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Spatial distribution of trace elements in the surface sediments of a major European estuary (Loire Estuary, France): Source identification and evaluation of anthropogenic contribution

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ABSTRACT

Assessing the extent of metal contamination in estuarine surface sediments is hampered by the high heterogeneity of sediment characteristics, the spatial variability of trace element sources, sedimentary dynamics and geochemical processes in addition to the need of accurate reference values for deciphering natural to anthropogenic contribution. Based on 285 surface sediment samples from the Loire Estuary, the first high-resolution spatial distributions are presented for grain-size, particulate organic carbon (POC) and the eight metals/metalloids identified as priority contaminants (Cd, Zn, Pb, Cu, As, Cr, Ni, Hg) plus Ag (an urban tracer). Grain-size and/or POC are major factors controlling the spatial distribution of trace element concentrations. The V-normalized trace metal concentrations divided by the V-normalized concentrations in the basin geochemical background showed the highest Enrichment Factors for Ag and Hg (EF; up to 34 and 140, respectively). These results suggest a severe contamination in the Loire Estuary for both elements. Intra-estuarine Ag and Hg anomalies were identified by comparison between respective normalized concentrations in the Loire Estuary surface sediments and those measured in the surface sediments at the outlet of the Loire River System (watershed-derived). Anthropogenic intra-estuarine Ag and Hg stocks in the uppermost centimetre of the sediment compared with rough annual fluvial flux estimates suggest that the overall strong Enrichment Factors for Ag (EF_{Ag}) and and Hg (EF_{Hg}) in the Loire Estuary sediments are mainly due to watershed-derived inputs, highlighting the need of high temporal hydro-geochemical monitoring to establish reliable incoming fluxes. Significant correlations obtained between EF_{Cd} and EF_{Ag}, EF_{Cu} and POC and EF_{Hg} and POC revealed common behavior and/or sources. Comparison of trace element concentrations with ecotoxicological indices (Sediment Quality Guidelines) provides first standardized information on the sediment quality in the Loire Estuary. The overall mean Effect Range Median quotients (m-ERM-q) results suggested that the Loire Estuary is mainly characterized by slightly toxic sediments even if ecotoxicological impacts have been previously reported on biota.

1. Introduction

Estuaries are among the most productive natural habitats. They are also dynamic transitional environments between continent and ocean, acting as bottlenecks for the transit of the majority of water, erosion/rock-weathering products, contaminants and migrating biological species from the watersheds to the coastal sea. As such, they also constitute ultimate or temporary sediment receptacles. However, because of the increasing urban and industrial development, estuaries are among the most threatened and vulnerable ecosystems in the world (e.g. Robb, 2014). These ecosystems have been facing different degrees of anthropogenic pressures during the last century, especially the pollution with chemical contaminants found in water and sediments, mainly as trace elements (e.g. Zwolsman et al., 1996; Galán et al., 2003; Meybeck et al., 2007; Morelli and Gasparon, 2014; Liu et al., 2016). Estuarine sediments have been identified as key factors in trace element transport from the continent to the ocean, making sediment management an important issue for coastal ecosystem protection (Förstner, 2009). Sediments can act as sinks for metals adsorbed on particles

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accumulating in estuaries. Conversely, they act as sources due to the release of sediment-bound metals by (i) desorption processes and other chemical transformations along the estuarine turbidity, salinity and redox gradients (e.g. Boyle et al., 1976; Elbaz-Poulichet et al., 1987; Boutier et al., 1993; Audry et al., 2006; Dabrin et al., 2009; Lanceleur et al., 2013), (ii) organic matter degradation (e.g. Masson et al., 2011; Petit et al., 2013), and/or (iii) sediment remobilization by anthropogenic (e.g. dredging; Robert et al., 2004) or natural events (e.g. tide effect, flood events; Coynel et al., 2007). These estuarine chemical or physical processes can strongly modify trace element distribution, partitioning budget, and behaviour. Consequently, sediments play an important role in metal cycling in estuarine/coastal environments, inducing potential ecotoxicological impact (Long et al., 1995; MacDonald et al., 1996; Long et al., 1998).

Few published studies investigated trace element contamination in the Loire Estuary, mainly because this system is considered as a less-polluted water-body (Robbe et al., 1985; Rode, 2010) compared with other large French estuaries (Gironde, Rhone, Seine). Previous studies in the Loire Estuary focused mostly on the distribution, speciation and behaviour of dissolved metals along the salinity gradients or in suspended sediments (Frenet, 1981; Figueres et al., 1985; Piron et al., 1990; Seyler and Martin, 1990; Boutier et al., 1993; Négrel, 1997; Waeles et al., 2004, 2009). The chemical composition of bed sediments collected in 11 sites in the Loire Estuary was investigated by Négrel (1997) for nine trace elements (Rb, Sr, Zr, Zn, Pb, Sn, La, Ce and Ba). Results showed a high spatial variability for Zn, Sn, and Pb, explained by a probable adsorption, co-precipitation and/or flocculation onto clay minerals, Fe oxyhydroxides and/or humic acid complexes. The same study also showed that half of the particles exported by the Loire Estuary are of fluvial origin (the other half consists of particles produced in situ in the estuary, e.g. by flocculation/precipitation processes, salting out of organic matter, or primary production which is particularly strong in the Loire Estuary (e.g. Etcheber et al., 2007). A more recent study based on trace element temporal dynamics in a sedimentary archive at the outlet of the Loire River watershed (Montjean-sur-Loire) has revealed a wide range of trace element contamination, resulting from mining, smelting and associated industries as well as from urban sources (Grosbois et al., 2012). In fact, recent metal concentrations in Loire River SPM are still high, compared to the fluvial sediment geochemical background (evaluated from pre-1970 sediment levels) despite a steady decrease in trace element concentrations (except Au) since 1980 as recorded in the sediment cores (Grosbois et al., 2012; Dhivert et al., 2016). The same authors concluded that the Loire riverine system must be considered as moderately to highly polluted for Cd and Hg, due to the metal persistency and additional input in the environment (e.g. from increasing urbanization or recent establishment of an industrial area/manufactory). Finally, the highly industrialized and urbanized Loire Estuary and its watershed are exposed to high anthropogenic pressure area inducing major degradations of ecosystem services and wildlife health (e.g. European eel; Blanchet-Letrouvé et al., 2014; Couderc et al., 2015).

The present work aims at investigating the current state of trace element contamination in the sediments of the Loire Estuary. We present the first high-resolution spatial distribution of concentrations and enrichment factors (EF) for the eight metals/metalloids identified as priority contaminants by the European Community Water Framework Directive (Cd, Zn, Pb, Cu, As, Cr, Ni, Hg; 2000/60/EC; Anonymous, 2000) and Ag (an urban tracer; Feng et al., 1998; Lanceleur et al., 2011a,b; Deycard, 2015) in the estuarine surface sediments along the whole salinity gradient. The trace element concentrations measured in this study were compared with ecotoxicological indices (ERL, ERM, m-ERM-q). The ERL and ERM guideline values define three ecotoxicological levels in chemical concentrations, when adverse effects were rarely (<ERL), occasionally (between ERL and ERM) and frequently expected (>ERM; MacDonald et al., 1996; Long et al., 1998). The pollutant-specific sediment quality guidelines (SQG) were also used for evaluating the possible adverse effects of toxic mixtures by calculating mean Effects Range Median quotients (m-ERM-q). We compare our results to the existing basin-scale geochemical backgrounds (Grosbois et al., 2012; Dhivert et al., 2015a) and ecotoxicological indices (MacDonald et al., 1996; Long et al., 1998) in order to (i) assess the degree of sediment contamination, (ii) identify contaminant sources explaining the observed anomalies, and (iii) delimit areas belonging to distinct sediment quality classes.

2. Material and methods

2.1. Study area and sampling sites

With a surface area of 117,054 km^2 (20% of France; Fig. 1) and a mean annual water discharge of 846 m^3/s varying from 80 to 5500 m^3/s (National water monitoring "Banque Hydro" database; station Montjean-sur-Loire), the Loire River is the longest river in France (1012 km). Before discharging into the Atlantic Ocean, it drains the crystalline bedrock (micaschists, gneiss, granites) of the Central Massif (in the southern part of the watershed), the Armorican Massif (in the western part), and the sedimentary bedrock of the Paris Basin Unit (in the central part), mainly composed of limestones, chalk, marl, and detrital siliceous rocks. The hydrological regime is pluvial, with snow-melt influence in the upper reaches, showing high water discharges in winter with long flood events and severe droughts in summer. Suspended Particulate Matter (SPM) is mostly derived from erosion of the crystalline rocks in the Massif Central during high water discharges. The overall rate of mechanical erosion in the watershed appears weak (~7 $t/km^2/yr$) although spatial variability exists within this territory (3–30 $t/km^2/yr$; Gay et al., 2014).

The Loire Estuary (~80 km long) is a macrotidal system with a maximum tidal amplitude of ~6 m at the mouth (Saint Nazaire; Fig. 1). Despite the large watershed, the estuary has a smaller surface area (~220 km^2) than other French macrotidal estuaries (e.g. Gironde Estuary, 650 km^2). The Loire Estuary constitutes the main source of drinking water for the all-western region of France. The estuarine water residence time was estimated between 3 and 30 days during flood and low water discharge periods, respectively (Gallenne, 1974). The tidal influence and saline intrusion respectively reach areas ~90 km (Ancenis) and 26 km (Cordemais) upstream from the river mouth, during average discharge conditions. The Loire Estuary features a permanent maximum turbidity zone (MTZ) representing a total sediment mass that comprised between 0.5 and 1.1 × 10^6 tons (Migniot, 1993), extending over 20 km on average and oscillating between Cordemais and Paimboeuf (Fig. 1; Migniot and Le Hir, 1994; Jalón-Rojas et al., 2016). The estimated residence time of SPM in the MTZ ranges from 0.7 month during flood events to 6–10 months during low discharge periods (Ciffroy et al., 2003).

The river-estuarine system is exposed to intense anthropogenic pressures from urbanized, agricultural, and industrial areas. The Loire is one of the most eutrophic rivers in Europe (Billen et al., 1986; Meybeck et al., 1988; Moatar and Meybeck, 2005; Etcheber et al., 2007; Minaudo et al., 2015, 2016) due to excess of nutrients and high phosphorus availability (anthropogenic point sources) combined to the river morphology which favours algal development (Minaudo et al., 2015). The large organic content of particles temporarily stored in sediments in the Loire Estuary can undergo microbial degradation after resuspension in the water column, inducing oxygen decrease and sometimes fish mortalities during the summer (Romana et al., 1990; Thouvenin et al., 1994; Abril et al., 2003; GIPLE, 2012). The most important urban areas are located for the fluvial part in the Upper Loire River reach with the Saint-Etienne conurbation (~390,000 inhab.) and in the Nantes conurbation (590,000 inhab.) for the estuarine part. The downstream watershed including the estuarine reach is highly industrialized, comprising (i) the 4th French seaport (Nantes-Saint-Nazaire harbour), (ii) the 2nd refinery (Donges with a capacity of 11.5 million tons/year