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Key factors influencing metal concentrations in sediments along Western European Rivers: A long-term monitoring study (1945–2020)

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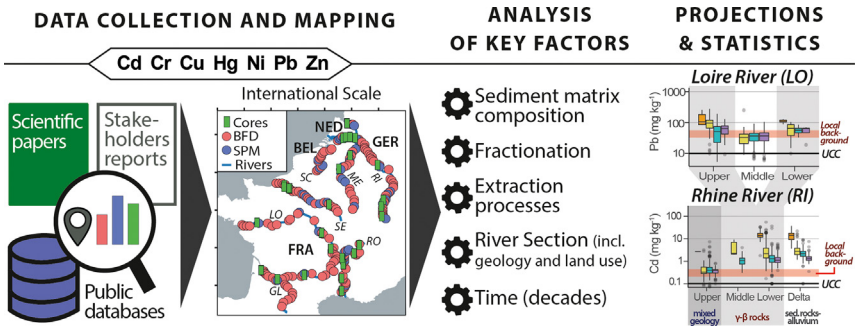
HIGHLIGHTS

- Assessment of metal contaminations in sediments along Western European Rivers
- Sediment monitoring and cores covering the period from the 1960s to the 2010s.
- Deciphering of spatial and temporal factors over contamination trends
- Secondary influence of the matrix-types and extraction process on metal levels

GRAPHICAL ABSTRACT



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ABSTRACT

Since 1945, a large amount of heterogeneous data has been acquired to survey river sediment quality, especially concerning regulatory metals such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Large-scale syntheses are critical to assess the effectiveness of public regulations and the resiliency of the river systems. Accordingly, this data synthesis proposes a first attempt to decipher spatio-temporal trends of metal contamination along seven major continental rivers in Western Europe (France, Belgium, Germany, and the Netherlands). A large dataset (>12,000 samples) from various sediment matrices (bed and flood deposits – BFD, suspended particulate matter – SPM, dated sediment cores – DSC) was set up based on monitoring and scientific research from the 1950s to the 2010s. This work investigates the impact of analytical protocols (matrix sampling, fractionation, extraction), location and time factors (related to geology and anthropogenic activities) on metal concentration trends. Statistical analyses highlight crossed-interactions in space and time, as well as between sediment matrices (metal concentrations in SPM ≃ DSC > BFD) and extraction procedures (also related to river lithology). Major spatio-temporal trends are found along several rivers such as (i) an increase of metal concentrations downstream of the main urban industrial areas (e.g. Paris-Rouen corridor on the Seine River, Bonn-Duisburg corridor on the Rhine River), (ii) a long-term influence of former mining areas located in crystalline zones, releasing heavily contaminated sediments for decades (Upper Loire River, Middle Meuse section), (iii) a decrease of metal concentrations since the

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1970s (except for Cr and Ni, rather low and stable over time). The improvement of sediment quality in the most recent years in Europe reflects a decisive role of environment policies, such as more efficient wastewater treatments, local applications of the Water Framework Directive and urban industrial changes in the river valleys.

1. Introduction

The industrial and urban development along European Rivers after 1945 led to major impacts and deteriorations of water and sediment quality. Metallic elements (Cd, Cr, Cu, Hg, Ni, Pb, Zn) have been largely released into rivers by human activities such as agricultural soil erosion, mining and industrial releases, waste waters, road and urban runoff (e.g. Callender, 2003). Due to their high particulate affinity, metal measurements focused on bed and flood deposits (BFD), suspended particulate matter (SPM) and dated sediment cores (DSC). Metal pollution surveys have been set up heterogeneously in space and time (variability of sampling stations and frequencies), on these matrices and in various environments such as in the main stream, secondary channels, backwater areas, dam reservoirs and lateral infrastructures (e.g. Vauclin et al., 2020). Metal-rich sediments may be stored for long periods in such environments, but they may also be remobilised during floods, flushing, dredging or restoration works, and transported further downstream as suspended particles (Qu and Kelderman, 2001; Audry et al., 2004a; Ollivier et al., 2006; Coynel et al., 2007; Taylor and Owens, 2009; Dhivert et al., 2015a; Le Gall et al., 2018). River sections, especially those located downstream of major and urban industrial centres in Europe, are still affected by highly polluted sediments, mainly inherited from the past as a legacy (e.g. Belgian rivers: Gao et al., 2013; Rhine-Volga-Danube Rivers: Winkels et al., 1998; Seine River, France: Le Cloarec et al., 2011; Le Gall et al., 2018; Moselle River, France: Le Meur et al., 2016; Tagus River, Portugal: Mil-Homens et al., 2009; UK Rivers: Walling et al., 2003). This long-term pollution is one of the largest issue complicating river management and restoration, especially to evaluate the improvement of the quality of water, sediment, aquatic and riverine habitats.

To assess metal pollution in river sediment, monitoring programs have been implemented since the late 1960s on watercourses with variable frequencies. The monitoring of sediment quality with respect to metal concentrations became more widespread and regular in the 1980s, under the supervision of Water Basin Agencies in several countries of Western Europe (e.g. after the Law on Water in 1964 in France). After 2000, increasing monitoring efforts were driven by the European Union regulation under the Water Framework Directive (WFD, 2000/60/CE). Accordingly, a large amount of data was produced on liquid and solid matrices along the rivers from local to national scale, or even at international scales on some transboundary rivers under the supervision of International Commissions (Rhine, Meuse and Scheldt Rivers). Previous syntheses emphasised the importance of an overview (Viers et al., 2009; Meybeck, 2013; Bravard, 2018; Damania et al., 2019): large spatio-temporal approaches of metal pollution in sediments along river networks are needed. Besides the issues due to the handling of international datasets, the diversity of methods used to produce the data generally limited large-scale studies. Indeed, for the last 60 years, a great variability of sampling and analytical protocols was used across countries and even in various watersheds within a country. For instance, sediments were sieved with variable meshes (2 mm, 63 or 20 μm), or even not sieved, and digested by various acids (hydrochloric (HCl), nitric (HNO_3) or hydrofluoric (HF) acids), or a mixture of substances such as *Aqua Regia* (HNO_3 + HCl) (Förstner and Salomons, 1980; Ackermann et al., 1983; Meybeck et al., 2018). Unfortunately, correction methods cannot be routinely used because of the irregular measurement of necessary ancillary data such as particle-size distribution and organic matter content, only available for recent surveys in general. Retrospectively, to produce a synthesis, questions may be raised regarding the influence of the heterogeneity of matrix parameters, sampling and analytical methods, which challenge the intercomparison of metal concentrations trends at a large spatial and temporal scale.

To address this issue, a large amount of data (including metal concentrations, grain-size, Total Organic Carbon – TOC content, location, sampling date and analytical protocol information when available) was collected based on past monitoring and research actions (1950s–2010s) along seven major rivers in Western Europe. By analysing this dataset (Table A.1, see also https://doi.pangaea.de/10.1594/PANGAEA.935416), the objectives of this research are (1) to decipher the variability of metallic pollution in sediments along the rivers, and (2) to reconstruct and intercompare the long-term evolution of sediment quality between rivers at an international scale. This work especially aims to assess the effects of the main factors influencing the variability of metal concentrations in river sediments (matrix, sampling and analytical effects, anthropogenic and geological influence). It also experiences the difficulty of interconnecting heterogeneous data at a large scale for identifying and quantifying spatio-temporal pollution patterns along European Rivers.

2. Materials and methods

Seven continental rivers of Western Europe were selected based on the data availability at national and international scales (Fig. 1): it includes four French rivers (Loire, French Rhône, Seine, Garonne-Lot River systems) and three transboundary rivers flowing from France to Belgium, Germany and the Netherlands (Rhine, Meuse and Scheldt Rivers). Only the freshwater sections of these rivers were considered; the estuaries were excluded due to the influence of tidal processes and salinity on sedimentation and on liquid/solid exchanges. In the following overview, the studied rivers were described from their upper to their lowest sections, according to two groups based on (i) hydrological (flow regimes and discharge), (ii) geological, (iii) river infrastructures and land-use in their drainage areas.

2.1. Flow regime and discharge of the studied rivers

The first group is composed by continental Atlantic rivers, draining the western Front of Europe (Fig. 1). It includes the Loire (LO hereafter, 1006 km), the Seine (SE, 775 km), the Garonne-Lot system (GL, cumulated length = 1132 km), the Meuse (ME, 950 km), and the Scheldt (SC, 350 km) Rivers. These river systems are mainly influenced by oceanic climate and characterised by high discharges in winter, with the occurrence of flash floods, and low discharges in the late summer (Descy, 2009). The interannual discharge ranges from 3 $km^3\ y^{-1}$ for SC to 27 $km^3\ y^{-1}$ for LO, and the sediment flux is comprised between 0.5 Mt. yr^{-1} for SC and 2.2 Mt. yr^{-1} for GL (FAO, 2016). ME, SC, and SE are typical lowland rivers, heavily equipped for navigation and flood control in the last 240 km for SC and the last 390 km for ME (Belgian and Dutch parts), while SE was rectified and/or bypassed upstream and downstream of Paris, along 600 km through dams and diversion canals (Foussard et al., 2010; Lestel et al., 2019). The LO and GL present higher elevation gradients as they start in the Massif Central and in the Pyrenees Mountains respectively. These two fluvial systems are less artificialised than the others, even if they also contain several major-to-small dams and hydro-electric power plants in their most upstream part; while embankments for flood protection, nuclear plant

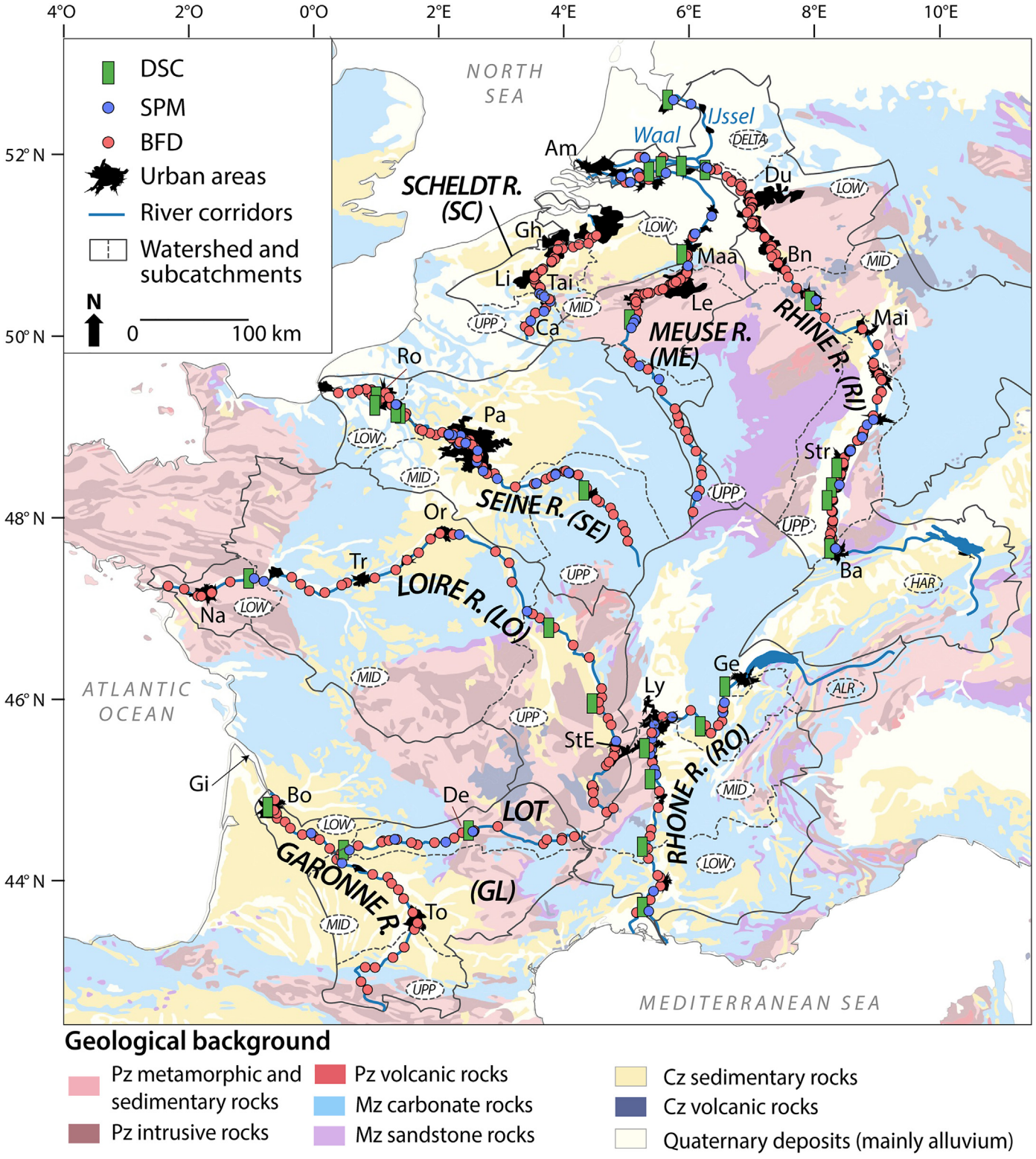

Fig. 1. Location of the studied rivers and sites. BFD = bed and flood deposits, DSC = dated sediment cores, SPM = suspended particulate matter. Main locations: Am = Amsterdam, Ba = Basel, Bo = Bordeaux, Bn = Bonn, Ca = Cambrai, De = Decazeville; Du = Duisburg, Gh = Ghent, Gi = Gironde estuary, Ge = Geneva, Le = Liège, Li = Lille, Ly = Lyon, Maa = Maastricht, Mai = Mainz, Na = Nantes, Or = Orléans, Pa = Paris, Ro = Rouen, StE = St-Etienne, Str = Strasbourg, Tai = Tournai, To = Toulouse, Tr = Tours. Geological background (Pawlewicz et al., 2002): Pz = Palaeozoic, Mz = Mesozoic, Cz = Cenozoic. Subcatchments: LOW = lower section, MID = middle section, UPP = upper section, ALR = Alpine Rhône (not treated), HAR = High and Alpine Rhine (not treated).

derivations, navigation and harbour facilities are mainly found in the middle and lower sections of these rivers (Dendievel et al., 2020a).

The second group includes the Rhône (RO) and Rhine (RI) Rivers, flowing from the Alps to the Mediterranean Sea and to the North Sea, respectively (Fig. 1). This study focuses on the sections located downstream of the Geneva Lake (considered as a natural decanter) for the French RO (545 km), and downstream of Basel and Constance Lake for RI (i.e. the last 816 km). The two rivers present a distinct

hydrological regime from upstream (snowmelt-fed regime with high summer flows) to downstream (rainfed regime supplied by winter-to-spring precipitations) (Sauquet et al., 2008; Uehlinger et al., 2009). They show a high discharge (RI at Lobith ~72 $km^3\ y^{-1}$; RO at Arles ~50 $km^3\ y^{-1}$) and suspended sediment load (up to 3.8 Mt. yr^{-1} for RI and 6.6 Mt. yr^{-1} for RO) (Middelkoop et al., 2010; Frings et al., 2019; Poulier et al., 2019; Delile et al., 2020). They were historically regulated and channelled (lateral/perpendicular dikes and by-passed sections) for flood and navigation control, to settle and resolve international water use conflicts, but also for electricity production (Tricart and Bravard, 1991; Eschbach et al., 2018; Arnaud et al., 2019; Vauclin et al., 2020).

2.2. Lithology and urban industrial land use

The two fluvial groups can also be differentiated based on geology and urban industrial zones (Fig. 1).

In group 1, SE and SC are alkaline rivers mainly draining sedimentary calcareous and chalk formations of Mesozoic and Cenozoic age (Fig. 1; Table A.2). On the SE, the Paris-Rouen corridor is densely populated (up to 4200 inhabitants km^{-2} on average; Table A.2) and well-known for hosting foundries and metal manufactories that released major pollution during the 19th and 20th centuries (GIP Seine Aval, 2010; Lestel, 2012). The SC system also drains major urban and industrial basins (Lille, Ghent) characterised by highly contaminated sediments (Charriau et al., 2011). Polluted sediments stored in the French-Belgian canals represent a major concern in case of floods and dredging remobilisation (Vandecasteele et al., 2003). The other rivers of group 1 are more contrasted from upstream to downstream. The LO and GL flow from crystalline and volcanic mountain ranges (Massif Central and Pyrenees), to middle and lower sections mostly constituted of sedimentary rocks and alluvial deposits (Fig. 1; Table A.2). Conversely, the ME rises in the eastern part of the Paris Basin in Mesozoic calcareous formations, before flowing across the Ardennes, which consist of metamorphic Palaeozoic rocks (slates, shales, quartzites). Downstream of Liège, the ME successively reaches Quaternary loamy plateaus, Miocene sand formations, peaty-clayey lowlands and moorlands in the lower section (Descy, 2009). All these rivers receive major tributaries characterised by typical metal contents such as the Lot River for GL (Audry et al., 2004a), the Geul River in the Middle ME (Rang et al., 1986), and the Allier, Vienne, Indre and Cher Rivers for LO (Dhivert et al., 2016). These rivers are also impacted by multiple historical urban industrial centres such as the Decazeville district on the Lot River, major mining sites of Wallonia (Southern Belgium) on the ME and the Saint-Etienne coal basin on the LO (see Fig. 1; Audry et al., 2004b; ICOMOS, 2012; Moatar and Dupont, 2016).

The lithology of group 2 is more complex because RI and RO originate from the Alps and flow across glacial formations as well as sedimentary basins with local felsic and mafic rocky outcrops (Fig. 1; Table A.2). The Upper RO is mainly supplied by fine sediments from the Arve River (Alpine rock flour), and then by the Ain and Saône Rivers draining molasse, moraines and limestones (Salvador et al., 2005; Dendievel et al., 2020b). Downstream, the RO receives metal inputs from (1) the Massif Central (granitic, metamorphic, and basaltic rocks: right bank tributaries), (2) calcareous subalpine zones (left bank tributaries), and (3) from the urban industrial zones of Lyon and the Gier Valley. (4) Small urban and industrial areas also coexist with farmlands along the RO Valley, while the connected hillslopes are covered with vineyards. The Upper RI, from Basel to Bingen am Rhein (near Mainz), flows into a 30-to-50-km-wide rift valley filled by Oligo-Miocene to Quaternary deposits. It receives tributaries from the Hercynian massifs (Vosges, Palatinate Plateau, Black Forest and Odenwald). The Middle RI begins after the confluence with the Main River, downstream of the Mainz-Frankfurt conurbation. The Middle RI valley is narrow (1 km wide) and incised the Rhenish Uplands composed by Late Palaeozoic slates, shales, greywackes, and volcanic rocks (Koster, 2005). The RI corridor is densely populated from Bonn to Duisburg in the Lower RI (415 to 528 inhab. km^{-2} on average), where it receives the Ruhr Valley inputs (coal industrial basin). Finally, in the delta area, the RI separates into several branches flowing to the west (Waal and Nederrijn/Lek) and to the north (IJssel).

2.3. Compilation of a large-scale dataset

Major and trace metal concentrations (Al, Fe, Cd, Cr, Cu, Hg, Ni, Pb, Zn), as well as ancillary data (TOC, grain-size) from bed and flood deposits (BFD), suspended particulate matter (SPM), dated sediment cores (DSC) were assessed by compiling a large dataset (>12,000 samples; Table A.1; see also https://doi.org/10.1594/PANGAEA.935416). A critical effort was made to assemble and treat information from academic publications and regulatory monitoring provided by governmental agencies or stakeholders at an international scale (France, Belgium, Germany, the Netherlands) (Table 1; see also acknowledgements). Based on the datasets validated by the producers, sampling locations, analytical protocols and units were checked, and data were selected based on a reliable sampling date or an age (derived from depth-age models for DSC) comprised between 1945 and 2020 (Fig. 2). Then, they were categorised according to the river section, decades, extraction protocols and sediment matrix.

Overall, 1.5% of the metal information refers the period before the 1970s ($n = 184$), 14.6% to that comprised between the 1970s and 1980s ($n = 1760$), and 83.8% from 1990 onwards ($n = 10{,}079$). Auxiliary data are available as follows: TOC content is available for 65.1% of the data ($n = 7823$), while grain-size data is available for only 12.8% of the data ($n = 15{,}035$).

When looking at the matrix level, 3156 samples collected at 515 BFD stations are considered along the rivers, but sampling frequencies and locations as well as the number of measured parameters followed diverse monitoring strategies. BFD data mainly come from regional Water Agencies and navigation authorities, and secondarily from sampling campaigns of research labs (e.g. Grosbois et al., 2006; Le Gall et al., 2018). Along RO and SE, the monitoring began in the 1980s and presented, since today, a greater focus downstream of Paris and Lyon conurbations than along the other sections (Fig. 1). Along LO and GL, a thorough monitoring of historically heavily polluted sections was achieved on the Saint-Etienne basin (Upper LO) since 1980, and along the GL continuum since 1990 (Lanceleur et al., 2011; Dhivert et al., 2015a; Gil-Díaz et al., 2019; Pougnet et al., 2019). In contrast, their middle sections were documented at a low sampling frequency (1 to 3 times in 30 years). The situation is more complex for Transboundary Rivers (ME, RI, SC), for which a limited set of parameters was monitored since the early 1950s at some locations. As an example, along the RI, the systematic control of water and sediment quality really took off after the Bonn commission in 1976, and intensified after the Sandoz chemical spill in 1986 (Giger, 2009). For the SC, the monitoring was – at first – implemented on the French stretch, and then, it was generalised to Belgium following the Helsinki convention in 1992, in order to manage water issues in Europe.

Metal concentrations in SPM were generally acquired at key stations (76 sites), i.e. before and after major confluences and conurbations (Fig. 1). The large number of samples ($n = 8117$) is due to high sampling frequencies (daily to quarterly in general). In France, SPM monitoring by using sediment traps spread in the 1990s. Other countries/organisations historically gave more priority to such mobile sediments. Indeed, along ME and RI, regular SPM measurements from unfiltered water began as soon as the late 1960s–early 1970s (Fig. 2), by relying on long-term monitoring stations such as Eijsden (Lower ME) and Lobith (beginning of the RI Delta). However, such protocol needs an adjustment of the data to be compared to sediment chronicles (see Sect. 2.5).

Table 1
Data sources along each studied river. AE = French Water Agencies ("Agences de l'Eau"): AG = Adour-Garonne; AP = Artois-Picardie; LB = Loire-Bretagne; RM = Rhin-Meuse; RMC = Rhône-Méditerranée-Corse; SN = Seine-Normandie. DREAL RA = Direction Régionale de l'Environnement, de l'Aménagement et du Logement, Rhône-Alpes (France). EDF = Electricité de France. FEA = Flanders Environment Agency (VMM, Belgium). IFREMER = National Institute for Ocean Science (France). ICPR = International Commission for the Protection of the Rhine. ONEMA = former Agency of Water and Aquatic Environment (OFB, France). OSR = Rhône Sediment Observatory (France). RWS = Rijkswaterstaat (The Netherlands). SPW = Service Public de Wallonie (Belgium). VNF = Voies Navigables de France. WSA = Wasserstrassen- und Schiffahrtsamt (Freiburg, Germany).

	Deposited sediments		Mobile sediments
River	Dated sediment cores (DSC)	Bed and flood deposits (BFD)	Suspended Particulate Matter (SPM)
GL: Garonne-Lot System	Grousset et al., 1999; Audry et al., 2004b; Castelle et al., 2007	AE_AG[1]; ONEMA[2]; Blanc et al., 1999; Barjhoux, 2011	AE_AG[1]; Audry et al., 2004a
LO: Loire	Grosbois et al., 2012; Dhivert et al., 2015a, 2015b	AE_LB[1]; DREAL RA; IFREMER[3]; ONEMA[2]	AE_LB[1]
ME: Meuse	Rang et al., 1986; Petit et al., 1987	AE_RM[1]; RWS[4]; SPW; FEA; Salomons and Eysink, 1981; Rang et al., 1986; Leenaers et al., 1988; Henry et al., 1990; Middelkoop, 2000	AE_RM[1]; RWS[4]; Salomons and Eysink, 1981; Petit et al., 1987;
RI: Rhine	Beursken et al., 1993; Middelkoop, 2000; Schulze et al., 2007	AE_RM[1]; RWS[4]; ICPR[5]; VNF/EDF/Strasbourg Port/WSA Freiburg; Salomons and Eysink, 1981; Middelkoop, 2000; Gocht et al., 2001; Heise et al., 2004	AE_RM[1]; RWS[4]; ICPR[5]
RO: Rhône	Dendievel et al., 2020b	AE_RMC[1]	AE_RMC[1]; OSR[6]
SC: Scheldt	–	AE_AP[1]; SPW; FEA	AE_AP[1]
SE: Seine	Van Metre et al., 2008; Le Cloarec et al., 2011; Vrel, 2012; Gardes et al., 2020	AE_SN[1]; IFREMER[3]; Meybeck et al., 2000; Grosbois et al., 2006; Barjhoux et al., 2018; Le Gall et al., 2018	AE_SN[1]; Tessier, 2003; Priadi et al., 2011

[1] French Water Agencies data portal: http://www.naiades.eaufrance.fr/.
[2] http://www.pollutions.eaufrance.fr/pcb/.
[3] ROCCHSED Programme. Data portal: https://wwz.ifremer.fr/surval/.
[4] https://waterinfo.rws.nl.
[5] http://iksr.bafg.de/iksr/.
[6] https://bdoh.irstea.fr/OBSERVATOIRE-DES-SEDIMENTS-DU-RHONE (Thollet et al., 2018).

The use of dated sediment cores (DSC) was also challenging because the sedimentation sites need to be well-characterised and dated (depth-age models based on known time makers are required). They were mainly performed by research labs (749 samples at 32 sites). The continuous or episodic nature of the sediment deposition relied on the geomorphic context and on the frequency of the stream connection. DSC provided powerful data for reconstructing pollution trends since 1945 (Fig. 2). A significant number of cores was available along GL, RI and SE Rivers (Grousset et al., 1999; Gocht et al., 2001; Audry et al., 2004b; Castelle et al., 2007; Schulze et al., 2007; Le Cloarec et al., 2011), although the RO was the most densely documented river thanks to six cores located at key points along the river (Dendievel et al., 2020b). Along the other rivers, DSC were mainly located in one or two key sections, such as the Upper and Lower LO (Grosbois et al., 2012; Dhivert et al., 2016), the Lower SE (Van Metre et al., 2008; Vrel, 2012; Gardes et al., 2020) and the RI Delta (Beursken et al., 1993; Middelkoop, 2000). For more information on sediment profiles, dating, grain-size, organic matter and metal concentrations of the cores, the reader is invited to refer to the publications listed in this paragraph (see also Table 1).

2.4. Analytical protocols

Heterogeneous sampling, treatments and analytical protocols were used over time, depending on technical developments and on national/international policies (Meybeck, 2013). Despite the systematic consultation of the laboratories involved in the metal analysis, some technical information was difficult to obtain or even lacking (mentioned as "undet." in Table A.1). After sampling, three types of sieving were generally used directly in the field or at the laboratory: (i) bulk fraction or <2 mm especially for BFD and some DSC (e.g. on GL and RO), (ii) <63 μm for other cores (e.g. on LO) and recent BFD (since 2000), (iii) <20 μm, a fraction especially studied on RI (Ackermann et al., 1983; Schulze et al., 2007). Two main types of extraction protocols were

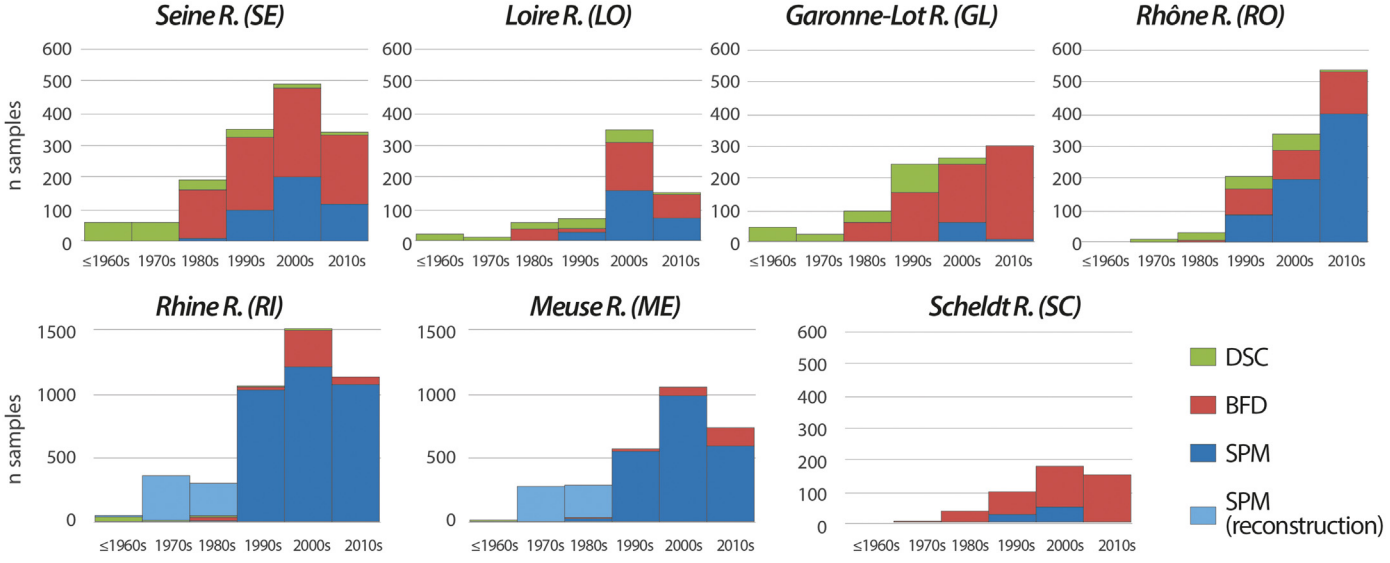

Fig. 2. Distribution of the number of samples with metallic element data according to matrice types, rivers and time. BFD = bed and flood deposits, DSC = dated sediment cores, SPM = suspended particulate matter.

used: (i) partial / pseudo-total procedure (PP hereafter) which includes *Aqua Regia* (HNO_3 + HCl), mainly used for SPM and BFD, (ii) total extractions (TE hereafter) using a multi-acid treatment (HNO_3, HCl, $HClO_4$, and HF), or fluoroboric acid (HBF_4) and borate fusion ($LiBO_2$-$Li_2B_4O_7$). PP and TE procedures correspond to 22% and 52% of the data, respectively, while 26% of chemical attack method remain undetermined (undet.). There was also a high variability of analytical equipment used for measuring metal concentrations such as atomic absorption spectrometry (AAS), inductively coupled plasma techniques associated with optical (especially for major elements such as Al and Fe) and mass spectrometry (ICP-OES and ICP-MS, respectively) or neutron activation analysis (NAA) for trace elements. Cold vapour fluorescence spectrometry or direct mercury analyser was used for Hg. The detection limits were irregularly mentioned (10% to 60% according to the river) and varied from 0.1 to 10 mg kg^{-1} for Al and Fe, 0.02 to 0.1 mg kg^{-1} for Cd, 0.001 to 10 mg kg^{-1} for Cr and Ni, 0.05 to 10 mg kg^{-1} for Cu, 0.01 to 0.2 mg kg^{-1} for Hg, 0.1 to 5 mg kg^{-1} for Pb and Zn.

Ancillary data such as grain-size was mainly measured by using laser diffraction granulometry (>70%). The Robinson pipette method was rarely used (<5%), while the method used remains unknown for ca. 25% of the data. The TOC was most often determined by sulfochromic oxidation, dry burning, pyrolysis RockEval or other guidelines (e.g. ISO 8245 1999 COT, NF EN 13137). These heterogeneous protocols lead to major limitations regarding the contribution of organic matter to the metal variability in sediments. For more information about the protocols, the reader is invited to refer to the original publications (see Table 1).

2.5. Data treatments

Descriptive and multivariate statistics were performed in *R* (R Core Team, 2018) to compare the data distribution between sediment matrices, fractions and extraction procedures on each river. Wilcoxon ranked tests and the Bonferroni post-hoc method were used to determine pairwise differences between samples (Hollander et al., 2014). The results were represented by boxplots. Given the large number of data, Pearson's coefficients (r) were calculated to test the relationship between metal concentrations, fine fraction (< 63 μm) and TOC contents. Finally, the dataset was transformed using a centred log-ratio (clr: Garrett, 2018). Then, the effects of sediment matrix, extraction procedure, spatial position (river section) and temporality (decades) on metal concentrations were tested with a four-ways ANOVA for dependant variables followed by a Tukey HSD post-hoc method, after a check of residuals' normality, the non-correlation of residuals with the studied factors, and the variance homogeneity (Yandell, 1997).

For the Lower ME and the RI Delta, metal concentrations in SPM prior to 1988 were reconstructed from unfiltered (dissolved and particulate phases) water measurements (expressed as mg L^{-1}). First, the Metal Mass Concentration (MMC) in SPM was estimated based on the difference between Total and Dissolved Phases (TP and DP), divided by Suspended Particulate Matter Concentrations (SPMC), as follows (1):

$$MMC = (TP - DP) / SPMC \quad (1)$$

Then, the relationship between MMC and metallic element concentrations measured in trapped SPM (MTrap) during a known period (between 1998 and 2018) was tested. Hence, when the correlation was statistically significant, linear regression models were used to correct metals in the RI and ME SPM before 1988 (see correlation tables and equations in Table A.3). Finally, in order to provide a rough estimation of the seasonal average, the data was smoothed by using a four-point running average. Thanks to this reconstruction, 358 and 153 samples were respectively added at Eijsden and Keizerveer from 1972 to 1988 (Lower ME), and 600 samples at Lobith from 1968 to 1988 (RI Delta). These reconstructed values represent ca. 8% of the whole dataset.

3. Results and discussion

3.1. Characterisation of the sediment matrix

The characterisation of the sediment matrix relies on the sample number and on the distribution of grain-size and TOC for each river (Fig. 3). Actually, grain-size and TOC from monitoring programs were acquired more systematically since 1996 and 2005, respectively.

The proportion of fine fraction (FF) – i.e. the percentage of sediment with a grain-size <63 μm – was analysed based on a least 133 samples by river (Fig. 3-A). The median FF reaches 90% in SPM, 78% in DSC, and 72% in BFD. Therefore, the FF in the different matrices was in general: SPM > DSC > BFD, with BFD containing the coarsest sediments. The RO, RI, ME and LO are the rivers where the finest sediment fractions were the most abundant in the samples (median > 70%), while sediments of the GL, SE and SC were coarser (56% < median FF < 69%).

The TOC data (expressed as % of sediment or SPM) is of particular interest, especially on ME and RI where the Rijkswaterstaat (the Netherlands) achieved long-term TOC monitoring (Fig. 3-B). All TOC

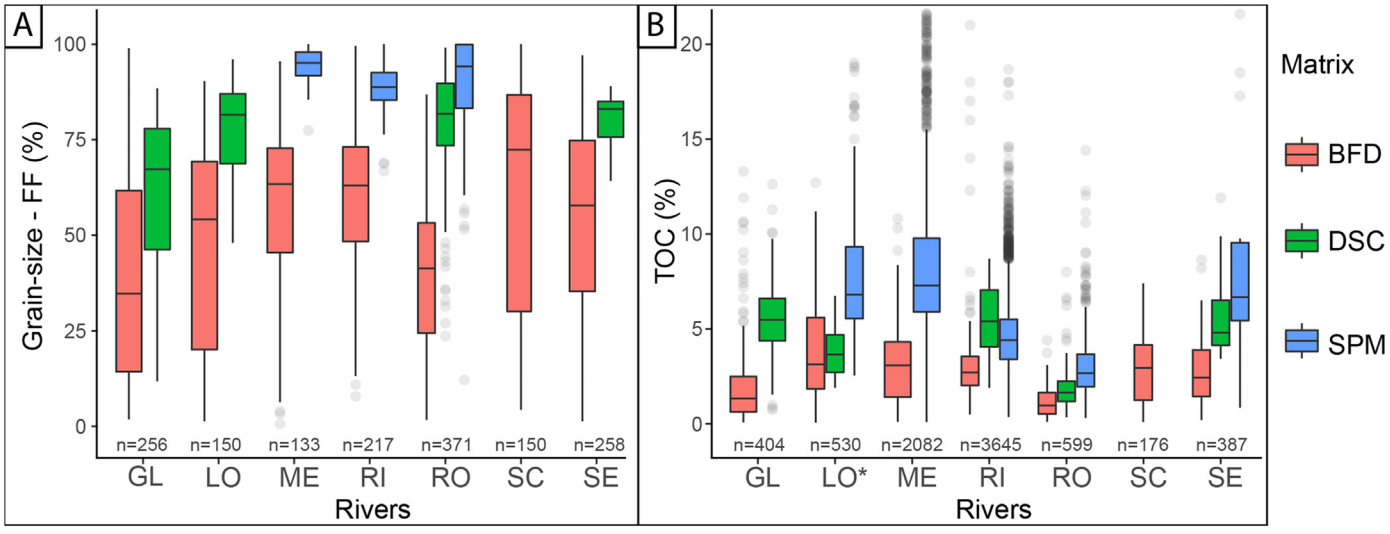

Fig. 3. A) Grain-size range (% of the fine fraction < 63 μm– FF) and B) Total Organic Carbon (TOC) percentage in the studied matrices and rivers. All distributions are statistically different, except for the TOC of the Loire River (LO) that is similar for BFD and DSC (asterisk mark). For river abbreviations, please refer to Figs. 1 and 2. Horizontal lines = medians, boxes = 25–75%.

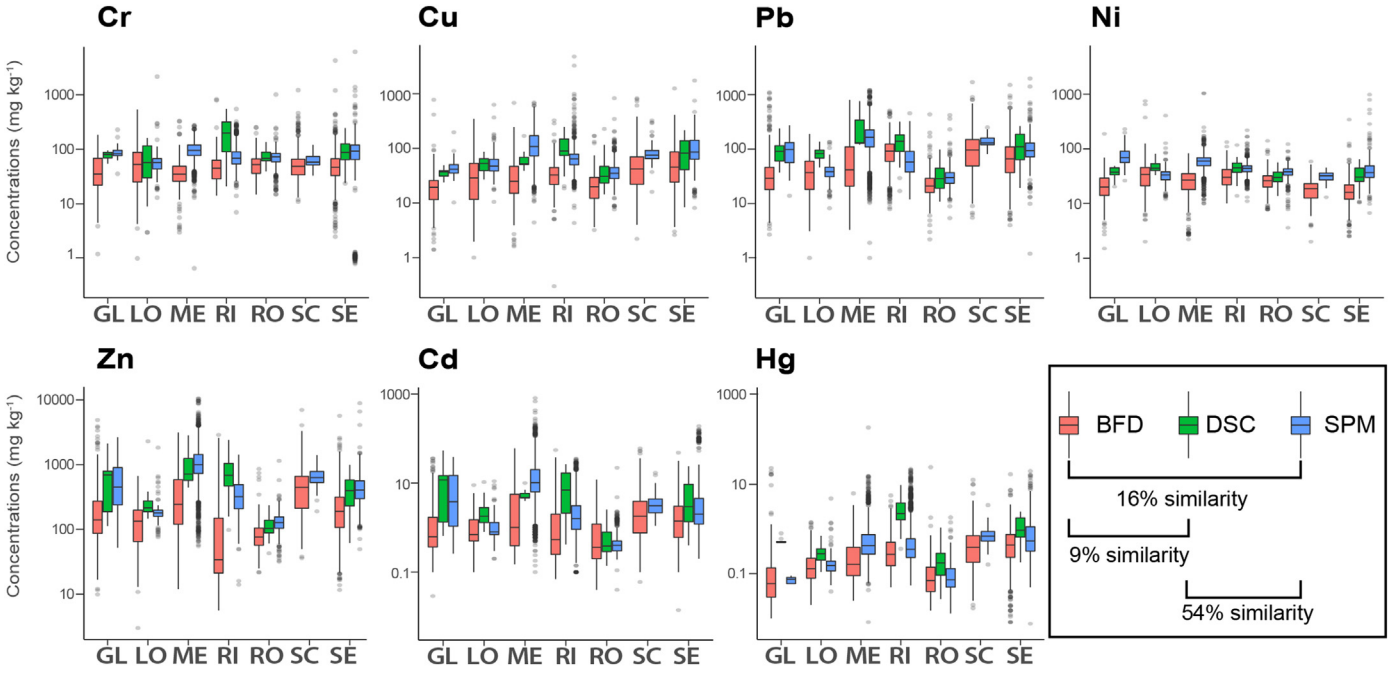

Fig. 4. Distribution of metal concentrations in sediments (all stations and time-periods) and statistical summary of the similarity between the different matrices, the whole dataset considered. Values are expressed in mg kg^{-1}. For river abbreviations, please refer to Figs. 1 and 2. Horizontal lines = medians, boxes = 25-75%.

levels are statistically different according to the sampled matrices within the rivers with, again, SPM being more concentrated than Cores and BFD. Only the LO presents BFD as rich in organic carbon as DSC according to the available data, probably because the cored sites shared similar characteristics to BFD on this river. The analysed sediments of the RO present the lowest organic content (2%; low eutrophication), while the LO, RI and ME offer organic-rich sediments (median of 4.4%, 4.8% and 6.9%, respectively). Such elevated TOC levels are in agreement with those previously found on these rivers characterised by a high organic supply from the watershed (Coynel et al., 2016; Grosbois et al., 2012; Middelkoop, 2000; Moatar and Dupont, 2016) and/or a high primary production (e.g. Etcheber et al., 2007; Minaudo et al., 2015).

Metal concentrations highly depend on the matrix characteristics such as grain-size, TOC and the date of sampling/deposit. For all metals, the concentrations are generally greater in SPM and DSC than in the BFD samples, especially for RI and SC (Fig. 4). For the other rivers, on average, about 25% of metal concentrations were similar within the three matrix types. Based on Kruskal-Wallis and Bonferroni tests, we highlighted that the distribution of metal concentrations between DSC and SPM was especially similar in 54% of the cases. This similarity relies on the high proportion of fine sediments in these two matrices (see above). This result can also be partly induced by the long-term coverage of DSC which can contain high metallic element concentrations inherited from past mining and industrial activities (Middelkoop, 2000; Grosbois et al.,

Table 2
Correlations (Pearson's r) between FF – the fine fraction (<63 μm fraction representing the grain-size distribution), Total Organic Carbon contents (TOC) and metallic element concentrations in all matrices. For FF, $n = 1594$ and for TOC, $n = 7040$. Colour code: light blue = poor negative correlation, white = no correlation, light red = poor positive correlation, pure red = clearly positive correlation ($r \geq 0.5$).

River	Parameter	Al	Fe	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Loire (LO)	FF	0.76	0.56	0.26	0.13	0.46	0.29	0.3	0.43	0.27
Garonne-Lot (GL)	FF	0.43	**0.69**	0.41	0.18	0.33	0.18	0.64	0.34	0.39
Meuse (ME)	FF	0.41	0.15	-0.06	0.52	0.14	-0.04	0.33	-0.05	-0.06
Rhine (RI)	FF	0.42	0.3	0.13	0.38	0.17	-0.02	0.34	-0.24	0.66
Rhone (RO)	FF	0.28	0.6	0.25	0.36	0.39	0.22	0.75	0.46	0.6
Scheldt (SC)	FF	0.72	0.54	0.45	0	0.73	0.37	0.71	0.62	0.5
Seine (SE)	FF	0.67	0.64	0.28	0.35	0.16	0.25	0.36	0.07	0.2
Loire (LO)	TOC	-0.12	0.1	-0.06	0.3	0.22	-0.14	-0.12	-0.21	0.05
Garonne-Lot (GL)	TOC	-0.01	0.57	0.53	0.23	0.58	0.48	0.43	0.5	0.52
Meuse (ME)	TOC	-0.31	-0.09	0.12	-0.04	0.25	-0.01	0.03	0.22	0.01
Rhine (RI)	TOC	-0.04	0.1	-0.19	-0.07	0.05	-0.09	-0.02	-0.05	0.05
Rhone (RO)	TOC	0.17	0.36	0.37	0.14	0.58	-0.11	0.33	0.23	0.3
Scheldt (SC)	TOC	0.58	0.66	0.43	0.18	0.83	0.45	0.73	0.63	0.6
Seine (SE)	TOC	0.36	0.57	0.28	0.39	0.39	0.36	0.41	0.17	0.3

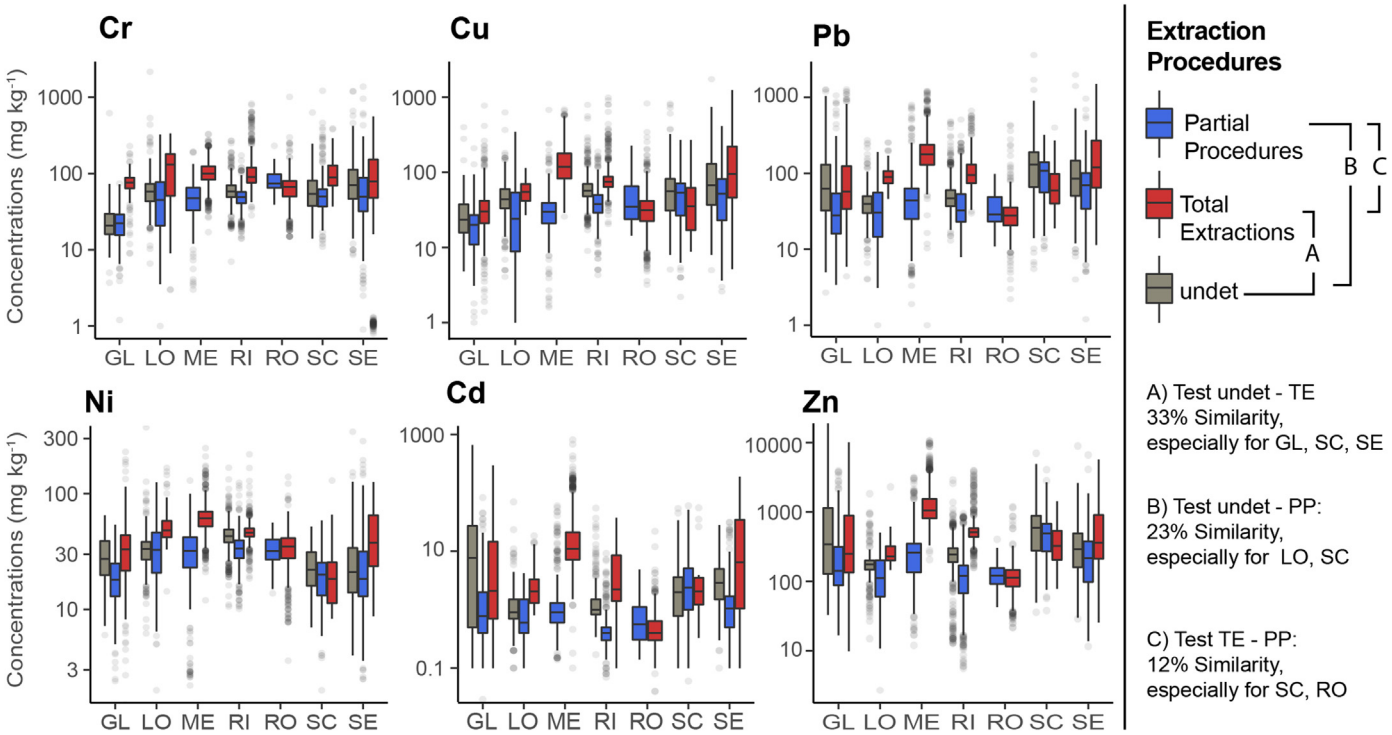

Fig. 5. Comparison of metal concentrations according to extraction procedures and summary of similarity tests. PP = partial procedures (*Aqua Regia*, acid nitric), TE = total extractions (multi-acid treatment or neutron activation analysis). The rate at the right of this figure (33% for A, 23% for B, 12% for C) indicates the degree of similarity between undet. Procedures and samples extracted with PP or TE. The mention "especially" indicates that the test results are mainly driven by samples from some specific rivers. For river abbreviations, please refer to Figs. 1 and 2. Hg was not considered due to specific analytical procedures for this element.

2012; Delile et al., 2020; Dendievel et al., 2020b). A lower level of similarity is observed between the metal levels in BFD and DSC (9%), and in BFD and SPM (16%), due to large differences of grain-size and organic matter between these matrices, as previously observed (Fig. 4).

3.2. Influence of the grain-size fractions and TOC contents

Relationships of metal concentrations with the grain-size fraction on one hand, and with TOC contents in the other hand, are summarised in Table 2. A highly significant and positive correlation is found between the fine fraction (FF) and Al or Fe (except for the ME) as clay minerals and iron oxyhydroxydes present small particle sizes and a high specific surface favouring metal sorption. In the absence of other geogenic elements monitored over the long-term (such as Sc, Th), Al and Fe could act as grain-size proxies in order to standardise metal concentrations (Schiff and Weisberg, 1999; Grosbois et al., 2006). However, the lack of data for these 2 elements during the early periods of monitoring greatly limited their use to build geochemical indexes based on lithogenic elements (such as Enrichment Factors or Geo-Accumulation Index). Indeed, Fe is available for 44% of the data, while Al is available for only 37% of the whole dataset and mostly during the most recent period (since the 2010s on the RO for instance). The other studied metals are also positively correlated with FF in general (Table 2), suggesting that they are mainly associated with the finest sediment particles (Ackermann et al., 1983; Buffle and van Leeuwen, 1992). The major exceptions are Cd, Hg, and Pb for RI, and all metals for ME which are not significantly correlated with the fine fraction. In these cases, the metal-bearing phases may be linked to coarser sediment fractions in these two rivers, and related to the presence of macroscopic slags coming from former mining zones in the Ardennes, Vosges or Black Forest massifs (Houbrechts et al., 2011).

Highly significant correlations are also found between metals and TOC for SE, RO, and especially for GL and SC river systems. The highest positive correlations with TOC are observed for Cu, which is widely known to being carried out by the organic matter (Buffle, 1988; Masson et al., 2011; Coynel et al., 2016). For SC, Pb, Zn and Cd have also been recognised as strongly linked to humic substances, playing a transfer vector role in this river (Charriau et al., 2011). The presence of negative correlations, or even the lack of correlation between metals and TOC on RI, LO and ME raises the question of the main bearing phases and the seasonal dynamics of organic matter production on these rivers. It is an additional argument to assume the presence of slags or ore particles, not linked to the organic matter, and inherited from past mining and industrial activities along these rivers, as evidenced on LO by Gautier et al. (2009).

Hence, RI and LO provided a subset of detailed data to analyse the fractionation effect on the BFD matrix (see Figs. A.1 and A.2 in the supplementary information online). On the RI, three fractions were analysed from 1999 to 2010 by stakeholders in charge of river monitoring (EDF, VNF, WSA): (i) total or <2 mm, (ii) <63 μm, (iii) <20 μm. A high resemblance in metal distributions was found in the Upper Rhine (Fig. A.1): apparently, the fractionation was not significant for Cd, Cu and Pb ($p > 0.1$). For the other metallic elements, a frequent homogeneity of distribution is also highlighted between the <2 mm fraction and the other fractions (71% of the cases), in particular with the fraction <20 μm. These similarities could be explained by relatively low amount of the coarse fraction in the analysed samples, the <20 μm fraction representing more than 60% of the bulk fraction (see Figs. A.3 and A.4 in the supplementary information online). On the LO, the Loire-Bretagne Water Agency (AE_LB) selected successively <2 mm (2000–2009) and <63 μm (2015–2018) sieved sediments to perform metal analyses. The tests presented a homogeneity of variances with similar distributions of metal concentrations between these 2 fractions ($p > 0.05$; Fig. A.2) even if the fine fraction is less abundant (see Fig. A.5 in the supplementary information online) than for the RI. Thus, the generally expected correlation between fine fractions and metal concentration is not obvious here. Although, the metal

concentrations measured in <63 μm could be lower than in the 2 mm fractions. However, these similarities are not very reliable as the particle-size distribution of bulk sediment was not available for all fractions and time periods. According to this exploratory approach based on these two river examples ($n = 318$), the sample fractionation displays a limited influence on metal concentrations when samples are mostly fine. It depends on the proportion of fine and coarse fractions of the bulk sample and more variability can be expected on the range of metal concentrations after the fractionation of coarse sediments (Faivre and Grosbois, pers. com.).

3.3. Influence of extraction procedures

According to Fig. 5, the samples digested by Total Extraction (TE) are generally more concentrated than the samples extracted with Partial Procedures (PP). This difference was already noticed by numerous works especially in case of lithogenic influence, such as sulphides for example (Cook et al., 1997; Sastre et al., 2002; Santoro et al., 2017). It also depends on the nature of the main metal-bearing phases, that is why it is generally important to consider separately the effects of the extraction procedures (e.g. Dendievel et al., 2020b). Along mining river sections (Lot, middle ME) where ore particles are present in river sediments (Sect. 3.2), the metals bounded to sulphide minerals are not usually dissolved/extracted in PP. Very significant differences are especially observed for Cr but also for Cd, Cu, Pb, or Zn to a lesser extent. It is in agreement with studies highlighting similar differences due to a significant part of residual metals contained in silicate minerals, such as nesosilicates (olivine, garnets, zircons) or tectosilicates (incl. quartz or feldspars; Cook et al., 1997; Sastre et al., 2002; Santoro et al., 2017). Noticeable exceptions are found for SC and RO, where the differences between TE and PP are not significant (Fig. 5). It could be explained by the lithology. In sedimentary rocks (chalk, limestone, and loam), the main metal-bearing phases (carbonates, oxides, and organic matter) can be efficiently extracted even by HCl-based methods (PP) such as *Aqua Regia* ($HNO_3 + HCl$), leaving few solid residuals. On the contrary, the metals linked to refractory minerals (e.g. Cr in chromite) are poorly recovered with PP extractions.

The statistical approach is also critical to interpret the samples for which the analytical procedure is not known (mentioned as "undet"), which represents 26% of the data. Based on Fig. 5, those "undet" samples present similar distribution of metal concentrations as TE procedures in 33% of the cases, especially for the samples coming from the GL and SE Rivers. Thus, on these rivers, a high proportion of "undet" was probably treated by using TE procedures. Similarly, 23% of the "undet" data presented a distribution compatible with PP, especially for the LO. These results suggest that "undet" data could be interpreted according to either TE or PP procedure, and should be considered separately.

3.4. Spatial and temporal variation of metal concentrations in rivers

Once the influence of grain-size, TOC and extraction procedure mentioned above are considered, this large-scale analysis also reveals very interesting spatial and temporal patterns of metal concentrations (Fig. 6):

(i) An increasing trend in metal concentrations occurred down the SE, RO, ME, RI Rivers. As an example, for Cd on the SE, the median concentrations in all the fractions considered increased from 0.8 ± 0.2 mg kg^{-1} in the Upper SE to ca. 4.2 ± 4.6 mg kg^{-1} in the Lower SE during the 1960s–1990s. Both values are significantly higher than the local geochemical background (Thévenot et al., 2007; Table A.4) and largely exceed the Upper Continental Crust (UCC) values for Cd (Rudnick and Gao, 2014). They also reached the Probable Effect Concentration for which a severe toxicity is likely to affect sediment dwelling species (PEC_{Cd} = 4.98 mg kg^{-1}, sediment quality guideline) defined by MacDonald et al. (2000), causing major concerns from the Lower Seine to the Channel (Meybeck et al., 2018). A slighter increase in metals is observed along the RO, Pb contents increased from 23 ± 6 mg kg^{-1} in the Upper RO to 30 ± 7 mg kg^{-1} in the Lower RO for instance, which slightly exceeds local geochemical background levels (Dendievel et al., 2020b). Similar trends are observed for Cu, Hg, Pb, and Zn (Fig. 6). It is certainly linked to emissions and releases of urban industrial zones located in the middle and lower sections of the studied rivers, such as along the Paris-Rouen corridor (Lower SE, France), downstream of Lyon and the Chemical Valley (Middle to Lower RO, France), from Bonn to the Ruhr Valley confluence (Lower RI, Germany) and from the Liège-Maastricht corridor to the RI-ME Delta (Belgium and the Netherlands).

(ii) Marked increases in metal concentrations are found along GL, LO, ME, SC and RI Rivers, downstream of local to regional pollution (mining and industrial zones) hotspots. For instance, substantial enrichments in Cd, Cu, Hg, Pb and Zn are found along the GL River system, especially downstream of the Lot confluence (Fig. 6). Indeed, a major pollution originates 350 km upstream (Lot River) from past mining and Zn-ore treatment (1847–1987) that impacted the river quality for decades with numerous environmental implications (sediment, water, freshwater and estuarine biota) (Audry et al., 2004b; Castelle et al., 2007; Lanceleur et al., 2011; Pougnet et al., 2019; Sivry et al., 2008). The Upper LO also presents enriched Cd, Cr, Hg, Ni, Pb and Zn contents, exceeding the local geochemical background levels (Table A.4), linked to the history of the coal mining district of Saint-Etienne (Dhivert et al., 2016). The long-term and long-distance influence of these coal mining-related activities is also known for persistent organic pollutant issues (PAH: Bertrand et al., 2015; PCBs: Dendievel et al., 2020a). In the Middle and Lower ME, two steps of major increases in Cd, Cu, Pb, and Zn concentrations are successively highlighted (Fig. 6). These sections receive contaminated sediments from the Geul River (draining the Ardennes mining basin) and wastewaters from Liège to Maastricht (Nienhuis, 2008; Rang et al., 1986). In the SC, a major increase of Cd, Cu, Hg, Pb and Zn (ca. 10 times the local background; and frequently > PEC threshold for Hg, Pb, and Zn) occurred from the Upper to the Middle SC, between Cambrai in France and Tournai in Belgium (Figs. 1 and 6; Table A.4), a zone mainly dedicated to textile and steel metallurgy (Cavallo, 1968). Finally, a well-marked rise of Cd, Cr, Hg, Pb and Zn occurred in the Lower RI and its delta, clearly exceeding the local geological background as well as the UCC (Eschbach et al., 2018; Vijver et al., 2008). These river sections are characterised by large population and historical industrial areas delivered metals through riverine releases and the specific supply from some tributaries like the Ruhr River (Bruggemeier, 1994; Middelkoop, 2000).

(iii) A significant temporal decrease of metal concentrations occurred from the 1960s to the 2010s for most river sections. For instance, Cd declined in all ME and RI sections until today: the median of all the samples on the RI decreased from 14 ± 2.8 mg kg^{-1} in the 1960s–1970s to 1.2 ± 0.3 mg kg^{-1} in the 2010s along the Lower RI and Delta. Even if it remains approximately two-fold higher than the local geological background, it also reveals a clear improvement of the river quality (Fig. 6). Decreasing temporal trends are also well noticeable for Cu, Hg, Pb and Zn on GL, RO, LO and SE. This sediment quality improvement can be related to several factors over time: the influence of regulation on releases and potential source reduction, the increased efficiency of waste water treatments as well as industrial changes characterised by an employment decline in the metallurgical sector of ca. −30% in France during the period 1990–2010 (Sedeno and Dupré, 2012), and -20% in 2000–2014 in the North Rhine-Westphalia Land for RI (Deshaies, 2017). In opposite to this general decline of metal concentrations in sediments over time, an increase of Cr is observed since the 1960s along the Garonne River itself (except for the Lot

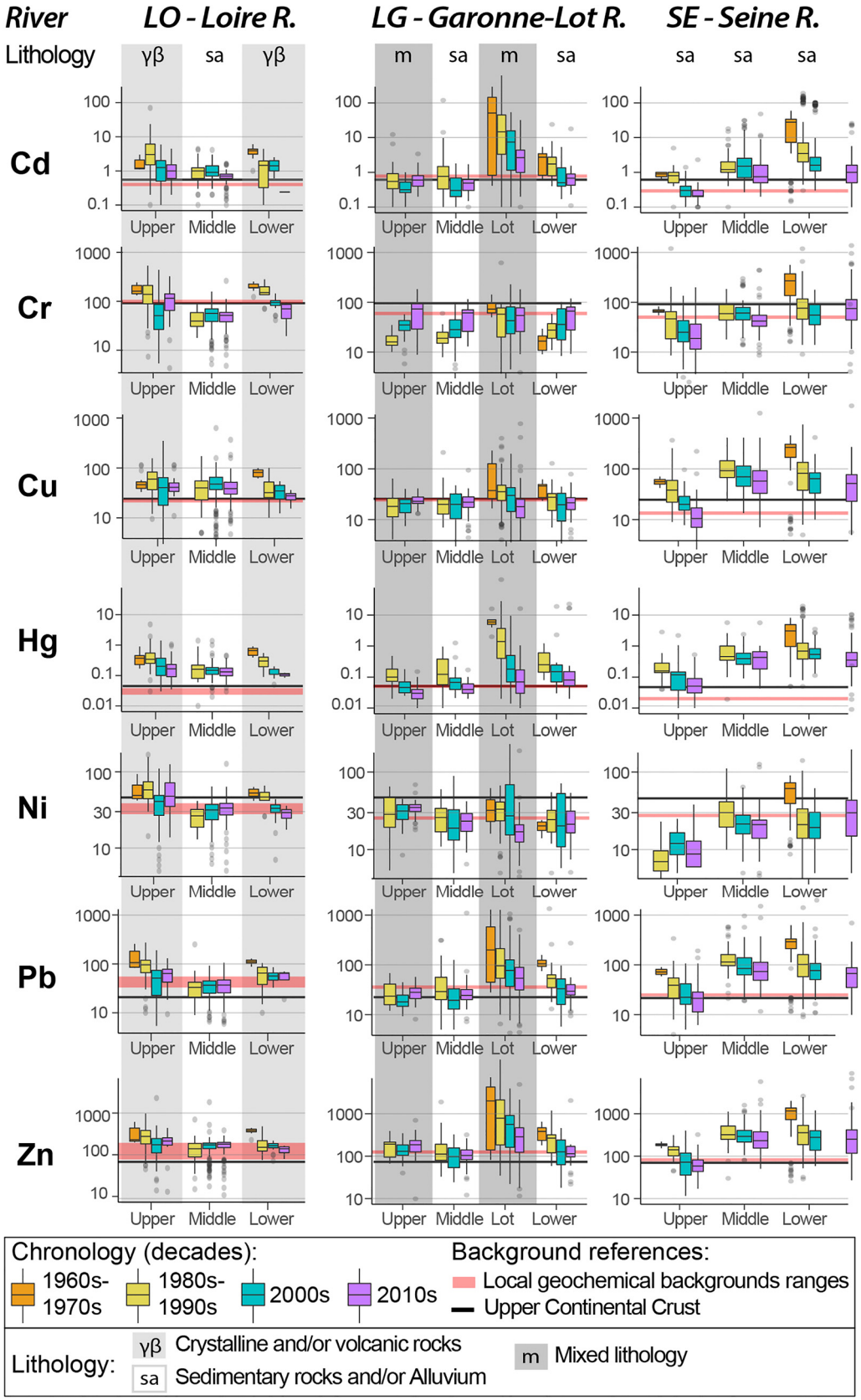

Fig. 6. Metal concentrations (mg kg^{-1}) in different types of sediments along the studied river according to four time-periods. Horizontal lines represent local geochemical backgrounds in red (see Table A.4) and the Upper Continental Crust values in black (UCC, after Rudnick and Gao, 2014). Vertical bars represent the main lithology of the river sections: γβ = crystalline and volcanic rocks, sa = sedimentary rocks or alluvium, m = mix of the previous two.

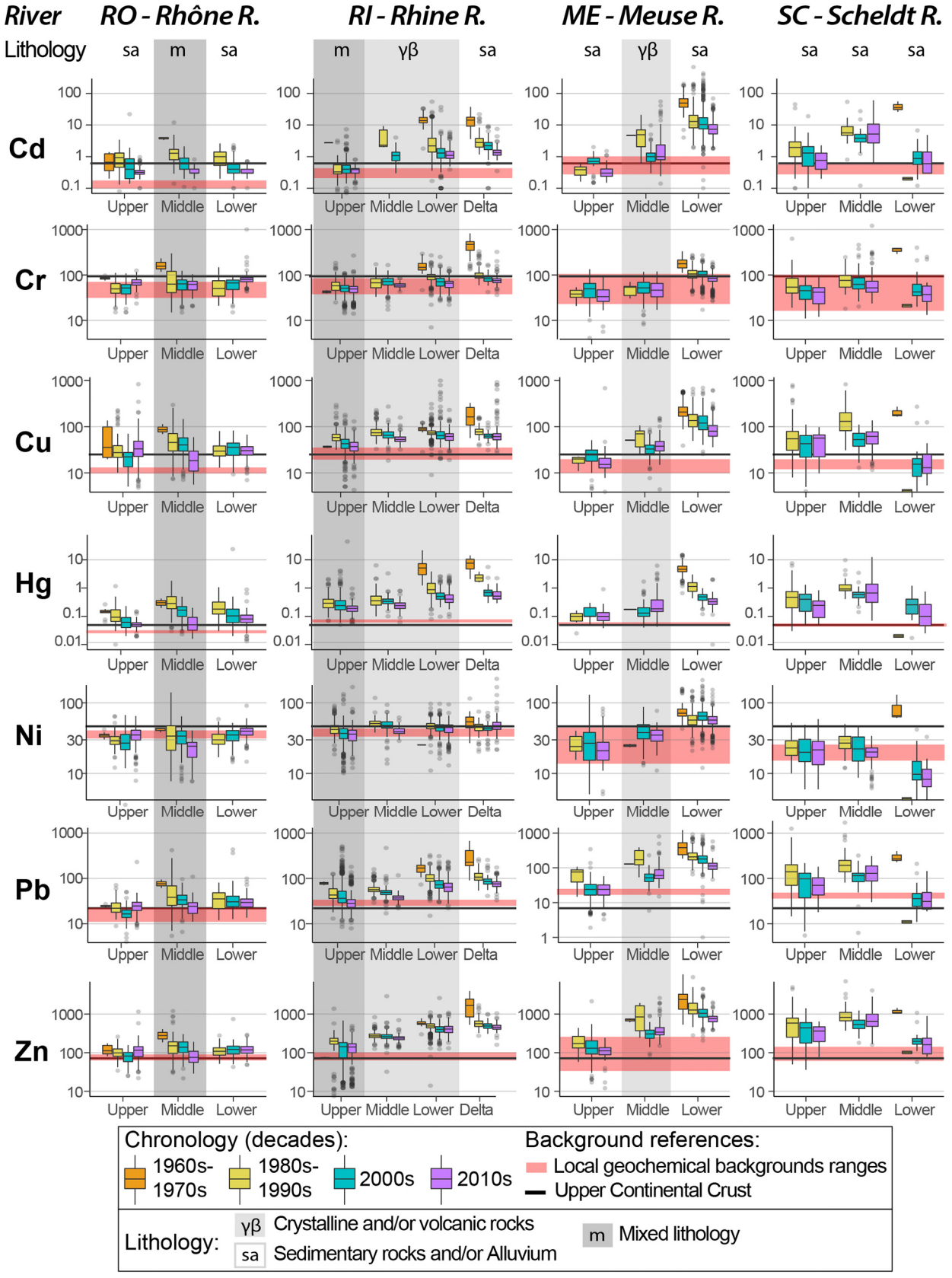

Fig. 6 (*continued*). *For more details, please refer to the first part of Fig. 6.*

River). It remains currently lower than the UCC, although it is approaching the critical PEC threshold of 111 mg kg^{-1} (Fig. 6; MacDonald et al., 2000). To our knowledge, this concern may be related to the transport of finer particles enriched in Cr, possibly increased by the water discharge decrease facing the Garonne River since 30 years (Etcheber et al., 2013; Habets et al., 2014). A slight increase in Cu, Cr, Ni, Pb and Zn is also observed recently in the Lower RO. In this case, the increase appears not to be related to an increase in metal concentrations. On the contrary, it is more likely driven by metal concentrations in SPM, linked to higher SPM loads during the 2010s (Delile et al., 2020).

(iv) Little variation was observed in space and time for several rivers (ME, RI, RO, and SC) for geogenic metal contents such as Cr and Ni. These metal concentrations generally remain in the UCC and local geological background ranges (Table A.4). They are also lower than the PEC which is of 111 and 48.7 mg kg^{-1} for Cr and Ni, respectively (MacDonald et al., 2000). These two non-ferric metallic elements could be brought to the sedimentary load by hillslope erosion and also by regular weathering of Palaeozoic Hercynian rocks supplied to the main stream by mountain tributaries (De Vos et al., 2006). These steady metal concentrations remain in line with the stable surface areas covered with farmland and forests in the drainage areas of these four rivers according to the Corine Land Cover Change survey (https://land.copernicus.eu/pan-european/corine-land-cover/lcc-1990-2000?tab=mapview).

3.5. Cumulative effects of analytical and environmental factors on metallic elements concentrations in river sediment

The meta-analysis of this large-scale dataset covering seven major Western-Europe basins and >12,000 samples highlights key messages, useful for the interpretation of metal concentration changes in the solid

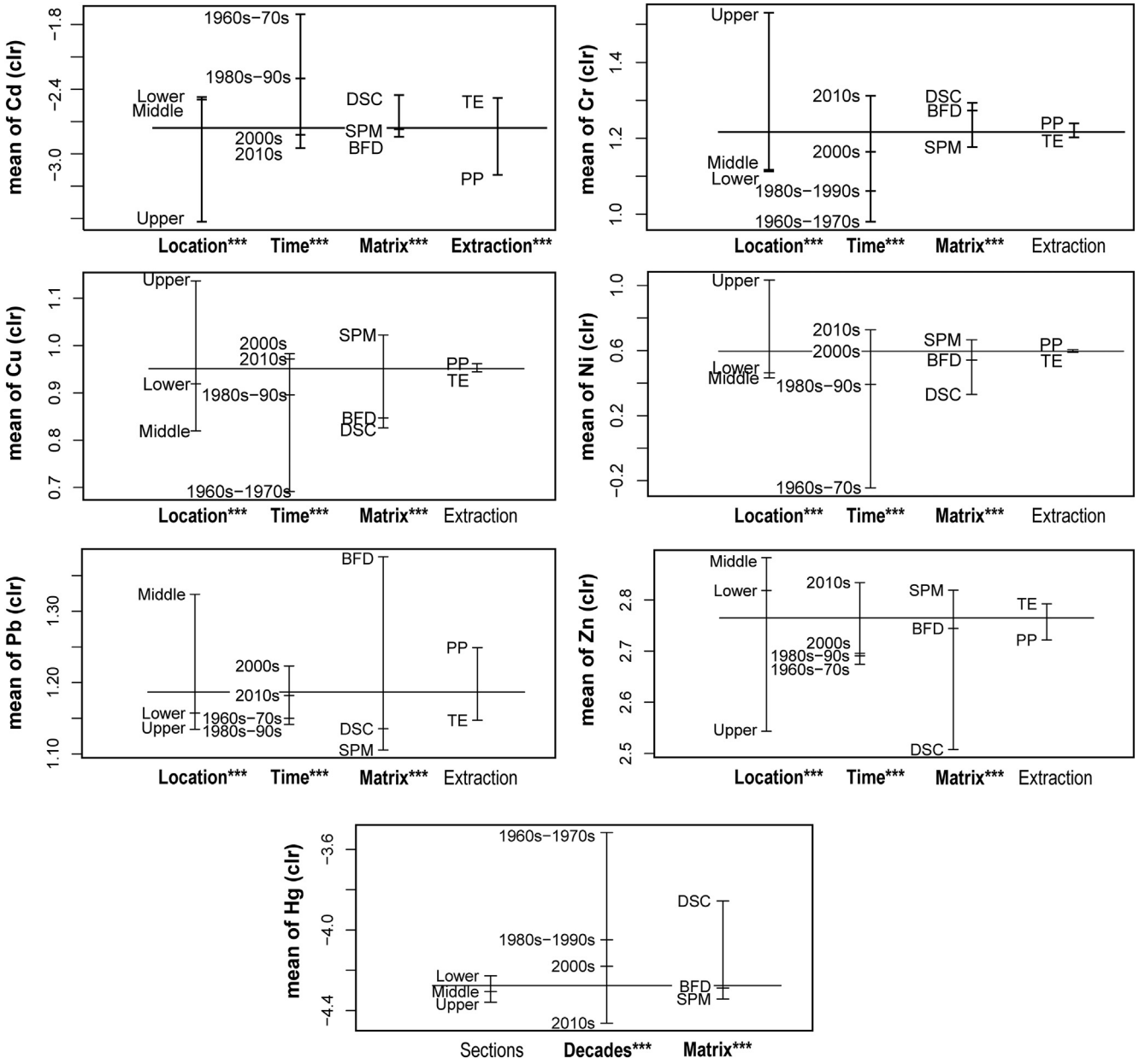

Fig. 7. Plot of univariate effects of the analysed factors on metal concentrations (clr = centred log-ratio) considering seven major Western European basins. A high scattering from the mean horizontal bar indicates very highly significant factor effects (***; see Table A.5 for p-values). Location, time and matrix-type are the 3 most significant factors influencing metal concentrations. The extraction protocol has a lesser significant influence on Cd, Cr, Cu, Pb, and Zn (extraction not tested for Hg).

fraction at a river corridor scale. The concentrations vary significantly depending on four factors: the type of matrix (BFD, DSC, and SPM), the heterogeneity of the extraction protocol (TE or PP), the spatial position along the river section (upper, middle or lower) and the sampling time period (decades). A four-ways ANOVA has been performed to test whether each factor effect and their interactions were statistically significant. A significance level of 5% was adopted. The *p*-values were <0.05 for most cases, implying a major influence of the studied factors on the metal concentrations (Table A.5).

At first, a statistically significant four-factor interaction between location, time, matrix-type and extraction is found for Cr and Cu ($p < 2.5e-3$). At a second level, a main effect of the interaction between location, time and, to a lesser degree, the matrix is evidenced for these two metallic elements, while the extraction type has a minor influence as also shown by univariate effect plots (Fig. 7).

For Cd, Ni, Pb and Zn, at least 3 statistically significant three-factor interactions are highlighted (Table A.5). Here again, the extraction method has the lowest influence according to the scores, except for Cd. Indeed, as Cd is generally present in small concentrations, little variations induced by the extraction method can even cause severe changes. At the two-ways ANOVA level, a significant interaction can be observed between paired factors for all metals, except for Cu and Ni which are less sensitive to location–extraction interactions. For Hg, the three-factor interaction between location, time and matrix is slightly significant and appears primarily influenced by (1) time and (2) location, i.e. the river section (Fig. 7; see Table A.5).

This analysis indicates that the largest effects are driven by the location along the rivers and by the sampling period of the sediment deposit. Actually, these two factors are influenced by geology and by the basin history, i.e. temporal variations of anthropogenic releases including urban, industrial and mining emissions. On Figs. 1 and 6, zones under crystalline and volcanic rock influence (felsic and mafic rocks) or presenting a mixed geology (mix of crystalline, volcanic and sedimentary rocks mainly) can be used to discuss the influence of these underlying factors. In some cases (e.g. Upper and Lower LO, Lot River section, and Middle RO), these regions may have a major influence on metal concentrations due to the presence of minerals more resistant to alteration. For instance, Cr and Ni which are mainly of geogenic origin (De Vos et al., 2006), are often much concentrated in these river sections (Fig. 6). This also applies to Cd, Hg, Pb and Zn. However, the increase in metals in crystalline and volcanic bedrock areas is not systematic. Indeed, a massive increase can occur in metal concentrations on the downstream parts of several rivers (Fig. 6). It is especially the case along RI and ME where a strong upward trend in metals occurred due to anthropogenic sources, regardless of the geological influence. It is also the case for SE and SC where no crystalline or volcanic rocks croup out along the main stretch. Thus, the concentrations appear more driven by urban industrial emissions and releases in the downstream part of these rivers than by geology.

To verify this hypothesis, a Factor Analysis of Mixed Data (FAMD) was performed in order to identify correspondences between quantitative data (metal concentrations: Cd, Cr, Cu, Ni, Pb, Zn) and qualitative variables (lithology, location, classes of population density; see table A.2 in the supplementary information) by using the PCAmix method in *R* (Chavent et al., 2017). This treatment corresponds to a mix between a PCA (Principal Component Analysis) for numerical data and a MCA (Multiple Correspondence Analysis) for the above-mentioned qualitative data. It can be used to identify the proportion of the total variation that can be attributed to changes in metal sources (natural versus anthropogenic origin). Due to the heterogeneity of the data, the results (calculated for both TE and PP extraction protocols) only explained 39% and 37.5% of the total variance on the two first axes, respectively (see Figs. B.1 and B.2 in the supplementary information). It can be attributed to major differences between river basins, stations and temporal variations at a river station. In both TE and PP cases, Cd, Pb and Zn were the best variables explaining the data, probably related to anthropogenic releases. This elemental triad is generally associated to the highest population densities (Q4), and to lower river sections characterised by sedimentary rocks or alluvium. Conversely, the concentrations in the upper and middle sections showed high correspondences with Q1 and Q3 population densities, found in crystalline and volcanic rock areas, and more importantly in mixed lithological sections (Figs. B.1 and B.2). Cu appears to have a less significant influence, while Ni and Cr do not show a close proximity to the location along the river, nor to lithology or population density.

All of these factors (lithology, river location, matrix type, extraction protocols) are critical to address a valid and meaningful comparison of spatial and temporal resiliency of hydrosystems at a large scale. This work underlined the difficulty to take into account seasonal metal variations with a higher resolution of such scale (e.g. Delile et al., 2020; Fan et al., 2021), and emphasises the need to adapt pollution indices (e.g. Geo-accumulation Index [IGeo], Enrichment Factors) to these factors to intercompare metal concentrations variations in river sediments.

4. Conclusions

Based on a dataset combining monitoring and scientific data (>12,000 samples), this work dealt with the variability of metal concentrations in sediments along seven major European fluvial corridors from 1945 to 2020. Facing heterogeneous sampling and analytical methods on the different rivers, this study quantified the influence of key factors influencing metal concentrations: sediment matrix type, TOC content, grain-size distribution and fractionation, extraction protocols, location and time.

The spatial (location) and time (decades) factors were the most significant factors. Indeed, major spatial and temporal patterns showed an increase of metal concentrations, especially Cd, Pb and Zn, along the river sections. It is closely related to population settings and geology in each watershed, both influencing the regional release of metal contaminants. This statement is in agreement with the impact areas of the main urban industrial hotspots, while former mined river sections generally contribute to increase the sediment contamination from the upper sections. A global decrease of metal concentrations in all sections since the 1960s–1970s onwards is related to international regulations and regional urban industrial changes. Secondary interactions such as the influence of the sediment matrix type (metal concentrations in SPM and DSC > BFD) were also highlighted. A frequent correlation between metal concentrations and FF content was especially observed, while the lack of correlation in some rivers suggests different metal-bearing phases probably due to the presence of macroscopic slags and ore particles. The extraction procedure had also to be considered because it explained significant differences for Cr, Cd, Cu, Pb, or Zn with higher metal concentrations derived from Total Extraction than from Partial Procedures, but it can be locally balanced by the substratum (i.e. for alkaline rivers, such as SC and SE). According to a subset of data on RI and LO Rivers, the particle size fractionation prior to analysis likely had a minor impact, mostly due to the domination of fine particles in the tested sample.

This approach gave critical evidences that improve the diagnosis of metallic pollution in worldwide rivers at large spatial and temporal scales. However, further efforts and works have to be undertaken to address remaining issues such as data corrections based on the influence of the above-listed factors, to find alternatives to the lack of TOC, grain-size or lithogenic elements (not acquired systematically during sediment surveys). In addition, this study underlined the need to adapt pollution indices to extraction modes and to lithological variations along the rivers. Responding these questions at a global scale will improve a consistent intercomparison of spatio-temporal trends and resiliency of river contamination.

Supplementary Information

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.149778.

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CRediT authorship contribution statement

André-Marie Dendievel (AMD): Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing – original draft, Visualization. **Cécile Grosbois:** Resources, Methodology, Writing – review & editing. **Sophie Ayrault:** Resources, Methodology, Writing – review & editing. **Olivier Evrard:** Resources, Methodology, Writing – review & editing. **Alexandra Coynel:** Resources, Methodology, Writing – review & editing. **Maxime Debret:** Resources, Methodology, Writing – review & editing. **Thomas Gardes:** Resources, Writing – review & editing. **Cassandra Euzen:** Resources, Writing – review & editing. **Laurent Schmitt:** Writing – review & editing. **François Chabaux:** Writing – review & editing. **Thierry Winiarski:** Methodology, Writing – review & editing. **Marcel Van Der Perk:** Resources, Methodology, Writing – review & editing. **Brice Mourier:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

We, the authors, declare that we have no conflict of interest.

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