



ORAL & ORAL POSTER PRESENTATIONS

PROCEEDINGS

Edited by Per Smolli, Kjetil Berntsen, Toralf Jølle

International Conference on
**RADIOECOLOGY
& ENVIRONMENTAL
RADIOACTIVITY**

PART 2

15-20 June 2008 - Bergen, Norway

Radionuclides behavior in natural water estimate based upon determination physicochemical state of their stable chemical analogs

E.V. Polyakov¹, N.A. Khlebnikov¹, V.T. Surikov¹, A.V. Trapesnikov², V.N. Udachin³, V.P. Remeza⁴

¹ Institute of solid state chemistry, UD RAS, 620041, Ekaterinburg, Pervomajskaya, 91 RF; ² Institute of plant and animal ecology, UD RAS, 624250, Sverdlovsk reg., Zarechny, a/b18, Biophysical Station, RF; ³ Institute of mineralogy UD RAS, 456301, Chelyabinsk reg., Miass, RF; ⁴ Scientific Engineering Co. ECSORB, 620014, Ekaterinburg, 8th March, RF

INTRODUCTION

Physicochemical factors play significant role in mass transfer of trace elements and their radionuclides in the environment. This is obviously true in particular for the migration of trace elements in the aquifer as well as in river water. Less obvious are means of an immediate determination of their chemical composition: *in-situ* radionuclides speciation is holding back by weak sensitivity of instrumental methods (Polyakov, Egorov, 2003). We evolve an approach, in accordance with which application both physicochemical methods and instruments for the experimental analysis forms of state of representative group of microelements in their natural abundance and state in the natural object could bring relevant information on the physicochemical behavior of their man-made radioactive chemical analogs in the same natural object (Polyakov, 2003). General aim of the investigation was to clarify the role of chemical composition of river Techa water in the transfer of man-made radionuclide in the vicinity of Mayak Production Association (South Urals, RF). The above formulated approach was used for the investigation of physicochemical state of Sr, U, REE and Th in the river Techa.

MATERIALS AND METHODS

Sampling procedures

Sampling of Techa river water was fulfilled to determine radionuclides and investigate their physicochemical state (speciation) and was carried out in the vicinity of the Muslumovo village, Chelyabinsk region, at spring (April) and autumn (October) periods of the years 2006-2007. Samples selection and preparation techniques conformed the recommendation of Public Health Ministry of the USSR (Burgasov, 1980), i.e.: (i) two parallel samples were being collected in each point of the middle part of the stream, (ii) the water samples were being filtered through cellulose cotton into the glass vessels (collectors), (iii) the samples were being acidified in the glass sampling vessels by concentrated HNO₃. In the case of samples preparation for the further speciation experiments the procedure of sampling differed from the described above in the points (ii) and (iii), i.e. no filtering and acidification was being carried out. For the radiochemical determination of ¹³⁷Cs, ⁹⁰Sr, ^{239/240}Pu in the samples of water the radionuclides were pre-concentrated and then adequate procedures of their selective determination were applied (Trapeznikov, Trapeznikova, 2006).

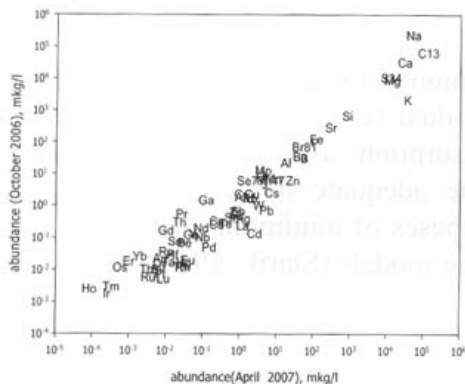


Figure 1. Example of seasonal variation the level of chemical elements in the water of river Techya. (samples were acidified before the analysis).

analysis of the filtered colloids in river water. The last was performed using the scanning microscope JEOL JSM -6460 LV.

Calculated fields of predominance for different species of Sr(II), U(VI), P3Э(III) and Th(IV) were based on the thermodynamic database (Kotrly, Sucha, 1985) and recent thermodynamic

Elemental analysis of liquid samples as well as elemental partitioning in ion-exchange and ultra-filtration experiments as a function of liquid phase pH were carried out by the inductively-coupled mass-spectrometry (Polyakov, 2007). Experimental investigation of physicochemical state of the trace elements with emphasis on the speciation of Sr(II), U(VI), P3Э(III) and Th(IV), the stable or long-lived chemical analogs of man-made radionuclides in river included application of such a techniques as ion-exchange (Schubert, 1948), ultra-filtration of water through nuclear track membranes (Kravets, 1997) and TiN-modified ones, scanning electron microscopy and local energy dispersive x-ray

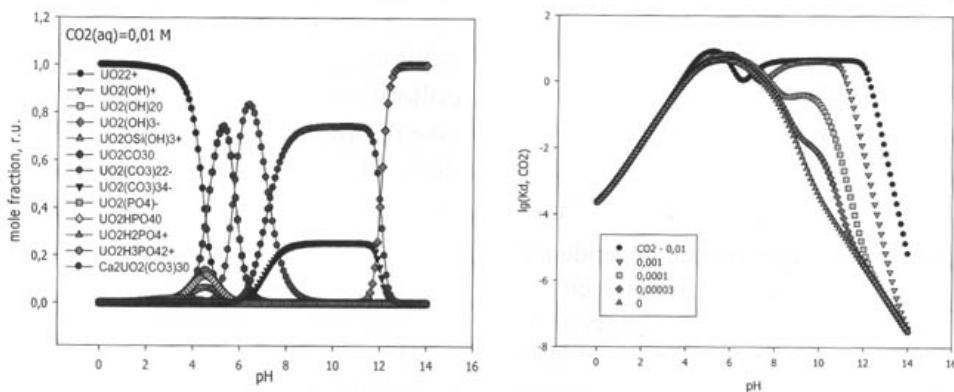


Figure 2. Calculated predominance area diagram for the U(VI) in river water (left); Calculated dependence of the U(VI) forms overall distribution coefficient (K_d) between river water and strong acid ion-exchanger (Na-form) as a function of CO_2 concentration in water in accordance with the accepted speciation model; numbers near the points depict concentration of soluble CO_2 , mole/l.

estimates of the formation constants for U(VI) and U(IV) solution species. Complexation constant for the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ species was taken from (Kelly, Kemner, Brooks, 2007). We have considered thermodynamics of complexation as well as the thermodynamic probability of sparingly soluble hydroxides, carbonates and phosphates of the above microelements formation in the river water medium.

Chemical identification of species composition was carried out in the framework of qualitative and quantitative analysis of alternative speciation models. All the models were based upon the thermodynamic (mass-action law) approach which allowed to describe impact the microelement species chemical composition and their abundance in the solution on the overall distribution coefficient K_d of this microelement between solution (fresh sample of the river water) and sorbent (strong acid cation-exchanger in Na-form). Assortment of the species in water and their

assumed capability (or incapability, as in the case of anion sorption by cation-exchanger) to interact with ion-exchanger were formulated as an individual resulting models, which yielded alternative isotherms of the microelement overall adsorption as a function of chemical composition of the solution. Procedure of selection the adequate model from the pool of alternative ones was based on the testing statistical hypotheses of minimum dispersion between observed K_d data and the estimate of K_d in the considering models (Starik, 1964; Egorov, 1975; Benes, 1980, Polyakov, 2003).

RESULTS AND CONCLUSIONS

Using the ion-exchange experimental data coupled with the results of ultra-filtration and thermodynamic modeling of the minor elements ion-exchange behavior, an immediate correlation

is estimated between seasonal variation of river water chemical composition (Fig.1), the concentration of soluble CO_2 in the water and fractional composition of all known chemical species of Sr(II), U(VI), $\text{P}3\text{O}(\text{III})$ and Th(IV) in it. Chemical state of Sr(II) and U(VI) is shown strongly depends on the level of carbonate species in the river water. Rise in the level of soluble carbonate may lead to the formation colloid suspension of CaCO_3 which is able to co-precipitate up to 10-15 % Sr(II) and up to 20% U(VI). CaCO_3 phase is supposed localized on the surface of mineral (complex Si-Al-O +Fe-O phase mixture) and biological (diatomic algae) suspensions. Size of the so formed intrinsic colloid is >3 mkm. The rest of Sr(II) exists in the form of aqua-cations. Uranium (VI) speciation in carbonaceous calcium contained water solution is so far contradictory problem. This is connected with the underestimate of the role of Na-Ca - UO_2 - CO_3 particles in the formation of the assortment of uranium-contained water soluble

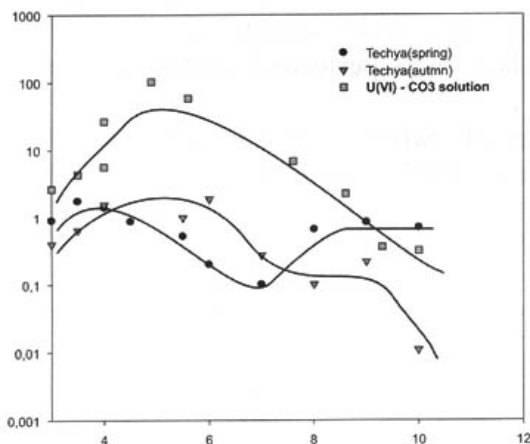


Figure 3. Points are experimental dependence of the K_d , ml/g (y-axes) for U(VI) between river water and strong acid ion-exchanger as a function of pH (x-axes); lines are result of least-square fitting of $K_d(\text{pH})$ model based function in which $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ complex is assumed capable to interact with cation-exchanger. Difference between spring and autumn data is connected with different soluble CO_2 and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ concentration in water samples.

ions and molecules (Davis, Curtis, 2003). As follows from the uranium(VI) diagram of predominance area (Fig.2), only $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ particles may be responsible for the discovered rise of the overall distribution coefficient K_d of uranium in the rang pH 8-10, in which negatively charged carbonaceous UO_2 -complexes exist if calcium is absent or hasn't taken into consideration in the aqueous solution (Fig.2,3). We have statistically proved hypotheses in accordance with which the adequate sorption model should include the positively charged and neutral particles formed by uranium as the particles responsible for it's sorption activity. This results indicate that uranium may be presented in the river water in the form of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ complex which concentration is to dramatically impact sorption behavior of the overall uranium in the freshwater. The sorption data indicate that the level of Ca - UO_2 - CO_3 complex is rather high in the spring CO_2 -saturated river water samples and low in the CO_2 -poor autumn ones. When CO_2 concentration in the river water is being descended to the level which is characteristic

for autumn period, the suspended CaCO_3 vanishes and fraction of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ in the water changes. Specific activity of Sr-90 correlates with this conclusions. Analogous procedure of modeling was applied to the ion-exchange and ultra-filtration data of the Th(IV) and REE in the river water. These microelements are found exist in the water as a hydroxo-complexes (<80%) and in the form of suspension with the particle size >3 mkm (<20%).

ACKNOWLEDGEMENT This work is supported by RF President grant HIII-725.2008.3

REFERENCES

P.N. Burgasov, 1980. The methods recommended for the sanitary control of radioactive substances level in the environment, Moscow. in Russian

Trapesnikov A.V., V.N. Trapesnikova, 2006. Radioecology of freshwater ecosystems. Ural Branch Russian Academy of Sciences. Ekaterinburg.

Polyakov E.V., 2007. Behavior of Ionic and Colloid Forms of Microelements in Colloidal Chemical Extraction from Humic Acid Solutions. *Radiochemistry (Springer)*. 49, 4: 432-436

Schubert J., 1948. The use of ion exchangers for the determination of physico-chemical properties of substances, particularly radiotracers, in solution-I, Theoretical. *J. Phys. Colloid. Chem.* 52, 340–350.

Kravets L.I., Dmitriev S.N., Apel P.Yu., 1997. Production and properties of polypropylene track membranes // *High energy chemistry*. 31: 108-113.

Polyakov E.V., Egorov Yu.V., 2003. Modern methods for the determination of physicochemical states of microelements in natural waters. *Russian Chemical Reviews*, 72, 11: 985-994

Polyakov E.V., 2003. Reaction of ion-colloid forms of state of microelements and radionuclides in aqueous solutions. Ural Branch RAS, Ekaterinburg, 2003.

Kotrlý S., Sucha L., 1985. *Handbook of chemical equilibria in analytical chemistry*. John Wiley&Sons, N-Y.

Davis J.A., Curtis G.P., 2003. Application of surface complexation modeling to describe uranium (VI) adsorption and retardation at the uranium mill tailings site at Naturita, Colorado. NUREG/CR-6820. U.S. Geological Survey. U.S. Nuclear Regulatory Commission. NRC Job Code W6813.

Kelly Sh. D., Kemner K.M., Brooks S.C., 2007. X-ray absorption spectroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations. *Geochimica et Cosmochimica Acta*, 71: 821–834.

Starik I.E., 1964. Principles of Radiochemistry, U.S. AEC report AEC-tr-6314.

Egorov Yu. V., 1975. Batch sorption of micro-components by oxyhydroxides. Atomisdat, Moscow (in Russian).

Benes P., 1980. Trace chemistry of aqueous solutions. Academia. Prague.