

Modelling multi-pollutant fate in a large river: Role of hydro-morphological and physicochemical parameters

**Cyril Garneau^{1,2}, Sabine Sauvage^{2,1}*, José-Miguel Sanchez-Perez^{2,1}, Yi Hong¹,
², Dominique Aubert^{3,4}, Anne Probst^{2,1}**

¹ Université de Toulouse; INPT, UPS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement), Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT), Castanet Tolosan, France

² CNRS; EcoLab (Laboratoire Ecologie Fonctionnelle et Environnement), Castanet Tolosan, France

³ Univ. Perpignan Via Domitia, Centre de Formation et de Recherche sur les Environnements Méditerranéens, UMR 5110, F-66860, Perpignan, France

⁴ CNRS, Centre de Formation et de Recherche sur les Environnements Méditerranéens, UMR 5110, F-66860, Perpignan, France

*sabine.sauvage@univ-tlse3.fr

Abstract: European rivers are facing multiple sources of pollution, including metals, pesticides and nutrients. To understand the factors controlling their transport, modelling can be used to predict their fate. Usually, however, only one class of components is considered, often neglecting inner interactions. This paper proposes a methodological approach towards understanding the main processes describing the fate of trace pollutants interacting with hydrological processes and suspended solids. The model is evaluated in the middle course of the Garonne River in France and developed in three stages, each integrating a new type of process. The first describes the hydromorphology of the sector studied and transport processes. The second adds the sorption-desorption of metals onto suspended solids in the water. The third and final stage makes the organic matter reactive, and therefore produced and consumed along the river. The influence of each process is quantifiable at each stage. Preliminary results for one data set suggest that the concentrations of two metals in the river cannot be explained by hydrodynamic processes alone. Furthermore, during low water conditions, many metals correlate significantly with dissolved organic carbon or particulate organic carbon, whereas these correlations do not exist during flood events. A contaminant model must therefore include hydrodynamics, sorption and organic carbon production and consumption.

Keywords: modelling; hydromorphology; organic matter; biogeochemical model; metals

1 INTRODUCTION

River contamination by heavy metals, pesticides and nutrients is a major environmental problem in European rivers. Several case studies have indicated that pollutant concentrations exceed critical limits, thus threatening the whole ecosystem along the food chain, including human water uses.

Modelling has been used for many years to predict water quality [Vanrolleghem *et al.*, 2001; Gassman *et al.*, 2007; Cole and Wells, 2008; Trancoso *et al.*, 2009; Brunner, 2010]. However, most models have only tackled a specific element or

single family of contaminants (nutrients and, more rarely, pesticides or heavy metals) and have not explored the combination and interrelations between these families. Moreover, little attention has been paid to environmental factors, such as river hydromorphology and physicochemical parameters, to explain the fate of multiple pollutants.

River processes are highly non-linear and pollutant transport is heavily linked to hydrology [Brunel *et al.*, 2003; Oeurng *et al.*, 2010], morphology [Bonvallet Garay *et al.*, 2001] and physicochemical conditions [Salvarredy-Aranguren *et al.*, 2008]. Dynamic modelling is therefore the solution to tackling the system's complexity.

Metals in the river can be considered as conservative tracers since they can change chemical form, but cannot be degraded by microbiological processes occurring in a river. However, metals are far from being inert in a river and any prediction of their fate must be undertaken with care. Dissolved/adsorbed metal partitioning has been tentatively modelled by speciation models such as MINTQA2 [Allison *et al.*, 1991], WASP [Ambrose *et al.*, 1993], WHAM [Tipping, 1994] or the Surface Complexation Model [Pokrovsky *et al.*, 2012]. These models allow the use of well-known equations such as the constant equilibrium K_d or the Freundlich or Langmuir equations. If adsorption is often assumed to be onto Al-Fe-hydroxides, "natural" waters are very rich in organic matter which is a great adsorbent [Tipping, 1994]. In this context, the WHAM model applied to rivers only considers interactions between metals and humic and fulvic acids, neglecting aluminium and iron oxides. While dissolved organic carbon (fulvic and humic acids) is a good adsorbent, particulate organic carbon cannot be ignored for major rivers. In order to model metal behaviour in rivers and its transport, either organic matter has to be considered as an inert input parameter or its fate modelled, for example using nutrient models.

The RWQM [Vanrolleghem *et al.*, 2001], Ce-Qual2 [Cole and Wells, 2008], PROSE [Even *et al.*, 1998] and WASP [Ambrose *et al.*, 1993] models simulate the fate of nutrients in rivers. Such models predict the evolution of nutrients such as nitrogen, phosphorus, carbon and biomass, but only consider the limited physicochemical parameters of the water, usually stopping with proxies, such as dissolved oxygen for the oxydo-reduction potential or alkalinity as an indicator of pH. Since nutrient modelling and metal modelling usually attempt to answer different questions (mainly eutrophication for the former and toxicity for the latter), both categories are rarely modelled in one single model with the exception of the WASP model. However, even in the WASP model, the user has to choose which modules to activate, namely the EUTRO module for biogenesis, and the TOXI module for toxicants.

Finally, the behaviour of trace contaminants, such as metals, cannot be described solely through nutrients and the sorption of metals onto organic matter. As observed by Oeurng *et al.* [2010], 85% of suspended matter can be transported during the flood event period, which accounted for 16% of the year in the Save river, a Garonne tributary.

Therefore in order to model the fate of metals, it is important to take into account (i) the hydrodynamic (hydraulic and transport) characteristics (the physical model); (ii) metal sorption onto organic carbon (the sorption model) and (iii) the fate of organic carbon (the biogeochemical model), since these are essential factors and processes in a river.

The objective of the study is to propose a methodology based on experimental and modelling approaches (i) to highlight the controlling factors (hydraulic, morphology, transport and physicochemical parameters) that can explain the fate of the multi-pollutants and their interactions (organic matter and metals) and (ii) to incorporate these relationships into dynamic modelling that integrates the system's complexity.

As a first step, the focus is on the effect of hydrology and morphology on the transport of metals.

2 METHODOLOGY

2.1 Study site

The Garonne River, a seventh-order river and the third largest river in France, is studied in its middle course near the city of Toulouse (south-west France). The Garonne River watershed is sourced in the Pyrenees and characterised by intensive agriculture in the alluvial flood plain. The river hydromorphology is characterised by a succession of gravel beds and deep water. It also has frequent meanders [Descy, 2009]. The hydraulic characteristics are very variable. For example during low water periods, flow velocity ranges from 0.3 m.s⁻¹ to 1.3 m.s⁻¹ and water height ranges from 0.1 m to 2.7 m [Sauvage *et al.*, 2003]. Finally, due to the shallow depth and presence of gravel beds, the epilithic biofilm growing on the river gravel beds is the primary source of organic matter [Boulêtreau *et al.*, 2006]. The middle course under study starts just before the city of Toulouse and continues for 80 kilometres. The mean annual discharge is around 200 m³.s⁻¹. Many small tributaries contribute to the Garonne. However, while their flows are negligible (up to 7 m³.s⁻¹), their contribution to pollution fluxes are not.

2.2 Data set

The model being developed is based on two data sets. The first consists of a tracer test conducted during 2007 and 2008 [E.A.T.C and SETUDE, 2008]. Conservative tracers (rhodamine and fluoresceine) were used to describe the behaviour of the river water under different hydrological conditions along the section studied. Three conditions were monitored, namely the low water flow (under 120 m³.s⁻¹ at the inlet and under 200 m³.s⁻¹ at the outlet of the section), medium water flow (180 m³.s⁻¹ at the inlet and 600 m³.s⁻¹ at the outlet) and a flood event (over 300 m³.s⁻¹ at the inlet and over 900 m³.s⁻¹ at the outlet).

The second data set was gathered during 2004 and 2005 where longitudinal profiles were sampled over an 80 km stretch of the Garonne River [Sánchez-Pérez *et al.*, 2006]. Physicochemical properties, biological nutrients and various metals (Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Mo, Cd, Sb, Pb and U) were measured. Two series of measurements were performed during a low water flow and a flood event with mean discharges at the outlet of 79 m³.s⁻¹ and 804 m³.s⁻¹. In all, ten points on the river and six tributaries were sampled for each profile.

Within the scope of this work, all the data was used to perform a statistical analysis and a subset of two metals was chosen to simulate a steady state. Cadmium (Cd) and lead (Pb) were selected because of their contrasting combinations with the dissolved fraction and the particulate matter respectively. Lead is therefore very sensitive to settling and resuspension.

2.3 Physical-based model

The physical-based model aims to isolate the influence of the hydromorphology by modelling the transport and settling of metals.

Three processes have to be included in this stage: the hydraulic equations, the advection-diffusion equations and the settling/resuspension of suspended solids. The equation considered is the St-Venant equation (a 1D-simplification of the Navier-Stokes equation) based on mass and momentum conservation. The St-Venant equation is calibrated with over 200 profiles from the Garonne River [Sauvage *et al.*, 2003].

Once the hydraulic model is calibrated, the movements of dissolved and suspended fractions are described by the advection/diffusion equation (1).

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + R \quad (1)$$

In equation (1), C is the concentration ($\text{g}\cdot\text{m}^{-3}$) of the soluble, U the flow velocity ($\text{m}\cdot\text{s}^{-1}$), D the diffusion parameter ($\text{m}^2\cdot\text{s}^{-1}$), R the reaction term ($\text{g}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$), t the time and x the position along the river.

The reaction term, R , can include decay or production equations. It can also include temporal effects not described by the advection/diffusion equation as transient storage. This storage includes water accumulating in dead ends or infiltrating the benthos, and has been successfully described by Runkel *et al.* [1999].

Once the hydrodynamic model is calibrated for hydraulic, advection/diffusion and settling/resuspension processes, it is possible to build a dynamic model that considers physical processes alone. If the observations can be explained by the hydrodynamic model, there is no need to complexify it further. However if there is a difference, the next stages in the modelling will attempt to explain it.

2.4 Adsorption/desorption model

The second stage in the development of the model is to add a sorption/desorption model. The partition between dissolved and particulate phases was significantly different for many metals depending on hydrological conditions. Some particulate phases were up to 20% greater during flood events. Therefore, a complex sorption model is required. Different codes are available (*e.g.* MINTEQA, WHAM, WASP, *etc.*) as well as many submodels, ranging from a simple K_d model, which can be either constant or linear with respect to pH or suspended solids (requiring one to three parameters) to the complex Humic Ion-Binding Model, proposed by Tipping [1994], which requires six parameters.

Since adsorption in natural waters is heavily dependent on the content of organic matter [Tipping, 1994], it is expected that viewing organic matter as inert (*i.e.* not being produced or consumed) will lead to significant inaccuracy, implying the need for a third layer of modelling.

2.5 Biogeochemical model

The final modelling stage in the attempt to build a multi-contaminant model is to add a biology component. Since metals adsorb strongly onto dissolved and particulate organic carbon (DOC and POC), these two components are the most important for modelling. Furthermore, organic carbon (OC) can be divided in two classes, namely labile OC and refractory OC. Labile OC is characterised by a fast decay dynamic and is mainly composed of epilithic biofilm produced in stream. Refractory OC decays much more slowly. Its principal source is the watershed soil erosion transported by run-off. Although various definitions exist, the CE-QUAL model considers labile OC as “fresh” OC in the sense that its decay will lead to the production of refractory OC. Of course, in the water all four forms, labile POC and DOC and refractory POC and DOC will be found.

These four forms are important. Labile OC serves as transient transport before being degraded or leaving the river section studied. Meanwhile refractory DOC might be considered an inert component over a river reach because of its long degradation time (CE-QUAL default decay parameters propose a half-life value of around 700 days). Suspended refractory POC can transport metals via adsorption processes, but once settled will act as a sink for metals. Although the bed sediments might be a source of metals for river water [Brunel *et al.*, 2003; N'guessan *et al.*, 2009], the first hypothesis was to consider this flux as negligible.

2.6 Simple steady state model for dissolved elements

The need for a complex model can be demonstrated by a simple mass-balance approach at steady state. During such conditions, the metal fluxes to the river section being modelled are constant, which allows neglecting transport equations of

advection and diffusion. Therefore a mass balance was performed on the two metals, Cd and Pb, which takes into account the fluxes from all tributaries along the section under study. This mass-balance was compared to observed data from the low water on 11 October 2005 and can be seen in the results.

2.7 Principal Component Analysis

Two Principal Component Analyses were performed on the profile of the Garonne River: the first during the low-water event of 11 October 2005 and the second on the profile of the flood event of 18 May 2005. In each case, eight physicochemical parameters (discharge, pH, dissolved oxygen, conductivity, turbidity, suspended particulate matter, DOC and alkalinity) and twenty-three chemical species (Si, Mg, K, Ca, Na, Cl, NO₃, SO₄, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Sb, Pb, U and Mo) were included. Cadmium was only considered in the low-water flow analysis as too much data on the flood event was missing. The data was centred and normalised to remove the units' bias.

3 PRELIMINARY RESULTS

3.1 Simple steady state model

Field measurements during low water occurred 20 days after the last precipitation. It can therefore be assumed that a steady state was attained. The profile of dissolved cadmium fluxes is plotted along the middle course of the Garonne for measured and predicted values (Figure 1). The modelled and measured data include the fluxes from tributaries. Between points 1 and 2, the biggest tributary (the Ariège river) enters the Garonne river before Toulouse with a net flux of Cd and Pb of 0.40 mg.s⁻¹ and 1.67 mg.s⁻¹ respectively. At point 3, the station is after Toulouse.

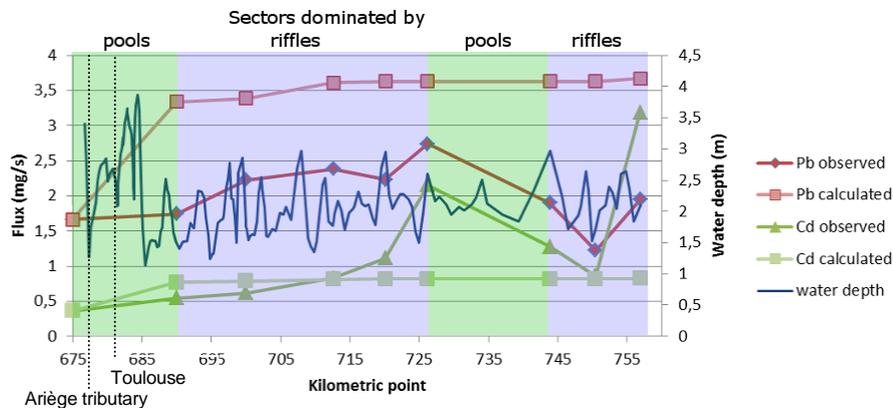


Figure 1. Modelled and observed dissolved fluxes of cadmium and lead transported along the Garonne River profile and water height, during a low water flow period of 80 m³/s at the outlet.

The results show that the trends for simulated and measured fluxes of Cd and Pb are convergent when the elements transported cross rapid and low-water depth sections in the second zone dominated by riffles. However, the fluxes are different and far from a steady state calculated by mass-balance when the elements cross the most lentic zones with a high water depth (zones dominated by pool characteristics) along the river profile and when the elements are transported in the last section dominated by rapid zones. The input fluxes from the tributaries cannot account for these variations.

The water height shows two deep zones, around Kilometric Point (KP) 690 and between KP 726 and 743. The first zone corresponds to the city of Toulouse where the river is canalised with different dams (high-water depth around 1.7 m and low

velocities). The second zone corresponds to a lentic zone before the Malause Reservoir at the end of the sector under study. These two zones correspond to the greatest mismatch between the model and the observations and can be linked to high sedimentation zones. The peaks of both species at KP 726 and KP 756 are also intriguing, since no tributary flux can contribute significantly and explain the fluxes observed.

Since the sediments should not be resuspending, the most probable explanation is that physicochemical conditions allow significant solubilisation of both metals trapped in the sediments. This zone is located just before the influence of the Malause reservoir.

3.2 Principal Component Analysis

Figure 2 (low waters) shows that DOC is highly correlated with the first axis. Furthermore, some species (Mo, Co, V, U, Sb, NO₃, As, Sc, Mn and Si) are correlated with DOC. The first group corresponds to metals mainly found in the dissolved fraction [Sánchez-Pérez *et al.*, 2006] with a high affinity to DOC. The second group (Al, Pb, Ca, SO₄) is correlated with suspended solids and discharge. Indeed, pH and redox potential are also significantly linked to the first axis. Since pH is a major parameter involved in sorption/desorption processes, its role cannot be excluded. Finally, it is worth noting that 50% of the variance of data is explained by the first axis.

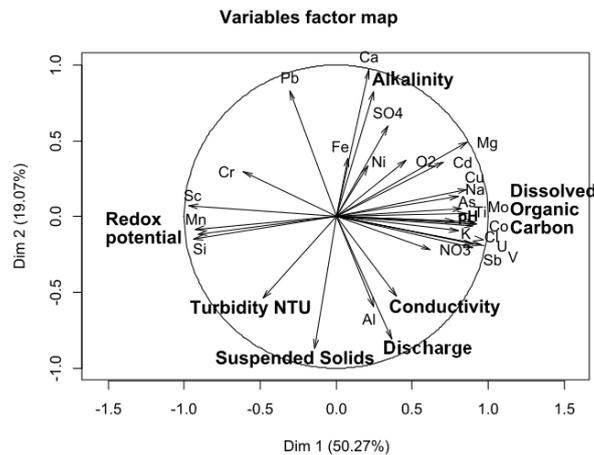


Figure 2. Principal Component Analysis of the data during low water flow in the Garonne River

While the first axis is linked to DOC, pH and redox potential, the second axis mostly mimics the information on discharge with the associated increased in physical parameters (turbidity, suspended matter *etc.*). On the opposite side of this axis, the link to alkalinity and calcium illustrates low discharge conditions and the dilution/concentration process. While an increase in discharge is also an indicator of the river going down, it is worth noting that the variables on the first axis are not overly influenced by their position along the river. In contrast, the metals mainly associated with the second axis mostly decrease with an increase in flow, pointing out the potential sedimentation in the course of the river, or at least a dilution since only concentrations are considered here. This point is well illustrated on the one hand by the positive relationship between particulate matter and discharge and on the other by the negative correlation with dissolved Pb. Finally, metals like Cr, Fe, Ni or Al are partly correlated with the two axes and thus cannot be clearly interpreted with respect to these axes.

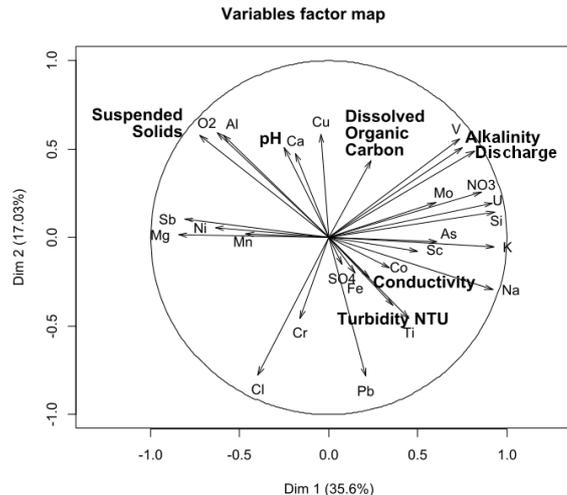


Figure 3. Principal Component Analysis of data during the 18 May 2005 flood event in the Garonne River.

The flood event conditions give a very different pattern (Figure 3). The variance explained by the two axes is less significant than during low-water flow conditions (53% versus 69%). No physicochemical parameter can be linked directly or significantly to the first axis and the variables are more divided. Many parameters are positively linked to axis 1, but discharge, suspended solids and alkalinity seem to be significant driving factors. Being halfway between the first two axes, they are good candidates for explaining the variability of Al, V, NO₃, U, Si, K, Na, Pb, Cl, Mg and Sb, whose variances are almost entirely explained by the two first axes. Lead is negatively correlated with the suspended solids, and the positive correlation with chloride suggests the probable strong influence of the dilution process. It is also worth noting that there is not a significant link between DOC and the components in the first two axes.

4 CONCLUSIONS

The transport of trace pollutants, such as metals in river water, cannot be modelled without an overview of the system at hand. It is now necessary, therefore, to consider the river and all the major processes affecting it. While PCA suggests that hydrodynamics are the major driving processes during flood events, this is not so true during low-water events. In these cases, sedimentation seems to capture a significant fraction of the lead in some sections, while other sections release large amounts. Therefore, the morphology seems to act on the physicochemical parameters driving the sorption/desorption of the metals.

This first study coupling modelling and measurements tested the approach and the first hypotheses on the effect of hydromorphology and physicochemical processes. It is now essential to demonstrate the role these processes play by integrating biotic and abiotic processes in the modelling approach to improve knowledge of the control parameters driving the transfer of multiple contaminants in rivers.

5 REFERENCES

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Susters: Version 3.0 User's Manual, 1991.
- Ambrose, R.B., T.A. Wool, and J.L. Martin. The Water Quality Simulation Program, WASP5: Model Theory, User's Manual and Programmer's Guide. U.S. Environmental Protection Agency, Athens, GA, US, 1993.
- Bonvallet Garay, S., S. Sauvage, and P. Vervier. Hydromorphological control of

- phosphorus in a large free-flowing gravel bed river: the Garonne River (France). *Regul. Rivers: Res. Mgmt.* 17(4-5): 461–472, 2001.
- Boulétreau, S., F. Garabetian, S. Sauvage, and J.-M. Sanchez-Perez. Assessing the importance of a self-generated detachment process in river biofilm models. *Freshwater Biology* 51(5): 901–912, 2006.
- Brunner, G.W. HEC-RAS River Analysis System – User's Manual. Institute for Water Resources, Hydrologic Engineering Center, Davis, CA, 2010.
- Brunel, C., M. Munoz, and A. Probst. 2003. Remobilisation of Zn and Pb in a mountain stream contaminated by mining wastes during a moderate flood event (Ariège, France). *Journal de Physique IV (Proceedings)* 107: 233–236.
- Cole, T.M., and S.A. Wells. CE-QUAL-W2: A Two-Dimensional, Laterally Averaged, Hydrodynamic and Water Quality Model, Version 3.6. Department of Civil and Environmental Engineering, Portland State University, Portland, OR, 2008.
- Descy, J.-P. 2009. Continental Atlantic Rivers. p. 151–198. In *Rivers of Europe*. Elsevier.
- E.A.T.C. and SETUDE. Etude de la propagation d'une nappe de pollution sur la Garonne. Syndicat Mixte d'Etude et d'Aménagement de la Garonne, 2008.
- Even, S., M. Poulin, J. Garnier, G. Billen, P. Servais, A. Chesterikoff, and M. Coste. River ecosystem modelling: application of the PROSE model to the Seine river (France). *Hydrobiologia* 373-374(0): 27–45, 1998.
- Gassman, P.W., M.R. Reyes, C.H. Green, and J.G. Arnold. The Soil and Water Assessment Tool: Historical Development, Applications, and Future Research Directions. Center for Agricultural and Rural Development (CARD) at Iowa State University, 2007.
- N'guessan, Y.M., J.L. Probst, T. Bur, and A. Probst. 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): Where do they come from? *Science of The Total Environment* 407(8): 2939–2952.
- Oeurng, C., S. Sauvage, and J.-M. Sánchez-Pérez. Dynamics of suspended sediment transport and yield in a large agricultural catchment, southwest France. *Earth Surf. Proc. Land.* 35(11): 1289–1301, 2010.
- Pokrovsky, O.S., A. Probst, E. Leviel, and B. Liao. Interactions between cadmium and lead with acidic soils: Experimental evidence of similar adsorption patterns for a wide range of metal concentrations and the implications of metal migration. *Journal of Hazardous Materials* 199-200: 358–366, 2012.
- Runkel, R.L., K.E. Bencala, and B.A. Kimball. Modeling Solute Transport and Geochemistry in Streams and Rivers Using OTIS and OTEQ. p. 120–127. In D. W. Morganwalp and H. T. Buxton, Charleston, 1999.
- Salvarredy-Aranguren, M.M., A. Probst, M. Roulet, and M.-P. Isaure. Contamination of surface waters by mining wastes in the Milluni Valley (Cordillera Real, Bolivia): Mineralogical and hydrological influences. *Appl. Geochem.* 23(5): 1299–1324, 2008.
- Sánchez-Pérez, J.-M., A. Probst, M. Gerino, S. Sauvage, D. Aubert, D. Devault, M. Tackx, S. Boulétreau, D. Dalger, F. Delmas, J.F. Dubernet, G. Durbe, M. Henry, F. Julien, P. Lim, G. Merlina, M. Mamoudou, E. Pinelli, J.-L. Probst, and P. Vervier. Fluvial transport and transformation of heavy metals, pesticides and biogenic elements in the Garonne river continuum system. In Paris, France, 2006.
- Sauvage, S., S. Teissier, P. Vervier, T. Améziane, F. Garabétian, F. Delmas, and B. Caussade. A numerical tool to integrate biophysical diversity of a large regulated river: hydrobiogeochemical bases. The case of the Garonne River (France). *River Research and Applications* 19(2): 181–198, 2003.
- Tippling, E. WHAMC—A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Computers & Geosciences* 20(6): 973–1023, 1994.
- Trancoso, A.R., F. Braunschweig, P. Chambel Leitão, M. Obermann, and R. Neves. An advanced modelling tool for simulating complex river systems. *Sci. Total Environ.* 407(8): 3004–3016, 2009.
- Vanrolleghem, P.A., D. Borchardt, M. Henze, W. Rauch, P. Reichert, P. Shanahan, and L. Somlyódy. River Water Quality Modelling: III. Biochemical submodel selection. *Water Sci. Technol.* 43(5): 31–40, 2001.