Redissolution of ^{226}Ra from sediments in a Spanish estuary affected by the phosphate industry: model comparisons in the frame of the IAEA EMRAS Project[1]

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Abstract. The Huelva estuary (SW Spain), a fully mixed tidal estuary, consists of two rivers: Odiel and Tinto. A phosphate fertilizer processing complex has been releasing NORM radionuclides directly into the Odiel River over several decades. As a consequence, high levels of ^{226}Ra, U and Th isotopes and other radionuclides have been measured in water, suspended matter and bed sediments of the estuary. Nevertheless, direct releases stopped in 1998 due to new regulations from the EU and, since then, a self-cleaning process has been observed. It consists of a continuous decrease in activity concentrations in water and bed sediments. The study by means of numerical models of the ^{226}Ra self-cleaning process observed in the estuary has been proposed as an EMRAS project task. A model has been proposed by each institute participating in the exercise. Models have different configurations and temporal and spatial resolutions. Some processes, for instance tides or uptake/release of radionuclides between water and sediments, are described in different ways. However, all are started from the same initial conditions, provided by the University of Seville model. The endpoint of the simulations is to give the temporal evolution of the total ^{226}Ra inventory in the bed sediments of the estuary and to estimate from it the sediment halving time. A brief description of the main features of each model will be provided and results will be compared and analyzed.

1. Introduction

During the last decades a number of projects have been launched to validate models for predicting the behaviour of radioactive substances in the environment. Such projects took advantage of the great deal of experimental data gathered, following the accidental introduction of radionuclides into the environment, to assess the contamination levels of components of the ecosystem and of the human food chain. For instance, BIOMOVS and VAMP projects stimulated intensive efforts for improving the reliability of the models aimed to predict the migration of ^{137}Cs in lakes and of ^{137}Cs and ^{90}Sr in rivers. Similar co-operative studies for model validation were never done for other important systems such as coastal waters and drainage areas. Moreover, apart from Cs and Sr, other long-lived radionuclides that may be of importance for the medium and long term effects related to the environmental contamination were not the object of equally extensive validation exercises.

The activities of the working group WG-4 (Aquatic Working Group) of the EMRAS project are aimed at filling some of the above gaps. Several priorities were selected for the new intercomparison exercises to be carried out in the frame of EMRAS: other radionuclides than Cs and Sr, extreme events, physical factors dealing with remobilisation and modelling radionuclide behaviour in coastal areas. The Huelva estuary is a scenario suitable for this study in the frame of EMRAS project.

The estuary is located in the south-west of Spain. It consists of a tidal, fully mixed estuary formed by the Odiel and Tinto rivers, which surround the town of Huelva (Fig. 1). The rivers join at the Punta del Sebo. From this point, they flow together through the same channel towards the Atlantic Ocean. An industrial area, including a complex dedicated to the production of phosphoric acid and phosphate fertilizers, is located next to the Odiel River. The fertilizer plants have been the main source of natural

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[1] Work carried out in the frame of the EMRAS (Environmental Modelling for Radiation Safety) project of the International Atomic Energy Agency.

radionuclides to the estuary — it is well known that the phosphate rock used as raw material by this industry contains significant amounts of natural radionuclides, mostly U, Th and Ra. The industrial processing of the phosphate rock leads to a redistribution of radioactivity. For instance, during the wet process for phosphoric acid production, 86% of U and 70% of Th present in the rock are transferred to the phosphoric acid itself, while 80% of the Ra content follows the so-called phosphogypsum path. This is a form of impure calcium sulphate removed as a precipitate during the process. Phosphogypsum is usually disposed into open air piles or discharged into rivers or estuaries, giving rise to a local radioactive impact. During 1990, for instance, 2×10^6 t of rock were processed and 3×10^6 t of phosphogypsum were produced [1]. These wastes were partially released directly into the Odiel river (20%) and conveyed with water through a pipeline to phosphogypsum piles (remaining 80%) located by the Tinto River (see Fig. 1), where such material is stored in the open air. The gypsum piles cover some 12 km^2 of the Tinto river bank. Since 1998 wastes have not been released directly into the Odiel River due to new regulations from the EU, although phosphogypsum is still being disposed of in the piles by the Tinto River. These new piles, however, are surrounded by dykes to prevent leaching to the river.

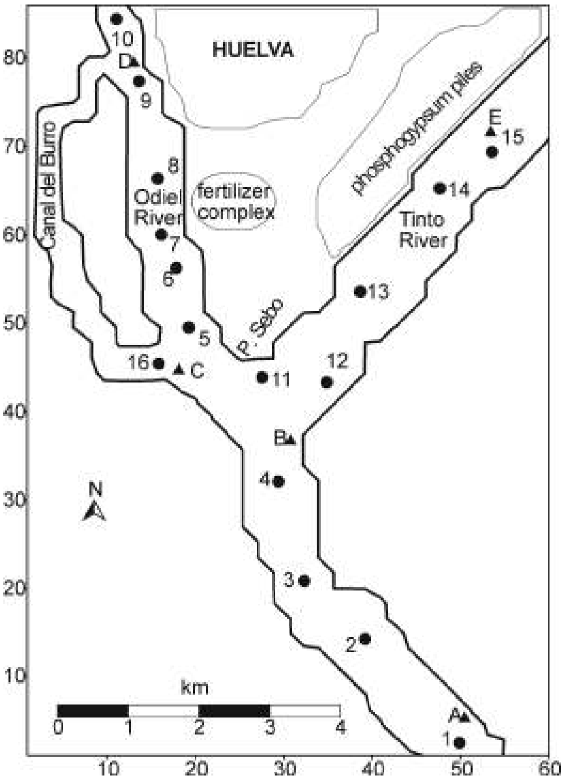

FIG. 1. The Huelva estuary showing points where samples were collected (circles) and points where current measurements are available (triangles). The location of the fertilizer complex and of the phosphogypsum piles is also shown. The Atlantic Ocean is approximately 1 km to the south of point 1. Each unit in the axis corresponds to 125 m

The time evolution of ^{226}Ra activities in water and sediments over the years 1999–2002 has been studied [1]. Results indicated that a self-cleaning process was taking place in the estuary as a consequence of the new waste policy, since a systematic and continuous decrease in activities was found in the water column and in bed sediments. The objective of this work consists of studying by means of different models the self-cleaning process that has been observed in the Huelva estuary. A general description of the scenario is given in the following section. Next, models participating in the exercise are briefly presented and finally results are discussed.

2. General description of the scenario

The estuary is very shallow (maximum depth around 19 m) and well mixed vertically due to the strong tidal currents, of the order of 1 m/s. The tidal range is about 2 m for the main tide M_2. Moreover, the stream flows of the rivers are very low (ranging from 0.5 to 70 m^3/s in usual conditions in the case of the Odiel River and even lower values for the Tinto River) and a fast dispersion of fresh water into a much larger volume of salt water occurs [2]. This mixing takes place upstream of the studied area and water salinity along the estuary may be considered constant and typical of seawater. Residual currents, due to the river discharges, are of the order of 1 cm/s over the estuary. The concentrations of suspended sediments in the estuary depend on tidal state. Thus minimum concentrations are expected during high and low water due to sedimentation during slack water periods. During ebb and flood periods, higher currents produce some erosion of the bed sediment. Seasonal variations must be expected as well. Nevertheless, net sedimentation rates are small and these processes have been neglected in previous modelling studies. Indeed, suspended matter concentrations of the order of a few mg/L have been measured along the estuary.

The information provided with the scenario is the following:

- Water depths with a resolution of 125 m.
- Initial conditions of the simulation. These are concentrations of ^{226}Ra in the bed sediment and in the water column over the estuary. These concentrations have been obtained from a run of a model developed at the University of Seville and correspond to concentrations at the moment when direct releases from the fertilizer complex were stopped. Initial conditions also provide the partition of Ra in the bed sediment between a fast and a slow-exchangeable phase.
- Boundary conditions. These are provided in order to solve the hydrodynamics of the estuary (tidal amplitudes and phases at the estuary entrance) and radionuclide dispersion. These last conditions consist of measured concentrations at the three open boundaries of the domain.
- Physical characteristics of the estuary: monthly averaged river flows, sediment characteristics and suspended matter concentrations. Limited information is available on the bottom sediment characteristics. In some of the sampling points indicated in the map of Fig. 1, bulk density, organic matter content and fraction of muds (particles <63 μm) were measured for samples collected in 1991.
- Kinetic rates for radium exchange (obtained from laboratory experiments) and average distribution coefficient in the estuary. Thus the modeller may decide between using a distribution coefficient or a kinetic model for describing the interactions between the dissolved and solid phase.

The endpoint of the exercise consists of providing the time evolution of the total ^{226}Ra inventory in the bed sediment and the time evolution of the mean radionuclide concentration in the water column. Models are started from the initial conditions and the system evolves without any external source of radionuclides. Thus, it may be determined whether a self-cleaning process of the system is actually predicted by the model. The time scale at which this process occurs is also of interest. Data files and a detailed scenario description may be downloaded from the EMRAS website [3].

3. Main characteristics of the models

A brief description of the models that have participated in the exercise is given below. Models range from box models in which the full estuary is divided into a small number of boxes to high resolution hydrodynamic and advection/diffusion models.

MASCARET (EDF R&D, France)

This is a 1D hydrodynamic system for simulating hydrodynamic flows, water quality and sediment transport [4]. In the present application, the hydrodynamic and pollutant transport modules of the model have been used. The interactions of dissolved radionuclides with the bed sediments have been described by means of two different approaches: a k_d-based model and a kinetic model consisting of two consecutive reversible reactions [5]. The hydrodynamic module solves the shallow water equations on a looped and branched network [6]. Equations are solved using implicit finite differences. The estuary geometry was described by means of 42 profiles extracted from the provided bathymetry. The model contains 250 sections with 50 m length in Odiel and Tinto and 150 m in the common channel. The monthly water flows were imposed at both the Odiel and Tinto rivers and water elevation was defined at the entrance of the estuary from the provided data for tides. The main M_2 and S_2 tides are considered. The 1D advection-diffusion equation in its conservative form is solved together with hydrodynamics. Time step for calculations is 60 s.

COASTOX (IMMSP, Ukraine)

This is a 2D depth-averaged model [7]. As in MASCARET, the hydrodynamics, including tides, and dispersion modules are solved on-line (simultaneously). To diminish the computational time (calculation time step scale of minutes) the simulation was provided for periods of 10–12 days for some values of the river discharges and then this hydrodynamics was replicated for other periods with the similar magnitude of the rivers discharges.The interaction of dissolved radionuclides with the bed sediment is described by means of a desorption coefficient and an adsorption coefficient, which is deduced from the k_d and the desorption coefficient. Thus, it is a kinetic model consisting of a single reversible reaction. The spatial resolution of the model is 125 m.

USEV (University of Seville, Spain)

The University of Seville model (2D depth-averaged) is described in [8]. Dispersion and hydrodynamics are solved off-line and standard tidal analysis is used to calculate tidal constants (amplitudes and phases) over the domain. These constants are stored and later read by the dispersion module for a fast computation of tidal currents. Thus, one year of dispersion calculations with a temporal resolution of 60 s takes a few minutes on an up-to-date PC. The interactions of dissolved radionuclides with the bed sediments are described through a kinetic model consisting of two consecutive reversible reactions [5]. Spatial resolution is 125 m.

ENEA model (ENEA, Italy)

The ENEA model is a box model based on quantitative evaluations and balance of radionuclide contents in the water system components (surface water, deep water, bottom sediment) accounting for the fluxes among these. The model structure is conceptually similar to the one adopted for the sub-model MARTE (Model for Assessing Radionuclide Transport and countermeasure Effects in complex catchments) [9] implemented in the Computerised Decision Support Systems MOIRA [10]. The water body is divided in three sectors. Each sector is sub-divided in three compartments: surface water, deep water and bottom sediment. A fourth compartment representing the sediment interface between bottom sediment and water is considered to simulate the quick interaction processes of radionuclide with particulate matter. The first order differential equations of the model were obtained by calculating radionuclide budget in the system compartments from the balance between input and output radionuclide fluxes. These are supposed proportional to the amount of radionuclide in the respective "source" compartment. Eddy diffusion (horizontal, between sectors, and vertical between surface and deep waters) is simulated by two-way fluxes that are calculated from the difference between radionuclide concentrations in two contiguous sectors. The radionuclide absorption by suspended matter and by the sediment interface layer is modelled according to the well-know k_d concept. The model is aimed at evaluating the radionuclide concentrations in the abiotic components of the water body averaged over 1 month, approximately. Consequently, the effects due to the tidal cycle are described as an average exchange of radionuclides between the sea and the estuary water. The simulation time step is 1 day.

4. Results and discussion

The time evolution of the computed ^{226}Ra inventory in the sediments of the complete estuary and the mean concentration in the water column obtained with the different models may be seen in Fig. 2.

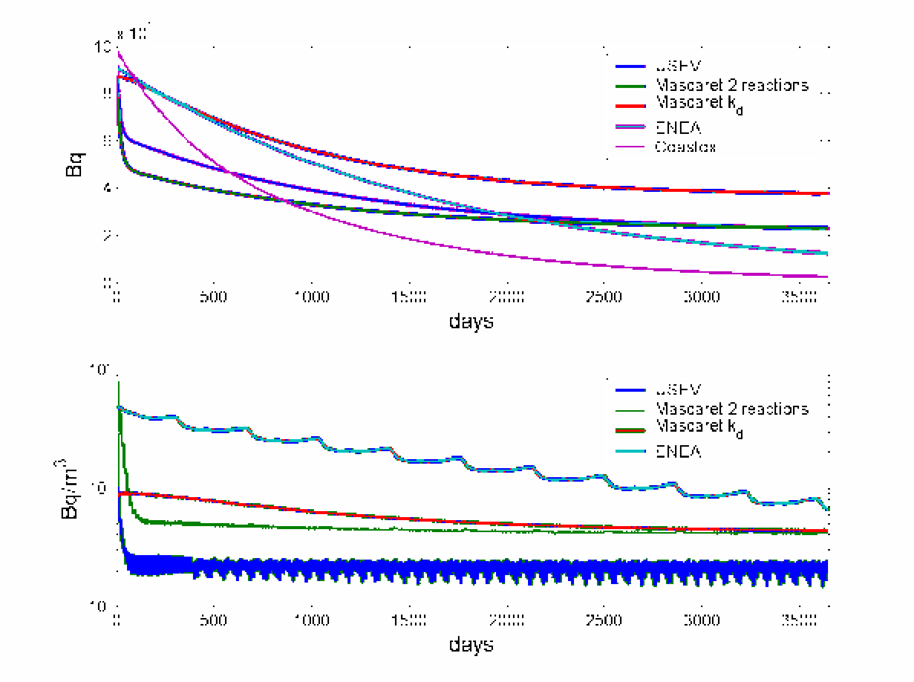

FIG. 2. Computed evolution of total ^{226}Ra inventory in bed sediments (upper) and average concentration in the water column (lower)

All the models predict a decrease of activity in both phases. Different behaviours may be observed for the sediment phase between models that use two-step kinetics (USEV and MASCARET 2 reactions) and models that use a single reaction or a distribution coefficient. In the former case, the first rapid reaction followed by a slower redissolution is clearly seen. In the second case, a continuous reduction in the inventory is obtained. A detailed view of the initial phase of the process is presented in Fig. 3, as well as the time evolution of the bed inventory after this initial phase.

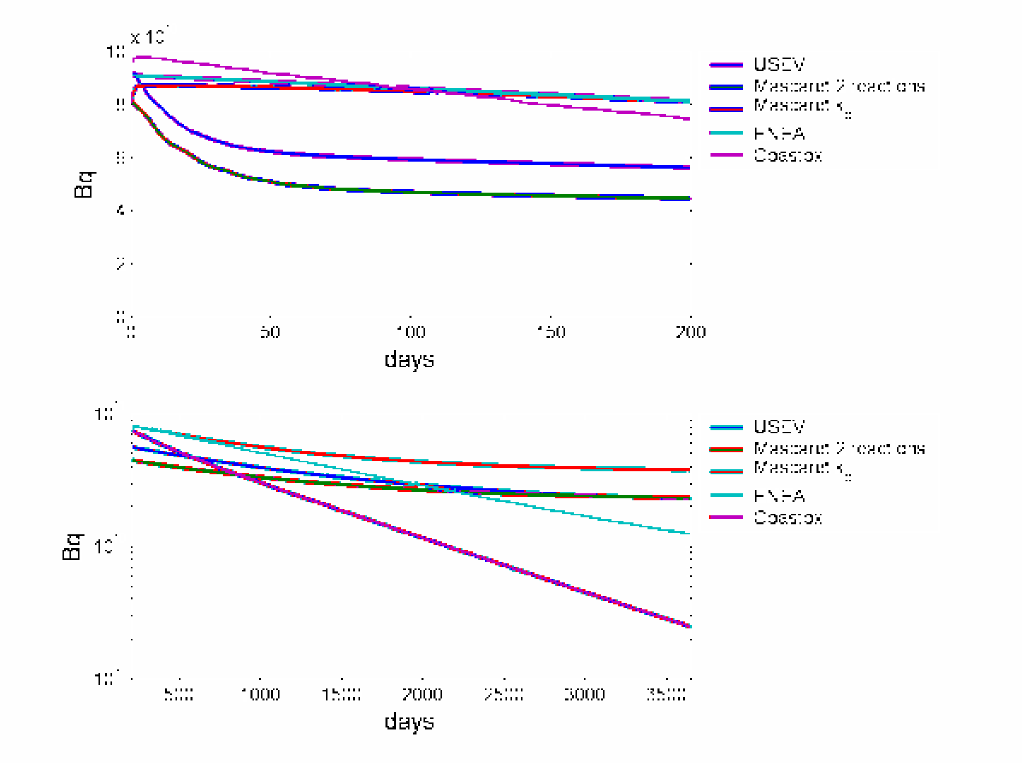

FIG. 3. Time evolution of computed inventories in the bed sediment at different time scales

It is worth commenting that there is a slight difference in the initial inventory in the bed sediment between MASCARET and the other models. This is due to the fact that MASCARET is a 1D model, thus ^{226}Ra concentrations in the bed provided in the scenario as 2D data had to be converted into a 1D structure and some activity was missing in process. From measurements in the estuary, it has been found [1] that the sediment half-time (time in which the ^{226}Ra sediment inventory decreases by a factor 2) is 630 days. The values of this half-time obtained with the different models may be seen in Table 1. Computed half-times range between some 400 and 1400 days, thus all models predict that a self-cleaning process of the estuary is occurring, and the order of magnitude of the process time scale is correctly estimated as well. Nevertheless, it seems that the main differences between the models appear in the initial stages of the process. Due to the difficulty in simulating this initial phase, strongly dependent on the kind of model adopted to describe water-sediment interactions, the trends shown in Fig. 3 (lower) have been fitted to exponential decay curves and the corresponding half-times derived from them are also presented in Table 1. Thus, model behaviours after the initial phase may be compared. It must be pointed out that the first halving-times are deduced from the full simulation for each model (from t = 0 to t = 3650 days, simply looking at the time when the total inventory in the bed is reduced by a factor 2) while the second ones (in the third column in Table 1) are obtained for each model after the initial dissolution phase (from t = 200 to t = 3650 days, after numerical fitting to an exponential curve). It can be observed that all models give very similar results at a longer time scale, if the initial phase of redissolution is not considered, with halving times ranging from 617 to 844 days.

TABLE 1. COMPUTED SEDIMENT HALF-TIMES OBTAINED FROM THE FULL SIMULATIONS AND AFTER THE INITIAL DISSOLUTION PHASE (from t = 200 days on).

Model	Half-time (days)	
	Full simulation	After initial phase
COASTOX	597	632
USEV	510	758
MASCARET 2 reactions	405	617
MASCARET k_d	1405	629
ENEA	1186	844

It may be questioned which is the most suitable water-sediment interaction description. Recent experimental [5] and modelling [11] evidence suggests that a 2-reaction kinetic model is more appropriate than a k_d or a 1-reaction model to describe both radionuclide uptake and release from contaminated sediments since the latter produces dissolution rates that are faster than those deduced from experiments and field measurements. However, no clear conclusion can be derived from this work. Indeed, all models produce acceptable values for the sediment half-time. The main differences between models appear in the initial stages of the redissolution process, but no experimental data are available to test which ones are giving a more realistic answer.

Sensitivity tests have been carried out to study the model response to changes in some of the parameters involved. A summary is presented in Fig. 4 for several parameters and models. One of the parameters is the sediment mixing depth (the sediment depth that interacts with the dissolved phase). Since ^{226}Ra concentrations in the surface sediment at the initial time are provided with the scenario description, reducing the mixing depth from the nominal value, 10 cm, to 1 cm clearly implies a reduction of the inventory in the initial time by a factor 10. Nevertheless the model output remains essentially the same, showing a self-cleaning process occurring at the same rate (results for the USEV model are shown). The COASTOX model has been tested with the nominal average sediment bulk density provided with the scenario (700 kg/m^3 from measurements) and a more standard value (1480 kg/m^3). Apart from the obvious change in the initial inventory, a similar cleaning process is obtained for both model runs. Finally, the MASCARET model has been tested with two k_d values. The mean value of the ^{226}Ra k_d measured in the estuary (36 samples), and provided with the scenario, is 9×10^3. The model has also been tested with a k_d of 1×10^3, which is closer to the value recommended by the IAEA [12] based upon a 20% of exchangeable Ra in coastal sediments (0.7×10^3). A reduction of the distribution coefficient makes the radionuclide more soluble and as a consequence there is a faster self-cleaning process over the first hundreds of days.

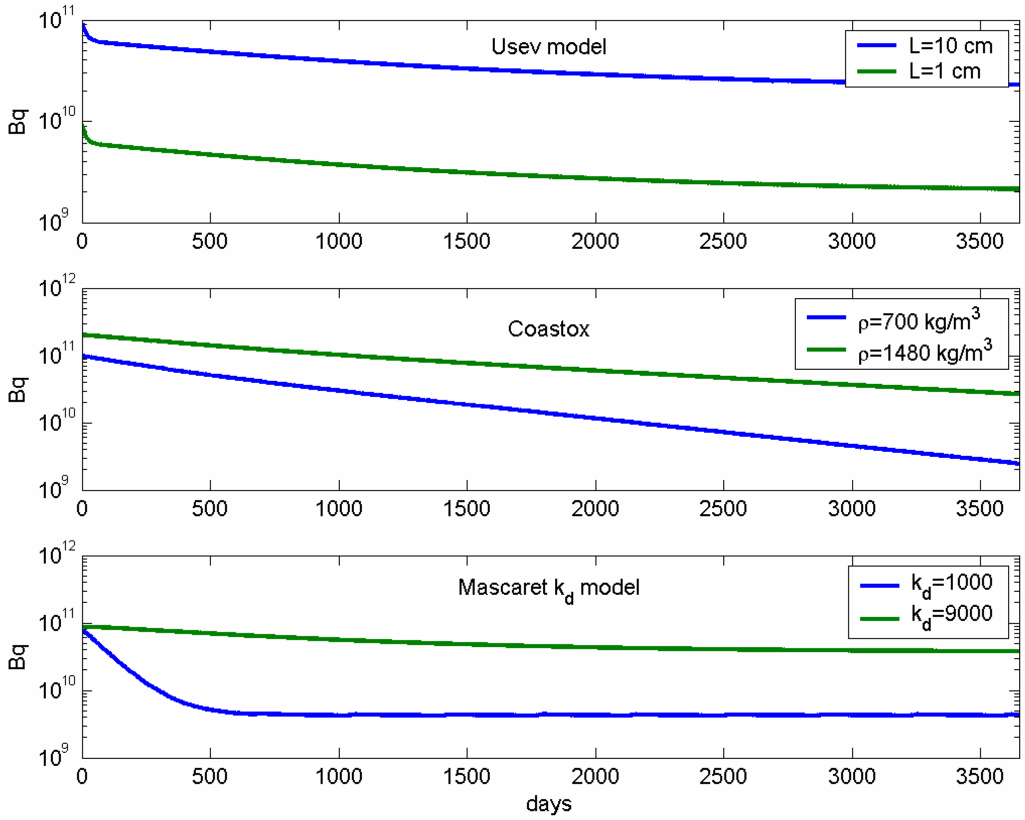

FIG. 4. Sensitivity of models to several parameters. The time evolution of the total ^{226}Ra inventory in the bed sediment is shown. Upper: sensitivity to the sediment mixing depth. Middle: sensitivity to the sediment bulk density. Lower: sensitivity to the distribution coefficient

5. Conclusions

Different models have been applied to simulate the self-cleaning process that has been observed in an estuary formerly affected by ^{226}Ra releases from a fertilizer complex. Models are very different in structure and resolution, from box models in which the complete estuary is divided into 3 compartments, to high-resolution two-dimensional models that explicitly solve tidal circulation. Water-sediment interactions are also described in different ways: distribution coefficients and kinetic models are used. In spite of these differences, all models predict that a self-cleaning process occurs and that the time scale of the process ranges between some 400 and 1400 days, i.e. a few years. The main differences between models appear during the initial phase of the cleaning process. A very good agreement between models is obtained if halving times are calculated after such initial phase. In this case they range from 617 to 844 days. This exercise also shows, as already stated [13], that a multi-model approach can be useful for the management of complex environmental assessment problems. The multi-model approach points out which are the conclusions that obtain the largest consensus among modellers and which are the ones that should be carefully handled.

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