

## DISPERSION OF RADIONUCLIDES IN AQUATIC ECOSYSTEMS: REMEDIAL ACTIONS.

R. El Mrabet, A. Laïssaoui, N. Dehbi

National Center for Energy, Sciences and Nuclear Techniques (CNESTEN), BP1382 RP, Rabat, 10001, Morocco

### ABSTRACT

Kinetic transfer coefficients are important parameters to understand and reliably model the behaviour of radionuclides in aquatic environments. In this work we present a review of laboratory tracing experiments to study the uptake of  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{133}\text{Ba}$  in natural aqueous suspensions from several aquatic systems (reservoir, river, estuary and sea).

The amount, nature and dynamics of the suspended loads highly influence the behaviour of particle-reactive radionuclides. The kinetics of this process has a very fast component. Changes in pH, temperature and in the electrical conductivity are influencing the uptake kinetics and the final partitioning of the radioactivity.

We developed a numerical model able to reproduce the observed kinetic uptake in all the studied cases. Then this model was adapted and incorporated into a kinetic reactive transport model for aquatic systems. In this way we are simulating some hypothetical scenarios of accidental releases of radionuclides in situations where the uptake kinetics is the main factor governing their short-term fate.

The model represents then a powerful tool to study basic processes in natural systems when it is coupled to the dynamic of suspended load concentrations. We are simulating several self-cleaning scenarios based in the enhancement of natural-occurring suspended load concentrations. An important reduction in the radionuclide concentrations in the dissolved phase can be obtained in most of the cases in a very short time (few hours) after the remedial action, what reduces the bioavailability of these pollutants and the risk on the environmental and human health. The basic processes studied here are applicable to other particle-reactive pollutants as many heavy metals.

**Keywords:**  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{133}\text{Ba}$ , Radionuclide, uptake experiments, kinetic model, aquatic systems, remedial actions.

### I. INTRODUCTION

Studies on radionuclide behaviour in natural waters are of interest because of their high particle-affinity, their complex chemical behaviour in natural systems, and their effect on human and environment health in relation to accidental spillage and planned release. In particular,  $^{241}\text{Am}$  and  $^{239}\text{Pu}$  behaviour in aquatic ecosystems has been widely studied [5], [13], [15], [17]. On the other hand, the enhancement of  $^{226}\text{Ra}$  (and its progeny) concentrations is the particular interest, among other, in the context of the uranium-fuel cycle and on the production of fertiliser from phosphate rock [8], [20], [21].

Interest in the uptake kinetics of radionuclides in natural aqueous suspensions has recently increased in order to understand and reliably model the dispersion of radioactive wastes in aquatic environments [19], [3]. The approaches based on the uptake kinetics are more appropriate than those based on the distribution coefficients,  $k_d$ . Moreover, [16] have discussed the constraints on the applicability of “in-situ distribution coefficient” values in the quantification of solute transport in natural waters.

[1] and [2] presented a basic microscopic theory of the distribution, transfer and uptake kinetics of dissolved radionuclides by suspended particulate matter. Scientific literature lists many examples of experimental studies on uptake kinetics of dissolved radionuclides by suspended loads [18], [6]. [14] studied the uptake kinetics of  $^{133}\text{Ba}$  in aqueous suspensions from estuary using a model of a single reversible reaction and a poor time-resolution for the initial uptake. The authors included the study of the effect on the uptake kinetics due to changes in salinity and suspended load concentrations. [10] studied the  $^{239}\text{Pu}$  uptake in several aquatic systems using a higher time-resolution. These authors used a model of two parallel plus a consecutive (weekly reversible or non-reversible) reactions and showed how 30% of Pu was transferred to suspended load in the first few minutes (with suspended load concentrations about 7-12 ppm). [11] extended their study to the  $^{241}\text{Am}$ , including the effect on the uptake

kinetics of suspended load concentrations and total surface area of particles per unit volume of solution. They found in the river naturally occurring suspended load concentrations of 860 ppm (after a rain episode). In these conditions, the uptake of 90% of the dissolved  $^{241}\text{Am}$  activity took place in less than 2 minutes.

The present work reviews the basic features of our experimental studies on  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  uptake and we then extend them to the uptake kinetics of  $^{133}\text{Ba}$  in natural aqueous suspensions formed with sediment and filtered waters of estuary. A model containing three reactions is also required to explain our present experimental results. The so calibrated equations describing the electrolytic reactions of Pu are then coupled with the ones describing the suspended load dynamics in a lake system. This way we are simulating several self-cleaning scenarios based in the enhancement of natural-occurring suspended load concentrations.

## II. THEORY OF ION EXCHANGE BETWEEN WATER AND SUSPENDED PARTICLES

The first reactive transport models for non-conservative radionuclides were based upon the equilibrium distribution coefficient,  $k_d$ . This parameter has always been a measure of sorption of contaminants to solids and is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid to the amount of the adsorbate remaining in solution at equilibrium. The widespread use of  $k_d$  is due to the need for a single parameter describing solid/solution distribution for the purpose of modelling the geochemical partitioning of radionuclides in steady state conditions. However, the use of distribution coefficients is limited by the fact that it can vary by 9 orders of magnitude between different nuclides and 3 orders of magnitude for any particular one [4]. This variation depends mainly on the solution composition and the nature of the solid substrate. On the contrary, recent models are based on kinetic rates of uptake/release of radionuclides between waters and the solid phases when short timescales are involved [22].

Recently, much experimental and modelling effort has been focused on determining those factors which affect the kinetics and the final equilibrium conditions for the uptake of pollutants in aqueous suspensions under dynamic or static situations. Some models include the kinetics as a one-step reversible or irreversible reaction which is often considered as a rough approximation [14]. However, data reported in the scientific literature show that the interaction of radionuclides with natural solids is often slow and is a two-to three-step process [1], [9]. Thus, a model taking into account a single reaction is generally unable to properly describe both sorption and release kinetics. It is worth noting that mathematical approaches using box models in the analysis of time-resolved sorption data are capable of providing kinetic parameters which are important in determining the mobility and rate of removal of radionuclides from the water column ([23], [12]). However, the values of parameters are often different, depending on the number of processes identified in the uptake curves.

Sorption of radionuclides by particles in aqueous suspensions can be regarded as a physico-chemical process through which the charges on the mineral lattice, generally negative, are compensated by ions of positive charge. This phenomenon can take place on the outer surfaces of the particles as well as on the inner surfaces of the pores, as shown in Figure 1 ([1], [7]). Thus, the whole volume of a particle is not really relevant to this process. One of the most common adsorption reactions in aqueous suspensions is ion exchange. In its most general meaning, an ion-exchange reaction involves the replacement of ionic species on a solid phase by another ionic species taken from an aqueous solution in contact with the solid; that is, a previously-adsorbed ion of weaker affinity is exchanged by the particle for a dissolved ion. Most metals in aqueous solution occur as charged ions and thus metal species adsorb primarily in response to electrostatic attraction.

The effect of surface charge on particles is that ions in the aqueous phase distribute themselves so that electrical neutrality is reached. Radionuclide adsorption is a statistical result of ionic collisions over the free surfaces of particles and of the probability of occurrence of different physico-chemical reactions. In most cases, collisions may take place over a non-active site on the surface of the particle and thus the exchangeable ion returns back into solution. Thus, only a fraction of all the collisions will be captured by uncompensated charges [1].

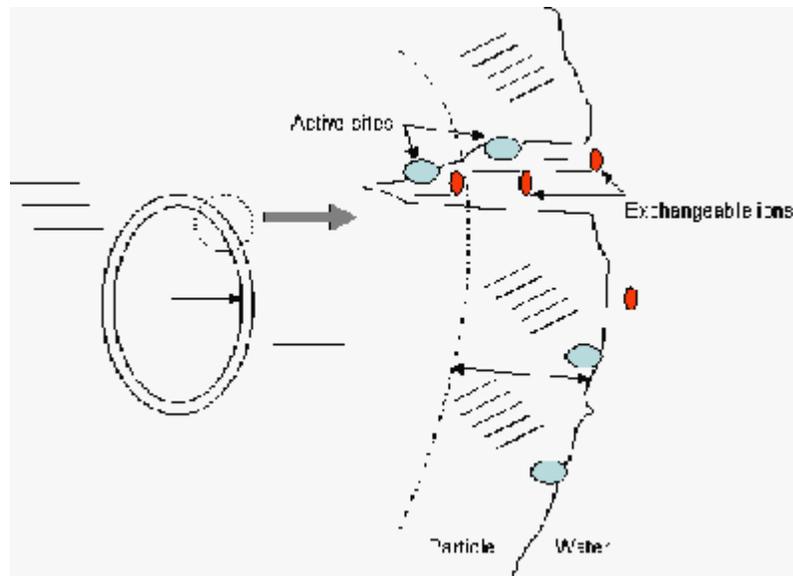


Figure 1. Schematic representation of a particle with its external surface layer.

A revision of the historic development of early theories on surface-electrolyte interactions can be found in [24], [25]. Some of these theories relate only to equilibrium conditions, such as the Gouy-Chapman diffuse double layer and Stern double layer theories or the application of Donan Principles to cation exchange. Non-equilibrium formulations, as presented in [25], often start from a governing differential equation with constant coefficients, which is stated for each specific adsorption case, such as the Langmuir approach, the Freundlich reaction, for mixed-order reactions, or the competition reactions. Furthermore, of all the complex reactions that take place in heterogeneous systems, the Langmuir adsorption is the most significant. It was originally proposed to describe adsorption of gas molecules onto homogeneous solid surfaces that exhibit one type of adsorption site. Many investigators have tacitly extended the Langmuir adsorption model to describe adsorption of solution species onto solid adsorbents including heterogeneous solids such as suspended particulate matter. It expresses the non-specific adsorption of ions at surfaces; non-specific means that all sorption sites are equal. This feature presents restrictions due to the number of active sites to be occupied which is limited by the available area. For this reason, Langmuir adsorptions show characteristic saturation phenomena. On the other hand, if the adsorption at heterogeneous surfaces is to be described where sites with different adsorption energy exist, then the Freundlich approach will be used to describe the equilibrium state.

### III. EXPERIMENTAL AND MODELLING STUDY OF THE UPTAKE KINETICS

Laboratory tracing experiments to study the uptake of  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{133}\text{Ba}$  in natural aqueous suspensions from several aquatic systems (reservoir, river, estuary and sea) are presented to illustrate the application of box models covering a large number of environmental situations and different reaction channels.

Water samples were collected from three different aquatic scenarios (river, estuary and reservoir). They were taken at the surface (less than 0.5 m depth) without perturbing the bottom sediments. In the laboratory the samples were stored in dark, and the tracing experiments were carried out as soon as possible. Table 1 summarises the relevant physical parameters.

Environment	PH	SPM (mg L <sup>-1</sup> )	Diameter $\phi$ 1 ( $\mu$ m)	Diameter $\phi$ 2 ( $\mu$ m)	SSA (m <sup>2</sup> g <sup>-1</sup> )	Main mineralogical or elemental composition‡
reservoir	8.4	7.37	0.30	19	0.28	CaCO <sub>3</sub> , calcite, muscovite
river	6.1	43	0.16	7.2-35¶	1.35	Calcite, quartz, illite, kaolinite, motormillonite
estuary-1	6.5	50	0.18	28	0.78	CaSO <sub>4</sub> ·2H <sub>2</sub> O, Bassanite, NaCl
estuary-2#	6.5	20000	0.20	0.3-11¶	1.08	N,O,Al,Si, S,K,Ca,Fe and Cu

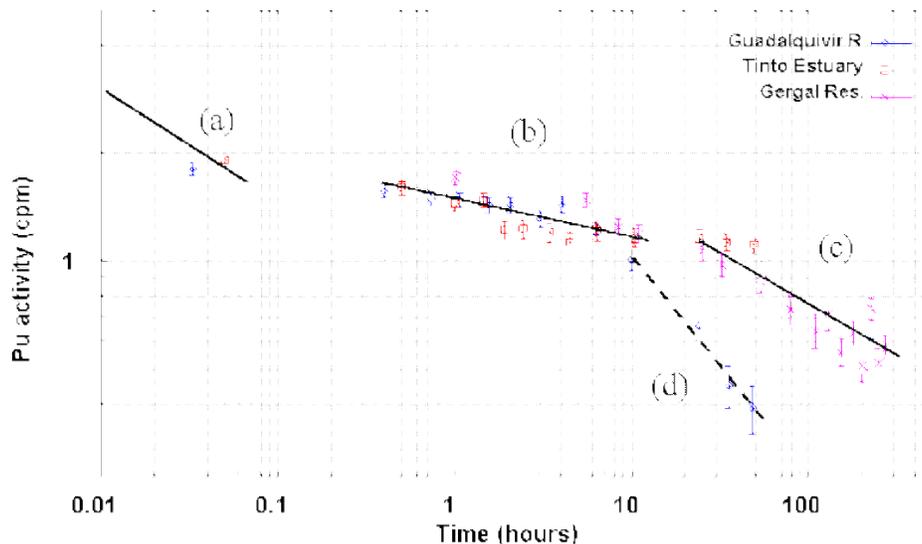
†  $\phi$ 1 is the most frequent diameter, and  $\phi$ 2 corresponds to particles with the highest percentage of volume. The specific surface area (SSA) is computed assuming a density of 2.10 g cm<sup>-3</sup> for solids.

‡ From XRF analysis and XRD microanalysis (this last for estuarine sediments).

¶ Two peaks, from higher to lower peak values. # Suspension formed with 20 g of sediment and 1 litre of natural decanted waters from the estuary. The granulometric analysis for this suspension corresponds to the fraction smaller than 100 $\mu$ m

**Table 1.** Granulometric and mineralogical analysis of the studied aquatic suspensions†

In each experiment one litre of water was transferred into a glass beaker. The suspensions were spiked with a known activity of the selected radionuclide and then continuously stirred to avoid any decantation. Aliquots (35-50 mL each) were sampled at different times after spiking. SPM was immediately removed from them by centrifugation (20 minutes at 4000 rpm). Then, 25 mL of the supernatant were transferred into a plastic container and acidified with 1 mL of concentrated HNO<sub>3</sub> to avoid adsorption of radionuclides onto the container walls. For <sup>239</sup>Pu and <sup>241</sup>Am (both are alpha emitters), 5 mL of acidified sample were transferred into a plastic vial and mixed with 15 mL of liquid scintillation cocktail (Pharmacia Optiphase 3) and measured with a Wallac Quantulus 1220TM liquid scintillation spectrometer. For <sup>133</sup>Ba the samples was prepared under standard counting geometry and measured by gamma spectrometry using an HPGe CAMBERRA detector. Results are summarised in Fig. 2 and Fig. 3.



**Figure 2.** Time evolution of <sup>239</sup>Pu activities in the dissolved phase corresponding to the three experiments (points with error bars). Continuous lines indicate the different sequences of the uptake kinetics. Suspended matter concentrations are: 7.37 ppm for the Gergal river, 12.6 ppm for the Guadalquivir river and 7.62 ppm for the Tinto estuary.

Three different regions characterised by different slopes can be distinguished in Figure 2: 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; 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. In region (c), the uptake (up to 50% of the remaining Pu in solution) continues during several days. Region (d) corresponds to a faster uptake of Pu from the dissolved phase, which is probably related to flocculation effects. The model of two parallel, reversible and concentration independent reaction followed by a consecutive, non-reversible (with saturation) and concentration independent reaction was successfully applied and the five kinetic coefficients were obtained. In all cases, the first parallel reaction is the faster. It transfers an important fraction of the dissolved Pu to the particulate phase (20% for estuarine waters, 30% for the reservoir and some 42-44% for the river). The period during which this reaction governs the global uptake is about 0.2 h. The application of a three-step model of single and effective oxidation state in this study allowed reaching a reasonable understanding of the Pu uptake curves. It also provided a set of kinetic parameters useful to describe the most relevant aspects of the electrolytic reactions of <sup>239</sup>Pu in the aquatic environment.

[10] concluded that a model of two parallel and reversible reactions, followed by a non reversible reaction (with saturation) could reasonably explain their experimental results, assuming the Pu in a single oxidation state: Pu(IV). The third reaction represents a small correction in all the cases, and in their study of <sup>241</sup>Am [11], they used a reversible approach for this third reaction. The first parallel reaction had a faster kinetics in all the cases, and the authors suggested that it should consist in a physis adsorption in accessible sites onto the particle surface, while the second parallel reaction would be related to the less-accessible sites (inner surfaces of pores and free-edges) and/or to the chemical-adsorption. The third (consecutive) reaction should correspond to a change of site (occlusion), nature or strength of the unions. Fig.3 shows a scheme of the model. The governing equations are:

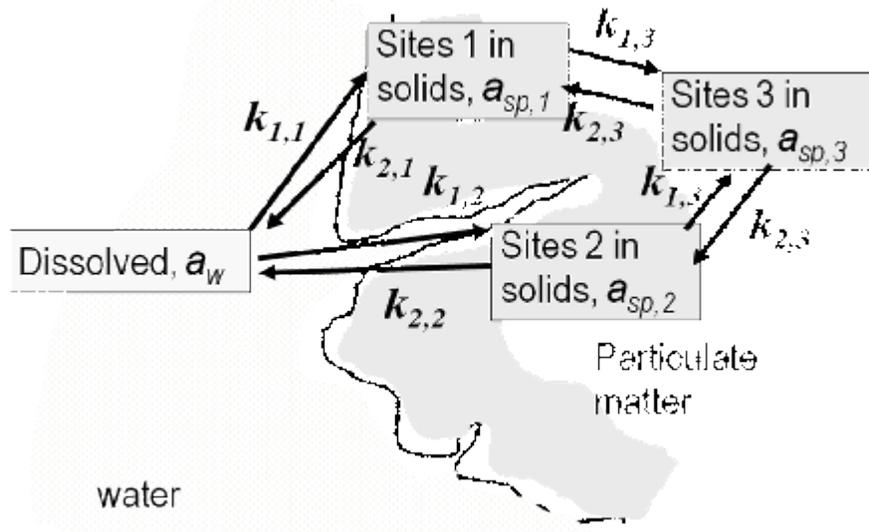
$$\frac{da_w}{dt} = -(k_{1,1} + k_{1,2})a_w + k_{2,1}a_{sp,1} + k_{2,2}a_{sp,2} \quad (1.1)$$

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

$$\frac{da_{sp,2}}{dt} = k_{1,2}a_w - k_{2,2}a_{sp,2} - k_{1,4}a_{sp,2} \quad (1.3)$$

$$\frac{da_{sp,3}}{dt} = k_{1,3}a_{sp,1} + k_{1,4}a_{sp,2} - (k_{2,3} + k_{2,4})a_{sp,3} \quad (1.4)$$

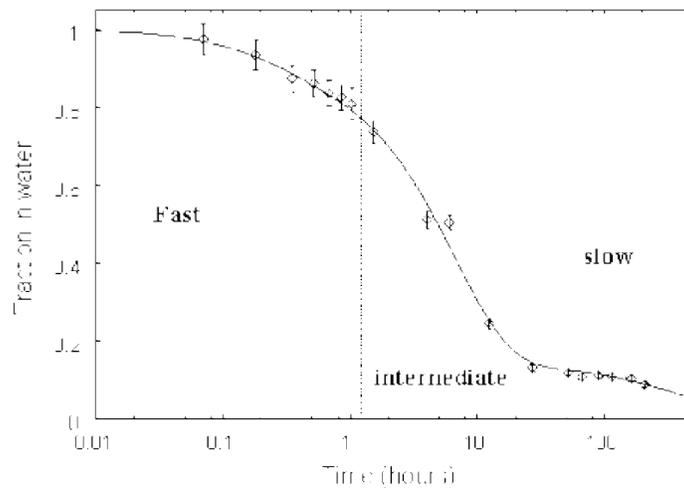
where  $a_w$  = concentration of the tracer in the dissolved phase, in Bq/l. All the activities are in units of Bq/l (or similar). In a first approach,  $k_{1,4}=k_{1,3}$  and  $k_{2,4}=k_{2,3}$ . The six kinetics transfer coefficients have units inversely proportional to time (s<sup>-1</sup> or h<sup>-1</sup>). The concentrations in solids are related to the corresponding specific activities (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  $a_{sp,3} = a^*_{sp,3} m_s$ .



**Figure 3.-** Scheme of the uptake kinetic model. It distinguishes three different sites in the particulate matter. Sites 1 and 2 have different accessibility and/or different nature or strength of the unions. They exchange radionuclides with the dissolved phase by means of two parallel, reversible and concentration independent reactions with kinetic coefficients  $k_{i,j}$ . Radionuclides from sites 2 and 3 can migrate to sites 3 (occlusion, or a change in the nature of the union). This reaction may be irreversible or weakly reversible. As a simple approach, it uses the same kinetics coefficients for channels  $1 \leftrightarrow 3$  and  $2 \leftrightarrow 3$ .

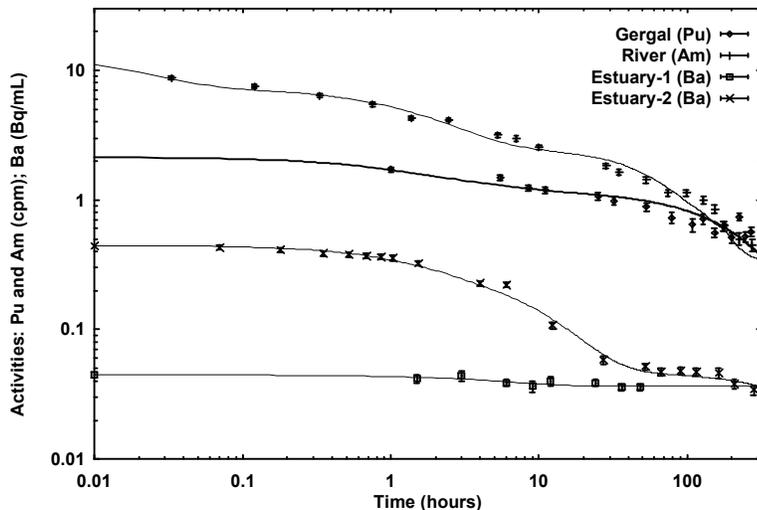
Equations 1.1 to 1.4 are numerically solved by means of a finite difference scheme. The parameter values are varied till get the best fit (shown in Fig. 4). The resulting parameter values are summarised in Table 2. Our present results show that the approach of a single reversible reaction used by [14] for  $^{133}\text{Ba}$  in natural aqueous suspensions is not applicable here.

Three processes can be clearly distinguished in the uptake curve; a fast adsorption during the first hour followed by a moderated reaction lasting some 20 to 30 hours and finally, an excessively slow reaction which draws the system to a saturation state.



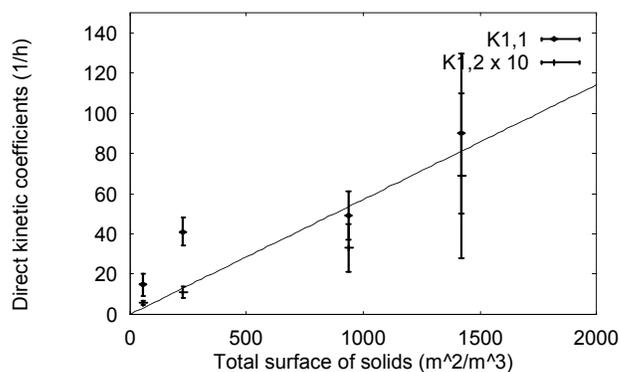
**Figure 4.** Time evolution of concentrations in the aqueous phase as the result of  $^{133}\text{Ba}$  adsorption by suspended particulate matter. The points are the experimental data.

Three different characteristic times can be, also, distinguished in the uptake curves in Fig.5. Consequently we need a model involving three reactions. A model of two parallel and reversible reactions, followed by a second step weakly reversible reaction explains the whole of our experimental results (see Fig.5).



**Figure 5.** Experimental uptake curves from our experiments (see Table 1).  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  activities (in cpm) in the 5 cm<sup>3</sup> aliquots of dissolved phase.  $^{133}\text{Ba}$  activity in water is expressed in Bq mL<sup>-1</sup>. The lines correspond to model results.

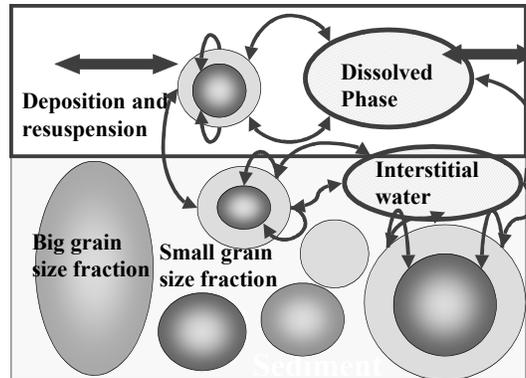
The partitioning coefficient  $k_d$  increases with pH and decreases with the concentration of competitive ions. The effect of electrical conductivity in the kinetic coefficients for  $^{133}\text{Ba}$  uptake was studied by [14]. In an independent series of experiments we studied the effect of total surface of solids per unit volume of solution in the uptake kinetics of  $^{241}\text{Am}$ . The two direct transfer coefficients (corresponding to the two parallel reactions) increased with SSA, as shown in Fig.6.



**Figure 6.** Direct transfer coefficients (in h<sup>-1</sup>) for the two parallel reactions versus total surface of solids per unit volume of solution. The second coefficient appears multiplied by a factor 10 for the sake of comparison.

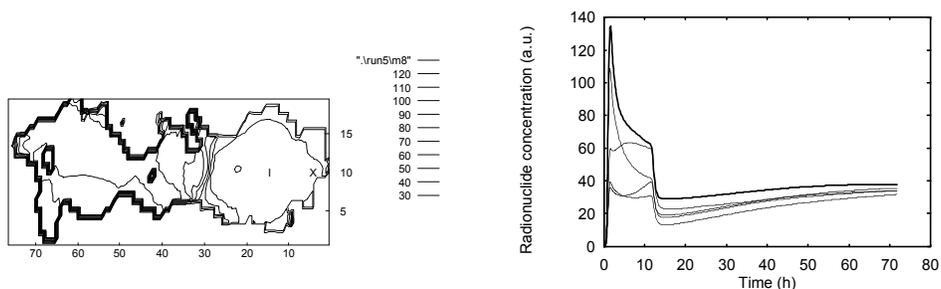
**IV- REACTIVE TRANSPORT MODEL FOR AQUATIC SYSTEMS.**

The model for the uptake kinetics has been incorporated into a more **general** model for radionuclide dispersion in the aquatic environment that simultaneously solves the advective and diffusive transport and the suspended matter dynamics [3] under tidal and/or wind forcing. Direct uptake by sediments was also considered, distinguishing two main grain sizes (small sizes can be resuspended). The basic processes included in the model are summarised in Fig.7.



**Figure 7.** Schematic representation of the processes involved in the reactive transport model.

An important application simulated the contamination of the Hårsvatten Lake (Sweden) by a hypothetical cloud containing  $^{239}\text{Pu}$  that uniformly entered over the whole lake area. Water circulation was forced by winds. 12 hours after contamination, SPM concentration were enhanced (natural episodic events or a remedial action). Activity in dissolved phase quickly decreased as shown in Fig.8. Consequently this remedial action has reduced the concentration of the Pu in water



**Figure 8.** Spatial map (left) and time series of concentrations (a.u.) at different locations (right) of Pu in dissolved phase in the Hårsvatten Lake after a hypothetical contamination episode followed by a remedial action.

## V. Conclusion

Kinetic box models are useful approaches to the analysis of time-resolved sorption data and are capable of providing transfer parameters which are important in determining the mobility and rate of removal of radionuclides from the water column. On the other hand, the box models represent an effective way of defining the number of processes involved in the adsorption in aqueous suspensions. A model taking into account a single reaction is generally unable to properly describe both sorption and release kinetics by suspended particulate matter in seawater. Higher order models such as “two-step” and “three-step” are most appropriate since the uptake of radionuclides by solid particles is usually a process where up to three steps can be distinguished: a fast kinetics (minutes), a moderate process (hours) and a slow sorption (days). However, the rationale for the selection of a model instead of another from the same category is still poorly established. This question should be seriously taken into consideration since it is determinant in interpreting the physical meaning of the transfer coefficients. One practical criterion able to discriminate among models is, from the authors’ point of view, the statistical analysis of the variability of  $k_{ij}$  with physico-chemical parameters. The best model should give a coherent response to changes in these environmental factors.

On the other hand, the use of kinetic transfer coefficients in predictive dispersion models of pollutants represents a powerful tool to study basic processes in natural systems. The simulation of a self-cleaning scenarios based in the enhancement of natural-occurring suspended load concentrations shows an important reduction in the radionuclide concentrations in the dissolved phase. This reduction can be obtained in most of the cases in a very short time (few hours) after the remedial action, what reduces the bioavailability of these pollutants and the risk on the environmental and human health. The basic processes studied here are applicable to other particle-reactive pollutants as many heavy metals.

Finally, investigation on the behaviour of radionuclides in aquatic environments is still of contemporary importance and there will be a continuing requirement for a research capability in this area for as long as nuclear power remains a significant contributor to world energy supply.

## REFERENCES

- [1] Abril, J.M. (1998a). Basic microscopic theory of the distribution, transfer and uptake kinetics of dissolved radionuclides by suspended particulate matter. Part I: theory development. *J. Environ. Radioactivity*. 41, 307-324.
- [2] Abril J.M. (1998b). Basic microscopic theory of the distribution, transfer and uptake kinetics of dissolved radionuclides by suspended particulate matter. Part II: applications. *J. Environ. Radioactivity*. 41, 325-342.
- [3] Abril J.M. and Abdel-Aal M.M. (2000). A modelling study on hydrodynamics and pollutant dispersion in the Suez Canal. *Ecological Modelling*. 128, 1-17.
- [4] Hamilton-Taylor J., Kelly M., Kershaw P. and Lambert C.E. Radionuclide aquatic pathways. In: *Radioecology after Chernobyl*, (eds.) Sir Frederick Warner and Roy M. Harrison. (1993), 177-274.
- [5] Assinder, D.J., Kelly, M., and Aston, S.R. (1985). Tidal variations in dissolved and particulate phase radionuclide activities in the Esk estuary, England, and their distribution coefficients and particulate activity fractions. *J. Environ. Radioactivity* 2, 1-22.
- [6] Benes P., Cernik M. and Lam Ramos P. (1992). Factors affecting interaction of radiocesium with freshwater solids II: Contact time, concentration of the solid and temperature. *J. Radioanalytical and Nuclear Chemistry*. 159(2), 201-218.
- [7] Eisma, D. (1993). *Suspended Matter in the Aquatic Environment*. Berlin: Springer.
- [8] Bolivar, J.P., García-Tenorio, R. & García-León, M. (1996). On the fractionation of natural radioactivity in the production of phosphoric acid by the wet acid method. *J. Radional. Nucl. Chem., Letters*. 214 (4), 77-78.

- [9] Barros H., Laissaoui A. & Abril J.M. (2004). Trends of radionuclide sorption by estuarine sediments. Experimental studies using  $^{133}\text{Ba}$  as a tracer. *Science of the Total Environment*. 319, 253-267.
- [10] El-Mrabet, R., Abril, J.M., Manjón. G. and García-Tenorio, R. (2001) Experimental and modelling study of plutonium uptake by suspended mater in aquatic environments from southern Spain. *Wat. Res.* 35(17), 4184-4190.
- [11] El-Mrabet, R., Abril, J.M., Manjón. G. and García-Tenorio, R. (2002) Experimental and modelling study of  $^{241}\text{Am}$  uptake by suspended mater in freshwater environments from southern Spain. *Wat. Res.* (Submitted).
- [12] Smith J.T., and Comans R.N.J. (1996). Modelling the diffusive transport and remobilisation of Cs-137 in sediments: the effects of sorption kinetics and reversibility. *Geochimistry and Cosmochimistry Acta* 60, 995-1004.
- [13] Kershaw P.J., Denoon, D.C., and Woodhead, D.s. (1999). Observations on the distribution of plutonium and americium in the Irish Sea sediments, 1978 to 1996: concentrations and inventories. . *J. Environ. Radioactivity* 44, 189-220.
- [14] Laissaoui A., Abril J.M., Periañez R., García León M. & García Montañó E. (1998). Kinetic transfer coefficients for radionuclides in estuarine waters: reference values from  $^{133}\text{-Ba}$  and effects of salinity and suspended load concentration. *J. Radioanalytical and Nuclear Chemistry*. 237 (1-2) 55-61.
- [15] Leonard, K.s., Mccubbin, D., Blowers, P., and Taylor, B.R. (1999) Dissolved plutonium and americium in surface waters of the Irish Sea, 1973-1996. *J. Environ. Radioactivity* 44, 129-158.
- [16] Mckinkley I.G. and Alexander W.R. (1992). Constraints on the applicability of “in-situ distribution coefficient” values. *J. Environ. Radioactiviy*. 15, 19-34.
- [17] Mitchell, P.I., Condren, O.M., Vitró, L.L., and McMahon, C.A. (1999). Trends in plutonium, americium and radiocaesium accumulation and long-term bioavailability in the western Irish Sea mud basin. . *J. Environ. Radioactivity* 44, 221-250.
- [18] Nyffeler U.P., Yuan-Hui Li and Santshi P.H. (1984). A kinetic approach to describe trace element distribution between particles and solution in natural aquatic systems. *Geochim. Cosmochim. Acta*, 48 , 1513-1522.
- [19] Periañez R. (1999). Three-dimensional modelling of the tidal dispersion of non-conservative radionuclides in the marine environment. Application to  $^{239,240}\text{Pu}$  dispersion in the eastern Irish Sea. *Journal of Marine Systems*. 22, 37-51.
- [20] Periañez R., García León, M. & Abril, J.M (1994a). Radium isotopes in suspended matter in an estuarine system in the Southwest of Spain. *J. of Radioanal. Nucl. Chem.* 183 (2), 395-407.
- [21] Periañez R., Abril, J.M & García-León, M. (1994b). A modelling study of  $^{226}\text{Ra}$  dispersion in an estuarine system in South-West Spain. *J. of Environ. Radioactivity* 24, 159-179.
- [22] Periañez. R. On the sensitivity of a marine dispersion model to parameters describing the transfers of radionuclides between the liquid and solid phases. *Journal of Environmental Radioactivity* 73 (2004) 101-115.
- [23] Robbins , J. A., Lindner, g., Pfeiffer, W., Kleiner, J., Stabel, H.H. & Frenzel, P. (1992). Epilimnetic scavenging of Chernobyl radionuclides in Lake Constance. *Geochimica et Cosmochimica Acta* 56, 2339-2361.
- [24] Arnold P.W. (1978). Surface-electrolyte interactions. In: *The Chemistry of Soil Constituents*. (eds.) Greenland and M. H. B. Hayes. Wiley, New York, ISBN 0 471 99619X.
- [25] Richter J. (1987). *The Soil as a reactor*. Catena Verlag, ISBN 3-923381-09-03.