Spatio-temporal assessment of the PCB sediment contamination in four major French river corridors (1945-2018)

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Short Summary

Polychlorinated Biphenyls indicators (ΣPCBi) from sediment cores, bed and flood deposits, suspended particulate matter and dredged sediments along the major French rivers (1945–2018) are compared with socio-hydrological drivers. ΣPCBi increased from 1945 to the 1990s due to urban and industrial emissions. They gradually decreased with the implementation of regulation. Specific ΣPCBi flux revealed amount of PCB-polluted sediments transported by French rivers towards European Seas over 40 years.

Abstract

Environmental pollution by Polychlorinated Biphenyls (PCBs) is a key concern about river quality because of their low degradation rates leading to their accumulation in sediments and living organisms. An original interdisciplinary work was conducted along the four main French rivers (Seine, Rhône, Loire and Garonne Rivers), which flow into major European seas. We completed a dataset based on sediment analyses provided by monitoring agencies, port authorities and research teams on different solid matrices (sediment cores, bed and flood sediments, suspended particulate matter, and dredged sediments). This dataset focused on the seven indicator PCB and their sum (ΣPCBi) from 1945 to 2018 (n ΣPCBi =1416). Special effort was put on the quality control to provide robust spatio-temporal information. Taking into account hydrological and human drivers, we outlined two main pollution trends: (1) from 1945 to 1975, a quick increase of ΣPCBi (up to 4 mg kg^{-1} dry weight, dw) and a sharp decrease in the 1980s on the Seine and Loire Rivers; (2) increasing but moderate ΣPCBi levels (50 to 150 µg kg^{-1} dw) followed by a decline after the 1990s on the Rhône and Garonne Rivers. In addition to these patterns, PCB emissions from urban and industrial areas or accidental events were significant on each river. Finally, when calculating specific flux, the Rhône River exhibited the uppermost ΣPCBi load (up to 12 µg m^{-2} $year^{-1}$ in 1977–1987), at least 25 % higher than those of the Seine and Loire Rivers, while the Garonne River showed a very low flux. In Western Europe, we confirmed that the Rhône, Seine and Loire Rivers contribute significantly to the PCB contamination of the seas, while French specific ΣPCBi fluxes are two orders of magnitude lower than those found in American or Asian Rivers. The dataset is available at https://doi.pangaea.de/10.1594/PANGAEA.904277 (Dendievel et al., 2019).

Keywords

Polychlorinated Biphenyls, Persistent Organic Pollutant, Rivers, Sediment, Cores, Monitoring, Historic pollution trends, Specific flux.

1 Introduction

The environmental pollution of river sediments due to Polychlorinated Biphenyls (PCBs) has become a concern as early as in the 1970s (Dennis, 1976; Müller, 1986). Indeed, PCBs were widely used as heat transfer fluids and insulating fluids for transformers and capacitors, while they had been utilised as wood, paper, plastic or ink additive since 1930 worldwide (Breivik et al., 2002a; De Voogt and Brinkman, 1997). Due to their high toxicity and their long persistence in the environment, the use of PCBs was banned in the USA (Toxic Substances Control Act of 1976) as well as in the Organisation for Economic Cooperation and Development member countries (OECD). In France, the use of PCBs was progressively restricted to closed systems, i.e. capacitors and transformers, by the order of 08/07/1975. Then, it was prohibited by decree in 1987 (n° 87-59). Old devices using PCBs are currently being dismantled after European Guidelines (national decrees: 2001-63 and 2013-301). To support these provisions, a global survey of PCBs in surface waters, sediments, fishes and bryophytes has started in the 1990s in France on behalf of the Survey and Control Network (RCS), jointly managed by the Water Agencies (WA) and the Regional Directorate for Environment, Development and Housing (DREAL). In charge of the local sampling and analyses, WA focused on seven PCB congeners (PCB-28, -52, -101, -118, -138, -153, -180) and their sum, referred to as ΣPCBi in the remainder of the text. These PCB indicators are generally found in high concentrations in the environment (e.g. sediment and biota), as well as in human food (IARC, 2016). Such provisions, taken at the worldwide scale, have led to a significant reduction of the quantity of PCBs found in the environment (Breivik et al., 2007; Wania and Su, 2004).

However, PCBs stored in the atmosphere, in soils and in hydrosystems still remain a major issue as revealed by recent studies on marine mammals and ice sheet contamination (Desforges et al., 2018; Hauptmann et al., 2017). Moreover, high PCB levels found in estuarine and riverine fauna – mussels, oysters, eels or fishes – are directly attributed to upstream sediment contamination (Blanchet-Letrouvé et al., 2014; Olenycz et al., 2015). In Europe and around the Mediterranean Basin, several studies focused on both sediment and biota concentrations in order to assess the relationships between particle pollution and accumulation in zooplankton, key invertebrates or bivalves, and fishes (Adda River, Italy: Bettinetti et al., 2016; Seine River, France: Chevreuil et al., 2009; Rhône River, France: Lopes et al., 2012; Thames River, UK: Lu et al., 2017; Elbe River, Germany: Schäfer et al., 2015; Nile River, Egypt: Yahia and Elsharkawy, 2014). Nevertheless, in most of these cases, understanding the PCB contamination transfer remains complex. Indeed, PCBs are stored in sediments from oxbow lakes, dams, soils, and dumping areas along rivers and coasts. This contaminated material is known to move through the system as suspended particulate matter (SPM) and could be submitted to successive deposition and remobilisation stages (floods, flushing, tidal effect, etc.). Diverse regulatory assessment and quality scale across countries (sampling frequencies and stations, analytical methods, limits of quantification, studied PCB congeners) complicate the estimation of PCB stocks in rivers at global scales. As for other pollutants, a more integrative research framework combining long-term data (i.e. sediment cores) and continuous/frequent monitoring of the various reservoirs (solid fraction, waters and biota), is needed to capture the spatial and temporal variability of the contamination by PCBs and to identify the drivers of this variability (Meybeck et al., 2018).

The current research aims at comparing PCB contamination in sediments along four major rivers with hydrological and human drivers over the period 1945–2018. In order to evaluate the magnitude of the PCB flux transiting from the rivers to the seas at a nationwide scale, we focused on the French rivers that flow into several major seas of the Northern Hemisphere (Loire and Garonne rivers: Atlantic Ocean; Rhône River: Mediterranean Sea; Seine River: English Channel and North Sea). These rivers are also known to have been strongly modified by anthropogenic activities since the 19th century to facilitate fluvial transport and, later on, for hydroelectricity and nuclear power purposes through the construction of dams, weirs and diversion canals (Tricart and Bravard, 1991; Parrot, 2015; Lestel et al., 2019). The occurrence of lateral structures narrowing and straightening the river stems (embankments on the Garonne River: Lalanne-Berdouticq, 1989; dikes and "épis de Loire": Barraud et al., 2013; "Girardon" structures on the Rhône River: Tricart and Bravard, 1991; etc.) also induced the storage of fine sediments with variable contents of organic pollutants in the floodplains (Vauclin et al., 2019).

Because historical data covering a wide range of locations along each river were required to approach spatio-temporal contamination trajectories, we compiled a dataset focusing on the sum of the seven indicator PCBs (ΣPCBi= PCB-28 + PCB-52 + PCB-101 + PCB-118 + PCB-138 + PCB-153 + PCB-180). ΣPCBi data were acquired on sediment cores, fresh bed and flood sediments and SPM or during dredging operation on the French rivers (Dendievel et al., 2019). We controlled data quality, spatial and temporal coverage to support our interpretation of the dataset and to maximize its robustness. This research also investigated how spatio-temporal contamination trends may be related to population, riverside land use (urban and industrial areas) and accidental PCB releases along each river. Finally, specific flux of ΣPCBi (µg m^{-2} $year^{-1}$) were calculated upstream of estuarine areas (km UEA). The results were compared to worldwide data in order to propose an integrative estimation of the mass contribution of the main French rivers to the global PCB pollution transferred to the neighbouring seas.

2 Methodology

2.1 Data collection on the studied rivers

Sediment contamination was assessed by collecting PCBi analysis results and associated ancillary data (total organic carbon content, grain size) at gauging stations located on the main stream and monitored for regulatory or scientific purposes. Significant effort was made to collect high quality information from multiple sources (harbour and navigation authorities, WA, DREAL, public research labs, etc.) at a national scale for the 1945–2018 period (initial total number of samples ~2300). The data came from four main sediment matrices:

- (1) Bed and flood sediments are assumed to be deposited sediments (monitoring: DREAL, WA, and ROCCHSED programme of the IFREMER). Sampling was performed by field operators since 1991–1995 on 135 stations distributed along the main rivers (see Fig. 1 and Supplement Table 1). Sampling frequencies ranged from once or twice a year to a unique sample in 30 years. All data – including sampling locations, dates, results and techniques if mentioned – were aggregated from 3 open databases and checked to avoid potential duplicates: (a) "naiades" supplied by WA (http://www.naiades.eaufrance.fr; accessed October 15, 2018), (b) the National Actions Plan on PCB (http://www.pollutions.eaufrance.fr/pcb/resultats.html; accessed January 15, 2019), (c) "surval" powered by the IFREMER (https://wwz.ifremer.fr/surval; accessed January 15, 2019). Academic studies on flood deposits were also included (e.g. Lauzent, 2017).
- (2) Suspended Particulate Matter (SPM) are considered as mobile sediments. SPM concentrations were monitored in the Rhône River by the OSR (Rhône Sediment Observatory) since 2011 at two stations: Jons and Arles, which are located upstream of Lyon and just upstream of the delta, respectively (https://bdoh.irstea.fr/observatoire-des-sediments-du-Rhône; accessed May 19, 2019). DREAL and WA were in charge of the SPM monitoring since 1993 on the Garonne River (three stations: upstream = Verdun-sur-Garonne; middle section = before the Lot confluence; downstream = Cadillac) and on the Loire River (four stations: upstream = Veauchette; downstream = La Possonnière, Montjean and Ste-Luce). We did not include SPM data from the Seine River because results were only available for "bulk water" (g L^{-1}) rather than for sediment. SPM were measured monthly to quarterly, sometimes bi-monthly, on the studied rivers.
- (3) Mobile dredged sediments were collected and analysed by harbour and navigation authorities. ΣPCBi data were provided by the Port of Rouen for the lower and estuarine sections of the Seine River with 5 stations monitored since 1992, and by the CNR (Rhône National Company) on the Rhône River with 81 sampling locations, mostly distributed next to hydraulic infrastructures or at river confluences.
- (4) Sediment cores deposited in reservoirs, oxbow lakes or channel banks were extracted by research teams of the INTERPOL consortium. Among French rivers, the Rhône River was intensively investigated with 13 cores analysed for PCBs contents along the river (Fig. 1). These studies provided vertical profiles of historical contamination on each river section since 1945 at least (Desmet et al., 2012; Mourier et al., 2014). On the other rivers, most analyses focused on lower sections to estimate the pollution trends at the river mouth: 3 cores were extracted downstream of Paris on the Seine River, providing records since 1945 (Boust et al., 2012; Lorgeoux et al., 2016; Vrel et al., 2013), 1 core was extracted from the Garonne River, downstream of Bordeaux, dating back to 1954 (Budzinski, Labadie and Coynel, pers. com.; Morelli et al., 2016; "Adapt'Eau" project) and 1 core from the Loire River, near Nantes (Desmet, personal communication; "Metorg" project) covering the period since the late 1970s. On the latter river, a second core was analysed for Persistent Organic Pollutants downstream of the industrial basin of Saint-Etienne (Fig. 1; Bertrand et al., 2015; Grosbois, personal communication; "Metorg" project).

2.2 Analysis and quality control

PCB-congener analyses in riverine sediments were performed according to several methods depending on stakeholders and research labs. It generally followed several steps. (1) Sampling was achieved by using Ekman grabs for bed and flood deposits, fluvial decanters for SPM, and hydraulic excavators for dredging. Cores at onshore and immersed sites were collected with percussion or piston corers (Cobra TT and UWITEC devices, respectively). Then, the samples were extracted in the laboratory and freeze-dried for conservation. Sieving was conducted when coarse sediment was collected (sieving to 2 mm or 63 µm). (2) According to our review, the extraction was usually achieved with a Soxhlet extractor or microwave-assisted, (3) before a purification via adsorption chromatography with sorbents such as silica, aluminium oxide, Florisil and activated carbon. (4) PCBs congeners were quantified by gas chromatography coupled with mass spectrometry (GC-MS) in selected ion monitoring (SIM) mode (for details, please refer to the related papers and sources cited in Table 1).

The quality control of monitoring data was one of the major challenges given the heterogeneity of data collected. Indeed, PCB results from bed and flood deposits, SPM and dredged sediment included frequent undetected values, outliers and variable limits of detection (LOD) or quantification (LOQ). LOQ for each PCB congener ranged from 0.01 to 20 µg kg^{-1} dw (highest LOQ observed among all congeners), depending on the analytical methods at the time of the analysis. For instance, a high LOQ of 20 µg kg^{-1} dw for each PCB congener was used for samples collected from the Garonne River over the 1994–2006 period. In addition, the low chlorinated compounds (PCB-LC: PCB-28, -52, -101, and -118) were rarely detected due to higher LOQ or lower concentrations. The highly chlorinated PCB congeners (PCB-HC: PCB-138, -153, and -180) were quantified at higher frequencies.

To process the original dataset (more than 12700 analyses on ca. 2300 samples), we considered two cases: (1) we integrated the results with all seven PCB congeners > LOQ, and (2) when only PCB-HC were quantified, a reconstruction was performed. For the latter, we estimated the ΣPCBi of each sample by using the original PCB-HC values, and relating it to the average percentage of PCB-HC in samples for which all PCB congeners were quantified from the same river and time. Such imputation-based method is more efficient than arbitrary substitution (e.g. half of LOQ), especially when undetected data dominate (Baccarelli et al., 2005; Helsel, 2006), which is a common case on the Loire and Garonne rivers. For this correction, ΣPCBi was calculated according to the following equation (1):

$$\Sigma PCBi \;=\; \frac{\Sigma PCB-HC \times 100}{MP\ PCB-HC} \quad (1)$$

where ΣPCB–HC is the sum of high-chlorinated PCB congeners measured in the sample (PCB-HC), i.e. PCB-138 + PCB-153 + PCB-180 (µg kg^{-1} dw), and MP PCB–HC is the mean percentage of the three PCB-HC in well quantified samples on each river (i.e. MP $PCB\text{-}HC_{Garonne}$= 63±11 %; MP $PCB\text{-}HC_{Loire}$= 68±12 %; MP $PCB\text{-}HC_{Rhône}$= 60±12 %; MP $PCB\text{-}HC_{Seine}$= 55±10 %).

As showed in Table 1, this step increased the proportion of validated monitoring data from 6 % to ca. 18 % for the Garonne River (48 samples), from 21 % to 36 % for the Loire River (147 samples), from 32 % to 44 % for the Rhône River (294 samples) and from 58 % to 76 % for the Seine River (343 samples). Table 1 also presents total organic carbon (TOC) and fine fraction content (% of clays and silts) in sediment. This additional data could not be used for normalisation because it was not systematically available for each sediment matrix or sample, and also because each basin has specific geochemical background signatures.

2.3 River system characterisation

River profiles, catchment surfaces, population in the drainage area and distances upstream of estuarine areas (km UEA) were collected by using Geographic Information System (GIS) data, as well as IGN tools and services (French National Institute of Geographic and Forest Information): Géoportail (https://www.geoportail.gouv.fr; accessed November 30, 2018), BD ALTI®, GEOFLA® and BD Carthage® (http://professionnels.ign.fr; accessed November 30, 2018). The annual average of water discharges (m^3 s^{-1}) along each river was computed according to the national databank of hydrological information (“Banque Hydro”; http://www.hydro.eaufrance.fr; accessed May 19, 2019). Other characteristics were collected from the European Corine Land Cover (2012) for urban and industrial areas (v.20b2, https://land.copernicus.eu/pan-european/corine-land-cover; accessed May 19, 2019), from *BASOL* (https://basol.developpement-durable.gouv.fr/home.htm; accessed February 11, 2019) and *BASIAS* (http://www.georisques.gouv.fr/dossiers/basias/donnees#/; accessed May 4, 2019) databases for the location of the sites where a PCB pollution was referenced after accidental spillage or after the deposit of contaminated sludge. The *QGIS* software (v.2.18.28) was used to merge and intersect all the data in a buffer zone of 1 km on both sides of each river.

2.4 Time series analysis and specific flux

The 1416 validated ΣPCBi data points (Dendievel et al., 2019) were analysed as a whole and representative for temporal trends since 1945 in *R* (v3.5.1, R Core Team, 2018) with the package “ggplot2” (v.3.1.1, Wickham et al., 2019). We used general additive models (gam) within the “stat_smooth” function to draw robust non-parametric models, little influenced by outliers and not truncated at the end. The basis dimension k was adjusted by using the “gam.check” function, available in the “mgcv” package (Wood, 2019). Chronological control was based on the date of sampling for regulatory monitoring data (bed and flood sediments, dredging and SPM) and on published chronological models for core data (e.g. Desmet et al., 2012; Lorgeoux et al., 2016; Mourier et al., 2014).

For the calculation of specific ΣPCBi flux, we estimated sediment flux according to water discharge (m^3 s^{-1}; available at http://www.hydro.eaufrance.fr) and reconstructed SPM concentrations using rating curves (relationships between water discharge and measured SPM concentrations). Specific rating curves were used for each river according to the existing literature and based on previously published data (Garonne River: Coynel et al., 2004; Loire River: Moatar and Dupont, 2016; Rhône River: Poulier et al., 2019; Seine River: GIP Seine Aval, 2008). This calculation was achieved at the gauging stations located just upstream of tidal influence zones (see locations on Fig. 1). The timescale was based on the monitoring network chronicles, and divided into four periods according to the data available: 1977–1987, 1987–1997, 1997–2007, and 2007–2017. Then, we used the average ΣPCBi concentration (cores and monitored sediments) from each lower river sections during these periods to calculate the yearly ΣPCBi load (t $year^{-1}$). Finally, in order to compare with international literature, we normalised this load to the drainage area at each gauging station to get specific flux of ΣPCBi (µg m^{-2} $year^{-1}$).

3 Results

3.1 Comparability of the results from different sediment matrices

The ΣPCBi distributions in each solid matrix were distinguished into two groups characterised by different hydro-sedimentary settings: (1) “deposited sediments” including bed or flood deposits and core sediments, (2) “mobile particles” including SPM and dredged sediments. ΣPCBi distributions between both groups in each river were tested (for details: see Suppl. Fig. 1). For the Rhône River, this comparison was achieved at the scale of the whole river during the period 2011–2018, because mobile particles were only available after 2011. In a similar way, we tested the distribution of ΣPCBi data from deposited and mobile sediments on the estuarine Seine (lower 50 km) and on the Upper Loire River (1012 to 750 km) since 1992 and 1991 respectively, because analyses on mobile sediments were available earlier (see. Suppl. Fig. 1). Regarding the Garonne River, we compiled all the available data since 1954 on the lower section (last 100 km). Wilcoxon tests demonstrated that the ΣPCBi distributions were not significantly different between the two groups ($p > 0.1$), and could therefore be suitable to support the discussion of the spatio-temporal contamination trends.

3.2 River and environmental settings

Physical settings and river modifications for navigation, flood control and electricity production could be considered as key factors influencing the sedimentation and the transport of polluted sediment. Accordingly, the studied rivers were divided into two groups based on the degree of water engineering disturbances and on flow rate trends (Table 2).

The first group is characterised by step-like longitudinal profiles due to heavy engineering caused by the installation of multiple hydroelectric plants and dams, changing the natural geomorphological dynamics. It comprises the Seine and the Rhône Rivers.

The Seine Valley is adapted for fluvial transport from and to Paris. It is equipped with 23 small dams and weirs currently managed by the Seine Navigation Service. The main hydraulic structure between Paris and Rouen is the Poses dam, which regulates the stream and stops tidal waters. Major tributaries flow into the Seine halfway between the source and the estuary, in urban areas around Paris Megacity. The junction with the Yonne, Marne and Oise Rivers occurs in this area (Fig. 2a to 2c). On the Lower Seine, the Eure River is the main tributary (annual discharge Q= 26 m^3 s^{-1}). At the estuary, the Seine River has a current discharge of ca. 600 m^3 s^{-1} (Suppl. Table 2).

The Rhône River corridor was also substantially modified for navigation purposes and hydroelectricity production. Several hundreds of “Girardon infrastructures” (dykes and groynes systems) were built to reduce the stream width and secondary channels were partly disconnected. Nowadays, 19 dams are managed by the CNR. The Upper Rhône is mainly supplied by Alpine rivers. The other main tributaries come in the medium and lower sections, in densely urbanized areas including Lyon, at the Saône River confluence (Q= 410 $m^3 s^{-1}$), Valence and Avignon at the Isère and Durance confluences respectively (Q= 333 and 180 $m^3 s^{-1}$). At the mouth (Rhône delta), the water flux culminates at ca. 1700 $m^3 s^{-1}$ with a high solid transport of 4–8 Mt of sediments each year (Fig. 2f).

The second group is composed by the Garonne and Loire Rivers which could be considered as less "structure-impacted" than those of the first group, although they are not devoid of hydraulic structures.

The Loire River is the longest French River (1012 km) and one of the main rivers flowing into the Atlantic Ocean (Bay of Biscay) in Western Europe. Its main stem is equipped with three major dams at La Palisse, Grangent and Villerest, managed for hydroelectricity and flood protection. Other significant hydraulic infrastructures are located in the Middle and Lower Loire River stretches (weirs, groynes, embankments and small reservoirs for navigation and nuclear plants management). Major confluences delineate each fluvial section: the Allier River (Q= 140 $m^3 s^{-1}$) is the downstream boundary of the Upper Loire; while the Cher, Vienne and Maine Rivers are at the transition between Middle and Lower Loire sections (Q=104, 203 and 127 $m^3 s^{-1}$, respectively). The water flux reaches ca. 870 $m^3 s^{-1}$ in the Lower section (Fig. 2k).

The Garonne River is equipped with high dams on its upper section (Pyrenees foothills), while only one section bypasses the main stream on the Middle Garonne, near the Golfech nuclear power plant. Water flux increases due to the contribution of successive tributaries from upstream (Ariège River) to downstream (Tarn and Lot Rivers; Fig. 2p). In the Lower Garonne, associated dikes and groynes channel the river which has a discharge of ca. 650 $m^3 s^{-1}$ in the Gironde Estuary. Sediment flux ranges from 0.9 to 3 Mt $year^{-1}$ in relation with hydrological conditions.

3.3 Land Use and Population

To decipher the spatio-temporal drivers of the ΣPCBi contamination trends in the studied rivers, we also acquired population and land use data for each river corridor (Fig. 2; see also Suppl. Table 2).

The first group (Seine and Rhône rivers) is highly populated halfway between the source and the estuary. This tipping point is also associated with the occurrence of major urban and industrial areas nearby the river. On the Seine River, a major increase in population and a concentration of industries occur in Paris Megacity, the largest urban centre in France (10.6 M_{inhab}; Fig. 2b and 2c). Other urban and industrial areas may be found in the Upper Seine (Troyes, and the Yonne confluence area), and in the Lower section (Rouen conurbation), although they remain small compared to Paris (Fig. 2b). Similarly, the Rhône River is characterised by increasing population densities with a demographic upsurge at Lyon (330 km before the sea). Near the Lyon metropolis (2.3 M_{inhab}), urban areas occupy up to 57 % of the river corridor and industrial areas cover 16 to 22 % of the surface area (Fig. 2h), in particular in the so-called "Chemical Corridor", south of Lyon.

The second group (Loire and Garonne rivers) shows more gradual increasing population densities along the river due to the regular presence of cities and towns (Fig. 2l and 2q). On the Loire Basin, urban (25 to 50 %) and related industrial areas (ca. 5 %) follow one another, such as Nevers, Orléans, Tours and Angers (Fig. 2m). However, two main historical industrial basins are also found: St Etienne Metropolis (404 K_{inhab}) in the Upper Loire (31 % urban and 19 % industries) and the Nantes Valley next to the Loire estuary (20 % urban and 30 % industries; 640 K_{inhab}). On the Garonne watershed, there are also two main cities and industrial areas (Fig. 2r): Toulouse, 370-280 km from the Gironde (32 % urban, 12 % industries; 760 K_{inhab}), and Bordeaux Metropolis (32 % urban, 19 % industries; 780 K_{inhab}), 50-25 km from the Gironde.

3.4 PCB pollution along the studied rivers

The spatial distribution of physical settings, land use and polluted sites is compared with the ΣPCBi spatial patterns in sediments along the rivers in Fig. 2d and 2e (Seine River), 2i and 2j (Rhône River), 2n and 2o (Loire River), 2s and 2t (Garonne River). Overall, maximum values (see Suppl. Fig. 2) were recorded on the Lower Seine River in the 1970s from Paris to Rouen (up to 5 mg kg^{-1} in the Darse des docks record in the Rouen Harbour; Vrel et al., 2013). On the Rhône River, the highest ΣPCBi found downstream of Lyon in 1995–1996, were somewhat lower (up to 2.4 mg kg^{-1}). On the Loire Valley, ΣPCBi was highest in the St Etienne Basin (Upper Loire) from 1966 to 2006 (up to 1.1 mg kg^{-1}), and in the Nantes Valley (Lower Loire) from 1973 to 1989 (0.6 to 1.2 mg kg^{-1}) and also sporadically in 2003–2008 (up to 1.4 mg kg^{-1}). ΣPCBi in the Garonne sediments are generally low and the maximum concentrations were recorded near the city of Toulouse in 1998 (only 145 µg kg^{-1}; see Suppl. Fig. 2).

Regarding the spatial patterns, the Seine River shows an increasing ΣPCBi trend in the downstream direction (Fig. 2d). Low ΣPCBi concentrations are measured upstream of Paris (median: 28±20 µg kg^{-1}), while an increase is obvious from Paris (median: 103±79 µg kg^{-1}) to Rouen (median: 318±348 µg kg^{-1}). This increase might be due to the co-occurrence of historical industries along the Seine River (such as smelters and papermaking industries of Vernon, ca. 200 km UEA) and from the Lower Eure Valley (ca. 140 km UEA), with long term release of fine sediments from Paris and the upper catchment areas (Fisson et al., 2017; Gardes et al., 2020; Tubergue and Arthus-Bertrand, 2009). Maximum ΣPCBi concentrations range from 0.5 to ca. 5 mg kg^{-1} in this area. A decline is observed in the lower 80 km, between Rouen and Le Havre, where ΣPCBi decrease to ca. 25±12 µg kg^{-1} in estuarine zones. On the Rhône River, based on 13 historical cores along the river, we highlight an increasing ΣPCBi trend from the Upper Rhône (median: 15±10 µg kg^{-1}) to the Middle Rhône section (median: 32±24 µg kg^{-1}). In addition, samples collected in the Chemical Corridor and near the Gier confluence (Middle Rhône) show very high contamination levels (ca 2 mg kg^{-1}). Then, according to the gam modelling, the Lower Rhône section presents a slight decrease of the PCB contamination (median: 24±18 µg kg^{-1}).

The global distribution of ΣPCBi in the Loire seems driven by two major areas (Fig. 2n): the industrial basin of St Etienne (Upper Loire; median = 153±101 µg kg^{-1}) and the Nantes Valley (Lower Loire; up to 1.4 mg kg^{-1}). Between these two sectors (i.e. Middle Loire), reduced ΣPCBi concentrations are recorded although the low density of observations is not sufficient to conclude (see Suppl. Fig. 2). The same applies to the whole Garonne River. Indeed, continental sections of the Garonne River lack accurate monitoring or historical data about persistent organic pollutants to propose a clear link between land-use and pollution levels (Fig. 2q, 2r and 2s).

According to *BASIAS* and *BASOL* databases, a variable number of PCB contaminated sites is reported along the rivers (Fig. 2e, 2j, 2o and 2t). These databases provide valuable insights into the main polluted sites (due to leaks or fires from electrical capacitors or transformers) that should be cleaned up in priority. High frequency of PCB-polluted sites is evidenced next to Paris and Rouen (Seine), Lyon (Rhône), Toulouse and Bordeaux (Garonne) conurbations. The spatial link between these sites and major urban or industrial areas is clear, probably due to the occurrence of electrical power centres specifically established to supply these areas. On the Loire River, this relationship is less obvious because numerous incidents took place along the river, from St-Etienne to Digoin, and Nevers for instance (Fig. 2o). Such divergences are most certainly due to an incomplete listing and/or survey of pollution events (Callier and Koch-Mathian, 2010).

4 Discussion

4.1 Temporal trends of the PCB contamination in the main French rivers

ΣPCBi temporal trends provide another important aspect of the fate of contaminant concentrations in sediments. Environmental histories could be described at different timescales according to the available data on each river: since 1945 for the Seine and Rhône Rivers, and since 1954 and 1973 for the Garonne and Loire Rivers, respectively.

Among the reconstructed trends, the Seine curve shows a close relationship with the estimated production inventory proposed by Breivik et al. (2002) (Fig. 3a and 3e). Thus, four main steps are highlighted for this river: (1) ΣPCBi gradually increased from 1945 to 1970, with a plateau at the end of the 1950s known at both local and global scales (Breivik et al., 2002a; Lorgeoux et al., 2016). (2) The Seine curve reached a maximum in 1975 with ca. 1800 µg kg^{-1} of ΣPCBi. Then, (3) it sharply decreased to ca. 300 µg kg^{-1} in the late 1980s and (4) to ca. 100 µg kg^{-1} in the 2000s (Fig. 3a). The current ΣPCBi contamination (2000–2018) on the Seine River remains relatively high from Paris to the Lower Seine section (Suppl. Fig. 2). Figures 2c to 2d suggested that the origin of the PCB pollution is located within Paris and Rouen urban and industrial areas, where accidental contamination could occur (more than 200 PCB polluted sites listed in Paris according to *BASIAS* and *BASOL* databases). Inputs from the Lower Seine Valley and from its tributary (Eure Valley), upstream of Rouen, may also be considered (Fig. 2d). The decline from steps (3) to (4) seems correlated with the prohibition of production, sale and purchase of devices using more than 500 mg kg^{-1} of PCB after 1987 (mainly electrical transformers) and their disposal according to the 1996 European Directive (transposed into the French law in 2003; Fig. 4-f).

The Loire record is shorter and presents high ΣPCBi concentrations in river sediments between 1973 and 1978 (1,200 µg kg^{-1}), before a quick decrease to 10 µg kg^{-1} after 2010 (Fig. 3b). These changes are likely linked with a global increase of PCB production and emission in Western Europe from 1930 to 1970 (steps 1 and 2), before a sharp drop after 1973 (step 3), linked to the national applications of global regulations (OECD) prohibiting the use of PCBs in open environments, following Breivik et al. (2002a, 2002b, 2007) (Fig. 3e). Indeed, The fast decrease of ΣPCBi in sediments in the late 1970s in the Seine and Loire Rivers (half-life $t_{1/2}$ ranges from 5 to 13 years) suggests a signal affected by the global reduction of PCBs emission (Rosen and Van Metre, 2010). Moreover, PCBi half-life decay ($t_{1/2}$) in the Seine and Loire sediments are also consistent with those measured on the Rhône River cores where $t_{1/2}$ is comprised between 2 and 13 years (Desmet et al., 2012).

For the Rhône River, the general additive model (gam) suggests a smoother and complex ΣPCBi trend (Fig. 3c). Indeed, the concentrations found in the 1950s are ca. 70 µg kg^{-1} and slightly increased to a plateau of ca. 80 µg kg^{-1} in the 1980s and 1990s. Then, a general decrease is observed after 1996. This model, based on a large number of data, confirms the first modelling attempt of Desmet et al. (2012) based on a lower number of observations (four cores). The long-term plateau effect is obviously linked to high ΣPCBi values during the 1980s and the 1990s. Maximum values ranged from 0.7 to 2.4 mg kg^{-1} in 1995–1996 (i.e. much higher than regulation levels). They originated from Givors and St-Vallier, two stations located downstream of the Lyon's "Chemical Corridor" and at the mouth of the Gier industrial Valley known for intensive mining, smelters, forges and factories since 1870 (Gay, 1996). Within Lyon (Fig. 2j), accidental contaminations of groundwater in abandoned or decommissioning industrial or commercial sites are recorded from the west (Vaise, 300 L of Pyralene spilled in 1995) to the north-east (Vaulx-en-Velin, 4,000 L in 2008). The reduction of PCBi levels in the Rhône River presents a time-lapse of about 20 years compared to the Seine and Loire Rivers trends. It could be due to accidental releases in the middle Rhône section, but it is also certainly linked with river management and hydrological settings. Indeed, the Rhône River is equipped with major dams and slide structures ("Girardon infrastructures") which can store contaminated sediments and release them later on. This heavy engineering also affects the continuity of sediment transport. In addition, the Rhône River has the highest SPM flux (9.5 – 14 Mt $year^{-1}$) and water flux (ca. 1,700 $m^3 s^{-1}$) in France, which has likely diluted the pollution levels measured in sediments. Its floods could also produce a massive remobilization of contaminated sediments (Ollivier et al., 2006). However, similar PCB patterns as those of the Seine River were found in some areas with continuous sedimentation on the Rhône River, such as "La Morte" (MTE core), "Arras-sur-Rhône" (ARS core) and at the Lake of Paladru (Desmet et al., 2012; Mourier et al., 2014). The PCBi trend on these sites is consistent with the global production of PCB in Western Europe (Breivik et al., 2002a).

On the Garonne River, a preliminary model can be applied carefully due to the few data > LOQ (Table 1; Fig. 3d). For a first attempt, ΣPCBi increased until 1980–1990 and then progressively decreased. Figure 3d displays a curved shape, although the lack of accurate monitoring data and of sediment archives (only one core) does not allow to distinguish local from long-distance pollution. In any case, median ΣPCBi concentrations in the Garonne River sediments vary from less than 20 µg kg^{-1} to ca. 70 µg kg^{-1} (see Suppl. Fig. 2). Low ΣPCBi concentrations could be due to high sedimentation rates upstream of the monitored sites; whereas the highest concentrations could be partly related to the reworking of polluted sediments by the 1993 and 1996 floods for instance. These general low values explain why the monitoring efforts were lower on this river; LOQs were also too high to investigate the spatial and temporal evolution of the contamination of this river.

4.2 Spatio-temporal distribution of the PCB contamination and implications for biota

To discuss spatial and temporal variations of contamination within each corridor, ΣPCBi concentrations in sediments were presented on the river sections for three main time windows: < 1997, 1997–2007, and 2007–2018 (Fig. 4). Despite the differences regarding the spatial distribution (Fig. 2d, 2i, 2n, 2s) or the temporal trends on each river (Fig. 3), a general decrease of the ΣPCBi contamination is found in each river section, with the highest values systematically observed before 1997 (except around Paris; Fig. 4). Otherwise, a major increase is observed in the downstream direction for the three time windows.

On the Seine River, this situation is the result of a major contamination of the river corridor from Paris to Rouen, linked with urban and industrial activities (Figs. 2a to 2e). However, in 1997–2007, ΣPCBi concentrations in fluvial sediments were higher in the Parisian stretch than in the lower section (Fig. 4a). It might be explained by a release of PCBs from accidental spills or waste discharges – mainly "Pyralene oils" from electrical transformers –, also contaminating soils and aquifers for a long period. Circa 20 sites show median concentrations above the lower effect level at which toxicity to benthic-dwelling organisms is predicted to be unlikely (threshold effect concentration – TEC = 59.8 µg kg^{-1} according to MacDonald et al., 2000). Among these sites, 16 are also above the approved level for dredging and relocation activities in France without further investigations (N1= 80 µg kg^{-1}, order of 14-07-2014). Further downstream, PCB concentrations in the Lower Seine section also frequently exceed the Environmental Assessment Criteria (EAC comprised between 0.6 µg kg^{-1} for PCB-118 and 40 µg kg^{-1} for PCB-153) used for the monitoring of coastal areas (OSPAR commission, 2009a). This pollution may have been dispersed down to the estuary where PCB contents increased in mussels (*Mytilus edulis*) from 1995 to 2006 (Tappin and

Millward, 2015). Moreover, according to the current OSPAR assessment maps (http://dome.ices.dk/osparmime/main.html; accessed February 14, 2020), PCBi concentrations in sediments, fishes, shellfishes and crustaceans along the Normandy Coast frequently exceed EAC for most of the PCB indicator congeners and are generally higher than those of the English Coast of the Channel.

In the Rhône sediments, low to moderate ΣPCBi concentrations were generally observed before 1997 and a gradual decrease is found from 1997 to 2015 (Fig. 4b). The Middle Rhône River receives especially high concentrations of these contaminants, linked to significant emissions from urban and industrial activities (Lyon conurbation, its "Chemical Corridor", and the Gier Valley). In addition, several sites of PCB production and release are located nearby Lyon such as the PCB treatment facility of Tredi (St-Vulbas), St-Auban in the Saône Basin or some local sources such as at the vicinity of the "Grand Large" Dam, as previously demonstrated by Desmet et al. (2012). The concentrations in the Lower Rhône corridor are very close to the Middle Rhône concentrations and suggest a long-distance diffusion of this pollution. On the Lower section, ΣPCBi concentrations are expected to be diluted by the high SPM flux coming from some tributaries, such as the Durance River (1 to 2 Mt year^{-1}; Poulier et al., 2019). Our hypothesis, based on the compilation of numerous data, clearly contrasts with the previous assumption – based on 8 cores of which only one was located on the lower section – which proposed an exponential increase of PCB pollution in the downstream direction (Mourier et al., 2014).

In all the Loire River sections, very high ΣPCBi levels are displayed before 1997 (Fig. 4c). In the Upper Loire, a major increase occurs in the St-Etienne Basin which is mainly supplied by two tributaries: the Ondaine and Furan Rivers (Fig. 2k). Currently (2007–2018), PCBs continue to accumulate at relatively high concentrations in this section. This issue is critical for sediment management and for wild species conservation. As an example, Lemarchand et al. (2014) demonstrated that PCBs were detected in all the analysed species, and found high contamination cases among European otters (*Lutra lutra*). Indeed, the Upper Loire Basin was historically one of the main coal extraction areas in France with a high density of urban population and industries (gas, weapons, tools…) until the 1980s. As for PAHs (Bertrand et al., 2015), the Ondaine-Furan corridor was likely the main contributor to the Upper Loire PCB contamination. In the Middle Loire River stretch, several urban and industrial zones are found (Nevers, Orléans, Tours), albeit the low quantity of available data does not allow to evaluate PCB pollution trends on those areas. In the Lower Loire, PCBi sums were very high before 1997 and probably induced a high toxicity level, above the French N2 level (i.e. contamination too high to discharge dredged sediments into the sea; the sediments must be treated or stored on terrestrial environment) and PEC thresholds (Fig. 4c). This local PCB pollution is related to urban, industrial, refining and harbour activities around the city of Nantes and the Port of St-Nazaire.

On the Garonne River, a decreasing ΣPCBi trend is highlighted in each section, from 1997 to 2017 (Fig. 4d). ΣPCBi concentrations around Toulouse (Middle Garonne) were the highest and suggest significant pollutant releases from the city conurbation. Few data were available for the Pyrenees foothills before 2010, although ΣPCBi concentrations are higher compared to those from the lower sections at the same period. One hypothesis could be the presence of local pollution sources derived from electricity production. Moreover, the PCB pollution in the Pyrenees is also demonstrated by the local prohibition to fish eel, barber, bream, carp and catfish in the Upper Garonne section since 2011 (according to prefectural orders collected by Robin des Bois, 2013). These observations illustrate the continuing need to challenge the PCB pollution issue (Brunet et al., 2007). Thus, current research underlines the need to acquire more precise monitoring and long-term data in several river sections that are poorly documented (e.g. Pyrenees foothills and Middle Loire, for the Garonne and Loire Rivers respectively).

Finally, the current ΣPCBi contents in all river sediments (2007–2018) suggest a relatively low toxicity. For this period, ΣPCBi concentrations are usually under ecotoxicological thresholds (such as TEC and EAC), and under the French regulatory level N1 ruling the management of dredged sediments. These relatively low ΣPCBi contents in current river sediments contrast with high ΣPCBi concentrations found in related biota. Indeed, PCB concentrations in freshwater fishes still exceed regulatory bench-marks for consumption in the middle Rhône Valley, along the Lower Seine and in the Upper Loire (Babut et al., 2012; Lopes et al., 2012; Vigreux-Besret et al., 2015). For instance, the Bay of Seine mussels are inedible due to median concentrations exceeding 300 µg kg^{-1} of PCB-153 – only one of the PCB-HC (Claisse et al. 2006). According to the OSPAR commission (2000), the French Atlantic coast is also contaminated by PCBs delivered by the Loire and the Garonne Rivers: high concentrations in mussels, oysters and fishes were found next to their estuaries, and likely originated from urban and industrial areas. Sediments frequently exceeded the EAC in the Loire Estuary, especially for PCB-118 which is the most toxic PCB-congener (OSPAR commission, 2017). At the Western European scale, high PCB contents in surface sediments and marine biota from Southern England, and from Spain (Eastern Biscay Bay and Catalonia as well) likely indicate that French rivers provide a significant amount of PCBs, transported by sea currents to these areas (OSPAR commission, 2009b).

4.3 Specific ΣPCBi flux and worldwide comparison

Mean annual ΣPCBi flux (kg year^{-1}) during four decades (1977–1987, 1987–1997, 1997–2007, 2007–2017) was calculated according to the mean ΣPCBi concentrations in the lower river part and the corresponding SPM/solid flux during the same decades. Then, it was normalised by respective catchment areas to obtain specific ΣPCBi flux expressed in µg m^{-2} year^{-1}. Such process allows an estimation of annual pollutant flux reaching the river mouths (Babut et al., 2016; Mäkelä and Meybeck, 1996).

Using this approach, we demonstrated that the ΣPCBi load was the highest on the Lower Rhône River, regardless of the time window (Fig. 5). Indeed, specific ΣPCBi $flux_{Rhône}$ reached 12±3 µg m^{-2} year^{-1} (more than 1 t year^{-1}) between 1977 and 1987. Moreover, the specific flux remained relatively high until 2007, exceeding 4 µg m^{-2} year^{-1}, before to be ca. 1.3 µg m^{-2} year^{-1} during the last decade. The Rhône River could be considered as one of the main contributors to the PCB pollution in the Western Mediterranean, where shelf deposits accumulated ca. 10–30 µg m^{-2} of PCBs a year (maximum = 45–65 µg m^{-2} year^{-1}) from Monaco to Catalonia (Marchand et al., 1990; Salvadó et al., 2012; Tolosa et al., 1997). The specific ΣPCBi $flux_{Rhône}$ remains in the low quartile of the most polluted rivers of the world, compared to American ones (ΣPCBi $flux_{Lakes\ Erie\ and\ Ontario}$= 0.2–11 mg m^{-2} year^{-1} from 1997 to 2000: Marvin et al., 2004; ΣPCBi $flux_{Mississippi\text{-}Louisiana\text{-}Florida\ Bay}$ = 12–390 µg m^{-2} year^{-1}: Santschi et al., 2001) and to Asian Rivers (e.g. ΣPCBi $flux_{Pearl\ Delta}$= 86–187 µg m^{-2} year^{-1} from 1980 to 1994: Mai et al., 2005).

The Seine specific ΣPCBi flux amounted to ca. 8.3 µg m^{-2} year^{-1} in 1977–1987, although they rapidly decreased below 1.5 µg m^{-2} year^{-1} after 1987 (Fig. 5a). Current specific ΣPCBi $flux_{Seine}$ can be estimated to ca. 0.35 µg m^{-2} year^{-1}; i.e. close to atmospheric flux measured by Chevreuil et al. (2009). According to Tappin and Millward (2015), the Seine River could be considered as a major source of micropollutants to the English Channel, supplying half of the PCB flux (ΣPCBi $flux_{English\ Channel}$ = 7.6 µg m^{-2} year^{-1} in the 1980s). The Seine River very likely contributed, together with the Thames and Rhine Rivers, to the North Sea PCB pollution. Some recent works also showed that a more local pollution, derived from small coastal rivers, apparently drives the PCB influx nowadays (Everaert et al., 2014; Nicolaus et al., 2015; Vandermarken et al., 2018).

The Loire River exhibited a ΣPCBi load as high as in the Seine River. Indeed, specific ΣPCBi $flux_{Loire}$ culminated at ca. 8.2±2 µg m^{-2} year^{-1} in the 1970s and 1980s, before a sharp decrease under 2 µg m^{-2} year^{-1} after 1987 (Fig. 5a). Its load exceeded the Seine load until 1997: 220–900 kg yr^{-1} versus 90–550 kg yr^{-1} (Fig. 5b). In the Loire basin, a high ΣPCBi flux originates from the Upper Loire and is mainly exported by the Furan/Ondaine tributaries in the St Etienne Basin (ca. 59–41 kg y^{-1} until 2007), due to high sediment loads (Gay et al., 2014). Finally, the Garonne River transported relatively stable amounts of PCBi from 1977 to 1997 (2 to 1.7 µg m^{-2} year^{-1}), before decreasing to less than 0.5 µg m^{-2} year^{-1} after 2007. All ΣPCBi fluxes display an asymptotic behaviour from 1977 to nowadays (Fig. 5), which revealed the persistence of non-null values of PCB in fluvial sediments in the future.

5 Data availability

The dataset presented in this study is freely available on the Pangaea portal at: https://doi.pangaea.de/10.1594/PANGAEA.904277 (Dendievel et al., 2019).

6 Conclusions

In this research, we provided an original intercomparison of PCB pollution trends along four major rivers – i.e. from source to estuary – of Europe (Seine, Rhône, Loire and Garonne rivers). The dataset targeted the sum of the seven regulatory indicator PCBs (ΣPCBi) through the collection of bed and flood sediments, SPM, dredged sediments and cores coming from both monitoring data and research projects. The quality of the data varied according to the studied hydrosystem: the Seine and Rhône rivers were well documented, whereas a rather low number of suitable ΣPCBi data was available on the Garonne and Loire rivers. After using a correction factor on low quality data, long-term ΣPCBi concentrations and flux were reconstructed over the last 80 years (1945–2018). Our results identified some major industrial and urban areas as PCBi sources, diffusing the pollution from the upper and middle river sections to downstream areas. Two major temporal trends were found, depending on the river: (1) major and highly concentrated ΣPCBi releases (up to 4 mg kg^{-1}) until 1975, followed by a sharp decrease until today occurred on the Seine and Loire rivers, and could be related to the implementation of environmental regulation. (2) Moderate ΣPCBi concentrations with a long-term diffusion until the 1990s are found on the Rhône and Garonne rivers. Sporadic increases (up to 2 mg kg^{-1}) due to urban or industrial releases and accidental discharges (old transformers and capacitors) also reduced the resilience of the studied hydrosystems. Specific ΣPCBi fluxes and loads since 1977 show that the Rhône River provides an important quantity of ΣPCBi to the sea, followed by the Seine and the Loire rivers. In contrast, low exports from the Garonne River were found. Despite the lack of a global evaluation of PCBs delivered by rivers to the seas over the world (Lohmann and Dachs, 2019), we highlight the important role played by French rivers in the PCB contamination (sediments and biota) of the seas (Western Mediterranean Sea, English Channel, Atlantic Ocean). For the future, it is important to insist on the necessity to (1) improve analytical performances for the acquisition of more reliable monitoring data on organic pollutants from river sediments and (2) to collect sediment cores at long-term accumulation sites in order to perform robust trend analyses and to better integrate the spatial and temporal contributions of pollution heritage.

7 Supplements

Two supplementary tables are provided with (1) the list of the sampling locations, including the geographic coordinates, the survey period and the number of samples used (Suppl. Table 1) and (2) hydrological and human settings in a buffer zone of 1 km on both side of each river, including the flow rates, population distribution, land use (urban and industrial areas) and number of PCB polluted sites (Suppl. Table 2). Two supplementary figures are also provided to detail the ΣPCBi distribution within the matrix groups on each river (Suppl. Fig. 1), and to compare the historical (1945–2018) distribution of ΣPCBi maxima along the rivers with the current situation (2000–2018; Suppl. Fig. 2).

Supplement Table 1 – List of the sampling locations, chronology and number of samples accepted and corrected

Supplement Table 2 – Hydrological and human settings along each studied river (Garonne, Loire, Rhône, Seine Rivers)

Supplement Fig. 1 – Comparison of the ∑PCBi distribution within the matrix groups. Distances are expressed in kilometres Upstream of Estuarine Areas (UEA). Graphics and Wilcoxon tests were performed with R (v. 3.5.1, R Core Team, 2018).

Supplement Fig. 2 – Comparison of the ∑PCBi maxima from 1945 to 2018 with current maxima (2000–2018) along the French Rivers.

Author contributions.

A-MD and BM were in charge of collecting, formatting, cleaning and analysing data. BM was also the head of the INTERPOL project. Hydrological and land use data were acquired by A-MD and QF. AC, BM, CG, FK, HB, MDebret, MDesmet, OE, PL, SA, SV, TG, TW and YC provided core data. Spatial analysis was performed by A-MD. Statistics, spatial figures and discussion were designed by A-MD, BM and with the help of SV and TW. All authors participated to the discussion and reviewed the draft manuscript.

Competing interests. The authors have no conflict of interest

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Tables and captions

Table 1 – Sources and quality of the data. Sediment matrices are divided into: deposited sediments (cores, bed and flood deposits) and mobile particles (SPM and dredged sediments). "PCBi analyses (initial)" represent the number of analyses initially collected from monitoring data, whereas "7 PCBi > LOQ" and "Imputed ΣPCBi" represent only the data discussed in this article. The number of sites corresponds to the sites where validated analyses (i.e. 7 PCBi > LOQ or imputed ΣPCBi) are available. WA = Water Agency.

Rivers	Matrix group	Solid matrix	Sites (n)	Time range	PCBi Analyses (Initial)	7 PCBi > LOQ	Imputed ΣPCBi	TOC (%)	Clays and silts (%)	Data Sources	References and Availability
Garonne	Depo-sited	Bed and flood sediments	23	1992-2017	223	16	25	1.3 ±1.9	89.7 ±5.0	Adour-Garonne WA; IFREMER (ROCCHSED); UMR CNRS 5805 EPOC	http://www.naiades.eaufrance.fr https://wwz.ifremer.fr/survail Lauzent, 2017
		Cores	1	1954-2011	12		-			UMR CNRS 5805 EPOC	Budzinski, Labadie & Coynel, pers. com.; Morelli et al.. 2016
	Mobile	SPM	3	1993-2014	52	0	7	1.8 ±1.0	-	Adour-Garonne WA	http://www.naiades.eaufrance.fr
Loire	Depo-sited	Bed and flood sediments	35	1994-2015	178	64	15	2.2 ±2.7	-	Loire-Bretagne WA; DREAL Auvergne-Rhône-Alpes; ONEMA; IFREMER (ROCCHSED)	http://www.naiades.eaufrance.fr http://www.rhone-mediterranee.eaufrance.fr/docs/PCB/donnees/bassin_LB/resultats-sedimentsLB_2013.xls http://www.pollutions.eaufrance.fr/pcb/resultats-xls.html; https://wwz.ifremer.fr/survail
		Cores	2	1973-2012	23		-			E.A. 6293 GeHCO	Desmet, pers. com; Grosbois, pers. com.
	Mobile	SPM	4	1993-2014	229	21	47	6.8 ±4.2	-	Loire-Bretagne WA	http://www.naiades.eaufrance.fr
Rhône	Depo-sited	Bed and flood sediments	30	1995-2016	318	73	53	1.07 ±1.2	78.4 ±30.7	Rhône-Méditerranée-Corse WA	http://www.naiades.eaufrance.fr
		Cores	13	1939-2017	327		-			UMR CNRS 5023 LEHNA	Desmet et al., 2012; Mourier et al., 2014
	Mobile	Dredged sediment	81	2006-2017	146	139	1	3.4 ±2.7	88.1 ±22.3	CNR	https://www.cnr.tm.fr
		SPM	2	2011-2016	209	13	15			OSR	https://dx.doi.org/10.17180/OBS.OSR
Seine	Depo-sited	Bed and flood sediments	47	1991-2016	362	212	58	3.5 ±3.0	81.7 ±9.1	Seine-Normandie WA; IFREMER (ROCCHSED); Port of Rouen	http://www.naiades.eaufrance.fr https://wwz.ifremer.fr/survail http://www.haropaports.com/fr/rouen
		Cores	3	1945-2015	222		-			UMR CNRS 8212 LSCE; UMR CNRS 6143 M2C	Boust et al., 2012; Gardes et al., 2020; Lorgeoux et al., 2016
	Mobile	Dredged sediment	5	1992-2018	88	65	8	1.0 ±0.9	-	Port of Rouen	http://www.haropaports.com/fr/rouen

Table 2 – River characteristics. Lengths are given following the SANDRE baseline datasets (http://id.eaufrance.fr/). *For the Rhône River, the length is representative of its French course. **Watershed surfaces are given upstream of the gauging stations where specific flux was estimated. The water-engineering column refers to groups defined in the text. SPM – Suspended Particulate Matter – discharges were based on existing literature (Copard et al., 2018; Coynel et al., 2004; GIP Seine Aval, 2008; Moatar and Dupont, 2016; Poulier et al., 2019).

River	Length (km)	Altitudinal range (m)	Watershed (km²)**	Flow rate (m^3 s^{-1})	SPM discharge (Mt $year^{-1}$)	Cumulated Population ($M_{inhab.}$)	Main Towns (downstream direction)	Water-engineering
Seine	775	445–0	65366	600	0.2–0.6	20.1	Troyes, Paris Megacity, Rouen, Le Havre	Group 1
Rhône	545*	347–0	89011	1700	4–8	12.2	Geneva, Lyon, Valence, Avignon, Arles	Group 1
Loire	1006	1551–0	110726	870	0.4–0.7	14.3	St Etienne, Nevers, Orléans, Tours, Angers, Nantes	Group 2
Garonne	529	1840–0	51257	650	0.9–3	5.9	Toulouse, Agen, Bordeaux	Group 2

Figures and captions

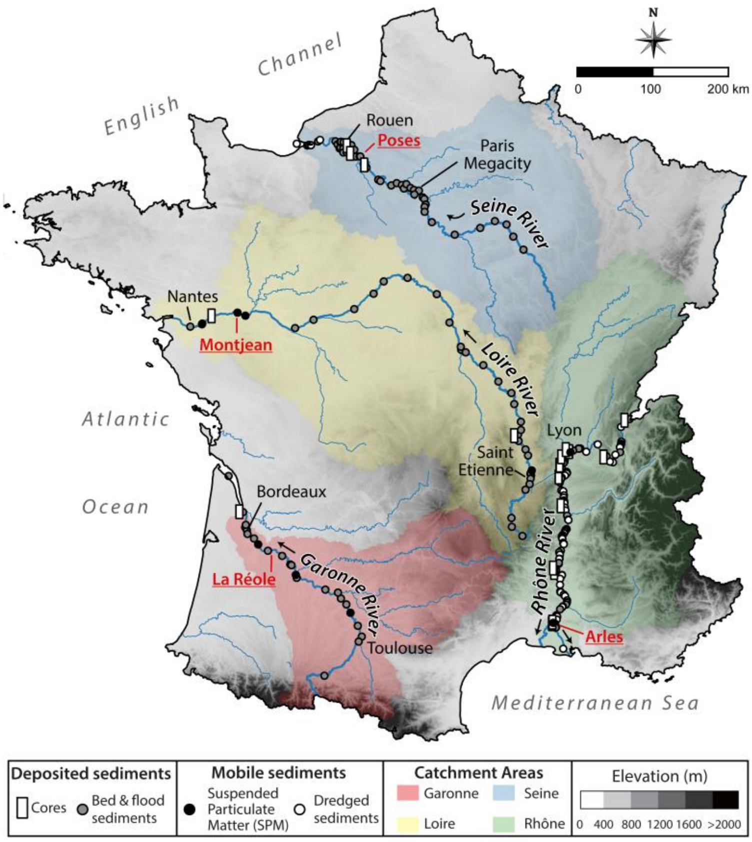


Fig. 1 – Location of sampling stations along the four main French Rivers (Garonne, Loire, Rhône, Seine). Main cities are reported in black whereas locations mentioned in red and underlined correspond to the four stations where specific flux was estimated.

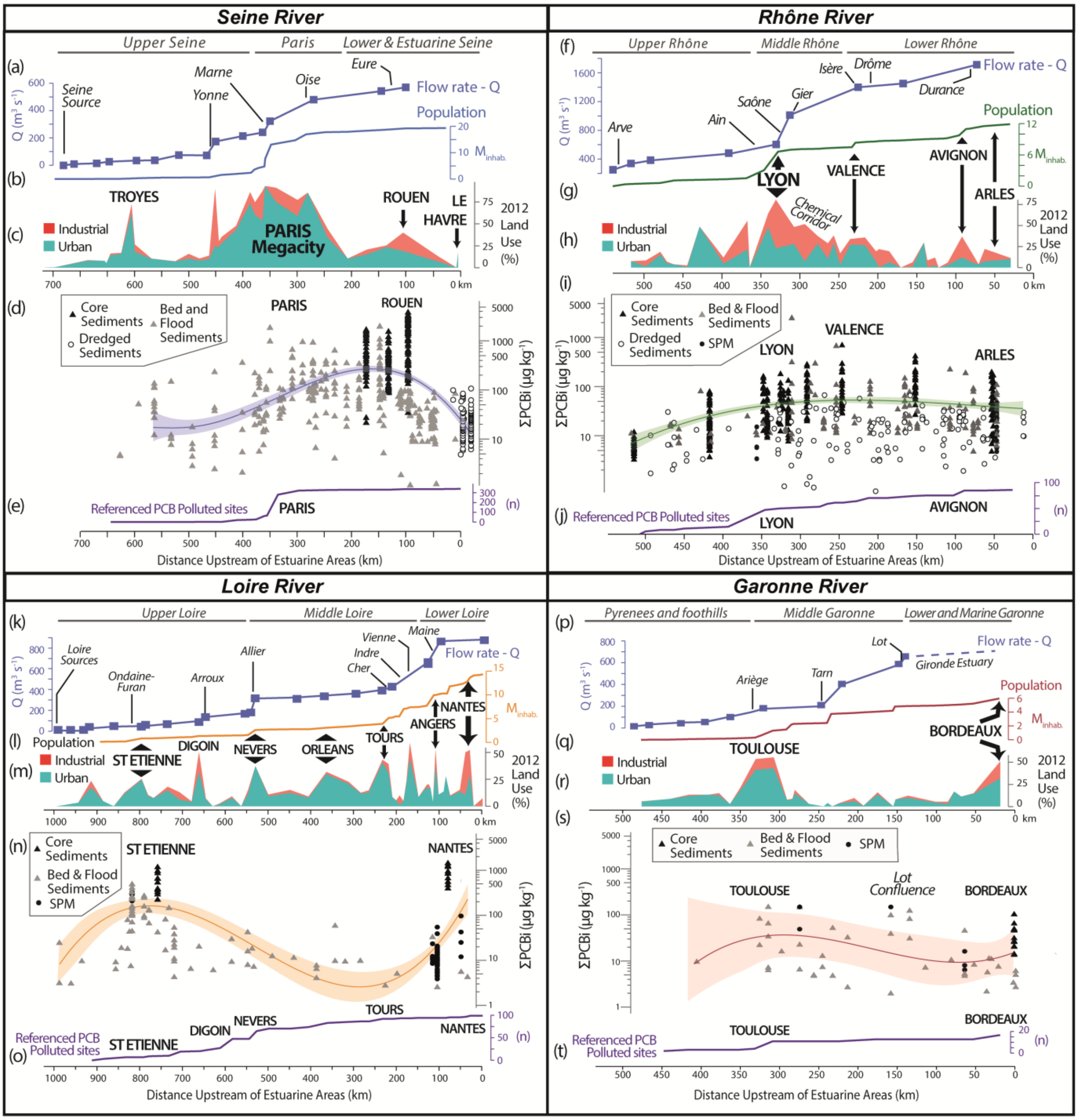


Fig. 2 – Main physical and socio-environmental information computed along each river corridor: a-e) Seine, f-j) Rhône, k-o) Loire, p-t) Garonne. Rivers discharges and their main tributaries are plotted in boxes a, f, k and p. Cumulated population in the watershed (expressed in $M_{inhab.}$) is represented in boxes b, g, l and q. The main urban and industrial areas within 1 km of the riverbed are shown with stacked area charts in boxes c, h, m and r. ΣPCBi in solid matrices are plotted all together according to a gam to represent the spatial variability of the PCB stocks during the period 1945–2018 (boxes d, i, n and s). PCB polluted sites referenced by the BASIAS and BASOL databases are represented by a curve cumulating the number of sites in the downstream direction. The distance scale is expressed in kilometres upstream of estuarine areas (km UEA).

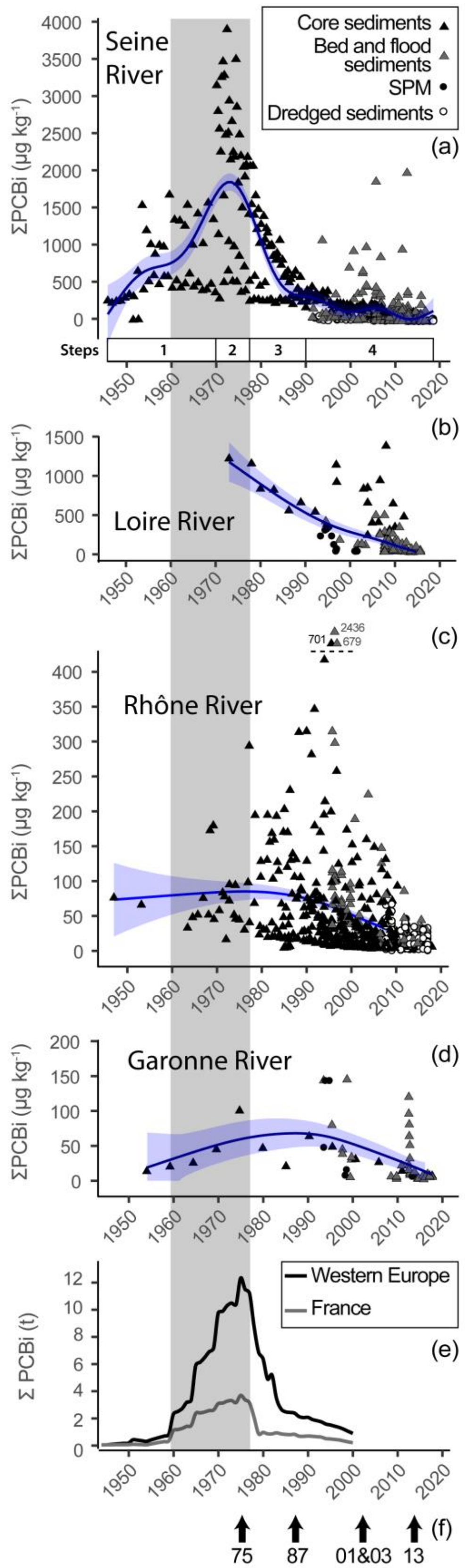


Fig. 3 – Estimated ΣPCBi trends in fluvial sediments since 1945 in the 4 rivers: (a) Seine River, (b) Loire River, (c) Rhône River, (d) Garonne River. The blue curve represents the gam modelling and the pale blue area its confidence interval. Steps 1, 2, 3, and 4 refer to the temporal trends cited in the text. (e) Comparison with global estimated emissions of ΣPCBi in tons for France and Western Europe (after Breivik et al., 2002a, 2007). (f) Regulation timeline: 75 = French restriction of PCBs in closed devices (order of 08-07-1975); 87 = prohibition of production, sale and purchase of devices using PCBs > 500 mg kg^{-1} (decree 87-59); 01&03 = removal of devices using PCBs > 500 mg kg^{-1} (decree 2001-63 and order of 26-02-2003); 13 = disposal of devices using PCBs > 50 mg kg^{-1} (decree 2013-301). The grey bar underlines the main period of PCBs production worldwide.

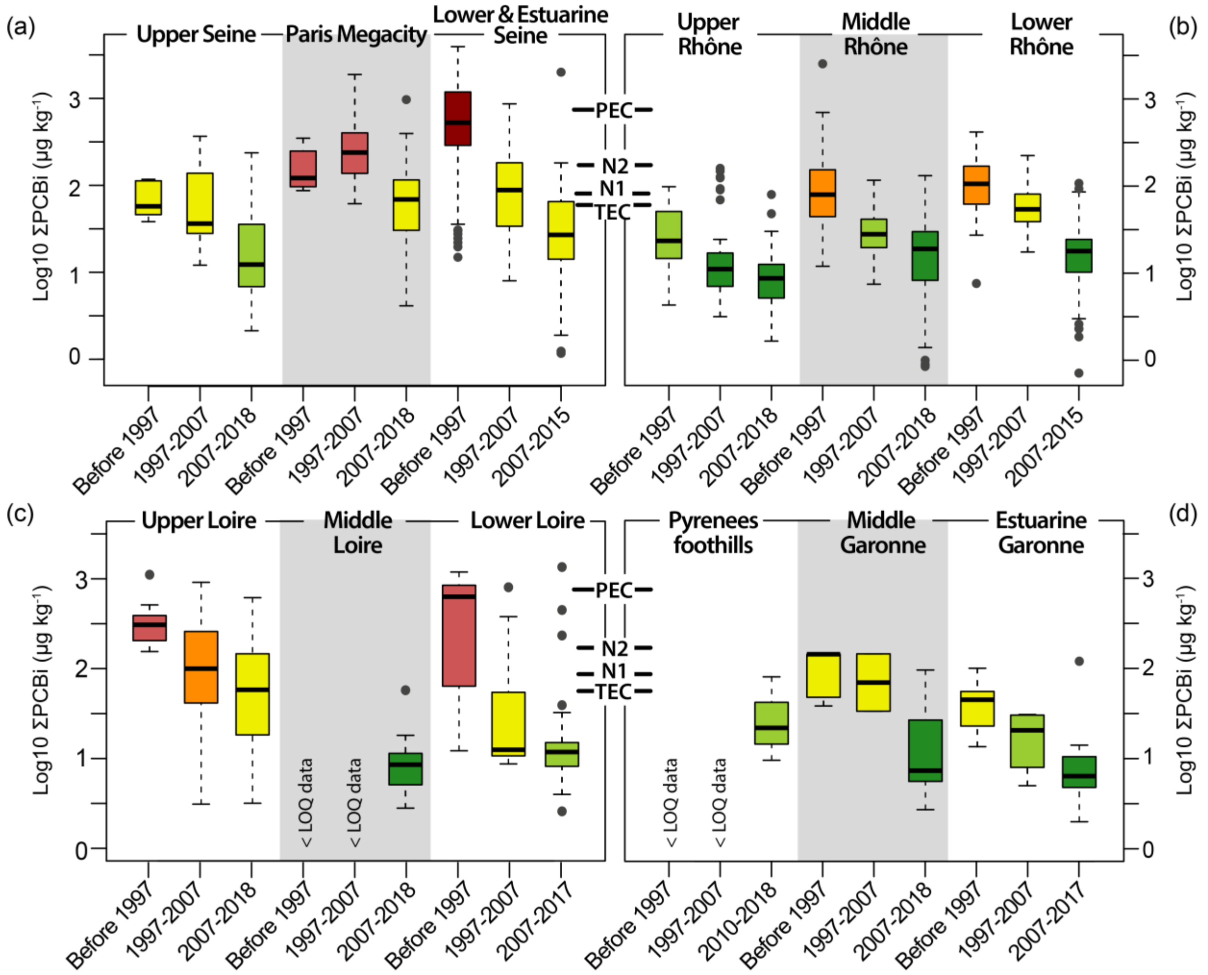
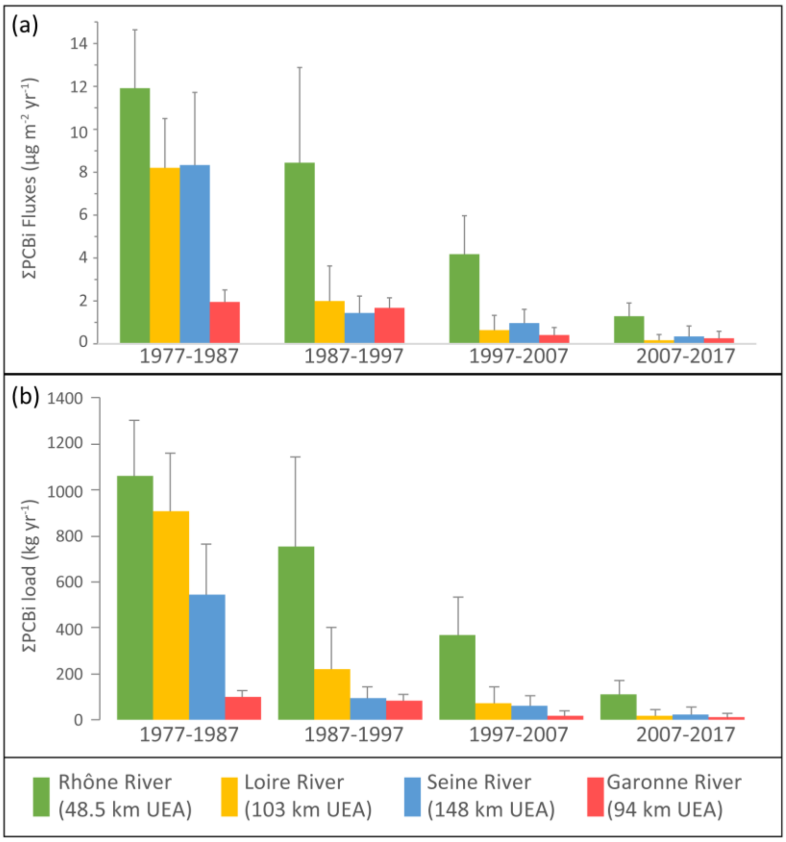


Fig. 4 – Detailed spatio-temporal distribution of ΣPCBi (log10 scale). (a) Seine River, (b) Rhône River, (c) Loire River, (d) Garonne River. Colours describe pollution levels in sediments, ranked from forest green (lowest levels) to dark red (highest levels). TEC, PEC, N1 and N2 refer to the main thresholds for PCBs: TEC (Threshold Effect Concentration) and PEC (Probable Effect Concentration) are of 59.8 µg kg^{-1} and of 676 µg kg^{-1} for total PCBs, respectively (MacDonald et al., 2000); French regulatory levels N1 and N2 refer respectively to 80 µg kg^{-1} and 160 µg kg^{-1} of ΣPCBi (order of 17/07/2014).



805 **Fig. 5 – Comparison of specific ΣPCBi flux (a) (unit: µg m^{-2} $year^{-1}$) and the mean annual load (b) on the French rivers (unit: kg $year^{-1}$).** Fluxes and loads are estimated at the lower station upstream of the tidal influence: Arles/Beaucaire for the Rhône River, Montjean for the Loire River, Poses/Poissy for the Seine River, and La Réole/La Magistère for the Garonne River (see locations on Fig. 1). The distance of each station to the sea is expressed as kilometres Upstream of Estuarine Areas (km UEA).