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Significance of floods in metal dynamics and export in a small agricultural catchment

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SUMMARY

High-resolution monitoring of water discharge and water sampling were performed between early October 2006 and late September 2007 in the Montoussé River, a permanent stream draining an experimental agricultural catchment in Gascogne region (SW France). Dissolved and particulate concentrations of major elements and trace metals (i.e. Al, Fe, Mn, As, Cd, Cr, Cu, Ni, Pb, Sc and Zn) were examined. Our results showed that contamination levels were deficient to moderate, as a result of sustainable agricultural practices. Regarding dynamics, metal partitioning between particulate and dissolved phases was altered during flood conditions: the particulate phase was diluted by coarser and less contaminated particles from river bottom and banks, whereas the liquid phase was rapidly enriched owing to desorption mechanisms. Soluble/reactive elements were washed-off from soils at the beginning of the rain episode. The contribution of the flood event of May 2007 (by far the most significant episode over the study period) to the annual metal export was considerable for particulate forms (72–82%) and moderate for dissolved elements (0–20%). The hydrological functioning of the Montoussé stream poses dual threat on ecosystems, the consequences of which differ from both temporal and spatial scales: (i) desorption processes at the beginning of floods induce locally a rapid enrichment (up to 3.4-fold the pre-flood signatures on average for the event of May 2007) of waters in bioavailable metals, and (ii) labile metals – enriched by anthropogenic sources – associated to particles (mainly *via* carbonates and Fe/Mn oxides), were predominantly transferred during floods into downstream-connected rivers.

1. Introduction

Naturally occurring in the earth's crust, trace metals are emitted by human activities (industry, mining, agriculture, cities...) and accumulate in the different compartments of the hydrosphere (Adriano, 2001), both in dissolved and particulate forms. Soils constitute the first repository areas, receiving most of the influx via atmospheric deposition, urban runoff, wastewater, industrial effluents and agricultural practices (Nicholson et al., 2003). Part of them may be available for plants and finally contaminate the food chain, exposing humans to elevated health risks (Oliver, 1997). In the meantime, anthropogenic metals sequestrated in soils during the dry season can episodically be washed-off during rain episodes and flushed to the river, particularly when runoff is important. Their ultimate fate in downstream-connected hydrosystems depends mainly on their form (Sparks, 1995; Jiang et al., 2011). Metals have natural affinities for particles, especially under neutral pH conditions, so that the major part of the river-transported metals is generally associated with suspended particulate matter. However, changes in physico-chemical conditions (pH, redox...) encountered during transport can cause their mobilization in the dissolved phase (e.g. Zwolsman et al., 1997; Elbaz-Poulichet et al., 2001, Brunel et al., 2003, Gundersn and Steinnes, 2003), where they become easily bioavailable. Determining the time and space scales over which these solid-phase metals are desorbed remains a critical factor in evaluating their bioavailability. It is fundamental, therefore, that the riverine transport pathways are well documented and that fluxes of metals are accurately estimated. These requirements can be met with an adequate sampling frequency (Syvitski and Morehead, 1999), especially in heterogeneous, small or medium scale watersheds, where discharge regimes and geochemical parameters are highly variable (Coynel et al., 2007).

To determine the key processes of metal transfer, partitioning and bioavailability, most efforts of researchers have focused on large-size river basins (e.g. Audry et al., 2004; Gaeiro et al., 2003; Ollivier et al., 2011) and estuary/coastal areas (e.g. Zhang, 1999; Roussiez et al., 2011, 2012), due to ever-increasing numbers of people living there and growing anthropogenic pressure on ecosystems. Conversely, little attention has been paid regarding

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small-scale and low population density catchments devoted to agricultural activities, especially on calcareous lands. To increase their crop production and make culture possible in nutrient-deficient lands, farmers commonly use a broad suite of fertilizers and pesticides. These products include a variable proportion of metals such as Cd, Cr, Cu, Ni, Pb and Zn as constituents or impurities (Nicholson et al., 2003). To reduce the risks of environmental and ecological damages, strategies have emerged to reconcile agricultural methods with the principles of sustainable development.

The Montoussé catchment is a small and minimally populated agricultural river basin in the Gascogne region (Southwestern France), with rotation of wheat and sunflower crops. In collaboration with the research laboratories in Toulouse and the GPN society (initially "Société Chimique de la Grande Paroisse"), farmers of the Montoussé catchment have developed over the last two decades a production strategy that fulfills the concept of integrated farming. This area represents therefore a suitable long-term observatory belonging to the French catchment observatory network (RBV). It is driven by EcoLab for measuring both the effectiveness and the benefits of such management practices in terms of contaminant export. In this context, the riverine fluxes of Al, Fe, Mn, As, Cd, Cr, Cu, Ni, Pb, Sc and Zn, both dissolved and particulate, have been reconstructed at the outlet of the Montoussé stream, over a one-year survey (October 2006 – September 2007), with a special emphasis on the environmental/ecological implications. Attention was focused on the significance of the discharge regime in metal yields and the accuracy of their estimates.

2. Materials and methods

2.1. Study area

The characteristics of the study area are fully described in Perrin et al. (2008) and Ferrant et al. (2012). Briefly, the Montoussé river basin (328 ha) is located 35 km west of the city of Toulouse (Southwestern France, see Fig. 1) and lies on a shallow calcareous substratum, which is relatively impermeable owing to its high abundance in clays. Consequently, the discharge of the Montoussé stream is mainly supplied by surface and sub-surface run-off. The thickness of alluvium varies from few cm in the overhanging formations (where Oligo-Miocene molassic deposits – called molasses – nearly outcrops) to a few meters in the lowest zones. The difference in soil elevation between plateau relics and outlet is 100 m.

The hydrological regime is mainly pluvial regulated by rainfall (see also Section 2.3), with a wet period running from October to May. Similar to the other rivers in the Gascogne region, the Montoussé stream undergoes very important inter-annual variations (Probst and Tardy, 1985). Although very small during summer (especially between July and August), the stream is permanent and feeds the Boulouze River, which itself opens into the Save River, i.e. one of the 3 main left-bank tributaries of the Garonne River (647 km length from Spanish Pyrenees to the Gironde estuary in France) draining the Gascogne region (Fig. 1). Importantly for our investigation on trace metals, the waters of Montoussé stream are neutral to alkaline (pH recorded between 2004 and 2006 exhibit a mean value of 8.1, according to Perrin et al., 2008). Calcium and alkalinity (HCO_3^-) are the major ions.

The river basin is characterized by low population density (29 inhab./km^2) and exclusively devoted to agricultural activities: ca. 86% of land cover is wheat and sunflower cultures with cropping management, with the remaining in pasture/grass areas (ca. 5%), woods (ca. 5%) and habitations (ca. 4%). Some general characteristics of the watershed are summarized in Table 1. Note that the annual rainfall measured for the study period (i.e. 640 mm between October 2006 and September 2007) is in line with the average for the last 20 years (i.e. 656 mm, Ferrant et al., 2012). The specific solid discharge of the Montoussé stream estimated in this study at 33.5 (±7.2) t km^{-2} yr^{-1} is in agreement with the value (i.e. 27 t km^{-2} yr^{-1}) given by Probst (1986) for the nearby Girou River, a right-bank tributary of the Garonne River draining a homogeneous

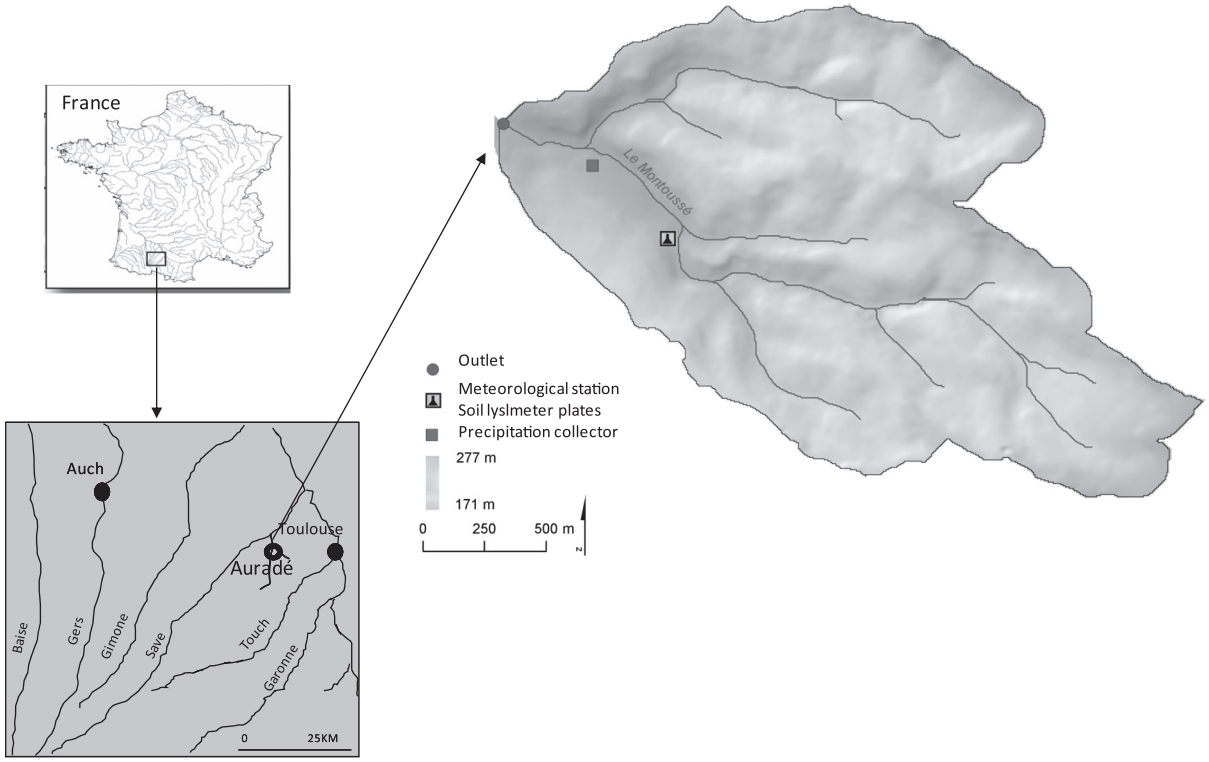

Fig. 1. Geographical location of the study area.