
²³⁹Pu sorption by suspended matter from Hueznar reservoir (southern Spain): Experimental and modelling study

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Abstract. Kinetic transfer coefficients are important parameters to understand and reliably model the behaviour of non-conservative radionuclides in aquatic environments. This report pertains to a series of radiotracer experiments on ²³⁹Pu uptake in natural unfiltered waters from the Hueznar reservoir (southern Spain). The experimental procedure ensures the preservation of environmental conditions and the dissolved Pu activity was measured by liquid scintillation technique. The data suggest that the main pathways for Pu uptake consist of two parallel and reversible reactions. We studied the effects of suspended matter concentrations and the specific surface area on the kinetic transfer coefficients.

1. INTRODUCTION

Studies on Pu behaviour in natural waters are of interest because of high particle-affinity of the radionuclide, its complex chemical behaviour in natural systems, and its effect on human and environment health because of accidental spillage and planned release.

Pu isotopes' behaviour in natural aquatic ecosystems has been widely studied by using in-situ distribution coefficients, k_d , including their dependence on oxidation state and the particle size of solids (Hetherington, 1976, 1978; Nelson & Lovett, 1978; Kershaw et al., 1992). Aston & Fowler (1984) studied the bioaccumulation of plutonium and suggested that Pu(III+IV) and Pu(V+VI) have similar behaviour. Sibley & Sanchez (1986) suggested that chemical oxidation-reduction of Pu occurs quickly in relation to bioaccumulation, and that reduction of Pu(V) to Pu(IV) is catalysed by surfaces and Pu(IV) is then partitioned between soluble and particulate phases by competition between complexation and adsorption reactions.

Interest in Pu 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 (Periáñez 1999, 2000; Abril & Abdel-Aal, 2000). 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, Mcknley & Alexander (1992) have discussed the constraints of the applicability of "in-situ distribution coefficient" values in the quantification of solute transport in natural waters.

Scientific literature lists many examples of experimental studies on uptake kinetics of dissolved radionuclides by suspended loads (Nyffeler et al., 1984; Benes & Cernik, 1992; Benes et al., 1992; Laissaoui et al., 1998). Bultman et al. (1998), studied the time dependence of Pu(IV) sorption by humic and fulvic acids chemically immobilized on silica gel.

2. MATERIALS AND METHODS

Water samples were collected from aquatic scenario in southern Spain: the Gergal reservoir (NW from Seville). Samples were collected at the surface (less than 0.5 m depth) without perturbing the bottom sediments. Four plastic bottles containing 25 litres each were transported to the laboratory, and stored in dark.

A granulometric analysis of the natural suspended matter present in the water samples was carried out with a Mater Sizer with 100 size bands ranging from 0.01 to 1000 μm . Scanning electron microscope (SEM) was used to study the morphology of natural particles from all the samples. The mineral composition was studied by X-ray diffraction (XRD).

In each experiment, a typical volume of 1 litre of water was transferred into a glass beaker. The sample was spiked with ^{239}Pu and continuously stirred (at constant state temperature) to avoid any decantation of the suspended matter. Pu came from a standard solution with concentration of 21.2 Bq/ml, in which it was presented as carrier free in 0.5M HNO_3 . The certificate solution contains other isotopes of Pu and a trace of ^{241}Am (less than 0.05%), being the isotopic abundance of the ^{239}Pu atoms greater than 99%. In terms of percentage of the activity of ^{239}Pu , the contribution of ^{240}Pu is 3.62%. In the presence of an oxidizing agent such as HNO_3 , Pu(IV) is by far the dominant specie (Cleveland, 1970). The time evolution of the activity concentration in the dissolved phase was followed by sampling aliquots at different times after spiking. A typical volume of 45 ml was selected for each aliquot. Suspended matter was removed by centrifugation (20 minutes at 4000 rpm). 35 ml of supernatant were transferred into a plastic container and acidified with 1ml of HNO_3 to avoid adsorption of Pu onto container walls. Finally, 5 ml of acidified sample was transferred into a plastic vial and mixed with 15 ml of liquid scintillation cocktail (Pharmacia Optiphase 3). Wallac Quantulus 1220TM liquid scintillation spectrometer was used for ^{239}Pu activity measurements.

Nephelometer was used to read the turbidity of the supernatant waters after centrifugation. In all the cases, turbidity was virtually identical to that obtained after filtration with a Nucleopore filter of 0.45 μm pore size. These supernatant waters will represent our operational definition for the *dissolved* fraction. This definition does not allow a more detailed study of the role of organic and inorganic colloids, but it represents a practical and usual simplification in these experimental works. Centrifugation was used instead of filtration as in a test experiment with distilled water, it was proven that some 10% of the Pu was retained in the filter. In another independent experiment in which filtered waters were used, we got that the specific activity of Pu did not decrease in the water with time.

Wallac Quantulus 1220TM liquid scintillation spectrometer was used for ^{239}Pu activity measurements. It is a low background counter and allows the measurements of alpha and beta activities, simultaneous and separately (Manjón et al., 1997). The pulse shape analyser (PSA) of the detector was optimised by measuring some ^{239}Pu standard samples, under typical measurement conditions, at different values of PSA threshold level and determining the alpha interference (defined as the fraction of alpha counts measured in the beta spectrum). A value of 55 was selected as working PSA level. If a higher value were selected, the alpha interference cannot be considered negligible and the counting efficiency decreases. When PSA is selected, background counts are acquired in the beta spectrum (the ^{40}K , present in the vial walls, is a beta emitter and represents the main contributor to the detector background) and the alpha background is negligible. It must be noted that alpha/beta separation is not totally efficient, and a portion of the beta emissions can be counted in the alpha spectrum. This beta interference decreases when the PSA value is increased. Therefore, the PSA value was selected as the maximum value at which the alpha interference is negligible. Alpha efficiency was determined by spiking 5 ml of the water samples with known amounts of ^{239}Pu .

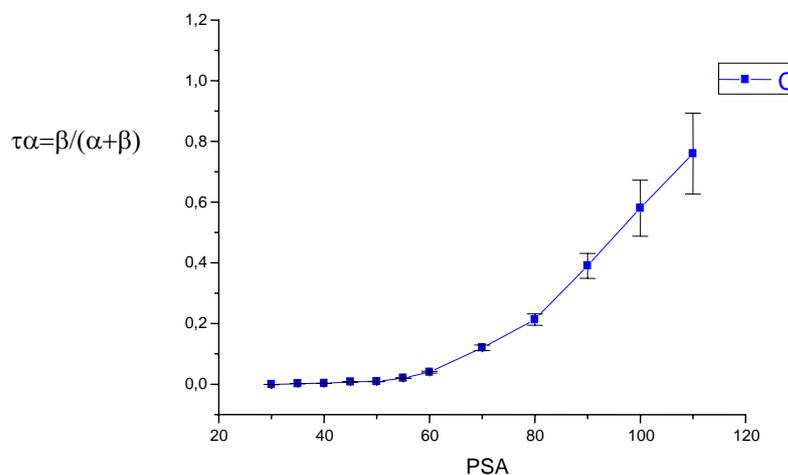


Figure 1. Optimization of the PSA of the Quantuls 1220 Best results correspond to PSA 55.

3. RESULTS AND DISCUSSION

Temperature, pH, electric conductivity and suspended material in water samples are reported in Table 1. The data on granulometric and mineralogic analysis of samples are reported in Table 2. The SEM micrograph of the samples revealed that the most common shape is the spherical one. The mineral composition was determined by X-ray diffraction using a Siemens Krystalloflex D-501 spectrometer with Cu-K_α radiation, and scanning the samples over the interval 3°-70° 2Θ.

Counting efficiency and background obtained with Wallac Quantulus 1220TM, using water samples collected in the Hueznar reservoir are reported in Table 3. LID is de detection limit, and MDA is the minimum detectable activity; counting time was 600 min in all the cases.

Table 1. Temperature, pH, electrical conductivity and suspended matter content in water samples measured just after collection. Data can be considered as environmental conditions.

Environment	Temperature (°C)	pH	Conductivity (mS)	Suspended matter (mg/l)
Hueznar reservoir	20.6	7.86	0.46	7.43

Table 2. Results from granulometric and mineralogic analysis. Diameter φ₁, in μm, corresponds to the most frequent diameter, and φ₂ is the diameter corresponding to particles with the highest percentage of volume. The specific surface area (S.S.A.) is computed assuming a density of 2.10 g cm⁻³ for all the solids.

Environment	Diameter φ ₁ (μm)	Diameter φ ₂ (μm)	S.S.A. (m ² /g)	Main mineralogical Composition
Hueznar reservoir	0.23	25	0.68	SiO ₂ Quartz, CaCO ₃ Calcite
Hueznar concen.	0.25	27	0.31	SiO ₂ Quartz, CaCO ₃ Calcite

Table 3. Counting efficiency and background obtained with Wallac Quantulus 1220TM, using water samples collected in different environmental scenarios. LID is de detection limit, and MDA is the minimum detectable activity; counting time was 600 min in all the cases.

Environment	Efficiency	Background (cpm)	MDA (Bq L ⁻¹)	LID (cpm)
Hueznar reservoir	0.77 ± 0.02	0.41 ± 0.04	0.16	0.037

In what follows we will apply to our data a model of two parallel, reversible and concentration-independent reactions. Pu will be considered in a single and effective oxidation estate: Pu(IV). This does not mean that other pathways or effects do not exist, but that they are smaller in comparison with these selected dominant effects (in the framework of the duration of the experiment and other experimental conditions). The equations for the system are:

$$\frac{da_w}{dt} = -(k_{1,1} + k_{1,2})a_w + k_{2,1}a_{sp,1} + k_{2,2}a_{sp,2} \quad (3.1)$$

$$\frac{da_{sp,1}}{dt} = k_{1,1}a_w - k_{2,1}a_{sp,1} \quad (3.2)$$

$$\frac{da_{sp,2}}{dt} = k_{1,2}a_w - k_{2,2}a_{sp,2} \quad (3.3)$$

Here, a_w is the activity concentration in the dissolved phase, and $a_{sp,1}$ and $a_{sp,2}$ corresponds to the concentration of radioactivity in the solid compartments, all the activities are in units of Bq per ml of bulk solution. The kinetics coefficients (k_{ij}) have units of h^{-1} . The concentrations in solids are related to the corresponding specific activities (denoted with *) by means of suspended load concentration, m_s , in units of g/ml: $a_{sp,1} = a_{sp,1}^* m_s$ and $a_{sp,2} = a_{sp,2}^* m_s$.

Equations 3.1 to 3.3 are solved numerically by a finite difference scheme, the parameter values are varied till get the best fit (i.e. minimum Q^2). The error, σ_k , of a parameter k is obtained from the curvature of its parametric line in the Q^2 function:

$$Q^2 = \sum_{i=1}^N \left(\frac{a_{w,Th} - a_{w,i}}{\sigma_{a,i}} \right)^2 ; \sigma_k^2 = \frac{2}{\left. \frac{\partial Q^2}{\partial k^2} \right|_{k_{\min}}} \quad (3.4)$$

$a_{w,i}$ and $\sigma_{a,i}$ are, respectively, the measured value of the activity concentration in water and its error (i ranges from 1 to N , the number of measured data) and $a_{w,Th}$ is the corresponding computed value.

Results from experiments are depicted in Fig. 3, 4, 5 and 6 which shows the time course of the total ^{239}Pu activity (given in cpm) in 5 ml in the supernatant waters.

The experiment performed with 7.4 ppm shows a simple kinetics and the precise shape of the uptake curve could not be obtained although the experimental effort in sampling during the first hours. It is due to the natural variability of the process which introduces fluctuations. However, it could be said that the characteristic time of the transfer is of the order of 12 hours, time in which some 15% of the dissolved radionuclides have been transferred to the solid phase.

In the literature, it has been shown that radionuclides which present a simple one-stage uptake in the presence of low levels of SPM (Laissaoui *et al.* 1998) are featured by a more complex kinetics when the concentration of particles rise (Barros *et al.* 2004). This is the case of our experiments, so the experiments performed with 17 and 30 ppm, both, shows a two step kinetics.

The experiment made with 17 ppm transferred more than 30% of the Pu in 12 hours, achieving a total transference of 40% at the end of the experiment. The experiment with the highest SPM concentration have transferred 45% of the radiotracer to the solid phase in the first 12 hours and about the 60% at the end of the experiment.

The kinetic coefficients of all three experiments are showed in the table 4, while figure 6 shows it dependency with the SPM concentration. In that figure it can be noted that the direct sorption coefficient increases as SPM rises, however the coefficient corresponding to the lower concentrations of solids (particularly those of 7.4 ppm) seems to be infravalored, it could be related with the relatively high uncertainties of the measurement and show a limitation in the experiments at low SPM content.

The distribution coefficient is a parameter that changes along the time until the situation is close to the equilibrium, in the case of the present experiments it doesn't happen during the first day. In order to gain information about the distribution of the radionuclide, and asses the fraction of radioactivity that still available after one day of the release we calculate de kd coefficient as:

$$k_d = \frac{a_w(t=0) - a_w(t)}{m_s a_w(t)}$$

It corresponds to the experimental distribution coefficients (calculated on the basis of the last experimental data point available) and not to the extrapolation of the obtained numerical solution of the equations 3.1 - 3.3. Here m_s represent the concentration of suspended particles (mg/l). The obtained values are respectively:

$$kd_{7ppm} = 29000 \pm 4600 \text{ (l/kg)}$$

$$kd_{17ppm} = 36800 \pm 5100 \text{ (l/kg)}$$

$$kd_{31ppm} = 40400 \pm 8500 \text{ (l/kg)}$$

The uncertainties are obtained by propagating the errors of all the involved values. If we compare the present values with those from the previous study of Pu uptake in similar environments (Figure 5 in El Mrabet et al 2001) we confirm that in the present environment the transference mechanisms are weaker. In fact the kd values for other similar environments (Tinto estuary, Guadalquivir river and Gergal reservoir) are above 100 thousand liters per kilogram after 24 hours, and in the Hueznar reservoir (with practically the same SPM concentration than the Gergal reservoir) we get less than half of that value. The same happens for the direct adsorption coefficients, in the referred paper they ranged between 1.1 and 12 h⁻¹, and in the present work we have found values between 0.015 and 0.6. It shows that we are in presence of a slower mechanism. Since the physical parameter of some of these environments are similar, particularly if we compare the two reservoirs (pH, electrical conductivity of the water, suspended load concentration, etc.) the differences in the strenght of the reactions should be related with the main mineralogical composition of the sediments and loads.

Table 4. Parameter values after fitting the experimental data with the model.

Experiment	ms (ppm)	k1,1(h ⁻¹)	k2,1(h ⁻¹)	k1,2(h ⁻¹)	k2,2(h ⁻¹)	χ
1	7.4	0.015 ± 0.007	0.057 ± 0.011	0*	0*	1.5
2	17	0.320 ± 0.060	0.88 ± 0.11	0.011 ± 0.002	0.009 ± 0.001	2.5
3	31	0.606 ± 0.090	1.80 ± 0.20	0.047 ± 0.014	0.040 ± 0.012	2.9

The χ -test is shown in the last column. Values marked with asterisk (*) means that this channel of reaction has not been included in the model. The 7.4 ppm corresponds to the natural SPM concentration in the Hueznar reservoir at the moement of the sampling. The higher SPM values have been obtained by decantation of natural waters.

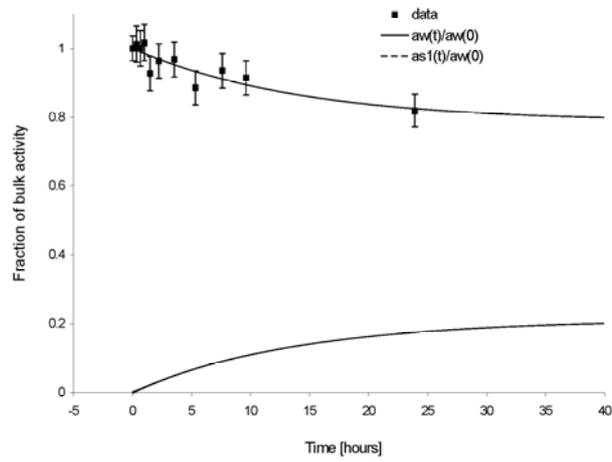


Figure 2. Experiment in the Hueznar with 7.4 ppm. First order model.

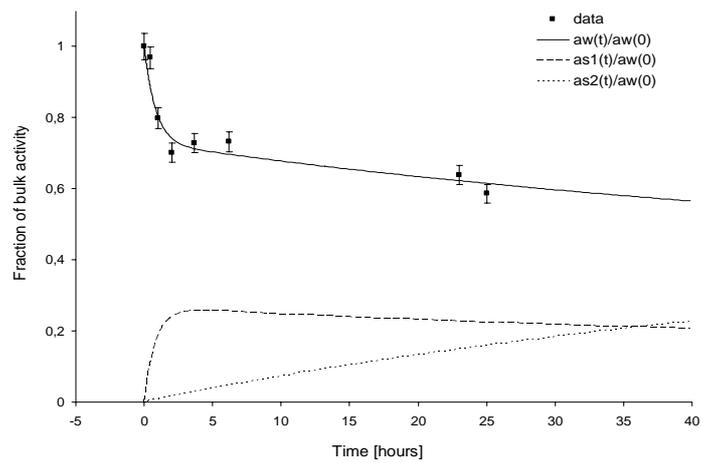


Figure 3. Experiment in the Hueznar with 17 ppm. Second order model.

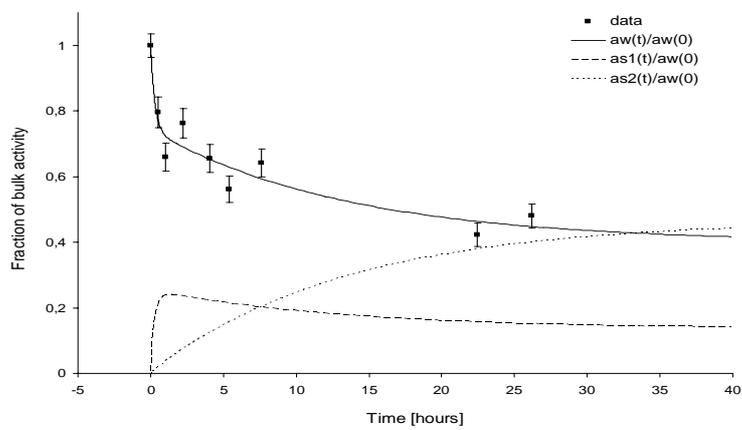


Figure 4. Experiment in the Hueznar with 30 ppm. Second order model.

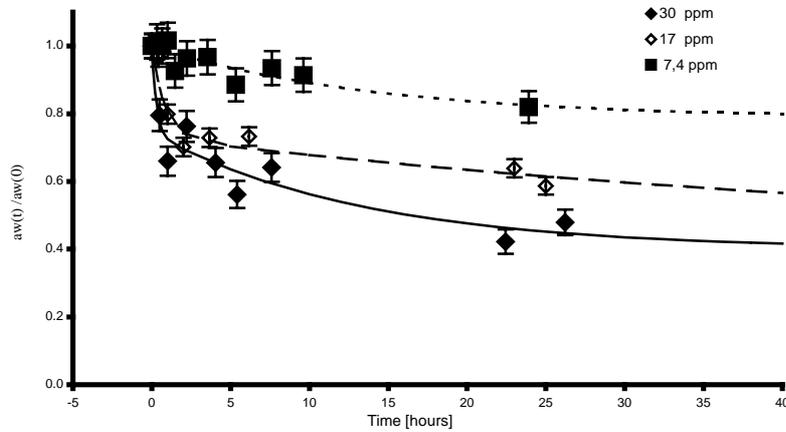


Figure 5. All experiments with 7.4; 17 and 30 ppm.

Acknowledgments

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