Contribution of modeling to the knowledge of trace elements behaviour and speciation in estuaries

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Abstract. Geochemical models are excellent tools for the understanding of trace elements dynamics, in particular in complex environments like estuaries. Their aim is to reproduce numerically the biogeochemical processes observed in the field or laboratory. The development and the use of this kind of tool requires :
- *in-situ* data on the distribution in space and time of the elements studied and relationship with the environmental variables.
- experimental data (mainly based on the use of radioactive analogues of the studied elements) for evaluation of model parameters and the validation of model assumptions.
The model must be capable not only of reproducing the distribution of metals between the dissolved and particulate phases, but also of evaluating the concentrations of various chemical species (especially those which are most bioavailable). The approach presented treats adsorption processes as a formation of complexes with functional surface groups (surface complexation model). The calculation of chemical species takes into account the presence of dissolved ligands. The model can integrate several types of "natural" particles (oxydes, particulate organic matter) and different types of surface sites. This approach requires the evaluation of various parameters (especially surface properties of natural particles). The usefulness and limits of this kind of approach are illustrated via an application with cadmium, cobalt and caesium using data collected in the Seine, Loire and Gironde estuaries.

1. INTRODUCTION

Progress in the field of the analysis of trace elements led to a better knowledge of the biogeochemical cycle of contaminants. But, the measurement of the concentration of an element in the various operational fractions (dissolved, particles, colloids...) does not allow a direct knowledge of the various species (free ions, organic and inorganic complexes...) present in the environment. However, this knowledge is necessary to the understanding of the dynamics of the different species, in particular those wich are most bioavailable, and is a prerequisite to the studies of the contaminant effects on the aquatic organisms.

In spite of the accessibility of the littoral environment, the interpretation of field data is not easy and their generalization is difficult because of the spatio-temporal variability of the different processes (physical, chemical and biological) which proceed there.

Mathematical modeling is a good tool to integrate this variability and the diversity of the processes concerned. It makes it possible to synthesize the observations, to understand and treat on a hierarchical basis the phenomena, and in the long term, to evaluate the effects of the modifications of the system on the speciation of the contaminants and their fluxes towards the ocean. This kind of tool must be based on the knowledge of the major processes (on the smallest possible scale) and of the key variables which control them. At present, the geochemical models of speciation make it possible to treat a great number of situations met in aquatic environment. The principal difficulty is related to the evaluation of the various model parameters which cannot be measured directly.

The aim of this paper is to show the usefulness and limits of this kind of approach (experimental evaluation of parameters linked to the sorption properties of natural particles and surface complexation modeling) which are illustrated via an application with cadmium, cobalt and caesium using data collected in the Seine, Loire, Gironde and Rhône estuaries. The data, model and experimental methods used are presented in greater detail in various reports and articles [1-13].

2. MODELING : PRINCIPLE AND REQUIRED DATA

The Cd, Co, Cs speciation during estuarine transit has been simulated using a surface complexation model (MOCO). The adsorption of Cd and Co on particles is treated as a formation of inner sphere complexes with functional surface groups (hydroxyls). Dissolved species are calculated via the solving of the equilibria describing the metal's complexation with various dissolved ligands (Cl^-, OH^-, SO_4^{2-}). This approach was detailed in various articles [13-17]. The model used (MOCO) and its application to Cd in the Seine estuary were presented by Gonzalez *et al.* [11]. For Co, the cationic exchange is also treated while for Cs only the cation exchange is considered. The competitor cations taken into account are Ca^{2+} and Mg^{2+} for Co and K^+ for Cs. The choice of modeled processes is based on studies on Cd, Co and Cs biogeochemistry in the estuarine environment.

MOCO can consider the various natural particle components (oxyhydroxides, organic matter, clay minerals) as individual adsorbent phases, or treat natural particles in a "global" manner. In this study, particles are treated "globally". This approach requires the use of mean sorption properties measured on particles from the various estuaries considered.

2.1 Required variables and parameters evaluation

The concentrations of the following variables are required by the model to simulate metals speciation: chlorides (calculated from measured salinity); hydroxides (calculated from pH); SO_4^{2-}, Ca^{2+}, Mg^{2+} and K^+ (calculated from salinity, assuming conservativity and using concentrations measured at the fluvial and marine boundaries); suspended matter concentration (SM).

The use of the surface complexation concept requires evaluation of a certain number of parameters linked to the sorption properties of natural particles. As most of these parameters cannot be measured directly, their evaluation necessitated a variety of experimental approaches [gonzalez et al, 98; gonzalez et al, in press] applied to particle samples taken throughout the estuaries. The parameters used by the model are as follows:
- the specific surface area of the particles (SSA in $m^2 g^{-1}$) measured via nitrogen adsorption using the BET method (COULTER SA 3100)
- the total concentration of surface exchanging sites of protons ([TS] in mol g^{-1} of SM) evaluated by potentiometric acid-base titration (ABT)
- the "mean" intrinsic surface acid-base constants of these sites (K_{a1} and K_{a2}), determined via adjustment of the experimental data obtained by ABT using FITEQL 3.2 [18-20]
- the "global" intrinsic complexation constant (Km_{int}) of these sites with regards to Cd and Co obtained via experiments based on the use of ^{109}Cd and ^{57}Co (particle samples taken throughout the estuary).
- the cation exchange capacity (CEC in mol g^{-1} of SM) estimated via measurements of which uses ammonium as an exchangeable cation.
- the "exchangeable" particulate fraction. The approach used to estimate this fraction [gonzalez et al, in press] is based on the comparison of measured natural metals coefficient of distribution with the coefficient of distribution of their radioactive equivalents (determined by adsorption experiments, on the same samples).

Due to the rough evaluation of the parameters of sorption, and their natural variability within the estuary, we carried out simulations with sets of minimal, mean and maximum values, in order to examine the sensitivity of the model to these significant parameters.

On the basis of these data, the model distributes total measured metals (minus the non exchangeable particulate fraction) among the different considered species. For each field measurement point, a system of non-linear equations is solved (balance of mass, charges, surface sites and electrostatic effect correction) to calculate concentrations of the various species (dissolved complexes and sorbed) at equilibrium.
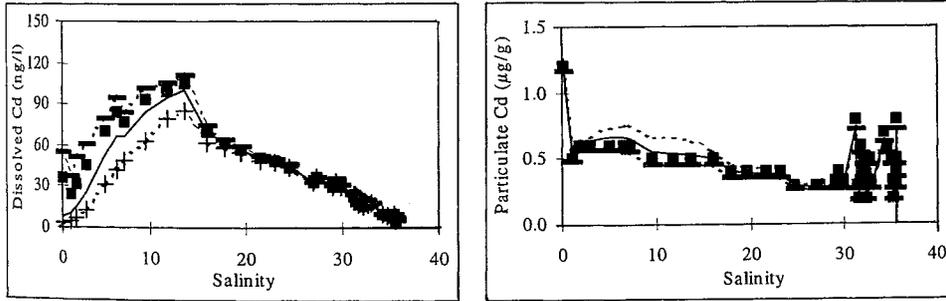
Co in the Seine estuary : Comparison between model results and measurements (■ Chiffoleau, personal communication).
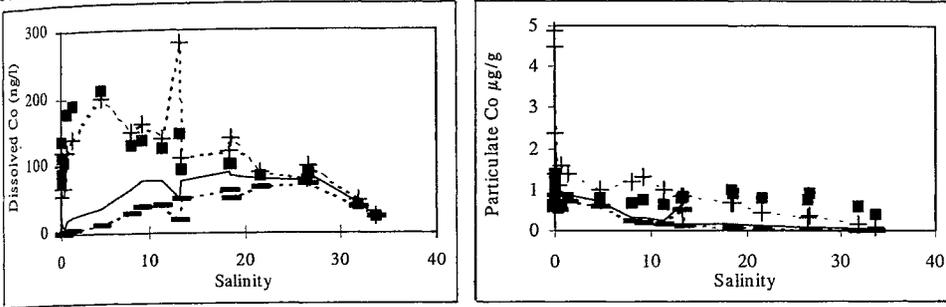
Cd in the Loire estuary : Comparison between model results and measurements (■ Boutier *et al*, 1993).
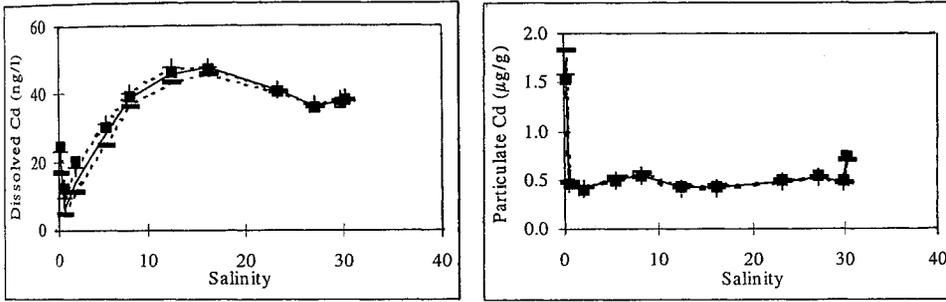
Cd in the Gironde estuary : Comparison between model results and measurements (■ Boutier *et al*, 2000).

[134]Cs and ^{137}Cs in the Rhône estuary : Comparison between model results and measurements (■ Martin and Thomas, 1990).
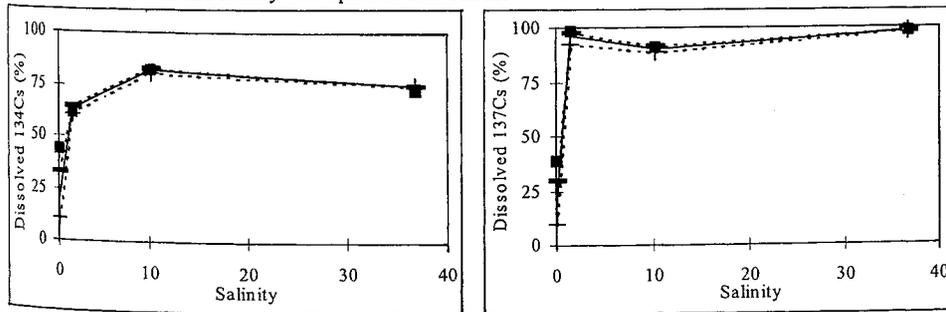

Figure 1 : Examples of simulations for Cd, Co, Cs in the Seine, Loire, Gironde and Rhône estuaries using mean (—), minimum (·) and maximum (+) values of the sorption parameters determined experimentally (■ measurements).

2.2 Comparison of measurements and simulations

The numerous campaigns realized by IFREMER allowed to obtain the major part of the data necessary for the simulations and for the validation of the model. The figure 1 shows some examples of the obtained results. To facilitate comparison of the simulation with field measurements, model results are given as "total dissolved cadmium" (sum of the various calculated dissolved species) and particulate Cd (calculated adsorbed + non-exchangeable).

The results show that metals distribution measured *in-situ* is comparable to that calculated by the model. Despite its simplifications, MOCO reproduces Cd, Co, Cs behavior and speciation in the estuaries in a satisfactory manner. One observes a significant solubilization of the three elements as soon as salinity increases:
- for Cd, explained largely by its stability in dissolved chlorocomplexes form and its rapid desorption during estuarine transit
- due to the competition for the same surface sites with major cations (Ca^{2+} and Mg^{2+} for Co, K^+ for Cs). It should be noted that this process is responsible for the significant Cs solubilization in the plume of the Rhone as soon as salinity increases.

It can exist significant differences between measurements and the results of the model, in particular for Cd and Co with low salinities and high SM concentrations. It is in these parts that the model is most sensitive to the value of the sorption parameters and to the quantity of metal exchangeable particulate fraction.

The model's limits are inherent to an efficient evaluation of sorption parameters (in particular with weak salinities) and the fraction of exchangeable particulate metals (in particular with high concentrations of suspended matter).

3. CONCLUSION

The application of a surface complexation model to simulate the behavior of Cd, Co and Cs in estuarine environment shows the usefulness and the limits of this approach.

The results indicate that the processes taken into account by the model explain well the dissolved / particulate distributions measured. Nevertheless, it can exist important discrepancies between the measures and the simulations in certain parts of the studied estuaries, particularly for Cd and Co. Various factors can be these gaps, for example:
- a single average type of sorbing particles is considered, their characteristics are little known and considered constant along the estuary
- processes which could be important in certain parts of the estuary (for example: coprecipitation with sulphides in anoxic zones, phytoplanctonic activity in the upstream part) were not taken into account.

The presented approach should be based, in an operational purpose, on the knowledge of numerous parameters estimated on the field or from laboratory experiments. The requirement is to be able to reduce at most the degrees of freedom of the model. A use of this model, in a purpose of forecast, requires a coupling to hydrosedimentary transport models [11 , 13] which reproduce accurately the spatio-temporal distribution of variables (salinity, SM) necessary for the calculations of trace metals speciation.

Acknowledgments

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