



# Anthropogenic sources and biogeochemical reactivity of particulate and dissolved Cu isotopes in the turbidity gradient of the Garonne River (France)



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## ABSTRACT

High precision MC-ICP-MS Cu isotope measurements were performed on suspended particulate matter (SPM) and filtered water sampled along the turbidity gradient of the fluvial Gironde Estuary (Garonne Branch), following a summer lasting period of low freshwater discharge. High Cu concentrations (up to ~200 µg/g) in particulate organic carbon (POC)-rich (up to ~14%) particles upstream from the Maximum Turbidity Zone (MTZ) coincide with the most negative  $\delta^{65}\text{Cu}$  values (down to  $-0.39\text{‰}$ ). This suggests the preferential uptake of light Cu isotopes by phytoplankton or anthropogenic contamination from  $\text{CuSO}_4$  fungicides related to intensive wine farming in the area ( $\delta^{65}\text{Cu} = -0.37\text{‰}$  for vineyard soils). Suspended particulate matter samples in the MTZ exhibit lower Cu concentrations (~35 µg/g) and heavier isotopic compositions ( $\delta^{65}\text{Cu} = -0.20\text{‰}$  in average), as recorded by other samples from the Gironde Watershed. Along the fluvial estuary, dissolved Cu is mostly enriched in heavy isotopes (up to  $\delta^{65}\text{Cu} = +0.21\text{‰}$ ), but negative signatures down to  $\delta^{65}\text{Cu} = -0.66\text{‰}$  occur near the city of Bordeaux. Release of dissolved Cu was attributed to the mineralization of organic matter with a total addition of ~600 ng/L in the fluvial estuary. Continuously decreasing amounts of dissolved Cu added with distance suggest that the observed Cu release evolved towards completion in the MTZ and contributed to negative values for dissolved Cu isotopes, as modeled by a Rayleigh process. Urban wastewater effluents probably also contribute to both (i) the dissolved Cu addition (10–20%) in the MTZ and (ii) negative Cu isotope signatures. Further work is necessary to assess the respective roles of anthropogenic sources and biogeochemical fractionation processes. Accordingly, the present study provides new insights into the potential of Cu isotopes for fingerprinting sources and mechanisms involved in the biogeochemical cycle of Cu in temperate aquatic environments impacted by anthropogenic activities.

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## 1. Introduction

Copper is a ubiquitous biolimiting micronutrient, involved as cofactor in enzymes and regulatory proteins in all living organisms (Semeniuk et al., 2009). Copper, as a base metal, is an essential economic resource sustaining industrial, agricultural and domestic activities. It becomes one of the most widespread and potentially toxic inorganic contaminants (De Oliveira-Filho et al., 2004) when lost into the environment, causing long-term potential threat to living organisms and aquatic ecosystems (Serra and Guasch, 2009). Once released, Cu is mainly transported to the marine environment by rivers and estuaries, where it can change its chemical forms due to

biogeochemical processes induced by biological activity and/or physico-chemical gradients.

Copper carrier phases are distributed through a continuous range of sizes including particulate, colloidal and dissolved Cu(II) ionic forms (operationally defined as  $<0.2\ \mu\text{m}$ ). Particulate Cu is carried onto SPM which is made of a complex mixture of various mineral phases and living/dead organic matter. All of them are potentially involved in Cu speciation 1) absorbed into living organisms or 2) precipitated/adsorbed onto freshly precipitated mineral and organomineral coatings; or 3) “tightly” bound within the crystalline lattice of detrital particles (Petit et al., 2009).

Copper, along the salinity gradients of estuaries at the global scale (Shank et al., 2004; Waeles et al., 2005; Audry et al., 2007) shows transient, seasonally dependent, conservative and non-conservative behaviors, due to salinity-induced desorption, adsorption and flocculation. These processes affect Cu speciation and are intimately related with primary production and organic matter degradation, owing to the

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high affinity of Cu for dissolved organic ligands (e.g. Gerringa et al., 1998; Wells et al., 1998).

These changes in speciation strongly influence the fate of Cu including its transport, persistence, bioavailability and toxicity. Therefore, studying the significance of Cu stable isotopes and their partitioning between particulate and dissolved phase is of special interest in estuaries affected by anthropogenic activities.

Biological assimilation and chemical precipitation (involving redox and/or non redox processes) may affect the isotopic composition of Cu, forming stronger chemical bonds and showing heavy isotope enrichment in its oxidized state (Balistrieri et al., 2008; Pokrovsky et al., 2008), and/or sorbed onto mineral surfaces (Pokrovsky et al., 2008). Applying results from in vitro experiments to natural systems would imply that particulate Cu in oxic surface waters should be mostly enriched in heavy isotopes if it resulted solely from chemical precipitation. This is in contrast with field data showing (1) heavy isotope enrichment in the dissolved phase of world rivers (Vance et al., 2008), attributed to strong binding dissolved organic ligands and (2) very light isotopic signatures in the particulate phase of the Itchen Estuary. There are also evidences of constant Cu isotopic compositions across the whole size range from 100  $\mu\text{m}$  to 1 kDa by filtration/ultrafiltration of river samples (Ilna et al., 2013), suggesting that there is not yet a clear picture on fractionation mechanisms of Cu isotopes in rivers waters.

Despite these apparent discrepancies between field and experimental data, the increasing amount of Cu isotope applications to environmental sciences (Chen et al., 2008; Petit et al., 2008a; Vance et al., 2008; Bigalke et al., 2010; Thapalia et al., 2010; Bigalke et al., 2011; El Azzi et al., 2013; Ilna et al., 2013) and the conceptual framework on fractionation processes provided by experimental approaches (Mathur et al., 2005; Pokrovsky et al., 2008; Kimball et al., 2009; Navarrete et al., 2011), comfort the promise of using Cu isotopic signatures in estuarine environments. However, in these multi-source, multi-process systems, isotopic studies are challenging and have to rely on well constrained case studies and/or well targeted environmental conditions.

Copper behavior in estuarine environments has mostly been investigated along salinity gradient, but data on Cu in the freshwater reaches of estuaries (i.e. influenced by dynamic tide) are generally scarce, although there is evidence for its high reactivity in these dynamic zones (Jarvie et al., 2000). In fact, during summer long-lasting low freshwater discharge periods, Cu addition occurs in the freshwater reaches of the Gironde Estuary and has been unequivocally related to

the mineralization of organic matter (Audry et al., 2006; Masson et al., 2011).

This study investigates the environmental significance of particulate and dissolved Cu stable isotopes in the Garonne Branch of the Gironde Estuary, under the specific environmental conditions outlined here above. It aims at evaluating the potential of Cu isotopes for tracking (i) different sources within the watershed and (ii) biogeochemical fractionation processes occurring in the fluvial estuary. In addition, the study complements current Cu isotopic data (e.g. Vance et al., 2008) acquired with sampling strategies not specifically designed to capture its non-conservative behavior.

## 2. Environmental setting

The Gironde Estuary (Fig. 1) is a major European fluvial–estuarine system draining about 80,000 km<sup>2</sup>, equivalent to 18% of the metropolitan French land surface. The Gironde system is known for chronic metal contamination due to the former Zn-ore refining industry of Decazeville (Riou-Mort/Lot/Garonne River continuum) that affects the estuary and the inshore coastal areas. This historical pollution still persists due to heavy contamination of reservoir sediments that are important secondary sources of metals (Coynel et al., 2007). In addition, intensive agriculture and wine industry in the watershed are major Cu sources to the Gironde Estuary (Masson et al., 2006), as observed in other river systems (e.g. Brun et al., 1998; Pietrzak and McPhail, 2004; Fernández-Calviño et al., 2008). Moreover, wastewater treatment plants in the urban agglomeration of Bordeaux (~1 million habitants) contribute to a substantial increase of metal concentrations in the Garonne Branch, especially in periods of low freshwater discharges (Deycard et al., unpublished results).

The Garonne River is the third largest river in France in terms of flow, with a catchment area of 56,000 km<sup>2</sup> (over 10% of the area of France). It is the main contributor to the Gironde Estuary with ~60% of the total water flux (28 km<sup>3</sup>/yr) and ~75% of the total SPM fluxes (1.8 Mt/yr) entering the estuary, in average for the period 1999–2009 (Lanceleur et al., 2011). Asymmetrical progression of the tidal wave towards the upstream estuary results in the presence of a Maximum Turbidity Zone (MTZ) with suspended particulate matter (SPM) concentrations in surface water that exceed 1 g/l. In periods of low freshwater discharges the MTZ expands within the Garonne Branch inducing suboxic conditions in the water column. During spring and summer, in conjunction with low turbidities, intense phytoplanktonic blooms may develop upstream from

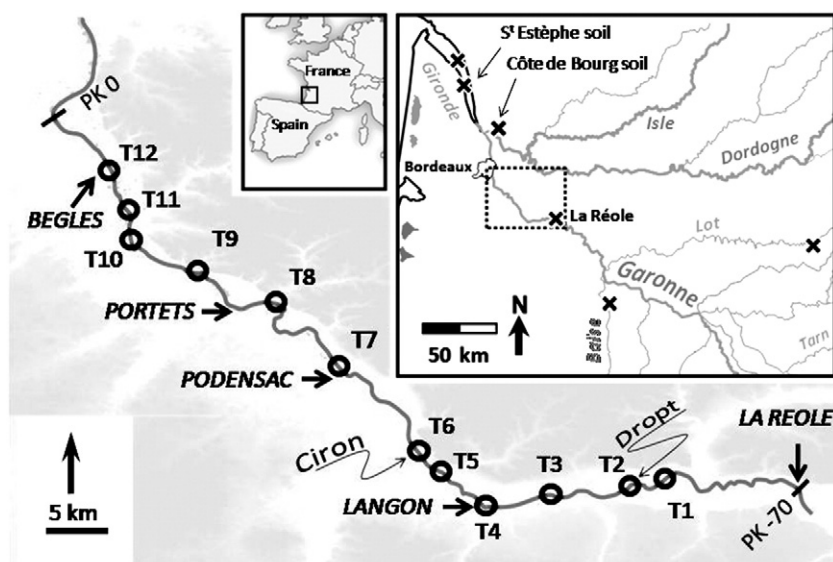


Fig. 1. Study area. Map of the Garonne–Gironde continuum and watershed with sampling locations (circles: longitudinal profile samples T1 to T12; crosses: watershed samples).

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