

## Experimental and modelling study of artificial radionuclides ( $^{239}\text{Pu}$ , $^{241}\text{Am}$ and $^{99}\text{Tc}$ ) uptake by suspended matter in environmental waters located in the south of Spain

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**Abstract.** The interest on transfer coefficients studies have increased recently, since they are important parameters required understanding and reliably modelling the dispersion of conservative and non-conservative radionuclides in aquatic environments. The approaches, based in the implementation of the uptake kinetics of dissolved radionuclides by solid particles, are more appropriate than those based in the use of the distribution coefficients,  $K_d$ . In this work, we present a series of tracing experiments to study the uptake of Pu, Am and Tc in natural aqueous suspensions from three aquatic systems (Gergal reservoir, Guadalquivir river, and the estuary of Tinto river) located in the South of Spain. The kinetic transfer coefficient for direct sorption depends on the total available surface of particles and on the concentration of active sites in the surface layer (what depends on the mineral composition, free edges, pores, coatings, etc.). In order to compare results from different environments and to fix the conditions of applicability of the derived coefficients, it is necessary to handle the particle size spectra and the mineral composition of natural occurring suspended loads. The time dependent uptake curves, covering up to a large period, are fitted to the numerical solutions calculated with different models of the uptake kinetics.

### 1. INTRODUCTION

Interest in Pu, Am and Tc uptake kinetics in natural aqueous suspensions has recently increased in order to understand and reliably model the dispersion of radioactive wastes in aquatic environments, especially when kinetic reactive transport models for tidal waters are used [1]. The approaches based on the implementation of the uptake kinetics are more appropriate than those based on the use of distribution coefficients,  $K_d$ . Moreover, [2] have discussed the constraints of the applicability of "in-situ distribution coefficient" values in the quantification of solute transport in natural waters.

In the scientific literature we can find many examples of experimental studies on the uptake kinetics of dissolved radionuclides by suspended loads. Thus, [3] obtained kinetic transfer coefficients for several elements from seawater onto particulate matter and surface sediments by using a model of two consecutive and reversible reactions and contact times of several weeks. [4] studied the effects of changes in suspended matter concentrations and temperature on the kinetic transfer coefficients of Co and Sr and discussed the use of models of two parallel and two consecutive reactions. [5] published the experimental determination of kinetic transfer coefficients for  $^{133}\text{Ba}$  in estuarine waters and studied the effects of salinity and suspended load concentrations. Although other authors have not obtained transfer coefficients, their studies have included the effect of sediment type, temperature, colloids, particle size and particle concentration on the uptake of radionuclides by sediments.

The present study reports the results of tracer experiments with  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{99}\text{Tc}$  in unfiltered waters from three aquatic systems in southern Spain. The experimental procedure retains the natural conditions, and Pu activity is measured by liquid scintillation.

### 2. MATERIAL AND METHODS

Details concerning the sampling, the physico-chemical characterisation of samples and the experimental and analytical procedures were presented in a previous work [6]. Consequently, we will briefly describe here only the most relevant aspects.

Water samples were collected from three different aquatic scenarios from the South of Spain. The first station was located the Gergal reservoir (NW from Seville). The second sample was collected in the Guadalquivir river, near the town of Seville. Finally a third sample was collected in the Tinto estuary, close to the Atlantic Ocean, during the low tide.

At each sample site, we filled four 25 l plastic bottles. Temperature, pH and electrical conductivity were measured just after collection. Samples were then carried to our laboratory and stored in dark during few hours. The tracing experiments generally begun at the following morning. We used a nephelometer to measure the suspended matter content.

In each experience, a typical volume of 1.0 l of water was transferred into a glass beaker. There, the sample was spiked with  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$  or  $^{99}\text{Tc}$  and continuously stirred in to avoid any decantation of the suspended matter. We followed the time evolution of the activity concentration in the dissolved phase by taking aliquots at different times after spiking. A typical volume of 45 ml was selected for every aliquot. Suspended matter was removed by centrifugation (20 minutes at 4000 rpm). Then, 35 ml of supernatant were transferred into a plastic container and acidulated with 1 ml of  $\text{HNO}_3$ , to avoid losses of plutonium by adsorption onto the container walls. Finally, 5 ml of acidulated sample was transferred into a plastic vial and mixed with 15 ml of liquid scintillation cocktail Pharmacia Optiphase 3.

A granulometric analysis of all the samples was carried out by using a Master Sizer instrument with 100 size bands, from 0.01 to 1000  $\mu\text{m}$ . A Scanning electron microscope (SEM) was used to study the morphology of natural particles from all the samples.

Results from experiments with  $^{239}\text{Pu}$  are depicted in Fig. 1, which shows the time course of the total  $^{239}\text{Pu}$  activity (given in cpm) in 5 ml in the supernatant waters.

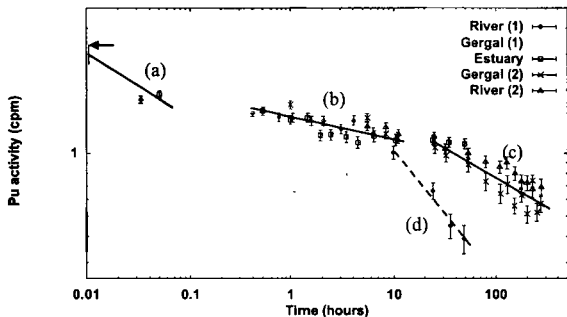


Fig. 1: Time evolution of  $^{239}\text{Pu}$  activities (in cpm) in the dissolved phase corresponding to the five experiments (points with error bars). Continuous lines indicate the different sequences of the uptake kinetics.

### 3. MODELLING APPROACHES

In what follows we will apply to our data a model of two parallel, reversible and concentration-independent reactions followed by a consecutive, non-reversible and concentration-independent reaction to derive the corresponding values for the kinetic coefficients (see discussion in section 4). The equations for the system are:

$$\frac{da_w}{dt} = -(k_{1,1} + k_{1,2})a_w + k_{2,1}a_{sp,1} + k_{2,2}a_{sp,2} \quad (1.1)$$

$$\frac{da_{sp,1}}{dt} = k_{1,1}a_w - k_{2,1}a_{sp,1} - k_{3,1}a_{sp,1} \quad (1.2)$$

$$\frac{da_{sp,2}}{dt} = k_{1,2}a_w - k_{2,2}a_{sp,2} - k_{3,2}a_{sp,2} \quad (1.3)$$

$$\frac{da_{sp,3}}{dt} = k_{3,1}a_{sp,1} + k_{3,2}a_{sp,2} \quad (1.4)$$

where  $a_w$  [Bq/l] is the tracer concentration in the dissolved phase;  $a_{sp,1}$  and  $a_{sp,2}$  [Bq/l] are the concentrations related to sites in solids participating in first and in second parallel and reversible

reactions, respectively. Similarly,  $a_{sp,3}$  [Bq/l] is the concentration in solids related to the non-reversible unions. The six kinetics transfer coefficients have units inversely proportional to time ( $s^{-1}$  or  $h^{-1}$ ). In the first instance we assumed a similar value for  $k_{3,1}$  and  $k_{3,2}$  coefficients. The concentrations in solids are related to the corresponding specific activities (in Bq/kg and denoted with \*) by means of suspended load concentration,  $m_s$ , in units of kg/l:  $a_{sp,1} = a_{sp,1}^* m_s$ ,  $a_{sp,2} = a_{sp,2}^* m_s$ , and  $a_{sp,3} = a_{sp,3}^* m_s$ .

We stated some initial values for kinetic coefficients in a computer code that numerically solves equations 1.1 to 1.4. The parameter values are then varied to get the best fit (i.e., minimises the summation of the weighted squared differences between numerical solution and observational data points). As each pathway is dominant over a region (or interval) in the uptake curve, an overall parameter fitting is not advisable. Thus, the fit is sequenced region by region and then refined overall. The graphical representation ensures the quality of the solution. The so derived parameter values are summarised in Table 1.

**Table 1.** - Parameter values after fitting experimental data (for case of 239-Pu) to a model of two parallel plus a consecutive and non-reversible reaction. The result of the  $\chi$ -test for the fitting is shown in the last column.

Experiment	$k_{1,1}(h^{-1})$	$k_{2,1}(h^{-1})$	$k_{1,2}(h^{-1})$	$k_{2,2}(h^{-1})$	$k_3(h^{-1})$	$\chi$
Estuary, 2 days, 7.62 ppm	1.9	8.2	0.19	0.28	0.0005	1.03
Gergal, 2 days, 7.37 ppm	1.1	2.6	0.05	0.25	0.009	0.95
River, 2 days, 12.6 ppm	12.3	17	0.09	0.20	0.055	1.55

In Figs. 2 to 6 we show the numerical solution for experiments with Pu, Am and Tc.

#### 4. DISCUSSION

From Fig. 1 (in case of Pu), in logarithmic scale, three different regions characterised by different slopes can be distinguished: region (a) corresponds to a fast reaction, lasting for few minutes, during which time up to 30% of dissolved Pu is transferred onto suspended solids. This corresponds to a fast physical-adsorption reaction (Pu is fixed by coulombian forces onto the external free surface of particles); in region (b), a second reaction governs the Pu uptake during 10-20 hours time, transferring up to 30% of remaining Pu in dissolved form. This reaction corresponds to physical adsorption onto the inner surface of pores and free-edges, and to the formation of reversible unions of a different nature and/or strength. In region (c), the uptake (up to 50% of the remaining Pu in solution) continues during several days (the duration of the experiments was too short to allow a conclusion concerning the final course of the reaction). This reaction may correspond to a slower process in which previously adsorbed Pu is transferred into the inner matrix of the particles or forms other non-reversible unions. Region (d) corresponds to a faster uptake of Pu from the dissolved phase. It is observed only in the first experiment with river waters and may be related to flocculation effects.

We observe the same situation in case of  $^{241}\text{Am}$ .  $^{99}\text{Tc}$  is considered as conservative radionuclide and the behaviour is different than of the Pu or Am.

In all cases (Pu and Am), the first parallel reaction is the faster. It transfers an important fraction of the dissolved radiotracer to the particulate phase,  $k_{1,1}$  is the rate of adsorption, and depends on the total available surface of particles per unit volume of solution (which in turn governs the number of physical collisions and thus,  $k_{1,1}$  should be proportional to  $m_s$ , if the rest of physical-chemical properties were preserved), and on the concentration of active areas (which governs the probability of reaction). The physical meaning of  $k_{2,1}$  and  $k_{2,2}$  is that of a probability of desorption, which implies the rupture of physical-chemical unions in sites associated with the two parallel reactions. From our interpretation,  $k_{1,2}$  does not depend directly on the total free surface of particles, but also on the existence and geometry of pores and free edges and the accessibility to the reaction sites. The third reaction is governing the long-term behaviour of the partition coefficient,  $k_d$ . Effectively, the transfer of radionuclides to the inner active areas frees the sites they occupied in the surface layer of particles. This enhances the uptake of radionuclides by the particulate matter.

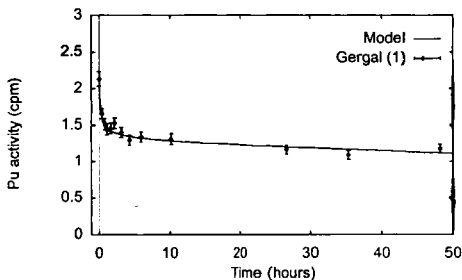


Fig.2: Time evolution of Pu activities (in cpm) in the dissolved phase corresponding to the serie of experiment for the case of the Gergal reservoir. Measured values appears with error bars, while continuous line corresponds to the best fit of the model.

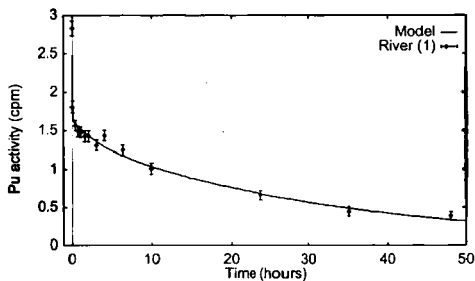


Fig.3: As in Figure 2 but for the case of the Guadalquivir river

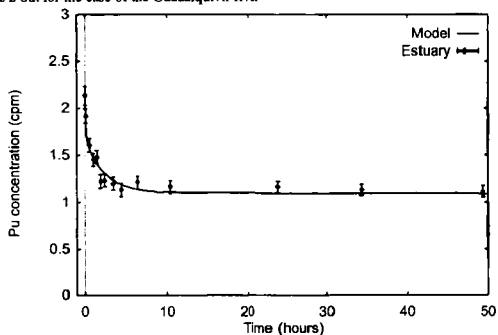


Fig.4: As in Figure 2 but for the case of the Tinto estuary

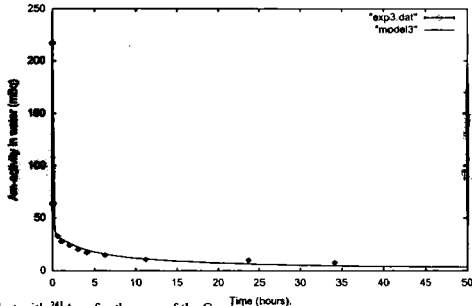


Fig.5: As in Figure 2 but with  $^{241}\text{Am}$ , for the case of the Guadalquivir river

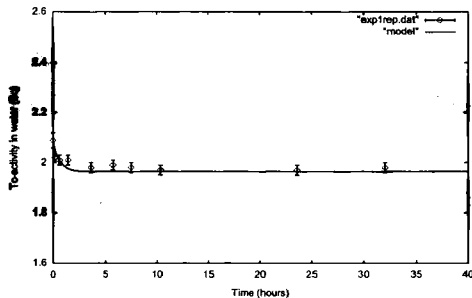


Fig.6: As in Figure 2 but with  $^{99}\text{Tc}$ , for the case of the Guadalquivir river

## 5. CONCLUSIONS

- 1.- In this work we applied a useful experimental procedure to study the uptake of Pu, Am and Tc by natural aqueous suspensions, based on the use of liquid scintillation technique.
- 2.- By using a model of a single and effective oxidation state, with two parallel reversible and concentration-independent reactions, followed by a consecutive non-reversible reaction, we obtained a reasonable understanding of the uptake curves.
- 3.- We have provided a set of kinetic parameters useful to describe the most relevant aspects of the electrolytic reactions of  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{99}\text{Tc}$  in the aquatic environments studied under environmental conditions prevailing during the sampling.
- 4.- The experimental results show that each pathway of reaction is governing the uptake at different stages, and some possible interfering and/or modifying factors are identified (storage, flocculation, competitive ions). This provides a good basis to improve the experimental set up to produce more accurate values for kinetic parameters

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