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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

Alexandra Coynel <sup>a,\*</sup>, Laureline Gorse <sup>a</sup>, Cécile Curti <sup>b,c</sup>, Jörg Schafer <sup>a</sup>, Cécile Grosbois <sup>d</sup>, Guia Morelli <sup>a,e</sup>, Emmanuelle Ducassou <sup>a</sup>, Gérard Blanc <sup>a</sup>, Grégoire M. Maillet <sup>f</sup>, Meryem Mojtahid <sup>f</sup>

<sup>a</sup> Univ. Bordeaux, UMR CNRS 5805 EPOC, Avenue Geoffroy Saint Hilaire, 33615 Pessac, France

<sup>b</sup> GEO-Transfert, ADERA, 162 Avenue Albert Schweitzer, 33608 Pessac, France

<sup>c</sup> I-Sea, 25 rue Marcel Issartier, BP 20005, 33702 Mérignac, France

<sup>d</sup> Univ. Tours, EA 6293, GéoHydrosystèmes Continentaux, Parc Grandmont, 37200 Tours, France

<sup>e</sup> Univ. Queensland, School of Earth Sciences, St Lucia, QLD 4072, Australia

<sup>f</sup> Univ. Angers, UMR CNRS 6112 LPG-BIAF, 2 bd Lavoisier, 49045 Angers, France

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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 highresolution 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 (EFAg) and and Hg (EF<sub>Hg</sub>) 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.

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#### 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

\* Corresponding author. E-mail address: alexandra.coynel@u-bordeaux.fr (A. Coynel).

http://dx.doi.org/10.1016/j.seares.2016.08.005 1385-1101/© 2016 Published by Elsevier B.V. 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

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 lesspolluted 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 pollutantspecific 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<sup>2</sup> (20% of France; Fig. 1) and a mean annual water discharge of 846 m<sup>3</sup>/s varying from 80 to 5500 m<sup>3</sup>/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<sup>2</sup>/ yr) although spatial variability exists within this territory (3-30 t/ km<sup>2</sup>/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<sup>2</sup>) than other French macrotidal estuaries (e.g. Gironde Estuary, 650 km<sup>2</sup>). 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  $1.1 \times 10^6$  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

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Fig. 1. Location of the study area with major tributaries and cities and map of the sampling sites in the Loire Estuary. The polluted sites and soils are extracted from the map of inventoried contaminated sites (http://basol.ecologie.gouv.fr/recherche.php).

& 230,000 bbl/day of crude oil), (iii) the largest coal-fired thermal electricity production in France (Cordemais), and (iv) various industrial activities (gas storage, aircraft industry, shipyards, etc.). Since 1993, the French Environment Ministry has kept a national register of sites (BASOL database; http://basol.ecologie.gouv.fr/) that have been reported as being actually or potentially contaminated and needing specific government action. Several polluted sites and 3 urban rivers (Erdre, Chezine and Sevre Rivers) are located in the Nantes Conurbation (Fig. 1).

### 2.2. Sampling strategy and analytical methods

A sampling campaign covering the entire Loire Estuary was conducted in September 2012 with the R.V. SURELL (CEREGE, Aix-Marseille) during the SEMHABEL cruise. Two hundred eighty five sediment samples were collected using a Van Veen grab, except for intertidal stations where samples (Fig. 1) were collected by hand at low tide (for more details see Mojtahid et al. (2016)). The uppermost sediment layer (~1 cm) was recovered using a PTFE spatula, placed into polyethylene bags, and stored at 4 °C and in the dark prior to further treatment in the laboratory. Samples were divided into two fractions: a first aliquot was retrieved for grain-size analyses and a second one was dried to constant weight in an oven at 50 °C, powdered and homogenised with an agate mortar for particulate organic carbon (POC) and trace element analyses.

Sediment particle size distribution was determined from fresh with a laser diffraction microgranulometer (MALVERN MASTERSIZER S) covering the range of 0.2–2000  $\mu$ m. The median grain sizes (D<sub>50</sub>) and the relative proportion of clay (<4  $\mu$ m), silt (4–63  $\mu$ m), sand (>63  $\mu$ m) were calculated for each surface sediment. Particulate Organic Carbon (POC) was determined in ~50 mg subsamples of dry and powdered sediment, previously acidified with 2 M HCl to remove carbonates, using a carbon/sulphur analyzer (LECO C/S-230) according to Etcheber et al. (2007) and expressed as POC %. Analytical error was within 5% (Coynel et al., 2005).

Total sediment digestions for particulate trace element analyses (Ag, As, Cd, Cr, Cu, Ni, Pb, Zn, V, and Al) were performed on representative

subsamples (30 mg of dry, powdered and homogenised sediment) in closed PP reactors (DigiTUBEs®, SCP SCIENCE) in a heating block (2 h at 110 °C) with 1.5 ml HCl (12 M Suprapur®, Merck), 0.75 ml HNO<sub>3</sub> (14 M) and 2.5 ml HF (22 M), as described in previous studies (e.g. Schäfer et al., 2002; Larrose et al., 2010). After evaporation to dryness (10 h at 110 °C), re-dissolution of the residues was performed with 0.25 ml HNO<sub>3</sub> (14 M) and 5 ml Milli-Q® water. After cooling, the solution was brought to 10 ml using Milli-Q water. Particulate trace element concentrations were measured by ICP-MS (X7 Series 2, THERMO) performed with external calibration under standard conditions. The analytical method was quality checked with international certified reference materials (IAEA 433; NIST 2702) to verify accuracy and precision. Accuracies were  $\geq$  93% for all trace elements analysed, with precision  $\leq$  4% (RSD). Particulate Al concentrations in 23 selected samples were analysed by Inductively-Coupled Plasma Optic Emission Spectrometry (ICP-OES 720, Agilent Technologies). Mercury concentrations were directly measured in ~50 mg aliquots of dry, powdered and homogenised sediments using a MILESTONE DMA 80 as described in Castelle et al. (2007). Replicated measurements of international certified reference materials for estuarine (IAEA 405; 0.79  $\pm$  0.06 mg/kg) and lake sediments (LKSD4; 0.18  $\pm$  0.003 mg/kg) were within the ranges of the recommended Hg values (0.81  $\pm$  0.04 mg/kg and 0.19  $\pm$  0.017 mg/kg, respectively).

### 2.3. Data processing

A comparison of trace element concentrations in sediments with regional reference concentrations is a prerequisite to assess metal/metalloid enrichments (e.g. Reimann and De Caritat, 2000, 2005; Coynel et al., 2009; Larrose et al., 2010; Grosbois et al., 2012). The regional geochemical background values of the Loire Estuary correspond to the concentrations in the bottom (360–400 cm; beginning of the 20th century) of a sediment core from Montjean-sur-Loire at the outlet of the fluvial watershed (Fig. 1; Grosbois et al., 2012 and unpublished data) and compared to other background values in the upstream part of the watershed (Dhivert et al., 2015a,b). These core levels correspond to

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Summary statistics (minimum, maximum and median values) of selected characteristics of the Loire Estuary sediments (0–1 cm; n: number of analysed samples = 285); grain size (D–50 in µm; diameter representing the 50th percentile on a cu-

trace element concentrations in sediments deposited before the major metal concentration increase in the whole fluvial system (Grosbois et al., 2012) at the whole basin scale when 3 different background levels were measured (Dhivert et al., 2015a).

The enrichment factors (EF) are defined as the measured trace element/X ratio (X = conservation element) in the sample divided by the background trace element/X ratio:  $EF = (C/X)_{sample}/(C/X)_{background}$ . Seven contamination degrees were established as suggested by previous studies (e.g. Essien et al., 2009; Larrose et al., 2010): EF < 1: no enrichment; 1 < EF < 3: minor enrichment; 3 < EF < 5: moderate enrichment; 5 < EF < 10: moderately severe enrichment; 10 < EF < 25: severe enrichment; 25 < EF < 50: very severe enrichment; EF > 50: extremely severe enrichment.

Sediment grain-size, POC and trace element concentrations and trace element EF were used as input data or calculated parameters for grid-based contour mapping using shoreline maps (IGN-Shom) to describe and analyse the spatial distribution in surface sediments at the Loire Estuary scale. For this geochemical mapping we used the ArcGis10<sup>®</sup> software with its spatial analyst toolbox and applied a nearest-neighbour algorithm, i.e. a geostatistical method (kriging), as the interpolation method.

The pollutant-specific Sediment Quality Guidelines (SOG), obtained in laboratory experiments using benthic organisms from the US Coasts (Long et al., 1998), can be combined for different elements in order to calculate mean Effect Range Median quotients (m-ERM-q). Mean ERM quotients take into account mixtures of contaminants present in sediment samples, including trace metals, PAHs and chlorinated hydrocarbons (Long et al., 1998). Experimentally determined relationships between the incidences of toxicity in amphipod survival tests and m-ERM-q support 4 classes of toxicity probability for biota which can be used as a management tool for assessing sediment quality in terms of adverse biological effects: low (m-ERM-q < 0.1), low-medium (m-ERM-q 0.11–0.5), medium-high (m-ERM-q 0.51–1.5) and high priority sites (m-ERM-q > 1.5).

### 3. Results

The ranges and median values for grain-size, POC and trace element concentrations of 285 surface sediments (Fig. 1) covering the whole estuary are summarised in Table 1. Results were compared with Upper Continental crust (UCC; Rudnick and Gao, 2003), the regional geochemical background of the Loire River (Grosbois et al., 2012), and the Gironde Estuary (Larrose et al., 2010 and unpublished data), one of the most polluted and studied French System (Table 1). Trace element concentrations were also compared with sediment quality guideline concentrations corresponding to the 10th and 50th percentiles of adverse biological effects: the effects-range-low (ERL) and effects-range-median (ERM) guidelines, respectively (Long et al., 1995). Complementary cumulative distribution functions of grain-size, POC and trace element concentrations describe spatial variability and show how often a respective value (grain-size or concentration) is greater than a given one (Fig. 2).

Grain-size compositions of surface sediments in the Loire Estuary are highly variable with the proportion of mud (silt + clay) and sand ranging from 0% to 89% and from 3% to 100%, respectively, for a median grain-size  $(D_{50})$  comprised between 9 and 777  $\mu$ m (Figs. 2 and 3). The spatial distribution of D<sub>50</sub> allowed the localisation of contrasting areas within the Loire Estuary (Fig. 3) which are closely related to the hydraulic conditions (Sanchez and Delanoë, 2006) in response to natural (i.e. tide and storm events) and anthropogenic factors (i.e. dredging of navigation channel and urban development). There is a general trend to increasing grain sizes from upstream to downstream. However, areas with relatively coarse sediments ( $D_{50} > 200 \mu m$ ) were (i) upstream Nantes, probably due to the narrowness of the strongly diked channel, (ii) in the island zone located upstream Saint Nazaire (e.g. Bilho Bank) and (iii) in the outer estuary (downstream from Saint Nazaire, e.g.

		D50 (µm)	POC%	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Λ
Loire Estuary $n = 285$													
Concentrations	Range (min-max)	9.7-778	0.02-3.80	0.02-3.06	0.53-47.7	0.01-3.33	2.02-315	 bdl-84.0	 bdl-0.37	0.88 - 68.6	1.49 - 104	3.87-349	2.35-255
Concentrations	Median	20.1	1.4	0.61	17.5	0.44	72.3	22.8	0.08	27.9	45.6	125	81.3
Enrichment factors (EF)	Range (min-max)			2.8-34	0.7 - 10.5	0.8 - 15.6	0.25-2.80	 bdl-6.9	 bdl-140	0.8 - 3.0	0.5-7.2	0.8 - 6.3	
Surface EF < 1	%			0	1.2	0	41.5	55.5	21.1	19.3	0.2	0.6	ı
1 < surface EF < 3	%			0	89.1	29.2	58.5	44.2	25.5	80.7	73.1	92.8	ı
3 < surface EF < 5	%			0	9.3	61.9		0.15	10.8		22.4	6.4	
5 < surface EF < 10	%			7.2	0.4	8.6		0.15	11	ı	4.3	0.2	ı
10 < surface EF < 25	%			91	0.001	0.2			25.6				
25 < surface EF < 50	%			1.8					3.1				
surface EF > 50	%			ı	ı				2.9				
Regional background	mg/kg	NA	NA	0.15	19.6	0.35	99.2	19.9	0.02	39.0	34.6	93.5	121.5
ERL	mg/kg			1.0	8.2	1.2	81	34	0.15	20.9	46.7	150	
ERM	mg/kg		,	3.7	70	9.6	370	270	0.71	51.6	218	410	,
UCC	mg/kg		,	0.055	4.8	0.09	92	28	0.05	47	17	67	97
Gironde Estuary n = 323	Range (min-max)	7.85-474	0.05 - 1.95	nd	3.06–37.4	0.011-2.09	1.34 - 140	0.493 - 40.1	0.001-0.366	0.883-48.4	4.97-83.8	3.95–323	NA
	Median	15.9	1.05	nd	18.7	0.48	78.4	24.5	0.16	31.7	46.8	168	NA
	EF (min-max)	I	I	nd	0.6-7.3	0.2-8.9	0.2-2.4	0.2-1.7	0.1-12.8	0.3-2.2	0.5-6.2	0.3-3.0	NA

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Table 1

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Fig. 2. Cumulative distribution functions of grain size, particulate organic carbon (POC%), and trace elements (V, Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn). Values for UCC (Upper Continental Crust, Rudnick and Gao, 2003), ERL and ERM (Long et al., 1995) are also indicated (the corresponding ERM values are not represented when these are considerably higher than the scale).

Mindin Bank). Between Cordemais and Saint Nazaire, in the navigation channel, the D50 distribution is dominated by alternating coarse and fine deposits, probably due to the Maximum Turbidity Zone (MTZ) migration and/or changing hydrodynamics.

In the Loire Estuary surface sediments, POC contents range from 0.02% (in sandy sediments) up to 3.80% (in fine sediments, generally in intertidal mudflats) with a median of  $1.4 \pm 1.0\%$  (Fig. 3). A POC decrease exists along the Loire Estuary with median values of 2.47%, 1.68%, and 0.08%, respectively for upstream, middle and downstream parts (Fig. 1). Surface sediments can be composed of a refractory POC fraction where terrestrial soil-derived material dominates (Abril et al., 2002). High levels of POC are observed near Nantes (Fig. 3) and could also be related to supply coming from wastewater treatment plants (e.g. in the Pirmil Channel in the left bank of the kilometric point (KP 55); Fig. 1).

The trace element concentrations in surface sediments (Table 1) ranged between 0.02 and 3.06 mg/kg (Ag); 0.53–47.7 mg/kg (As), 0.01–3.33 mg/kg (Cd), 2.02–315 mg/kg (Cr), <bdl-84 mg/kg (Cu), <bdl-0.37 mg/kg (Hg), 0.88–68.6 mg/kg (Ni), 1.49–104 mg/kg (Pb), 3.87–349 mg/kg (Zn), 2.35–255 mg/kg (V), and show a general decrease from upstream to downstream (Fig. 4). Average trace element concentrations are consistently higher than both UCC (Rudnick and Gao, 2003) and the regional background concentrations (Grosbois et al., 2012), except for (i) As and Cu concentrations that are only higher than UCC and (II) Ni and Cr showing values consistently lower than UCC and regional geochemical background. The highest trace element concentrations are generally comprised between ERL and ERM values, except for Ni where the maximum value is similar to ERM (Table 1 and Fig. 2). Note that the mean Ni value for ERM is equivalent to UCC, i.e. not necessarily attributed to anthropogenic sources.

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Fig. 3. Spatial distribution of median grain size (D50; µm) and particulate organic carbon (POC) concentrations.

The spatial variations of both POC and trace metal concentrations, expressed as the ratio of standard deviation to the mean concentration, range between 37% and 82% according to the following relative order: Pb < As < Ni = V < Cr < Zn < Ag < Cu = Cd < POC < Hg.

### 4. Discussion

#### 4.1. Relationship between trace element concentrations, POC and grain size

Trace elements in the Loire Estuary surface sediments are highly correlated between each other and are positively correlated to fine-grained sediments (i.e. clay  $<4 \mu m$ ) and POC (%), and negatively correlated to sands and D<sub>50</sub> (Table 2). These results suggest that grain-size and/or POC are major factors controlling the spatial distribution of trace elements. In fact, trace elements are mainly adsorbed onto the particle with the largest specific surfaces resulting in the highest concentrations in fine sediments with a low D<sub>50</sub> (e.g. Ackermann et al., 1983; Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999; Windom et al., 1989, Herut and Sandler, 2006). The elevated POC contents (up to 3.80%) recorded in sediments are in agreement with data from a previous study (Etcheber et al., 2007), which linked the average POC content in the SPM of the MTZ (supplying surface sediment during deposition) of the Loire Estuary (~3.25%) to the high supply of organic material (including a strong contribution of phytoplankton) coming from the watershed. These POC values are higher than those in the sediments of the Gironde Estuary, ranging from 0.05 to 1.95% for a median value ~1.0% (Larrose et al., 2010). Therefore, organic matter could also represent an important carrier phase for some trace elements, especially Cu (r = 0.90; Table 2) as observed in other French systems (e.g. Masson et al., 2011). In fact, particulate concentrations of Cu and other trace elements (e.g. Cd, Hg) in sediments depend, at least partly, of organic matter mineralization and/or related redox gradients (Audry et al., 2006; Petit et al., 2013). However, in the Loire Estuary sediments, correlations of Cd and Ag with grain-size (or POC) are weaker than for other elements (e.g. Hg, Table 2). Both metals are highly sensitive to salinity and a large percentage of particulate Cd and Ag in freshwater particles can be desorbed by chloro-complexation along the salinity gradients as observed in many estuaries worldwide (e.g. Boyle et al., 1976; van der Weijden et al., 1977; Elbaz-Poulichet et al., 1987; Zwolsman and Van Eck, 1993; Luoma et al., 1995; Chapman and Wang, 2001; Chiffoleau et al., 2001; Garnier and Guieu, 2003; Waeles et al., 2004; Dabrin et al., 2009; Lanceleur et al., 2013). Kinetics of phase exchanges and the resulting partitioning also depend on solid/liquid ratios (e.g. SPM concentrations; Tang et al., 2002; Choe et al., 2003; Masson et al., 2009; Deycard et al., 2014), which may exceed several g/l in the MTZ of macrotidal estuaries. Accordingly, the above observations suggest that geochemical reactivity along the estuarine salinity, turbidity and redox gradients may influence the spatial distribution of these elements in surface sediments in addition to grain size.

#### 4.2. Spatial distribution of enrichment factors (EF)

The trace element concentrations in the surface sediments of the Loire Estuary are similar to those measured in the Gironde Estuary (known for its historical metal contamination; Larrose et al., 2010). By comparison with other highly industrialized and/or urban world systems, the maximum values measured in the Loire Estuary are relatively weak (UK estuaries, Bryan and Langston, 1992; Scheld Estuary, Zwolsman et al., 1996; Bilbao Estuary, Cearreta et al., 2000; Seine Estuary, Cundy et al., 2007 and Hamzeh et al., in press; Toulon Bay, Tessier et al., 2011; Moreton Bay, Morelli and Gasparon, 2014). Based on the previous observations, we selected three trace elements as representative of the eight measured elements (Fig. 4): Hg being representative of trace elements with high affinity for grain-size and/or POC), Cd and Ag as being less correlated to grain-size and/or POC (Fig. 4). As observed for grain-size (expressed as D50) and POC, the Hg, Ag and Cd spatial distributions are very patchy and any well-defined spatial gradient could be enhanced. These concentration maps show areas with relatively high concentrations near Nantes and Cordemais (for Cd and Hg up to 3.3 mg/kg and 370 µg/kg, respectively) and Saint-Nazaire (for Cd and Ag up to 1.90 mg/kg and 3.0 mg/kg, respectively; Fig. 4). Such apparent

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Fig. 4. Spatial distribution of Hg, Cd and Ag concentrations in the surface sediments of the Loire Estuary.

anomalies may result from many factors and their assessment (intensity, origin, etc.) requires an adequate approach.

Given that trace element concentrations vary depending on the sedimentary matrices (e.g. particle size, Table 2), we cannot directly compare the concentrations from one sample to another to understand longitudinal (upstream-downstream) gradients and/or to localize metal/metalloid sources. The assessment of element concentrations in heterogeneous samples from fluvio-estuarine systems requires normalisation to reduce particle size and/or sedimentary matrix geochemical influence (Ackerman, 1980; Daskalakis and O'Connor, 1995; Herut

Table 2

Correlation matrix of median grain size (D50;  $\mu$ m), proportion of clay, silt, and sand (%) in sediments, POC contents (%), and trace element concentrations (mg/kg). All correlations are significant (Student test, p < 0.001; n = 285).

	V	Cr	Ni	Cu	Zn	As	Ag	Cd	Pb	Hg	POC%	D50	Clay%	Silt%	Sand%
V	1														
Cr	0.95	1													
Ni	0.96	0.94	1												
Cu	0.85	0.85	0.93	1											
Zn	0.83	0.82	0.89	0.92	1										
As	0.82	0.78	0.85	0.79	0.76	1									
Ag	0.72	0.77	0.77	0.80	0.74	0.60	1								
Cd	0.69	0.81	0.79	0.84	0.77	0.63	0.89	1							
Pb	0.77	0.73	0.84	0.86	0.83	0.79	0.63	0.70	1						
Hg	0.63	0.62	0.70	0.81	0.73	0.64	0.55	0.65	0.77	1					
POC%	0.75	0.70	0.81	0.90	0.83	0.71	0.58	0.61	0.76	0.79	1				
D50	-0.62	-0.59	-0.64	-0.63	-0.59	-0.45	-0.46	-0.48	-0.49	-0.57	-0.69	1			
Clay%	0.65	0.60	0.66	0.66	0.59	0.52	0.41	0.47	0.57	0.61	0.71	-0.78	1		
Silt%	0.69	0.65	0.74	0.80	0.73	0.60	0.52	0.56	0.66	0.70	0.86	-0.86	0.86	1	
Sand%	-0.70	-0.65	-0.74	-0.79	-0.72	-0.60	-0.52	-0.55	-0.66	-0.70	-0.86	0.86	-0.88	-1.00	1

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and Sandler, 2006). Aluminium, Ti and other crustal elements are commonly used for normalisation (e.g. Windom et al., 1989). However, recent work has shown that the massive use of Al in coagulation/ flocculation processes during the treatment of urban wastewater may lead to anthropogenic Al enrichment in sediments influenced by these wastewater outfalls (J. Wasserman, personal comm.) which may possibly limit its use for normalisation (grain-size correction) in such areas. Because V is a crustal element (as Al, Ti, Cr) and thus mainly controlled by the fraction of fine grained sediment as evidenced by the significant negative correlation (R = -0.62, p < 0.001, n = 285; Table 2) between grain-size (i.e. D50) and V concentrations, we have selected V as the conservative element for normalization of all the other trace element concentrations, analysed simultaneously with V. In addition, this choice was supported by a strong correlation between V and Al values (r =0.94; p < 0.001) analysed in selected samples (n = 23) covering a large range of metal concentrations and grain-size along the salinity gradient.

Enrichment factors (EF) were then estimated as the ratios between the V-normalised trace element concentrations in sediment samples and the respective V-normalised concentrations in the sediment from the regional geochemical background (V = 121 mg/kg). The krigingbased spatial distribution maps of EF classes allowed for the qualitative assessment of sediment contamination in the Loire Estuary and served as the support to estimate the surface areas associated with EF ranges (Figs. 5 and 6; Table 1).

It is considered that EF values of ~1 (0.8–1.2 considering analytical uncertainty and biogeochemical reactivity in estuaries; Larrose et al., 2010) reflect regional rock composition and EF values clearly above 3 reflect non-natural weathering processes, suggesting anthropogenic sources. With 98% (Ni) and 99% (Cr) of EF values lower than 2 for the whole Loire Estuary surface sediments, Cr and Ni are defined as not enriched (Fig. 5; Table 1). Other elements, such as As, Cd, Cu, Pb and Zn typically show moderate enrichments (3 < EF < 5), except in limited areas (mainly near Nantes), where higher EF values occur, reaching up to 6 for Zn and 7 for Cu and Pb, suggesting local moderately severe

enrichment (5 < EF < 10; Fig. 5). In the same zones, EF of up to 10 for As and 15 for Cd point out to the severe enrichment (10 < EF < 25). The surface areas containing sediments with moderately severe to severe contaminated sediments represent ~0.2% for Cu and Zn, ~0.4% for As, ~4% for Pb, and ~9% for Cd of the Loire Estuary surface (~220 km<sup>2</sup>). Two elements (Hg and Ag) show the highest contamination in the Loire Estuary surface sediments, attributed to innerestuarine anthropogenic sources (Figs. 5 and 6). For Ag, the spatial distribution of interpolated EF values suggests that ~91% of the Loire Estuary surface displays severe contamination by Ag, a classical and emerging metallic contaminant (Lanceleur et al., 2011b). The surfaces showing moderately severe contamination ( $\sim$ 7%; 5 < EF < 10) plot in the estuary mouth area, whereas, the surface sediments characterized by very severe enrichment (<2%; EF > 25) locate next to the urban agglomerations of St Nazaire and Nantes, supporting the potential of Ag in sediments to serve as an urban tracer despite its reactivity (e.g. formation of chlorocomplexes) in brackish waters (Table 1; Fig. 5). For Hg, EF values suggest an overall important contamination of the Loire Estuary surface sediments, although in the estuary mouth, uncontaminated sediments (EF ~1) cover ~21% of the total surface area (Fig. 6). In the central (from KP15 to KP40; Fig. 1) and upstream (from KP40 to KP70; Fig. 1) estuary EF values are clearly higher with severely contaminated (10 < EF < 25) areas representing 25% of the whole estuary surface and even very severely (EF > 25) between Cordemais and Saint Nazaire covering 6% of the surface (i.e. ~13–14 km<sup>2</sup>; Table 1; Fig. 6).

The elevated EF found can be attributed to the local deposition of particles issued from important multi- sources like urban inputs (runoff and sewers), industrial activities and various metal ore deposits implying associated past metallurgical activities (e.g. coal mining and burning; exploitation of Ag-Cu-Pb-Sn-Zn, Ag-Pb-Sb, Sn-W and Au-As-Sb districts located within the crystalline Central and Armorican Massifs; http://www.stebarbe.com/industriecharbon.htm;

sigminesfrance.brgm.fr). Indeed during the intense economic development in the 1950–1980s, the river system has subsequently been



Fig. 5. Spatial distribution of enrichment factors (EF) for Cr, Ni, Cu, Zn, Pb, As, Cd, and Ag.

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Fig. 6. Spatial distribution of Hg enrichment factors (Hg-EF), and POC-normalized Hg concentrations.

affected by severe metal pollutions and specially for Ag, Cd and Hg at the whole basin scale, in Sb in the upstream part and Bi more in the downstream part of the basin (Grosbois et al., 2012; Dhivert et al., 2015a, 2016). Industrial activities declined since the 1980s in the whole fluvial basin, corresponding to a slow decrease of metal enrichment in fluvial sediments up to nowadays, correlated to important environmental directives (Grosbois et al., 2012; Dhivert et al., 2016). However, EF values stay high in the Loire Estuary and could be attributed to supplementary sources within the estuary reaches (intra-estuarine), including wastewater and inputs from drainage areas directly adjacent to the estuary, which add to fluvial inputs entering the estuary at Montjean-sur-Loire.

4.3. Origin of anomalies: intra-estuarine vs watershed-derived

The strong EF values found for Ag and Hg may originate from either the Loire watershed upstream from Montjean-sur-Loire (located at the



**Fig. 7.** Spatial distribution of positive Ag and Hg anomalies ( $\sigma$ Ag and  $\sigma$ Hg) attributed to intra-estuarine sources calculated as the difference between the respective recent normalized concentrations in the surface sediments of the Montjean core (i.e. watershed-derived; Grosbois et al., 2012) and concentrations measured in the Loire Estuary surface sediments. Only positive values for Hg and >0.5 for Ag are reported.

upstream limit of tidal influence, i.e. the fluvial entry to the estuary) or more local sources within the estuary reaches (intra-estuarine). For both elements, the positive difference between the respective recent normalized concentrations in the surface sediments of the Montjeansur-Loire core (i.e. watershed-derived; Ag = 0.7 mg/kg and Hg =160 µg/kg; Grosbois et al., 2012) and those in the Loire Estuary surface sediments were considered as anomalies (oAg and oHg) and attributed to intra-estuarine sources. The spatial distribution of these anomalies pointing at intra-estuarine sources suggest two outstanding areas of Ag anomalies, one near Nantes in the Pirmil Channel ( $S = 1.2 \text{ km}^2$ ) and the second near Saint-Nazaire ( $S = 1.3 \text{ km}^2$ ; Fig. 7). Similarly, two areas of Hg anomalies appeared between Cordemais and Donges S = 3.9 km<sup>2</sup>) and the second one near Nantes, identical with that of Ag  $(S = 0.6 \text{ km}^2; \text{ Fig. 7})$ . Based on the surface areas of these anomalies, the density of the wet sediment ( $d = 0.625 \text{ t/m}^3$ ) and the respective trace element concentrations, we estimated the respective additional (anthropogenic) Ag and Hg stocks in the uppermost centimetre of the sediment. Results suggest that the Ag stocks derived from intraestuarine sources are 8.0 kg near Nantes and 6.2 kg near Saint-Nazaire, and the respective Hg stocks are ~0.3 kg near Nantes and 1.1 kg between Cordemais and Donges. The respective estimated total Ag and Hg stocks in the entire estuary are 26 kg and 2.2 kg (Fig. 7). However, these estimates only consider the upper centimetre of the surface sediment and, thus, neglect the stocks of anthropogenic intra-estuarine Ag and Hg deeper in the sediment, which are probably much greater than what has been inferred from the Hg and Ag patterns in historical records (1900-2009) of the Loire River sediments (Grosbois et al., 2012). Nonetheless, assuming that the upper centimetre of the sediment reflects recent sedimentation, the magnitude of these rough estimates seems consistent for example, with the annual Ag inputs from Bordeaux Urban Agglomeration WWTPs (wastewater treatment plants) into the Gironde Estuary (~29.6 g/day, 10.8 kg/yr; ~1 million inhabitant equivalents; Deycard, 2015). Considering the annual SPM flux of ~0.3- $0.5 \times 10^6$  t/yr calculated at the entrance of the estuary at Montjeansur-Loire (unpublished data and Minaudo et al., 2016) and the Ag and Hg concentrations in the <63 µm-sieved surface sediments (Grosbois et al., 2012), representative of SPM transport, a rough annual particulate Ag and Hg flux estimates of 210-350 kg/yr and 48-80 kg/yr, respectively can be proposed for evaluating the contribution of the Loire River System. Considering that the surface areas of these anomalies are locally restricted and account for low Hg and Ag stocks with regard to the annual Hg and Ag flux estimates at Montjean-sur-Loire, the overall strong EF observed in the entire Loire Estuary sediments for Ag and Hg are probably due to watershed-derived inputs (e.g. erosion of contaminated land, industrial waste heaps as observed in other systems; Coynel et al., 2007), highlighting the importance of controlling incoming fluxes by sediment management in the watershed.

#### 4.4. Identification of potential intra-estuarine sources

The maximum EF anomalies for Ag and Hg (but also for Cd, Cu and Zn) are found near the Nantes conurbation, on the left bank (Pirmil Channel; Figs. 1, 5 and 6). This is partly attributed to urban trace element inputs, including effluents from the highly urbanized Erdre and Chezine watersheds and to domestic and/or industrial effluents from WWTPs. Indeed, previous work on the Gironde Estuary reported that, during low freshwater discharge periods ( $Q < 200 \text{ m}^3/\text{s}$ ), and despite high removal trace metal rates (~80%) during the treatment process, the Bordeaux WWTPs (~1 million inhabitant equivalents) contribute 300% for Ag, 43% for Zn, ~30% for Cu and 5% for Cd to the respective total (dissolved + particulate) fluxes in the Gironde Estuary freshwater reaches (Deycard et al., 2014; Deycard, 2015). Given the roughly similar sizes of the Bordeaux and Nantes agglomerations, WWTP effluents in Nantes probably contribute relatively high amounts of dissolved and particulate trace elements to the estuarine surface water, receiving annual SPM fluxes via the Loire River of  $\sim 0.3-0.5 \times 10^6$  t/yr (2009 to 2012; estimated at Montjean-sur-Loire; unpublished data and Minaudo et al., 2016), i.e. less than half the SPM load entering the Gironde Estuary during dry years (Coynel et al., 2004). In the lowsalinity conditions, the major part of these metal inputs may rapidly associate with MTZ particles (either by flocculation or adsorption), followed by sedimentation. Additional sources from industrial activities, such as the Wilson Dock of the Nantes-Saint-Nazaire Harbour are located in the current cruise terminal area in the Pirmil Channel. Although this dock ceased heavy harbour activities in 2007, pertaining only the cruise terminal, the associated marina (Trentemoult) and some boat mooring upstream, historical sediment pollution probably persists, as found in many other harbours (Tessier et al., 2011; Briant et al., 2013; Pougnet et al., 2014). Other industrial sources, such as a steel and fertilizer companies in the surroundings and vineyards in the Sèvre River (flowing into the Pirmil Channel; Fig. 1) watershed may also contribute to trace element inputs into the Loire Estuary, as reported for other systems (Masson et al., 2006; El Hadri et al., 2012).

The strong Hg enrichment (EF > 20; Fig. 6) found in the Central Loire Estuary surface sediments between Cordemais and Saint Nazaire may be due to potential emissions from the Donges refinery and/or the Cordemais plant, the largest French power plant, including two coalfired units and two oil-fired units. Both companies declare to individually release 30 kg/yr of annual Hg flux into the atmosphere (DREAL, 2015). Depending on atmospheric and hydrodynamic conditions, a major part of this Hg emission may probably be deposited in the surroundings of the Loire Estuary, including adjacent land surfaces (e.g. within a radius ~50 km from the point of emission) and contribute to Hg accumulation in sediments either by direct deposition on the water surface or by runoff. This assumption is supported by results of Polycyclic Aromatic Hydrocarbon (PAH) measurements in some of the sediment samples analysed in the present study, published in Mojtahid et al. (2014), showing spatial coincidences of maximum PAH levels and with Hg EF. The predominance of heavier PAHs in these samples point at a pyrolytic origin (coal burning or exhaust gas), rather than petroleum origin, and the common distribution patterns suggest similar intra-estuarine sources and transport pathways for both PAHs and Hg in the Loire Estuary surface sediments. Compared to historical Hg concentrations reported for the Loire Estuary waters (up to 20 µg/l Robin and Ottmann, 1976) and SPM (up to 1.6 mg/kg in 1980-1982; Figueres et al., 1985 and 1 mg/kg in 1991-1993; Coquery et al., 1997), the recently measured maximum Hg concentration in surface sediments (0.4 mg/kg; this study) suggests a clear improvement of the Hg contamination status, despite the overall high EF at the estuary scale. Note that maxima values lower than 0.4 mg/kg in the current surface sediments are yet high comparatively with 0.02 mg/kg for the Loire geochemical background and 0.05 mg/kg for natural background generally estimated for other World estuary (Figueres et al., 1985; Castelle et al., 2007). In the Saint Nazaire sector, EF values are relatively moderate whatever the trace element (except for Ag), despite the presence of shipyards and various terminals (oil, coal, LNG, ...), suggesting that the EF anomaly observed only for Ag can be attributed to a WWTP located in this area.

#### 4.5. Role of estuarine processes vs sources in trace element spatial distribution (role of POC, normalisation grain-size and/or POC?)

Positive significant correlations were found between  $EF_{Cd}$  and  $EF_{Ag}$  (r = 0.71),  $EF_{Cu}$  and POC concentrations (r = 0.76), and  $EF_{Hg}$  and POC concentrations (r = 0.88) for EF values < 10 (Fig. 8). The positive correlation between  $EF_{Cd}$  and  $EF_{Ag}$  reflects that observed for their total concentrations in sediments (Table 2), and is most likely due to their similar behaviour along the salinity gradient in estuaries (chloro-complexation, see above) and/or common sources (Fig. 8). Local EF maxima occur in the downstream estuary, where advanced desorption is expected (i.e. particulate Cd and Ag depletion), pointing towards common urban sources (e.g. Saint Nazaire, see above) as the dominant control.

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**Fig. 8.** Positive significant correlations between  $EF_{cd}$  and  $EF_{Ag}$ ,  $EF_{Cu}$  and POC concentrations, and  $EF_{Hg}$  and POC concentrations. Surface sediments were distinguished for 4 salinity domains: oligohaline (0 < S < 5), mesohaline (5 < S < 18), polyhaline (18 < S < 30) and euhaline (30 < S < 35).

However, desorption efficiency in estuaries depends on several factors such as SPM concentration (e.g. uncomplete/retarded desorption in the MTZ) and particle residence time in the estuarine salinity gradient (Lanceleur et al., 2013). As surface sediments integrate particles that have undergone various conditions during variable residence times, it is impossible to attribute precise salinity values to a given location in the estuary and the surface sediments at this site. Gallenne (1974; see Mojtahid et al., 2016) proposed the subdivision of the Loire Estuary into 4 salinity domains: oligohaline (0 < S < 5), mesohaline (5 < S < 18), polyhaline (18 < S < 30) and euhaline (30 < S < 35). Based on this classification, the highest EF values generally occur in the oligohaline area, whereas the lowest EF<sub>Cd</sub> and EF<sub>Ag</sub> typically are in the euhaline area. In fact, EF<sub>Cd</sub> continuously decrease along the Loire Estuary to reach EF = 1 in the euhaline area, whereas  $EF_{Ag}$  do not fall below 4-5 (with no significant difference for mesohaline, polyhaline and/or euhaline sectors). These results clearly suggest that both desorption processes and inner-estuarine anthropogenic sources control the observed spatial distribution of Cd and Ag in the Loire Estuary surface sediments.

Copper and Hg are known to have a high affinity for organic matter (e.g. Coquery et al., 1997; Petit et al., 2013). The regression curves obtained for the correlations between EF<sub>Cu</sub>, EF<sub>Hg</sub> and POC% have logarithmic shapes (Fig. 8) and, despite some scattering, reproduce the relationships between these parameters, except for very high anomalies (EF > 10), probably due to dominance of local anthropogenic sources. Coquery et al. (1997) demonstrated that organic associations, through sulphydryl groups, were a major control factor for the spatial Hg distribution in the Loire Estuary. These authors observed a good correlation between particulate Hg in SPM and the chlorophyll *a* concentrations, suggesting that primary production plays an important role in the estuarine Hg dynamics, particularly during high water discharges of the Loire River (Coquery et al., 1997). The salinity subdivision did not reveal significant differences in EF<sub>Cu</sub> and EF<sub>Hg</sub> between the different zones, except for the euhaline domain where very low POC% concentrations prevail because of the dominant sand fraction. Previous works in other estuaries have reported lower particulate Cu and Hg concentrations in the saline estuary, compared to the freshwater end-member (Figueres et al., 1985; Cossa and Noel, 1987; Elbaz-Poulichet et al., 1987). This decrease could be attributed to the mineralization of POC, releasing dissolved trace metals as observed for both Hg and Cu in the Gironde Estuary (Cossa and Noel, 1987; Petit et al., 2013). However, the OM degradation along the Loire Estuary is not obvious to see, maybe because of the recent decline of eutrophication in the Loire fluvial-estuarine system. Indeed, in the 1980s, excess nutrients caused severe eutrophication with very high chlorophyll *a* concentrations (up to 300 µg Chl. *a*  $L^{-1}$ ) in the Middle Loire System because of the high phosphorus availability (anthropogenic point sources) combined to the fact that the river morphology favours algal development (Minaudo et al., 2015). Previous studies highlighted the severe oxygen depletion of the water column in the summer, mainly attributed to the oxidation of the particulate OM, previously accumulated in the MTZ, due to resuspension of anoxic "fluid mud" at spring tides (Thouvenin et al., 1994; Abril et al., 2002, 2003). This process possibly releases trace elements associated to either OM or redox-sensitive mineral phases (e.g. Mn and Fe oxy/hydroxides; Audry et al., 2006). In the recent years, chlorophyll a concentrations show clearly lower levels ( $<70 \,\mu g \, Chl. \, a \, L^{-1}$ ) due to phosphorus removal from wastewaters (Minaudo et al., 2015), resulting in lower autochthonous POC production. However, autochthonous POC is still dominant during phytoplankton blooms in summer (Minaudo et al., 2016), contributing up to 50% of the total POC load and resulting in high POC concentrations in SPM and sediment, compared to other French estuaries (Etcheber et al., 2007). Overall, reduced nutrient loads in the Loire Estuary may explain the decrease of labile POC and the subsequent homogenisation of POC concentrations in sediments, except in areas where hydrodynamic processes and the dilution by sands are dominant. If the amount of labile POC and the frequency/intensity of anoxia in the water column have been reduced, it may be expected that recently the sediments in the Loire Estuary release less trace elements to the water column than in the 1980s.

The above observations show that despite the normalisation by lithogenic elements, other constituents of the sediment matrix (such as OM content) may partly control the spatial distribution and the

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estuarine cycle of trace elements, especially those having a high affinity with organic matter.

Accordingly, few studies suggested to double-normalize by both lithogenic elements and POC as a tool to identify trace element anomalies in sediments (e.g. Horowitz, 1991), especially when comparing sediments in fluvial-estuarine systems. Based on POC-normalized Hg concentrations (expressed in µg/kg; Fig. 6), we arbitrarily subdivided the obtained Hg/POC into 3 classes: Hg/POC < 40; 40 < Hg/POC < 80; Hg/POC > 80 respectively considered as representing 'deficit', 'normal' or 'excess' Hg levels. The lowest Hg/POC values occurred in the Loire Estuary mouth, where low SPM levels (compared to the MTZ) favour Hg photo-reduction and subsequent evasion of dissolved gaseous Hg into the atmosphere, causing a deficit (with respect to POC) in particulate Hg (i.e. Hg/POC < 40). Photochemical processes may play an important role in estuarine Hg budgets, unless high SPM concentrations limit light penetration (e.g. in the Gironde Estuary; Castelle et al., 2009). The major part of the central and upstream Loire Estuary sediments shows 40 < Hg/POC < 80, suggesting 'normal' values without anomalies in the relationship between Hg and POC. In contrast, several sectors in the central/downstream estuary show Hg/POC > 80, i.e. excess Hg compared to POC (near Nantes between Cordemais and Saint-Nazaire; Fig. 6). Interestingly, nearly all of these areas coincide with zones, where the  $EF_{Hg}$  is >10, suggesting strong Hg contamination of these sediments, which cannot be explained by high OM contents. If POCnormalisation tends to confirm the geochemical Hg anomalies obtained from EF<sub>Ho</sub> in the strongly contaminated parts of the Loire Estuary, it represents a complementary approach for elements with high affinity to OM, but cannot replace grain-size normalisation by lithogenic elements.

### 4.6. Sediment quality assessment for trace elements in the Loire Estuary

Mercury and Ag are of particular concern for sustainable estuary management because they are the most toxic metals, suspected of causing toxic effects (e.g. Bryan and Langston, 1992; Luoma et al., 1995; Boening, 2000; Flegal et al., 2007). This part aims at assessing sediment quality and evaluating chemical risks on the biota. Even if the trace element concentrations in the Loire Estuary sediments are lower than in other systems, sediments with values that comprised between ERL and ERM are frequently observed for Ni, Pb, As and Hg. Sediments in these areas should be considered with caution because possible negative environmental consequences cannot be excluded (Fig. 2). Although the use of sediment quality guidelines (SQG) to correctly predict the presence and absence of acute toxicity has been the subject of debates, many studies have used these reference values as a standard method for identifying the probability of biological effects (e.g. Larrose et al., 2010; Tessier et al., 2011; Cao et al., 2015; Rodriguez-Iruretagoiena et al., in press). One main limitation of the mean Effects Range Median quotients (m-ERM-q) is the fact that it seems impossible to analyse and integrate all inorganic and organic pollutants in one study. To our knowledge, little information on organic micro-pollutants in the Loire Estuary sediments is available to date. A recent study reported that high PAH concentrations occurred on selected surface sediments near the shipyard of Saint-Nazaire (>7000 µg/kg) and near the shoreline areas (~700 µg/kg) associated with fine-grained sediments (Mojtahid et al., 2016). In contrast, investigations on aquatic organisms have been more documented due to their potential use in biomonitoring (Marchand, 1987; Lemarchand et al., 2012; Munschy et al., 2013; Blanchet-Letrouvé et al., 2014; Couderc et al., 2015). Consequently, in our study, the m-ERM-q for the Loire Estuary surface sediments were calculated for the eight priority contaminants Zn, Cd, Pb, Cu, Cr, Ni, As, and Hg as follows:

$$m - ERM - q = \frac{\sum_{i=1}^{n} (C_i / ERM_i)}{n}$$
(1)

where *Ci* is the concentration of the pollutant *i* in the sample, *ERMi* is the experimentally defined effect concentration for the pollutant *i* and *n* is the number of studied pollutant i (i.e. n = 8 in this study with Zn, Cd, Pb, Cu, Cr, Ni, As, and Hg).

A m-ERM-q map of the sediments for the whole Loire Estuary displays the areas with toxicity risk potential, at least for the eight priority contaminants studied (Fig. 9). The comparison of the Loire Estuary m-ERM-q with those of previous studies for the same trace metals (e.g. Larrose et al., 2010; Tessier et al., 2011; Rodriguez-Iruretagoiena et al., in press) provides additional information setting the Loire Estuary sed-iment quality in a larger context. The m-ERM-q values obtained for the Loire Estuary range between 0.009 and 0.52. The highest m-ERM-q values (>0.3) correspond to Hg and Ag hotspots as described above (Fig. 7) and for which high PAH concentrations were also reported (Mojtahid et al., 2016).

The m-ERM-q classes (<0.1; 0.1–0.5; >0.5) represent 12%, 87% and <1% of the Loire Estuary surface area, respectively with a median value ~0.21 considered as a low-medium priority site referring to the classification. These results suggest that the major part of the Loire Estuary contains slightly toxic or non-toxic sediments, comparable to those observed in the Gironde Estuary, known for its multi-metal contamination (Larrose et al., 2010). Both Atlantic coast estuaries are less impacted than the Toulon Bay (Mediterranean sea, France; Tessier et al., 2011) or the Nerbioi-Ibaizabal Estuary (Bay of Biscay; Atlantic Ocean, Basque Country; Rodriguez et al., in press) where the m-ERM-q reach values clearly higher than 1.5. Despite this relatively low m-ERM-q, ecotoxicological impacts have been already reported in the Loire Estuary. The French mussel watch biomonitoring programme has reported high Hg concentrations in the Loire mussels compared to those from the Baie de Somme, considered as an unpolluted environment (RNO, 1995; Boisson et al., 1998). Furthermore, a study on sentinel species was conducted on fish-eating species (e.g. osprey) from the Loire fluvialestuarine system because they integrate the global contamination of the watershed (Lemarchand et al., 2012). Even if Hg concentrations in osprey tissues were highly variable from one individual to another (<limit of detection-16.3 mg/kg ww), the overall values in specimen from the Loire Estuary are higher than those reported for other environments in Europe, US or Canada. Sediment dwelling bivalves (Macoma *balthica*) have been successfully used as biomonitors of the chronic Hg and Ag contamination in the Loire Estuary (Boisson et al., 1998). Consequently, the results obtained by the first systematic and spatiallyresolved sediment quality assessment for eight inorganic priority contaminants (this study) in the Loire Estuary converges with those from these various biomonitoring studies, despite the heterogeneity in the approaches.

### 5. Conclusions and perspectives

This study presents the current contamination state for inorganic trace element priority contaminants, based on 285 surface sediment samples collected in September 2012 across the entire Loire Estuary. The first high-resolution maps of concentrations and enrichment factors (EF) using basin geochemical background values were established for the eight metals/metalloids identified as priority contaminants (Cd, Zn, Pb, Cu, As, Cr, Ni, Hg), and Ag (an urban tracer). Among all the studied trace elements, Hg and Ag have the highest EF in the surface sediments of the Loire Estuary.

Despite generally decreasing trace element concentrations in fluvial sediments from 1980 to 2009, Hg and Ag concentrations and EF indicate severe contamination in the Loire Estuary surface sediments. Intraestuarine Ag and Hg sources were identified by comparison between the respective normalised concentrations in the Loire Estuary surface sediments and those measured in the surface sediments of a core collected at the outlet of the Loire River System (i.e. watershed-derived).

Anthropogenic Ag and Hg stocks in the uppermost centimetre of the sediment, compared with rough annual fluvial flux estimates, suggest

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Fig. 9. Spatial distribution of mean-ERM-quotient indices for the surface sediments of the Loire Estuary.

that the overall strong  $EF_{Ag}$  and  $EF_{Hg}$  are mainly due to watershedderived inputs, highlighting (i) the need of high temporal hydrogeochemical monitoring to establish reliable incoming fluxes and (ii) the importance of controlling trace element inputs into the estuary through improved sediment management in the watershed.

Comparison of trace elements concentrations with ecotoxicological indices (Sediment Quality Guidelines-SQG) provides the first standardized information on the sediment quality in the Loire Estuary. The highest m-ERM-q (>0.3) correspond to Hg and Ag hotspots. Geochemical mapping allowed delimiting the slightly toxic areas of the Loire Estuary, providing detailed knowledge useful for sustainable estuary management. The overall m-ERM-q results suggested that the Loire Estuary is mainly characterized by slightly toxic or non-toxic sediments, yet similar to those in the Gironde Estuary, known for multi-metal pollution causing deleterious effects in wildlife aquatic organisms and human health risks.

Because the highest EF (i.e. maximum of pollution) was observed in a historical sediment core from the Loire River watershed between 1945 and the late 1970s (the "thirty glorious years" of the French economy), it is likely that the most contaminated sediments in the Loire Estuary are located a few tens of centimetres below the sediment-water interface. Therefore, these "old" sediments may represent a potential secondary trace element source during remobilization due to dredging and/or major flood events. Furthermore, current sources of trace elements in the aquatic environment are not yet all identified. Future studies should integrate emerging contaminants (such as Rare Earth Elements, Platinum Group Elements or Ag- and other metal-nanoparticles) to provide timely information for a more sustainable estuary management. Indeed, new high technologies (photovoltaic systems, vehicle emission control, hybride vehicles, LED, mobile phones, etc.) imply the emission of emerging potentially highly toxic contaminants, which are also excellent tracers of urban activities, sources and transfers to natural systems (e.g. Rauch et al., 2005; Cobelo-Garcia et al., 2011, 2015). Their current importance is such that several of these elements have now been labelled as 'technology-critical elements' and initiatives at national and European levels are underway to evaluate their environmental processes to understanding potential human health threats (Cobelo-Garcia et al., 2015).

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