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

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**Abstract.** The physicochemical state of radionuclides of Sr, U, REE and Th(IV) and their natural analogs in the river Techya (Chelyabinsk reg., RF) is analyzed in connection with seasonal variations of the chemical composition of water. It is shown that the chemical state of Sr(II) and U(VI) strongly depends on the level of $CO_2$ in the river water. A high level of soluble carbonate leads to co-precipitation of to 10–15% Sr(II) and to 20% U(VI) on the surface of mineral $(Ca - Si - Al - O + Fe - O$ phase mixture) and biological suspensions with the size of >3 micron. The rest of Sr(II) exists in the river water in the form of aqua-cations. Uranium (VI) is present in the water as a set of hydroxo- and carbonate complexes which do not interact with the cation-exchanger and in the form of $Ca_2UO_2(CO_3)_3$ which may be involved in the ion-exchange interaction. Th(IV) and La (III) are found to exist in the water as hydroxo-complexes (<80%) and in the form of suspension (<20%). When the concentration of $CO_2$ in the river water decreases to the level typical of the autumn period, the suspended $CaCO_3$ vanishes and the fraction of $Ca_2UO_2(CO_3)_3$ in the water changes.

## 1. INTRODUCTION

Physicochemical factors play a significant role in the mass transfer of trace stable and radioactive elements in the environment. This is obviously true in particular for the migration of trace elements in the aquifer and river water. Less obvious are the means of immediate determination of their chemical composition: *in-situ* radionuclides speciation is holding back by weak sensitivity of instrumental methods [2]. In this work, we employ an approach, in which both physicochemical methods and instruments for experimental analysis of the state of representative groups of microelements in their natural abundance and natural objects are used to give relevant information on the physicochemical behavior of their man-made radioactive chemical analogs in the same natural objects [3]. The aim of this study is to clarify the role of the chemical composition of the Techya river water in the transfer of man-made radionuclides in the vicinity of the Mayak Production Association (South Urals, RF). The above approach is used for the investigation of the physicochemical state of Sr, U, REE and Th in the river Techya.

## 2. MATERIALS AND METHODS

Sampling of the Techya river water was carried out in the vicinity of the Muslumovo village, Chelyabinsk region, in spring (April) and autumn (October) 2006–2007 to determine radionuclides and investigate their physicochemical state (speciation).
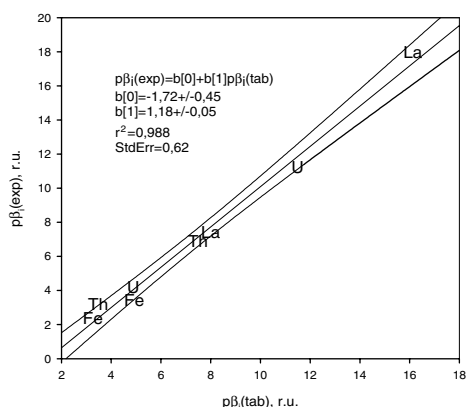
**Figure 1.** Linear correlation between tabulated (tab) [1] and experimentally estimated (exp) negative logarithms of stability constants of i-th hydroxo-complexes formation $p\beta_I$ proved at 90% confidence level.
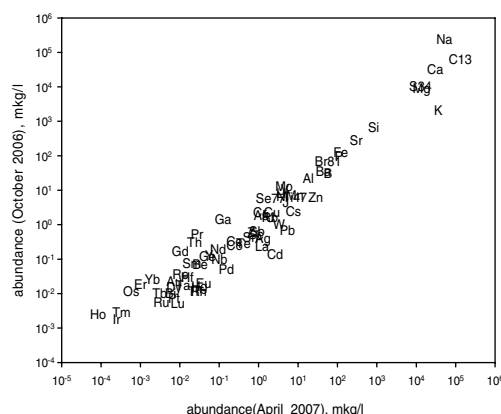
**Figure 2.** Example of seasonal variation of the level of chemical elements in the Techya river water (samples were acidified before analysis).

Samples selection and preparation techniques met the recommendations of the Public Health Ministry of the USSR [4], i.e.: (i) two parallel samples were collected in each point in the middle part of the stream, (ii) water samples were filtered through cellulose cotton into glass vessels (collectors), (iii) the samples were acidified in glass sampling vessels by concentrated $HNO_3$. In the case of samples preparation for further speciation experiments, the sampling procedure differed from that described above in points (ii) and (iii), i.e. no filtering and acidification were carried out. For radiochemical determination of $^{137}Cs$, $^{90}Sr$, $^{239/240}Pu$ in the water samples, the radionuclides were pre-concentrated and then adequate procedures of their selective determination were applied [5].

Elemental analysis of liquid samples and elemental partition in ion-exchange and ultra-filtration experiments as a function of liquid phase pH were carried out using inductively-coupled mass-spectrometry [6]. In the experimental investigation of the physicochemical state of trace elements with emphasis on the speciation of Sr(II), U(VI), REE(III) and Th(IV), which are stabile or long-lived chemical analogs of man-made radionuclides in the river, the following techniques were used: ion-exchange [7], ultra-filtration of water through nuclear track [8] and TiN-modified membranes, scanning electron microscopy and local energy dispersive X-ray analysis of the filtered particulate matter in the river water. The latter was performed using a scanning microscope JEOL JSM-6460 LV.

The calculated fields of predominance for different species of Sr(II), U(VI), REE(III) and Th(IV) were based on the thermodynamic database [9] and recent thermodynamic estimates of the formation constants for U(VI) and U(IV) solution species. The complexation constant for the $Ca_2UO_2(CO_3)_3^0$ species was taken form [10]. In the calculations we took into consideration the thermodynamics of complexation and the thermodynamic probability of formation of sparingly soluble hydroxides, carbonates and phosphates of the above microelements in the river water medium.

Chemical identification of the species composition was carried out in the framework of qualitative and quantitative analyses of alternative speciation models. All the models were based on the thermodynamic (mass-action law) approach which allowed us to describe the impact of the chemical composition of microelements species and their abundance in the solution on the overall distribution coefficient Kd of these microelements between the solution (a fresh sample of the river water) and the sorbent (strong acid cation-exchanger in Na-form). The assortment of the species in the water and their assumed capability (or incapability as in the case of anion sorption by cation-exchanger) to interact with the ion-exchanger were formulated as individual resulting models, which yielded alternative isotherms of the microelement overall adsorption (Kd) as a function of the chemical composition of the solution.
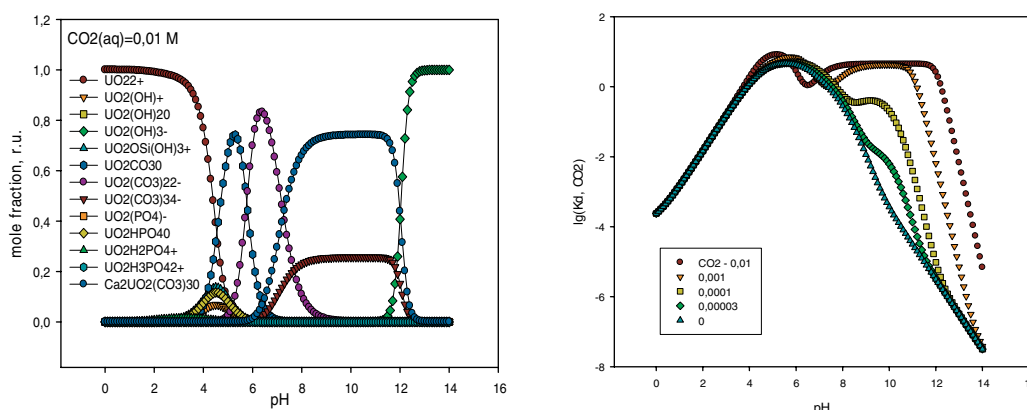
**Figure 3.** Calculated predominance area diagram for U(VI) in river water (left); Calculated dependence of the U(VI) forms overall distribution coefficient (Kd) between river water and strong acid ion-exchanger (Na-form) as a function of $CO_2$ concentration in water in accordance with the accepted speciation model; numbers near the points depict the concentration of soluble $CO_2$, mole/l [10, 11].

The selection procedure of an adequate model from among alternative ones was based on the statistical testing hypotheses about the minimum dispersion between the observed Kd data and the estimated Kd in the considered models [12–14].

One of the crucial methodological limitations on the state of the art speciation procedures in general and the selected chemical speciation procedure in particular concerned the lack of standard solutions with required chemical forms of the state of the elements under investigation [2]. A specific physicochemical behavior of individual chemical complexes of elements in a solution does not make it possible to single out pure individual forms of the state (because they are tied in the solution with each other by reciprocal transformations). Owing to this limitation it is reasonable to search for such standard solutions of the considered microelements, which would allow researchers to establish certain quantities of the individual forms of the state *a priori* and thus verify the reliability of the selected speciation procedure by way of experimental determination of these quantities of the individual forms of the state in the same standard solution. As an optional avenue of this search, we showed that equilibrium aqueous solutions, in which an array of *a priori* thermodynamically predictable complexes of microelements is created by changing the background electrolyte content, could serve as the required standard solutions [3]. We used this idea for the verification of ion-exchange procedure of microelements chemical complexes identification under selected experimental conditions.

Aqueous solutions of hydroxo-complexes of La(III), Fe(III), U(VI) and Th(IV) at the "micromole per liter" level of concentrations were used for verification. The selected low level of microelements concentration and the proper relation between the mass of the ion-exchange resin and the volume of the solution allowed us to avoid sorption concurrence and work within the Henri's Law region [15]. The verification procedure included the following steps. Experimental dependences between Kd and pH were estimated in the series of solutions with different pH at a constant ion strength for individual microelements in chemical mixtures using a strong acid cation-exchanger in the Na-form as a sorption material. Then the accepted ion-exchange sorption model was employed to calculate the best fit estimate of the experimental Kd-pH dependence with the use of the least-square based approach described elsewhere [2, 7, 12–14]. Experimental values of stability constants for the i-th hydroxo-complexes ($p\beta_i = -\log_{10}\beta_i$) of La(III), Fe(III), U(VI) and Th(IV) deduced from the estimated parameters of the sorption model were then compared with the corresponding data from [1]. Statistical results of this comparison allowed us to conclude that the above ion-exchange speciation procedure provides reliable information about microelements speciation at the 90% confidence level (see Fig. 1).
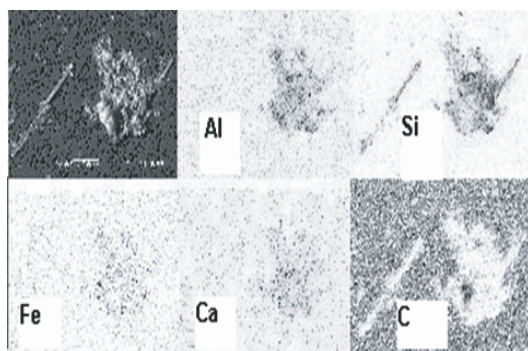
**Figure 4.** Scanning electron microscopy visualization of particulate matter filtered off by the TiN membrane filter from a sample of fresh river water; energy dispersive local analysis data for Al, Si, Fe, Ca and carbon distribution in the same particulate matter sample are depicted for comparison. Black dots on the upper left picture are 3 microns membrane orifices.
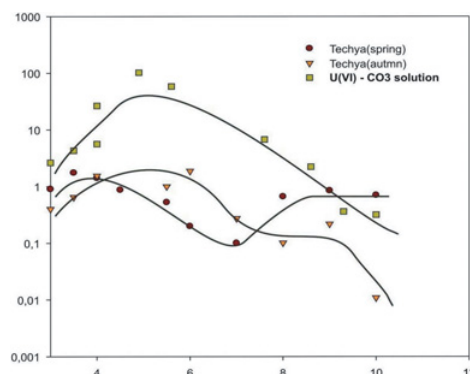


**Figure 5.** Points are experimental dependence of the Kd, ml/g (y-axes) for U(VI) distribution between river water and strong acid ion-exchanger as a function of pH (x-axes); lines are the least-square fitting result of the Kd(pH) model, in which the $Ca_2UO_2(CO_3)_3^0$ complex is assumed to be capable to interact with the cation-exchanger. Difference between spring and autumn data is connected with different concentrations of soluble $CO_2$ and $Ca_2UO_2(CO_3)_3^0$ in water samples.

The described speciation procedure was also applied for experimental determination of Sr(II), U(VI), REE(III) and Th(IV) in fresh samples of the Techya river water. The core element of the procedure consisted in *a priori* identification of the assortment of the considered chemical species. The assortment included a total list of thermodynamically probable complexes, which might be formed between the analyzed cations of Sr(II), U(VI), REE(III) and Th(IV) and the major inorganic anions ($OH^-$, $H_2PO_3^-$, $HCO_3^-$, $H_3SiO_4^-$) detected in the river water. The decision about the compliance of the ion-exchange speciation model to the experimental data was based on the result of testing the statistical hypothesis about the minimum dispersion between experimental and calculated Kd values. In the case of a positive result for the statistical procedure, a conclusion was made about reliability of the selected assortment of chemical species included in the model. In the case of a negative result, the hypothesis was rejected and a part of the assortment which was initially considered to be responsible for the ion-exchange interaction with the resin was changed. For example, the initial speciation model included only positively charged ions of U(VI), REE(III) and Th(IV) as subjects of ion-exchange interaction, but later on molecular complexes (such as $UO_2(OH)_2^0$, $La(OH)_3^0$ etc.) were taken into consideration. The calculations were reiterated until compliance between the observed and calculated Kd-pH values was achieved.

## 3. RESULTS AND CONCLUSIONS

Based on the ion-exchange experiment data and the results of ultra-filtration and thermodynamic modeling of the minor elements ion-exchange behavior, an immediate correlation was established between the seasonal variation of the river water chemical composition (Fig. 2), the concentration of soluble $CO_2$ in the water and the fractional composition of all the known chemical species of Sr(II), U(VI), REE(III) and Th(IV) in the water. The following information on the qualitative and quantitative physicochemical characteristics of the analyzed chemical elements was obtained.

### 3.1 Speciation of U(VI)

Thermodynamic analysis of the chemical state of U(VI) in the river water in the presence of major inorganic anions showed that it depended most strongly on pH and the concentration of $CO_2$ in the

water (Fig. 3). The experimental data supported this conclusion. In accordance with ultra-filtration data, at the highest observed levels of inorganic carbon ($CO_2$) in the river water, to 20% U(VI) was detected in the form of suspended mineral (complex $Ca - Si - Al - O + Fe - O$ phase mixture) and biological (diatomic algae) particles. The size of the so formed colloid-suspended particles was estimated to be >3 microns (Fig. 4). The rest of U(VI) in the river water was found to exist in the form of ionic species smaller than 3 nm, and could be attributed to aqua-complexes of U(IV).

Speciation of these complexes in natural carbonaceous and calcium-containing water solutions is so far a contradictory problem. This is connected with underestimation of the role of $Na - Ca - UO_2 - CO_3$ particles in the formation of uranium-containing water soluble complex ions and molecules [11]. The diagram of the U(VI) complexes predominance area in the river water (Fig. 3) shows that uncharged $Ca_2UO_2(CO_3)_3^0$ particles may be responsible for the observed increase in the overall distribution coefficient Kd in the pH range from 8 to 10. Only negatively charged carbonaceous $UO_2$-complexes existed in this pH interval when Ca(II) was absent or was considered to be in the aqueous solution (Figs. 3, 5). We have proved statistically hypotheses, in accordance with which an adequate sorption model should include both positively charged and neutral particles formed by U(VI) species responsible for their sorption activity. These findings indicate that uranium was present in the river water mainly in the form of the $Ca_2UO_2(CO_3)_3^0$ complex and its concentration should dramatically impact the sorption behavior of the overall U(VI) in the fresh water samples . The sorption experiment data indicate that the level of the $Ca - UO_2 - CO_3$ complex was rather high in the spring $CO_2$-saturated river water samples. When the concentration of $CO_2$ in the river water decreased to the level typical of the autumn period, the fraction of $Ca_2UO_2(CO_3)_3$ species in the water changed.
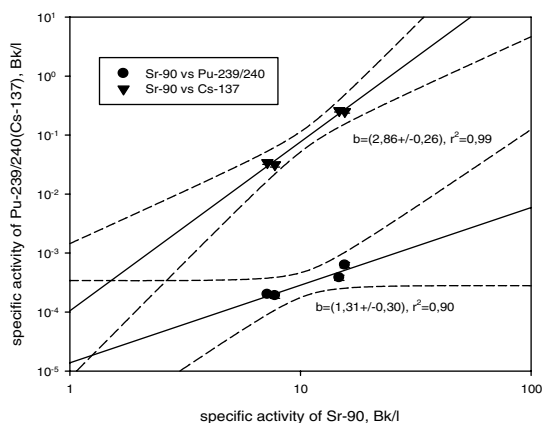


**Figure 6.** Correlation between abundances of Sr-90, Cs-137 and Pu-239/240 in the samples of Techa river water, collected in spring 2007. Dotted lines depict 90% confidence intervals of *log*-linear regressions; b is a slope of the regression lines.

### 3.2 Speciation of Sr(II)

Thermodynamic calculations indicated the probability of the sparingly soluble $CaCO_3$ phase formation in the spring $CO_2$-saturated ($\sim$50 mg free soluble inorganic carbon per liter) river water at pH above 7.7. When the concentration of $CO_2$ in the river water decreased to the level typical of the autumn period ($\sim$3 mg free soluble inorganic carbon per liter), the water system became undersaturated with respect to $CaCO_3$ and this phase vanished from the solution. Ion-exchange speciation experiments confirmed that the chemical state of Sr(II) strongly depended on pH and the level of carbonate species in the river water. As follows from ion-exchange data, the artificial increase in pH of river water at high (spring) levels of soluble $CO_2$ enhanced sorption of all IIa group elements Ca(II), Sr(II), Ba(II) by the surface

of suspended mineral and biological (diatomic algae) particles at pH above 7.7. The same behavior was observed for these microelements in the river water when the ion-exchange resin was absent and partition between water and the walls of silicon flasks was the only sorption process. At the natural river water pH of 7.0–7.5, maximum 10–15% Sr(II) was found in the form of suspended particles tentatively associated with the $Ca - Si - Al - O + Fe - O$ phase mixture (Fig. 4). At pH < 7, the distribution coefficients of Sr(II), Ca(II) and Ba(II) between the river water and the ion-exchanger did not depend on pH which is characteristic to the behavior of aqua-cations of these elements. Thus, natural isotopes of Sr(II) existed in the river water predominantly in the form of simple cations.

The above conclusion was indirectly supported by comparison of the mutual correlation of specific radioactivity levels of Sr-90, Cs-137 and Pu-239/240 in the Techa river water (see Fig. 6) . Unlike Sr-90 and Pu-239/240, fixation of Cs-137 by illitic clay minerals, which are the main components of the river bottom sediments, was very high [16]. Sr and Pu radionuclides were able to migrate from the bottom sediments to the river water through the mechanism of chemical solubility of their readily extractable forms [5]. An almost linear correlation between the level of Sr-90 and Pu-239/240 specific activity in the water found experimentally (Fig. 6) seems to be in agreement with the mechanism of chemical solubility of Sr- and Pu-enriched sediments [16]. On the contrary, a rather high slope b ($\sim$3) of the logarithmic linear regression between Cs-137 and Sr-90 specific activities may be a testimony of the connection between Cs-137 and the $Ca - Si - Al - O + Fe - O$ phase suspended matter.

### 3.3 Speciation of La(III) and Th(IV)

Isotherms of ion-exchange sorption of Th(IV), La(III), Ce(III) and the rest of rear earth elements in the river water samples were found to be identical to that of the solution used earlier for verification of speciation procedures. The application of the ion-exchange sorption model to these data allowed us to conclude that Th(IV), La(III), Ce(III) and other REE exist in the water as hydroxo-complexes ($<\sim$80%) and in the form of a suspension with particle size >3 microns ($<\sim$20%).

### 4. CONCLUSION

To estimate the state of microelements such as Sr(II), U(VI), REE(III) and Th(IV) in natural water, we used a physicochemical approach which included (i) selection of a reference system and verification of the speciation procedure, (ii) experimental determination of the microelements Kd response to the variation of the chemical composition of natural water, (iii) extraction of chemical information about individual species of the considered microelements using a coupling speciation model and experimental data. It was established that the assortment of natural isotopes of Sr(II), U(VI), REE(III) and Th(IV) in the river water included ions, hydroxo-complexes and adsorption states associated with the $Ca - Si - Al - O + Fe - O$ phase mixture. In accordance with ultra-filtration data, simple ions and hydroxo-complexes were predominated forms of the state of these microelements. The physicochemical state of U(VI) in Ca(II)-reach river water was much more complicated and was represented mainly by the $Ca_2UO_2(CO_3)_3^0$ complex which was able to interact with a strong-acid cation-exchanger and did not interact with weak-acid inorganic ion-exchangers [17]. The chemical composition of the determined forms of U(VI), Th(IV) and REE(III) in fresh water does not contradict the contemporary view on the actinide speciation and migration properties in aquatic systems [18]. It is obvious that artificial radionuclides of the elements under consideration introduced in the river water will be present in the water in the same equilibrium physicochemical assortment and will obey in the same sorption behavior as their natural isotopes.

### Acknowledgments

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