



Modelling trace metal transfer in large rivers under dynamic hydrology: A coupled hydrodynamic and chemical equilibrium model



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ABSTRACT

Trace metals (TMs) in rivers experience a complex chemistry that affects their partitioning between the dissolved and particulate fractions. Predictive modelling of this partitioning is challenging, particularly under variable hydrodynamic conditions in rivers. This paper presents a coupled hydrodynamic–geochemical model for trace metal dynamics in rivers, to highlight key parameters and set a basis for developing simplified models. A coupled model based on the hydrodynamic model MOHID and the chemical speciation model WHAM was applied to the middle part of the Garonne River (SW-France). The predictions of the coupled model are compared to those of a fixed K_d partitioning model.

The model accurately simulates trace metal behaviour under varying hydrological conditions. The importance of the riverbed geomorphology and the diurnal variations in pH on TM concentrations in the water column are underlined. The sensitivity analysis ranked all physico-chemical parameters according to their influence on TM behaviour.

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1. Introduction

Rivers are a preferential pathway for solid and dissolved material export from continents to oceans. Therefore, they are susceptible to high input fluxes of pollutants from the watershed. One class of such pollutants comprises the trace metal elements (TMs) which, in contrast to many other classes of pollutants, are highly persistent in sediments since they cannot be degraded and they provide a delayed source of contamination to the river by leaching and erosion. TMs are also a potential risk for human and ecosystem health (Oliver, 1997). In order to assess their toxicity, it is important to consider not only the dissolved concentration in the water (Caruso et al., 2008; Di Toro et al., 2001), but also the chemical speciation of the TMs. Furthermore, even if a significant fraction of complexed TMs is not readily bioavailable, these complexes can also react rapidly to changes in physicochemical conditions and act as a buffer on the free metal concentration (Di Toro et al., 2001).

Transport of TMs in river follows different pathways depending on physicochemical form. Dissolved and colloidal TMs are transported with the bulk water flow with a contribution of diffusion. The presence of transient storage zones, such as dead arms or the hyporheic zone, can induce more complex patterns of dispersion in the water column (Bencala and Walters, 1983; Bottacin-Busolin et al., 2011; Runkel et al., 1999). TMs bound to suspended particulate matter (SPM) are transported with the flow, but may also deposit to the riverbed. Deposited material may itself be subsequently eroded. The association of TMs and SPM varies a number of factors, including the chemical composition of the water and SPM. Detaching instream biofilm can generate particulate organic matter (Boulètreau et al., 2006; Graba et al., 2012) while many sources of material, organic or mineral, can contribute to SPM loads via runoff erosion (Ludwig et al., 2005) or in-stream erosion (Allen et al., 1999). Overall, however, the organic matter content is often related to the SPM concentration of a river (Meybeck, 1982; Semhi, 1996; Veysy et al., 1996) which, in turn, depends on the river hydrology (Oeurng et al., 2010; Probst and Bazerbachi, 1986; Semhi, 1996). Furthermore, complex river geometry may influence SPM dynamics. Successions of riffles and pools can, under specific hydrological conditions, lead to successive erosion and deposition

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zones (Garneau et al., 2015) while larger hydraulic obstacles such as dams and weirs, create high deposition zones.

The overall partitioning of TMs between the SPM and the water column, expressed as the partition coefficient (Kd), results from the chemical processes affecting TM speciation. The Kd has been extensively documented for most elements (Allison and Allison, 2005) and is, indeed, far from a constant: it varies depending on the chemical composition of the water and the SPM (Cao et al., 2006; Christensen and Christensen, 2000; Dai and Martin, 1995). The variation of the Kd should not be seen as resulting from a single geochemical process, but from a combination of simultaneous binding processes to ligands in the water and on the SPM. Weak binding includes electrostatic sorption (Drever, 1997), for example to fixed-charge clays. Specific binding to stronger adsorbents (e.g. carbonates, organic matter, iron or manganese oxides) can further reduce the mobility of TMs. This gradation of chemical strength between TMs and SPM can be identified by sequential extractions (Leleyter and Probst, 1999; Tessier et al., 1979).

Many different model frameworks can compute the chemical speciation of TMs such as PHREEQC (Parkhurst and Appelo, 1999), MINTEQA2 (Allison et al., 1991), CHESS (Santore and Driscoll, 1995) or WHAM (Tipping et al., 2011a) and thus in principle compute Kds as a function of the water chemistry. At the opposite scale, models working at the river or watershed scale often use very simple partitioning models. The WASP model (Ambrose et al., 1993), for example, implements a fixed Kd while the SWAT model (Neitsch et al., 2009) considers TMs as inert tracers and simulates them by applying mass-balance relationships in the rivers.

Modelling the state of TMs (dissolved or particulate) in natural waters has been the objective of many studies. Complex chemical models have been applied to a wide range of situations, from groundwater quality assessment (Stigter et al., 1998; van Breukelen et al., 2003) to surface water geochemistry (Thorstenson and Parkhurst, 2002), acid mine drainage (Chapman et al., 1983) or to waters characterized by high concentrations of organic matter (Lofts and Tipping, 2000; Weng et al., 2002). These models are usually applied to laboratory experiments since they require a detailed description of the physico-chemistry of the water and of the SPM. One exception is the TICKET model (Farley et al., 2011, 2008) which uses the MINTEQA2 and WHAM V models in a spatial framework with slow dynamics to model chemical gradients (i.e. groundwater, sediment or lake models). Large scale applications have also been performed on samples from rivers (Ji et al., 2002; Lindenschmidt et al., 2006; Lofts and Tipping, 2000; Runkel et al., 1999), lakes (Cao et al., 2006; Farley et al., 2008) and at the soil – water interface (Almàs et al., 2007; Shi et al., 2007) or the sediment – water interface (Caruso, 2004; Perriñez et al., 2004). The models used ranged from very simple fixed Kd to a complex representation of the variability of the Kd using speciation modelling.

Very few studies have attempted to study the detailed geochemistry of large rivers over long time scales (e.g. a year) to integrate varying hydrological conditions and to dynamically predict in-situ partitioning and fate of TMs. To our knowledge, even where regular and relevant measurements exist (Aubert et al., under revision; Davide et al., 2003; Sánchez-Pérez et al., 2006), no study has coupled complex geochemistry with physical processes such as hydrology and hydrodynamics. By coupling speciation and hydrodynamic models, it is possible in principle to dynamically describe TM geochemistry.

Considering the extensive experimental knowledge about the behaviour of TM in rivers and the limited modelling options to simulate TM sorption-desorption under varying hydrological conditions, the objective of this study was to simulate metal transport by coupling a chemical speciation model with a hydrodynamic

model integrating heterogeneous morphology. The WHAM chemical model (Tipping et al., 2011a) and the MOHID hydrodynamic model (Trancoso et al., 2009) were chosen for their physical and conceptual bases. This MOHID – WHAM coupled model was compared with MOHID coupled to a fixed Kd sorption – desorption model. These two approaches were then used to a) evaluate the ability of the coupled model to simulate TM behaviour along a large river exhibiting variable hydrology and morphology, b) evaluate the influence of a variable Kd model on the predicted partitioning between dissolved and particulate phases and its influence on the transport of TMs and c) apply sensitivity analysis to the coupled model to highlight the key parameters and processes controlling the transfer and fate of TMs in a large river.

With the knowledge obtained by the complex coupled MOHID – WHAM model, it will then be possible to propose simpler conceptual models based around the parameters that exert the most influence in describing TM fate in rivers. The considered study site was the Garonne River in its middle course (South-West of France).

2. Material and methods

The coupling of a hydrodynamic model and a chemical model was done in two steps. The first step was to setup the hydrodynamic model. Once the hydraulics, the transport of dissolved elements and the transport, erosion and sedimentation of SPM were calibrated, the chemical model of sorption – desorption was added to describe the behaviour of the TMs. Finally, a series of assumptions were made to provide input to the chemistry model. These assumptions are listed and justified for the case of the Garonne River.

2.1. The MOHID hydrodynamic environment

The hydrodynamic model was generated with the MOHID (<http://www.mohid.com/>) modelling framework written in FORTRAN 95. The River Network module (Trancoso et al., 2009) was used to simulate water flow and TM transport in the river. MOHID implements the full St-Venant equations in one dimension. A modelled river is thus discretized into nodes and reaches, allowing both temporal and spatial modelling. When available, the use of numerous river profiles allows for a fine description of the morphology of the river by describing the river profile and elevation at each node (Sauvage et al., 2003). Calculations are performed using a finite-volume approach and require the calibration of a single parameter, the Manning roughness coefficient, an empirical coefficient which depends on a number of factors such as the surface roughness or vegetation affecting the flow.

Two modules of MOHID were activated to transport TMs, namely the transport of suspended elements through advection – dispersion, and the erosion and deposition of SPM. Following Garneau et al. (2015), the transient storage model One-dimensional Transport and Input Storage (OTIS) was added to the River Network model (Bencala and Walters, 1983). OTIS is a conceptual model which considers a storage zone under the river. Exchanges between the river and the storage zone are strictly vertical and depend on two parameters, namely the exchange rate α (s^{-1}) and the cross section of the storage zone A_s (m^2). The variation of concentration in the river and the storage zone is driven by equations (1) and (2).

$$\frac{dC}{dt} = \alpha(C_s - C) \quad (1)$$

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