Mobility of trace metals in freshwater sediments: a modelling coupling solid-liquid exchanges, biogeochemical reactions and interstitial diffusion

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INTRODUCTION

In freshwater systems, trace metal pollutants are transferred into water and sedimentary columns under dissolved forms and fixed onto solid particles. Accumulated in the sedimentary areas, these latter ones can constitute important stocks of matters and associated pollutants. The mobility of the stocks of pollutants is mainly depending on the erosion, on the interstitial diffusion of the mobile phases (dissolved and colloidal) and on the bioturbation. In this context, this communication presents an analysis of the mobility by interstitial diffusion by comparing experimental results and modelling.

This topic involves two main points: 1) Trace metal fractionation between their mobile (dissolved and colloidal) and non mobile (fixed onto the particles) forms; 2) Interstitial diffusion of the mobile phases.

The first point is governed by sorption/desorption processes at the particle surfaces. In the sedimentary column, these processes are regulated by physico-chemical parameters as pH, potential redox, concentrations and nature of particles. In sediments, these parameters are mainly influenced by biochemical reactions resulting from the oxidation of the organic matter by the microbial activity: oxic respiration, denitrification, manganese hydroxides and iron hydroxides reduction, sulphate reduction, methanogenesis (Froelich, Klinkhammer et al. 1979). In this context, this work proposes a model coupling these biogeochemical reactions to sorption/desorption processes of trace metals and interstitial diffusion. In order to evaluate this model an experimental protocol has also been developed to obtain the vertical distributions of the predominant physico-chemical parameters and solid-liquid fractionations of metals (Fe, Mn, Co, Cu, Ni, Pb, Zn) in natural sediment cores. The first comparisons realised on cores collected in the Durance and Rhône rivers allows to identify the gaps and the efficiencies of the modelling approach.

MODELLING

The modelling procedure follows four steps:

1) Biogeochemical reactions,
2) Evolution of pH in the sedimentary column,
3) Solid-liquid fractionation of trace metals in the sedimentary column,
4) Interstitial diffusion of the mobile phases.

1) Biogeochemical reactions

The aim of the biogeochemical model is to provide the vertical evolutions of the chemical conditions along the sedimentary column. This model considers 21 chemical species divided in two categories: mobile phases including dissolved and colloidal forms and non mobile phases associated to solid particles as clays. The vertical variations of these species and of their forms are written under the general equation given by Berner (1971):

$$\boxed{\frac{\partial C}{\partial t} = \sum \textbf{\textit{Biogeochem ical Reactions}}}$$

The reactions are modelled according the approaches developed by Wang and Van Cappellen (Wang and Van Cappellen 1996; Van Cappellen and Wang 1997; Wijsman 2001). It considers the primary reactions of organic matter oxidation (aerobic respiration, denitrification, Mn oxide reduction, Fe oxide reduction and sulphate reduction) and the secondary reactions that are the precipitation of carbonate and sulphide phases with dissolved Fe and Mn and the eventual re-oxidation by O_2. In our case, the model has been completed with the geochemical processes of calcite dissolution.

For the primary reactions, the kinetic are based on Michaelis-Menten kinetics: the rate of each degradation pathway is not only depending from the reactivity of organic matter but also from the availability of the electron acceptor (Van Cappellen and Wang 1997).
For the secondary reactions, bi-molecular reaction rate laws are used to describe the reactions kinetics (Wang and Van Cappellen 1996; Rickard and LutherIII 1997; Rickard 2006).

2) Evolution of pH

pH is required to determine the trace metals fractionation between their dissolved and particulates form. Contrary to Wijsman et al (2001), pH is not here considered as a forced function. It is calculated from the ionic species concentrations issues from the resolution of the biogeochemical reactions previously described. From these concentrations, pH is determined by considering acido-basic equilibrium, mass conservation and electroneutrality.

3) Solid-liquid exchanges of trace metals:

The modelling of the solid-liquid exchanges is performed for five trace metals: Co, Cu, Ni, Pb, Zn. The main hypothesis is that these processes can be considered at the equilibrium because they are faster than the biogeochemical reactions and the interstitial diffusion. This hypothesis conducts to write the equilibrium ratio between the concentration of the metal under its dissolved $[Me]_D$ ($mol.L^{-1}$) and particulate forms p $[Me]_P$ ($mol.kg_{dry}^{-1}$):

$$Kd(Me)_P = \frac{[Me]_P}{[Me]_D}$$

These coefficients are depending on the pH deduced from the resolution of the biogeochemical model and on the trace metals and particles couples. The considered particles are oxides of iron and manganese under their colloidal and particulate forms, clays, precipitates of carbonates and sulphide and particulate organic matter.

4) Interstitial diffusion

The interstitial diffusion along the sedimentary column concerns the dissolved and the colloidal forms of the biogeochemical and trace metals species. This process is described by the first Fick's law (Boudreau 1997; Boudreau 1999):

$$\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial z}\left(D_{sed} \cdot \frac{\partial C_D}{\partial z}\right)$$

Where, D_{sed} ($m^2.s^{-1}$), the coefficient of interstitial diffusion, is given by:

$$D_{sed} = \frac{D_{sw}}{1 - \ln(n(z)^2)}.$$

In this relation D_{sw} ($m^2.s^{-1}$) is the coefficient of molecular diffusion in water and n(z) is the porosity, which is given in our case by the calibration of the Athy's relation (Boudreau 1997) on the experimental data:

$$n(z) = n_\infty + (n_0 - n_\infty)\cdot e^{-\tau\cdot z}$$

Where, n_0 and n_∞ are respectively the porosities at the sediment water interface and at infinitive depth and τ is the attenuation coefficient (cm^{-1}).

EXPERIMENTAL METHOD

The relevance of the modelling approach is determined by confrontations with empirical data. Achieve this one must be applied an experimental protocol, able to measure the vertical distributions of the main physicochemical parameters and of the solid-liquid fractionations of metals along cores of natural sediments. This experimental protocol is divided in four parts:

1) Sampling of natural sediment cores in rivers.
2) Analysis of the vertical profiles of pH, redox and dissolved O_2.
3) Under nitrogen-saturated atmosphere, vertical sectioning of the cores and separation of pore water and solid sediment of each layer.
4) Analysis of each phase: organic matter (TOC analyser), nutriments (Ionic Chromatography, metal contents (ICP-AES), grain size distributions (size analyser), density of the solid matter, water contents and porosity.

APPLICATIONS TO DURANCE RIVER SAMPLES

As illustration, this paper presents an application of the model and of the experimental protocol to natural sediment cores collected in the Durance Rivers in July 2007. Figure 1 shows that the sediment becomes totally anoxic from 2 cm of depth. The conditions become more and more acid owing to the mineralization of the organic matter. These physicochemical changes cause the reduction of manganese hydroxides. Dissolved manganese can then diffuse towards the oxic zone where it can be re-precipitated into oxide or precipitated with carbonate. The model reproduces correctly these behaviours (Fig. 1).

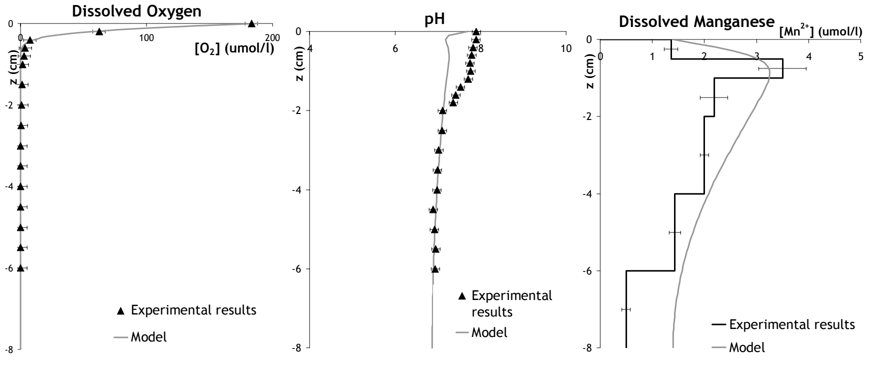

Fig.1*: Profiles of dissolved oxygen, pH and dissolved manganese*

Figure 2 shows that the behaviour of nickel is mainly depending on manganese (profile of dissolved Ni is similar to Mn profile). The sequential extraction shows that fixed Ni is principally associated to manganese oxides. Consequently, the reduction of manganese involves the release of absorbed Ni. The released Ni can then diffuse towards the oxic zone where it can be sorbed again onto the particles or associated to carbonate phases by coprecipitation. At the image of nickel, the transfers of trace metals in sediments are principally associated to the behaviours of Mn and Fe oxides and carbonated and sulfurized phases. The objectives of the study are the simulation of the ratio between fixed and dissolved metal. The first step has thus consisted in the identification of the main processes of liquid-solid exchange for each studied trace metals.

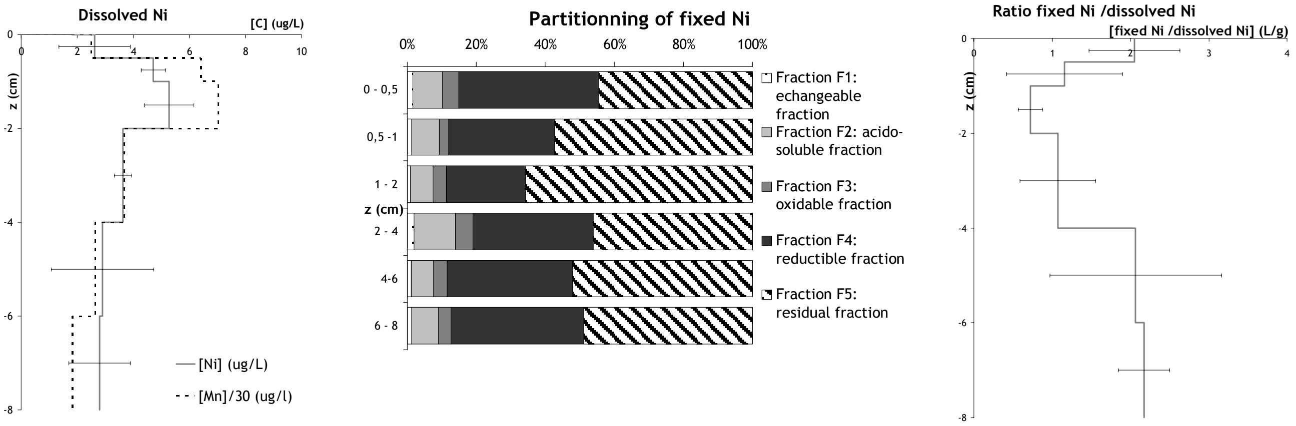

Fig.2: *Behaviour of Ni in the sedimentary column.*

CONCLUSIONS

A modelling and an experimental protocol dedicated to assess the interstitial diffusion of trace metals in sediments are still in a step of development. This paper presents their first applications to natural sediment cores collected in the Durance river. The results show that the model describes correctly the vertical behaviour of nutrients and pH. The next step of these developments will be the achievement of the modelling of solid-liquid fractionation of trace metals (Co, Cu, Ni, Pb, Zn).

This global approach is developed in view to analyse the behaviour of trace metals in freshwater sediments and to help to the improvement of the parameterization of operational and simpliest approaches.

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