing water plants. This is indirectly confirmed by close shapes of the concentration vs. chloride content plots for both biogenic elements, despite essential difference in their chemical properties. Published data [28] suggest that the biological removal of the dissolved mineral phosphorus and silicon species was also observed in the vegetation period at the mouths of the majority of other rivers in the world.

The conducted studies revealed major chemical transformation of the dissolved matter runoff in the river mouth areas. The lowest potential risk is posed by microelements that are actively removed from solution via interaction with seawater. The microelements that exhibit a conservative behavior occupy an intermediate place; their concentrations are determined mainly by the hydrophysical processes of mixing of the river water and seawater, while sorption–desorption and other intra-basin processes are of subordinate

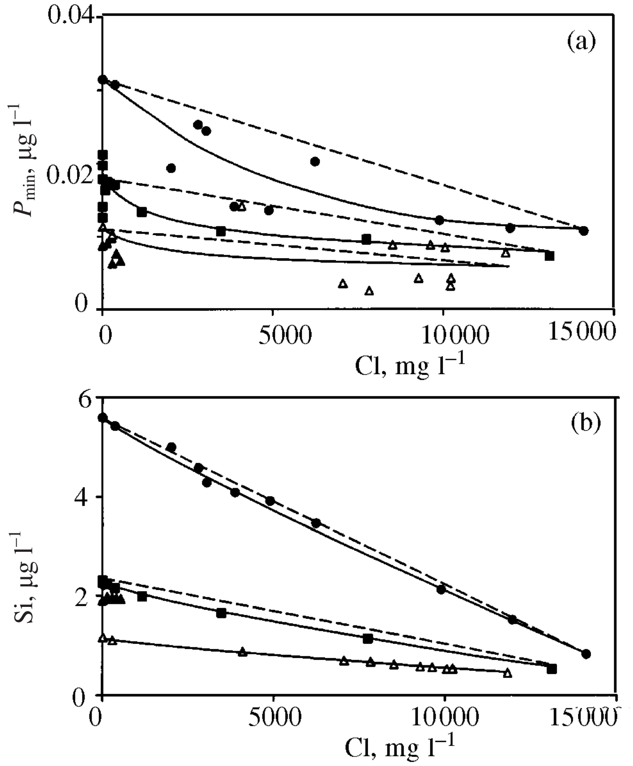

Fig. 7. Concentrations of dissolved (a) mineral phosphorus and (b) silicon vs. chloride content at the mouth of Northern Dvina in (●) April, (■) June, and (▲) August, 2003 [29], and (Δ) Onega in August, 2004.

importance. The most sensitive to anthropogenic contamination are components whose concentrations strongly exceed those calculated by the conservative mixing equation.

The overviewed results of the joint activities of Russian and French scientists demonstrate a wide scope of research in the field of environmental geochemistry.

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