

Oriented Chemical-Thermodynamic Modelling of the Speciations of Heavy Metals (Cu, Cd, Pb) in Fresh-Water Reservoirs

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Migration, bioavailability and toxicity of heavy metals (HM) in natural waters depend on their distribution on separate fractions (so-called 'forms of maintenance'). Usually 'dissolved' and 'suspended' parts are distinguished, state and amount of the latter, including plankton community, being essential in dynamics of pollutants deposition into the bottom sediments (BS). However, the "dissolved" part frequently prevails, and HM speciation in it plays a key role in the all mentioned relations. In turn, the last depends on ion composition, Eh, pH, temperature of waters, nature and concentration of the dissolved organic matter (DOM). Taking into account daily, seasonal and spatial variability of these parameters in fresh superficial waters, it is necessary to expect inconstancy of HM distribution not only in different, but even in one reservoir. At the same time the low levels of HM concentration in superficial waters and high lability concerning equilibria not only in separate subsystems, but also in system as a whole result in difficulty or impossibility of reception of the required detailed information about a state of HM by direct methods of chemical analysis even only in one aqueous phase.

Our approach to the description of HM state in the 'dissolved' part (i.e., quote distribution under the formed by HM chemical forms (speciation)) is based on the oriented chemical-thermodynamic modelling (taking into account the constructive principle of locality and partiality of any internal equilibria [1]). The last is carried out with addition the selected reference data on an inorganic subsystem, analytical data and experimentally obtained integral parameters (K^* and C_L^*) of HM ions binding by fragments of DOM in conditions of a particular reservoir [2]. HM distribution between 'dissolved' and 'suspended' parts, and in a case of 'active' experiments on influence of the increased concentration TM – both dynamics of such distribution and deposition into BS is analyzed also.

The method was realized for study of a state of Cu(II), Pb(II), Cd(II) in the fresh reservoirs of Western Siberia: in Novosibirsk Reservoir (NR) located in the south (zone of high technogeneuous loading) and small northern lakes (SNL). Besides ion composition and total HM content, K^* and C_L^* were determined by ionometry with ISE on Cu^{2+} , Cd^{2+} , Pb^{2+} . Let's note, that the determination of these parameters in conditions of low concentration ($n \cdot 10^{-7}$ – $n \cdot 10^{-9}$ mole/l) HM is a separate complex task. To dissolve this task, we offer to base on the analysis of known auxiliary functions, for example, Leden's function of metal, at ionometric titration of a portion of water by the solution of M(II) salt.

The investigated reservoirs considerably differ on a number of the important indexes: in the summer period for NR the high mineralization ($\Sigma_{ion} = 140 \pm 10$ mg/l), the weak alkaline medium (pH = 8.9 ± 0.3) and prevalence of carbonate alkalinity above humic one ($Alk_{carb}/Alk_{hum} \approx 7-8$) are typical, whereas for SNL it is found Σ_{ion} from 2 up to 30 mg/l, pH from 4.5 up to 6.5, Alk_{hum}/Alk_{carb} from 0.7 up to 10 [3]. Therefore, despite of approximately equal (at pH=6.0) values of K^* and C_L^* in 'dissolved' part of waters of both types, in summer in NR hydroxo- and carbonate forms (with the small contribution of binding with DOM) dominate, and in SNL the bonded with DOM forms for Cu(II), Pb(II) and aqua-ions for Cd(II) do. In a winter period in reservoirs of both types there is a downturn of pH and increase mineralization, that reduces quote of hydroxoforms, and for SNL it is observed the significant (in 1.5–10 times) increase of the total HM concentrations both in 'dissolved' and 'suspended' part. The fact of approximately equal average annual total HM concentrations in both types of reservoirs (in spite of the difference of technogeneuous loads) is also of interest. It allows to suppose the same 'containing' ability of aqueous bed in relation to HM. For SNL, besides the level of total HM concentrations, the significant quote of their aqua-ions can be an essential factor of negative influence on aquatic organisms.

So, the oriented chemical-thermodynamic modeling allows to receive the detailed information on the chemical forms of HM in natural waters, and on this basis to predict ecological risk of pollution of particular reservoirs in their current condition. Let's note, that the further perfection of a method is also bound up with increase of reliability of determination and application of integral parameters of HM ions binding by DOM fragments. The combination of a method with an "active" experiments, for example, complex on-line modelling of influence of the increased concentration of pollutants on whole biohydrocenoses with using of mesocosms, is most effective.

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[1] V. I. Belevantsev, *Journal of Structural Chemistry*, **39** (1998) p. 224.

[2] B. S. Smolyakov et. al., *Chemistry for Sustainable Development*, **3** (1996) p. 539.

[3] B. S. Smolyakov et. al., *Chemistry for Sustainable Development*, **7** (1999) p. 575.