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Historical records, sources, and spatial trends of PCBs along the Rhône River (France)

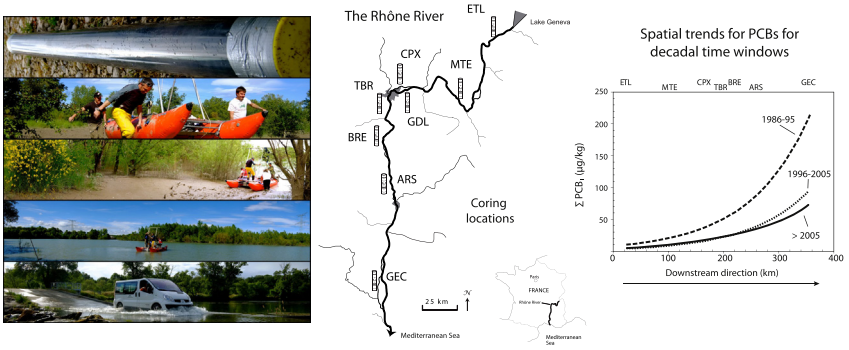
Brice Mourier [a,*], Marc Desmet [b], Peter C. Van Metre [c], Barbara J. Mahler [c], Yves Perrodin [a], Gwenaëlle Roux [a], Jean-Philippe Bedell [a], Irène Lefèvre [d], Marc Babut [e]

[a] Université Lyon 1, UMR 5023 Ecologie des Hydrosystèmes Naturels et Anthropisés, ENTPE, CNRS, 3, Rue Maurice Audin, 69518 Vaulx-en-Velin, France
[b] Université de Tours, GéHCO EA 6293, 37000 Tours, France
[c] U.S. Geological Survey, 1505 Ferguson Lane, Austin, TX 78754, USA
[d] UMR 8212 (CEA, CNRS, UVSQ), LSCE, Bât. 12, avenue de la Terrasse, F-91198 Gif-sur-Yvette Cedex, France
[e] Irstea, UR MALY, rue de la Doua, CS70077, F-69626 Villeurbanne, France

HIGHLIGHTS

- We reconstructed spatial and temporal trends in PCBs using eight sediment cores.
- PCB concentrations in sediments of the Rhône increase exponentially in a downstream direction.
- Concentrations of PCBs at the downstream sites remained elevated into the 2000s.
- Hierarchical clustering of PCB congeners identified differences within and between sites.
- PCBs in sediment downstream from Lyon are unlikely to decrease over the short term.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite bans on PCB use since 1975 (open systems) and 1987 (closed systems), concentrations of PCBs in riverine fish in France continue to exceed regulatory levels. We present historical records of PCB concentrations in sediment cores from eight sites on the Rhône River, from Lake Geneva to the Mediterranean Sea. Maximum PCB concentrations (sum of seven indicator PCBs) increase downstream, from 11.50 µg/kg at the most upstream site to 417.1 µg/kg at the most downstream site. At some sites peak concentrations occur in sediment deposited as recently as the 2000s. Hierarchical clustering (five clusters) identified differences in PCB congener profiles within and between sites. Exponential models fit to decadal time windows indicate that rapid reductions in concentrations during about 1990–2000 have slowed, and that it might be decades before target concentrations in sediment that correspond to regulatory thresholds in fish will be reached at some sites.

1. Introduction

Rivers receive a multitude of persistent organic pollutants (POP), including polychlorinated biphenyls (PCBs), that are transported principally by particulate matter (Viers et al., 2009). PCBs are released into the environment by improper disposal, leakage, incineration, and volatilization (Breivik et al., 2002). PCBs do not readily degrade, and can

* Corresponding author at: University of Limoges, Groupement de Recherche Eau Sol Environnement, 123 Avenue Albert Thomas, 87060 Limoges Cedex, France.
E-mail addresses: brice.mourier@unilim.fr (B. Mourier), marc.desmet@univ-tours.fr (M. Desmet), pcvanmet@usgs.gov (P.C. Van Metre), bjmahler@usgs.gov (B.J. Mahler), yves.perrodin@entpe.fr (Y. Perrodin), gwenaelle.roux@entpe.fr (G. Roux), jeanphilippe.bedell@entpe.fr (J.-P. Bedell), irene.lefevre@lsce.ipsl.fr (I. Lefèvre), marc.babut@irstea.fr (M. Babut).

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move through food webs and bioaccumulate in the fatty tissues of fish and mammals (Hammond et al., 1972). The chemical quality of sediment is a major concern for public policy makers and for stakeholders (e.g., environmental managers, navigation and power supply companies) because of the potential effects on aquatic biota and, ultimately, human health.

In France, PCBs still are of major concern (Agence nationale de sécurité sanitaire, 2011), despite a ban in 1975 on their use in open systems (e.g., hydraulic fluids, coatings) and another in 1987 on their use in closed systems (e.g., transformers, capacitors) (Chevreuil et al., 1988). Contamination of sediment and fish by PCBs in the Rhône River system was reported as early as the 1980s (Andre and Lascombe, 1988; Brodhag, 1989; Santiago et al., 1994). New regulation on dioxins and related chemicals in foodstuffs was introduced in 2006 and amended in 2011 (European Commission, 2011), and it was reported that the load of dioxin-like PCBs in fish is correlated to that of the sum of the so-called indicator PCB [International Union of Pure and Applied Chemistry (IUPAC) congeners 28, 52, 101, 118, 138, 153, and 180] (ΣPCB_I) concentrations in sediment (Babut et al., 2009). This led to an extended investigation of fish contamination throughout the Rhône River catchment (Babut et al., 2011, 2012) and in other French river basins. As a result of PCB contamination, commercial fishing and fish consumption currently (2013) are banned in the main channels of the Rhône and Saône (the largest tributary to the Rhône River) Rivers from upstream of Lyon to the Mediterranean Sea, and there are bans along reaches of numerous tributaries (Eaufrance, 2011).

Identification of long-term trends in PCB contamination can contribute to a better understanding of current (2013) risks and can assist in evaluation of the effectiveness of environmental legislation aimed at reducing the impact of human activities in the basin. However, datasets at a multi-decadal time scale (e.g., 20–50 years) on PCBs in water, sediment, and fish are not available for the Rhône River or, indeed, for most major rivers. One way to overcome this limitation is to reconstruct contamination histories through the use of natural sediment archives. In lakes and reservoirs with negligible post-depositional processes (e.g., bioturbation, porewater transport, biotransformation), sediments provide a record of contaminant inputs and other environmental changes over decadal time scales (Eisenreich et al., 1989; Van Metre et al., 1997; Van Metre and Mahler, 2005). In some riverine systems, sediment accumulates in off-channel depositional zones over long periods, creating multi-decadal records of contaminant histories (Van Metre et al., 1998; Desmet et al., 2012).

We have previously reported trends in PCBs in sediment cores from three secondary-channel depositional areas along the Rhône River and one reference site (Desmet et al., 2012). Here we expand that analysis to eight locations in the Rhône River basin to characterize the contamination levels, sources (through the distribution of PCB congeners), and spatial and temporal trends in PCBs at the basin scale.

2. Methods

2.1. Site selection

Sites for collection of sediment cores were chosen to evaluate the upstream–downstream distribution and temporal trends of PCB-contaminated sediment and to assess the potential effects of major industrial areas and tributaries (Bourbre, Saône, Gier, and Isère rivers) (Fig. 1). Sediment cores were collected during May 2008–February 2011 at eight sites in or adjacent to the Rhône River corridor 23 to 354 km downstream from Lake Geneva (Table 1; Supplementary information Figs. S1–S8). PCB trends from three of the eight sites chosen for this study [La Morte (MTE), Crépieux (CPX), and Ile du Beurre (BRE)] were presented in Desmet et al. (2012). All eight sites currently (2013) are connected to the Rhone River and likely subject to continual sediment deposition.

The two most upstream sites, Gravière des Etournels (site ETL) and MTE, are in a relatively non-industrialized part of the Rhône River basin (Fig. 1). Site ETL is 23 km downstream from Lake Geneva, and is a former quarry that became inundated when it was abandoned in 1980 (Supplementary information Fig. S1). Site MTE is 104 km downstream from Lake Geneva and is in a secondary channel at the downstream end of a cutoff meander of the Rhône River that is open to the river at its downstream end (Supplementary information Fig. S2). The Grand Large (site GDL, Supplementary information Fig. S3) and site CPX (Supplementary information Fig. S4) sites (171 and 175 km downstream from Lake Geneva, respectively) are downstream from site MTE and upstream from Lyon. GDL is a small reservoir of 160 Ha (the main part of the river is diverted around Grand Large), and site CPX is an inundated former quarry adjacent to the old channel of the Rhône River upstream from Lyon. Both sites are assumed to record the effects of PCB inputs from a PCB treatment (incineration) facility about 40 km upstream from Lyon, smaller cities between Lyon and site MTE, the Bourbre River, and non-point emissions from the northern part of the greater Lyon urban area. These four sites (ETL, MTE, GDL, and CPX) are referred to hereinafter as upstream sites.

Four sites are downstream from Lyon. Table Ronde (TBR), 12 km downstream from the confluence of the Rhône and Saône Rivers in Lyon, is a small embayment on the right bank that is open to the old Rhône River channel at its downstream end (Supplementary information Fig. S5). Ile du Beurre (site BRE) is 22 km downstream from TBR, and is in a secondary channel in a forested wetland adjacent to the Rhône River (Supplementary information Fig. S6). Site BRE was chosen because of its location downstream from the Lyon metropolitan area and the industrial corridor that extends to the south of the city. It also is downstream from the confluence with the Gier River (Fig. 1), which, like the Bourbre River, has a comprehensive ban in place on the consumption of fish because of PCB contamination (Eaufrance, 2011). Arras (ARS) is 41 km downstream from site BRE and upstream from the city of Valence, is an off-channel basin created by the construction of a dam in 1971, and is open to the old Rhône River channel at its downstream end (Supplementary information Fig. S7). The most downstream site, Lône de la Grange Ecrasée (site GEC), is a secondary channel downstream from the confluence with the Isère River (Supplementary information Fig. S8). The watershed of the Isère River includes several historical PCB production and disposal facilities. These four sites (TBR, BRE, ARS, and GEC) are referred to hereinafter as downstream sites.

2.2. Core collection and sediment description

Before coring, the study sites were surveyed using a GPSMAP® 521 s sounder (Garmin Ltd., Southampton, UK) to map the depth of the water. Several short cores were taken and inspected visually to evaluate the spatial nature and extent of major sedimentary facies. Water depth and the reconnaissance cores were used to guide site selection and coring locations. Sediment cores were collected with a UWITEC® corer (Uwitec, Mondsee, Austria) fitted with a 2.0-m-long, 63-mm- or 90-mm-diameter plastic liner with a core catcher at the bottom. From a cataraft, an extension rod was used to push the corer gently into the sediments. Multiple 63-mm diameter cores were collected at sites MTE, CPX, and BRE. 90-mm-diameter cores were collected at each of sites ETL, GDL, TBR, BRC, ARS, and GEC, and all descriptions and measurements for each site were performed on the same core.

Sediment cores ranged in length from 0.5 to 1.40 m. Core liners were cut near the sediment–water interface and capped for transport to the laboratory. At the laboratory, cores were sub-sampled at a 1-cm interval for grain size analysis and at a 3- or 4-cm interval for analysis of PCBs, total organic carbon (TOC), and radionuclides. For each of sites ETL, MTE, GDL, TBR, ARS, and GEC cores, all sub-samples for analysis of PCBs, TOC, radionuclides, and grain-size distribution were obtained from one core. At sites CPX and BRE, sub-samples from one core were analyzed for PCBs, TOC, and grain-size distribution (primary core) and samples from a second core were analyzed for grain-size distribution and radionuclides (radionuclide core). Grain-size distribution was

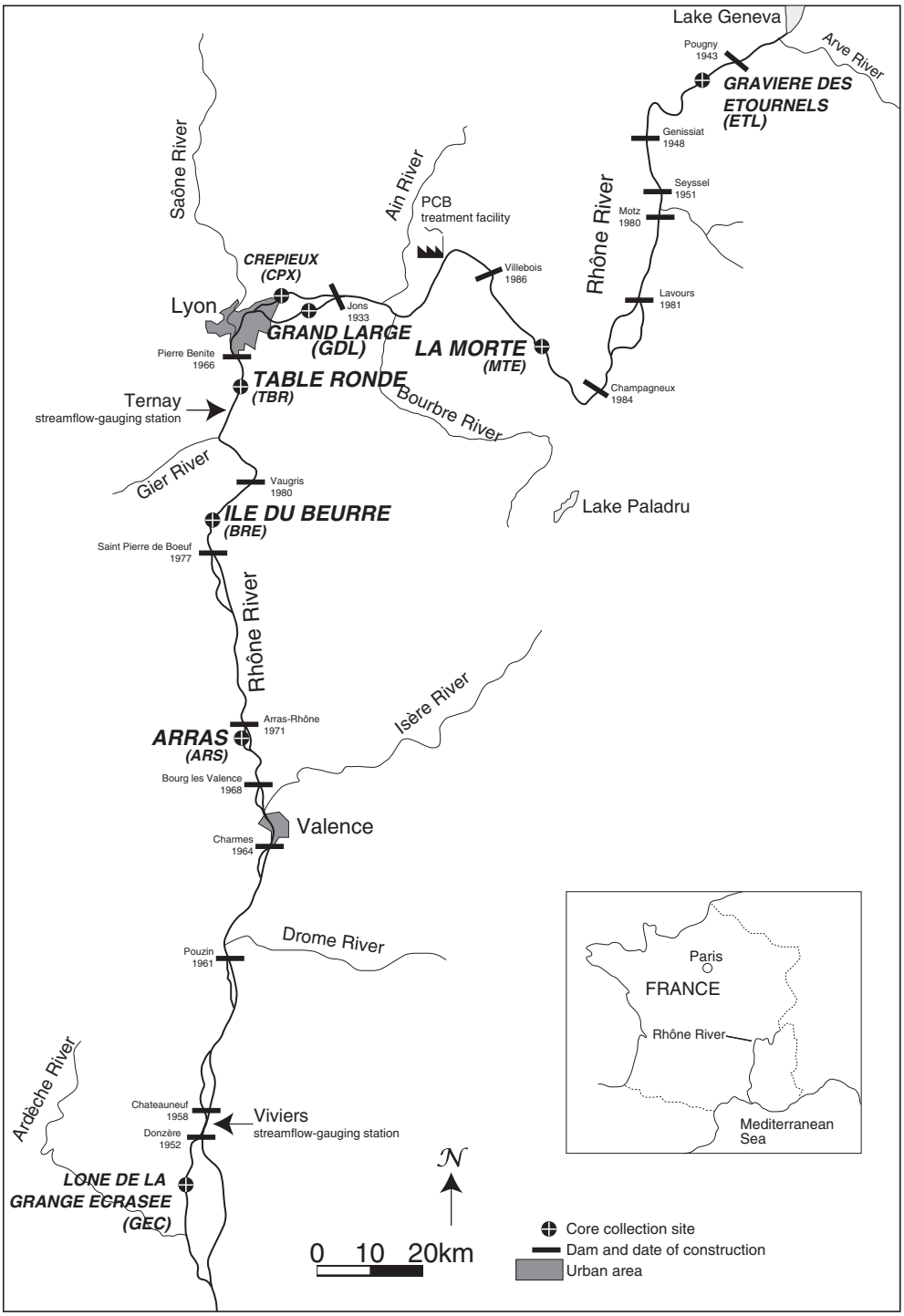

Fig. 1. Map of the study area (Rhône River basin, France) and locations of sediment core collection.

used at sites CPX and BRE to help correlate the primary and radionuclide cores so that dates could be assigned to the primary core.

Dry bulk density was determined as the difference between wet and dry mass divided by the volume of the container. Grain-size distributions were determined by sonicating and then analyzing each sample with a Mastersizer 2000® laser mounted with a hydro SM small-volume dispersion unit (Malvern Instruments, Worcestershire, UK). Grain-size mean, mode, sorting, and skewness were computed using the Gradistat program (Blott and Pye, 2001). Cumulative volumetric percentages of sand (>63 μm), silt (4–63 μm), and clay (<4 μm) were determined for each depth interval (<63 μm, i.e. silt and clay together, hereinafter fine fraction).

2.3. Analytical methods

Sediment samples were analyzed for radionuclides at the Laboratoire des sciences du climat et de l'environnement (LSCE), Gif sur Yvette, France. Following drying, sub-samples from each core were analyzed for radionuclides by counting for at least 24 h using low-noise gamma spectrometry. Gamma emissions were detected with a germanium

Table 1
Characteristics of sediment-core collection sites and sediment cores.

Site name (abbreviation)	Fluvial setting	X (Latitude)	Y (Longitude)	Distance from the outlet of Lake Geneva (km)	Core ID	Core length (cm)
Gravière des Etournels (ETL)	Former quarry	5.935603	46.131889	23	ETL 10-02	98
La Morte (MTE)	Secondary channel	5.554050	45.701586	104	MTE 08-03	69
Grand Large (GDL)	Reservoir	4.972078	45.778453	171	GDL 09-07	55
Crépieux (CPX)	Former quarry	4.916314	45.803050	175	CPX 08-01	78
					CPX 08-02	94
Table Ronde (TBR)	Small embayment on the right bank	4.799633	45.610754	197	TBR 09-01	123
Ile du Beurre (BRE)	Secondary channel	4.782072	45.476389	222	BRE 08-01	106
					BRE 08-03	98
Arras (ARS)	Off-channel basin	4.807308	45.132542	263	ARS 10-02	135
Lône de la Grange Ecrasée (GEC)	Secondary channel	4.655806	44.390028	354	GEC 11-04	100

detector and used to quantify specific activities of ^{226}Ra, ^{228}Ra, ^{40}K, ^{210}Pb, and ^{137}Cs (Pinglot and Pourchet, 1995).

Samples were prepared for measurement of organic carbon by drying, sieving to 2 mm, and grinding to <200 μm, in accordance with standard NF ISO 11464 (Groupement d'Etudes Méthodologiques pour l'Analyse des Sols, 2011), and acidifying with aqua regia (a mixture of concentrated nitric and hydrochloric acids). Total organic carbon was analyzed by high-temperature combustion (1250 °C) in accordance with standard NF ISO 10694 (Groupement d'Etudes Méthodologiques pour l'Analyse des Sols, 2011).

PCBs were analyzed by the EUROFINS laboratory, Saverne, France (www.eurofins.fr), which is accredited in accordance with ISO 17025. In brief, 5 g of dried, homogenized sediment was extracted for a minimum of 8 h with toluene/acetone (90/10 v/v) in a Soxhlet apparatus. A mixture of isotope-labeled internal standards used for identification and quantification of native congeners was added prior to extraction. The sample extract underwent a clean-up step using gel permeation chromatography. Clean-up consisted of sequential passes through silica, aluminum oxide, Florisil, and active carbon columns. Prior to extraction, the standard 13C12-123789-HexaCDD was injected to allow the quantification of isotopic labels. The sample extract was analyzed by high resolution gas chromatography–high resolution mass spectrometry (HRGC/HRMS) with a VG-AutoSpec in selected ion monitoring (SIM) mode. Laboratory quality control consisted of periodic analysis of blanks and certified reference materials. Analytical results for environmental samples were not blank-corrected.

The interpretations that follow are based on ΣPCB_I, commonly used in European national regulations to ensure food safety (e.g., Royal Order, 2000). Quantification limits for PCB_I ranged from 0.02 μg/kg (PCB 52) to 0.05 μg/kg (PCB 153).

2.4. Statistical methods

Hierarchical clustering (Ward's method) was used to classify the samples according to their congener compositions (Ward, 1963); this method of hierarchical clustering gives compact clusters and clear hierarchies (Aitchison, 1986; Martin-Fernandez et al., 1998). Relative concentrations of PCB congeners (% of ΣPCB_I) were used so that the magnitude of the concentrations would not influence the result. Distances between PCB congener compositions were measured as Euclidean distances between centered log ratios (CLR) (Aitchison et al., 2000). The results were interpreted from a dendrogram, a branching diagram that represents the relationships of dissimilarity among a group of entities. Following clustering, compositional differences between clusters were evaluated using a discriminant analysis (DA) (Kachigan, 1991). Discriminant analysis is a statistical procedure for identifying boundaries between groups (here, clusters) of objects (here, samples) on the basis of quantitative predictor variables (here, PCB congeners). The objects are expressed as linear combinations (factors) of the predictor variables; the centroid of each group in the factor space is determined and the probability that each object is classified into the correct group is evaluated. The confusion matrix evaluates the consistency of classification of samples into groups by the clustering and DA methods, providing a measure of confidence in the results. Data preparation and multivariate analysis were performed by using CoDaPack V2 (Thió-Henestrosa and Martín-Fernández, 2005) and XLSTAT V3.05 (Addinsoft, Paris, France), respectively.

To evaluate spatial trends in PCB contamination at the Rhône River basin scale, PCB_I concentrations for three time windows were evaluated relative to distance downriver, i.e., from the outlet of Lake Geneva. Regression models (exponential, linear, and piecewise linear) were fit to median values for the three time windows for which there are data from a sufficient number of sites (1986–1995, 1996–2005, and post 2005).

3. Results

3.1. Age dating

Peak ^{137}Cs activity, a primary date marker, was used to estimate sediment deposition dates in the cores. Two date–depth markers inferred from the ^{137}Cs profile can be identified in European sediment cores: a peak in ^{137}Cs activity (1963) corresponding to the height of releases associated with world-wide nuclear weapons testing (Beck and Helfer, 1990), and a second (1986) peak corresponding to the Chernobyl accident. The Chernobyl ^{137}Cs peak was identified in almost all of the cores (Supplementary information Figs. S1–S9). Changes in grain-size distribution provided secondary date markers. Changes were interpreted as indicating onset or cessation of a land-use activity (e.g., quarrying), timing of major flood events, or a change in connection with the Rhône River (sites ETL, CPX, and BRE) (Supplementary information Fig. S1, S3, S6–S9). Flood-event facies identified in the cores were matched to flood flows measured at the nearest streamflow-gauging station (Ternay or Viviers, Fig. 1).

Age dates for MTE, CPX, and BRE cores, presented in Desmet et al. (2012), were based on ^{137}Cs peaks and changes in grain size matched to floods. Age dates for the ETL core were based on a ^{137}Cs maximum at a depth of 44–45 cm interpreted as the Chernobyl accident and an increase in the percentage of silt and clay at a depth of 72–73 cm in the core, interpreted as indicating the cessation of quarrying (Supplementary information Fig. S1). Age dates for the GDL core were estimated on the basis of the ^{137}Cs profile and on variations in grain size corresponding to dredging in 2005 (Supplementary information Fig. S3). However, the age–depth model was difficult to define at this site because sediment deposition was disturbed by reservoir management (Babut et al., 2011). At sites TBR and GEC, sediment deposition rates were too high (or core lengths were too short) to observe the complete ^{137}Cs maximum related to the Chernobyl accident. Estimated date of sediment deposition at these sites is based on grain-size changes that correspond to floods that occurred in the early 1990s and 2000s (Supplementary information Figs. S5, S8). Age dates for the ARS core were based on a single pronounced ^{137}Cs peak that occurred at a depth of 95–97 cm and interpreted as corresponding to the Chernobyl accident (Supplementary

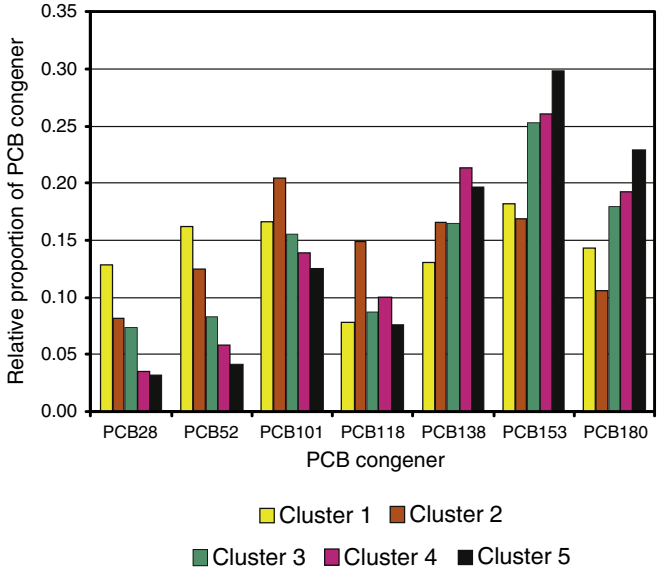

Fig. 2. Proportions of the seven indicator PCB congeners for centroids of five clusters.

information Fig. S7). The age model was refined on the basis of a slight decrease in percentage of silt and clay in the upper part of the core that matched well with floods in the early 2000s.

3.2. Indicator PCB (PCB_I) concentrations

PCB_I were measured in 248 sediment samples. Three or more congeners with concentrations below the detection limit were measured in four samples; those samples therefore were excluded from the dataset for statistical analysis. For two samples, the concentration of an undetected congener (PCB 101) was estimated by multiplying the median proportion of the congener in the adjacent layers by the sum of seven congeners in the layer with the non-detection. Sediment samples deeper than 51 cm at site ETL (11 samples) were excluded from statistical analysis because the deposits were interpreted as having been remobilized (Supplementary information Fig. S1). Samples with an absolute standardized residual greater than 2 (outliers) were evaluated: two were excluded (one collected from site BRE and the other from site ARS) from subsequent statistical analysis because the total PCB concentration was atypically high relative to that in adjacent layers, and because the PCB profile (in both cases, a presumed positive bias of PCB 52) was not consistent with that of most of the other measurements.

PCB_I concentrations and profiles varied considerably within and between the sites sampled for this study, both in timing and magnitude of peak concentrations (Figs. 2 and 3). Maximum PCB_I concentrations were lowest upstream (e.g., maximum ΣPCB_I concentration of 11.50 μg/kg at ETL) and increased downstream to a concentration of 417.1 μg/kg at GEC (Fig. 3). Maximum concentrations measured for this study exceeded those measured in sediment in several other European rivers, such as the Sava River (the largest tributary to the Danube) (<4 μg/kg) (Heath et al., 2010), the Vistula River, Poland (64 μg/kg) (Dmitruk et al., 2008), and the Po River, Italy (4.1 μg/kg) (Viganò et al., 2008).

Temporal patterns of ΣPCB_I concentrations vary from upstream to downstream. Concentrations at site MTE are highest in the 1970s and decrease monotonically to the top of the core; concentrations at site ARS generally decrease from the mid-1980s onward. Concentrations in PCB concentrations at the other six sites are more variable. At ETL, CPX, BRE, and GEC, concentrations of PCBs were elevated and variable in the late 1980s and mid-1990s, decreased in the late 1990s, and have remained relatively stable since. At GDL and TBR, maximum concentrations occurred in the 2000s (ΣPCB_I of159.8 μg/kg in 2003 at GDL and 131.5 μg/kg at TBR in 2007). At GDL, a progressive increase occurred in the early 1980s until 2005, but the ΣPCB_I maximum at TBR was brief, occurring only during 2007–08.

3.3. Spatial trends in PCBs at the scale of the Rhône River and changes through time

Exponential regression models used to evaluate changes in PCB concentrations in a downstream direction for three time windows (1986–1995, 1996–2005, and post 2005) provided a good fit to the data ($r^2 = 0.92$, $r^2 = 0.96$, $r^2 = 0.94$, respectively; $p = 0.03$). Site GDL was excluded from this regression because its age model was not consistent with those from the other sites (Supplementary data Fig. S3). Linear and piecewise linear regression models had acceptable but lower r^2 (0.71–0.96), and residuals were substantially higher than those from the exponential models.

The exponential models illustrate spatial and temporal trends in PCB concentrations in Rhône River sediment (Fig. 4). PCB concentrations generally increase from upstream to downstream, regardless of the period considered. Concentrations decreased substantially from about 1986–95 to 1996–2005 and to a much lesser extent from 1996–2005 to post 2005–top of core. The decreases are more marked at downstream sites than at upstream sites. The apparent slowing of the rate at which PCBs are decreasing indicates that PCB inputs to the Rhône River might be continuing, particularly downstream from the greater Lyon area.

Median ΣPCB_I values for downstream sites TBR and BRE for the 1986–95 time window diverge from the exponential model for this period (Fig. 4). The median for TBR is less than that predicted by the regression model for this period, whereas the median for BRE is greater than that predicted (and greater than that predicted by the exponential models, to a lesser extent, for the 1996–2005 and post-2005 time windows). The watershed of the Rhône River downstream from the city of Lyon is much larger than it is upstream, because it also includes the watershed of the Saône River, whose confluence with the Rhone River is at the downstream end of Lyon (Fig. 1). A mean ΣPCB_I concentration of 18.7 μg/kg ($n = 6$, ± 16.6) was measured in sediments samples collected from the downstream end of the Saône River after 2007 (Eaufrance, 2011). The change in watershed size might explain the considerable dilution of PCB concentrations observed at TBR. Conversely, at BRE and downstream, local PCB sources might be superimposed on the general contamination pattern.

3.4. PCB congener profiles

Cluster analysis provides some insights into patterns of PCB congeners. On the basis of the dendrogram distances (Supplementary information Fig. S10), all samples were assigned to one of five clusters. Clusters 4 and 5 contained the most samples ($n = 97$ and 70, respectively), and clusters 1, 2 and 3 contained far fewer ($n = 21$, 18, and 25, respectively). In the DA, two factors were sufficient to describe 97% of the variance; the separation of the PCB congeners in the two-dimensional factor space indicated that samples were distinguished to a large extent by degree of biphenyl chlorination (Supplementary information Figs. S10 and S11a). The confusion matrix confirmed the integrity of the clustering: less than 10% of the cluster analysis classifications were reclassified into a different cluster by the DA (Supplementary information Fig. S11b and c).

Despite variability within and between sites, some patterns among PCB profiles can be identified (Fig. 3). Cluster 1 is characterized by low-chlorinated biphenyls (PCBs 28, 52, and 101), and samples in cluster 1 mostly are from GEC, the most downstream site. In the GEC core, the dominance of cluster 1 extends from about 1990 to the top of the core. Cluster 2 is composed mainly of *tetra–penta*-chlorinated biphenyls (PCB-52, PCB-101, and PCB-118). This assemblage, characterized by relatively low-chlorinated biphenyls, was common for GDL samples deposited from the 1980s to 2005. Congener profiles at sites

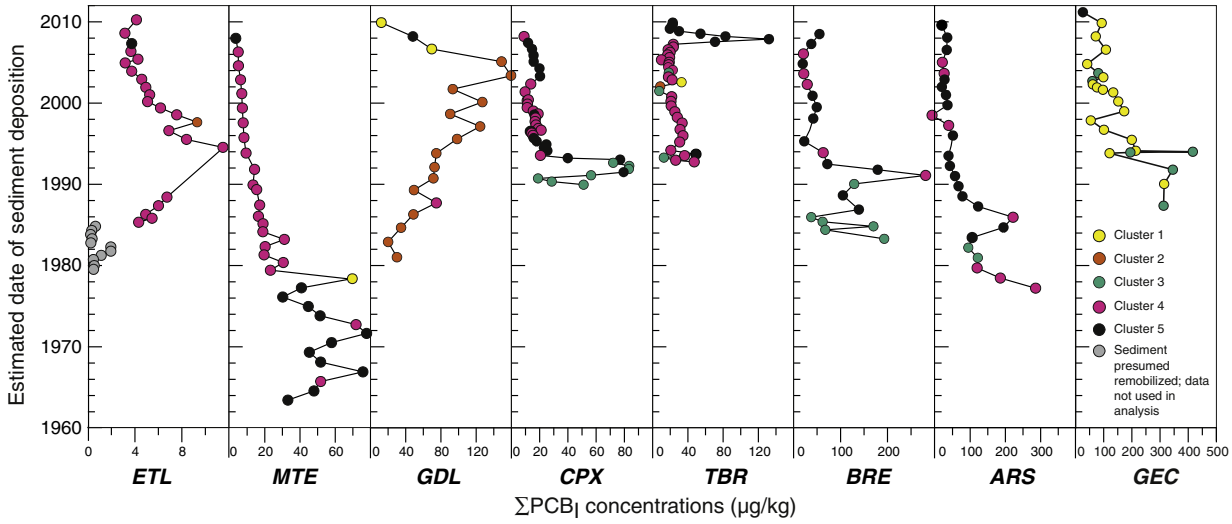

Fig. 3. Profiles of the sum of the concentrations of the seven indicator PCBs (ΣPCB_I) in sediment cores collected from the Rhône River basin, France. The color of each symbol corresponds to its PCB congener assemblage cluster (Fig. 2).

GEC and GDL differ from those at other sites, indicating that PCB contamination at these sites might be affected by local sources. Samples in cluster 3 are primarily samples from the lower parts of cores collected from sites CPX and BRE, and, to a lesser extent, from cores collected from sites TBR and GEC. These sediment intervals correspond to flood deposits in the early 1990s and 2000s at sites CPX, TBR, and GEC (Supplementary information Figs. S3, S5, and S8) and to removal of debris in 1984 at site BRE (Supplementary information Fig. S6). Cluster 4 is dominated by *penta–hexa–hepta*-chlorinated biphenyls (PCB-118, PCB-138, PCB-153, and PCB-180), and more samples are in cluster 4 than in any other cluster. Samples in cluster 4 are abundant at upstream sites ETL, MTE, and CPX, and at downstream site TBR (sediment deposited prior to 2007). Cluster 5 is characterized by high proportions of *hexa*- and *hepta*-chlorinated biphenyls (PCB-153 and PCB-180). Upstream site samples in cluster 5 consist of deeper sediments collected at site MTE and the most recently deposited sediment collected at site CPX. Downstream site samples in cluster 5 include recently deposited sediments represented by TBR, BRE, and ARS cores. Recently deposited sediments in the TBR core, which include the PCB maximum, are in cluster 5 whereas older sediments are in cluster 4.

4. Discussion

4.1. Implication for sources

A general upstream–downstream pattern of increasing PCB concentrations indicates a relation between PCB contamination and drivers, such as the catchment area and the cumulative upstream population (Fig. 4B). Cumulative area and upstream population are correlated ($r^2 = 0.985$, $p < 0.0001$), and we hypothesize that they are proxies for emissions, as suggested by others (e.g., Breivik et al., 2002). However, population is neither the only nor the main driver of trends in historical PCB concentrations along the upstream–downstream gradient. Regardless of the decade, considerable variations are observed between the median concentrations, the models, and the cumulative population.

Trends in PCBs at sites MTE and ARS are consistent with widely reported patterns in PCB contamination (e.g., Eisenreich et al., 1989; Van Metre et al., 1997) in which the highest concentrations coincide with maximum use and environmental release in the 1960s and 1970s and marked decreases since. At other Rhône River sites, however, relatively high concentrations persist into the 1990s, inconsistent with this pattern, indicating that PCB inputs might have continued to occur in the basin following regulation. The PCB peak at TBR during 2007–08 is an example of this (Fig. 3). We hypothesize that local PCB releases (in addition to those from the PCB treatment facility upstream from Lyon) have occurred upstream from this site in the past decade.

PCB distribution and trends also are affected by sediment flushing events and floods. Floods can cause bank erosion, resulting in inputs of less-contaminated sediment in some cases, or in inputs of more-contaminated sediment in others (e.g., Lecce and Pavlowsky, 1997; Rozan and Hunter, 2001). Floods also can mobilize upstream PCB sources, and major hydro-sedimentary events therefore can affect congener compositions. At sites CPX, TBR, and GEC, the data indicate a mixed congener assemblage (cluster 3) that corresponds to flood deposits.

A potential PCB point source to sediments deposited at sites GDL, CPX, and downstream is the PCB treatment facility upstream from Lyon (Fig. 1), which is authorized to release small amounts of PCBs into the Rhône River (Eaufrance, 2011). Because PCBs are treated and disposed of at this facility, its regulation differs from that of PCB use in France. The magnitude and timing of PCB discharges at the facility are consistent with temporal trends in PCBs at site CPX (Desmet et al., 2012), but they are more difficult to interpret at site GDL. At site GDL, PCB concentrations increased until 2005 and the congener mixture (cluster 2, higher proportions of low-chlorinated biphenyls) is distinct from that at the other sites. The trend at site GDL might be attributable to PCB inputs from upstream tributaries (e.g., the Bourbre River) and (or) management operations in the Grand Large (e.g., dredging). Mean ΣPCB_I concentrations measured in surficial sediment of the Bourbre River range between 201.3 μg/kg (1986–1995) and 25.9 μg/kg (post-2005) (Eaufrance, 2011).

Overall, PCB_I concentrations are higher at sites downstream from Lyon (TBR, BRE, ARS, and GEC) than at sites upstream from Lyon (ETL, MTE, GDL, and CPX). This pattern indicates that, although the PCB treatment facility is a source, it is neither the only source nor the most important. The substantial increase in PCB_I concentrations in the downstream direction can be explained only by other PCB sources in the greater Lyon metropolitan area and from tributaries to the Rhône River downstream from Lyon. Potential sources include the City of Lyon, the industrial corridor downstream from Lyon, the Gier River (a tributary that flows into the Rhône River between TBR and BRE), the Isère River (a tributary that flows into the Rhône River at Valence, between ARS and GEC), and perhaps other tributary watersheds (Fig. 1), consistent with sources evoked by Santiago et al. (1994). High concentrations of PCBs were measured in a sediment core collected from the Gier River (ΣPCB_I of 115–160 μg/kg

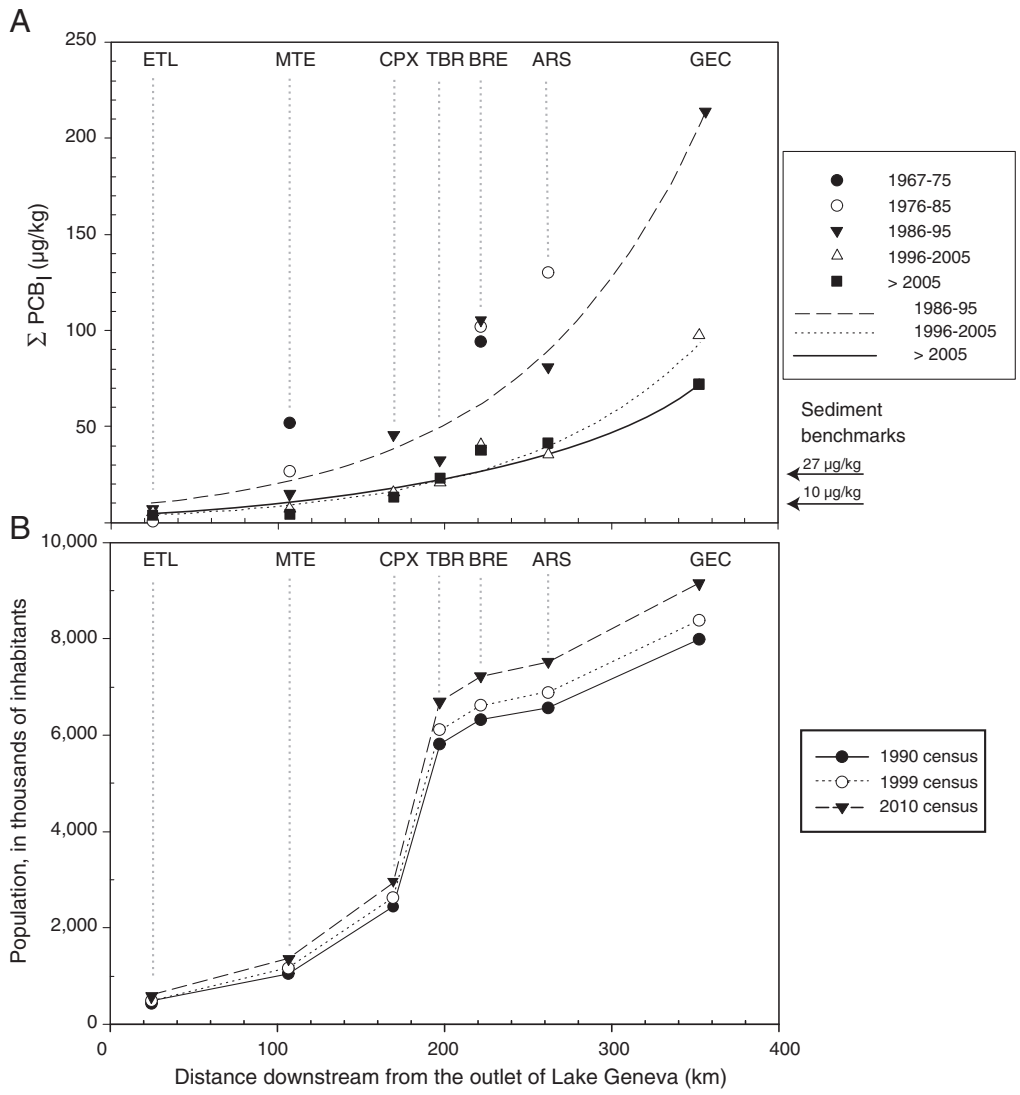

Fig. 4. (A) Median ΣPCB_I concentrations in sediment core samples for decadal time windows. Site GDL is excluded because sediment at this site was disturbed by reservoir management activities. Two-parameter exponential models were fit to the 1986–95, 1996–2005, and post-2005 time windows (adjusted r^2 of 0.92, 0.96, and 0.94, respectively). Data for the 1967–75 and 1976–85 time windows were not modeled as insufficient data were available for many of the sites. Arrows indicate sediment benchmarks calculated from BSAFs models that correspond to PCB thresholds in fish (Lopes et al., 2011; Babut et al., 2012). (B) Cumulative population in the catchment upstream of each sampling site. Census data from L'Institut national de la statistique et des études économiques (INSEE) (http://www.insee.fr/fr/themes/detail.asp?reg_id=99&ref_id=base-cc-evol-struct-pop-2010).

since 1986 and up to 940 µg/kg in the 1970s) (Babut et al., 2011) and in sediment from the Isère River (EauFrance, 2011). The hypothesis of other PCB inputs from the Isère River is consistent with a difference in congener mixture at site GEC (relatively low chlorinated congeners, cluster 1) relative to those upstream (Fig. 3). In the Rhône River delta, PCB concentrations are lower than in sediments collected at site GEC for the most recent period (post-2005) — the mean ΣPCB_I for suspended sediments collected since 2008 near the mouth of the Rhône River is 24.1 µg/kg (n = 122) (EauFrance, 2011; SORA Station).

4.2. Time and system recovery

Results from this study and that of Desmet et al. (2012) provide empirical evidence that environmental regulation of point sources enacted since 1975 and 1986 reduced the PCB burden recorded in sediments. They also provide an indication of the time required for PCB levels to decrease, particularly at downstream sites. Regulation of point sources, however, has not prevented exceedances of the fish-consumption regulatory threshold set in 2008 and revised in 2011 to 6.5 pg toxic equivalency factor (TEQ)/g wet weight (ww) for all species but eel, for which the threshold was set at 10 pg TEQ/g ww (data for fish available at http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB/basepcb/index.php) (European Commission, 2011). The question thus arises: How much more time is required until PCB concentrations in surface sediment are consistent with regulations for fish consumption? The ΣPCB_I concentration in sediment that corresponds to the fish regulatory limit depends on the approach used and the data involved. Using biota–sediment accumulation factors (BSAFs) over a large spatial scale, the sediment benchmark for ΣPCB_I was determined to be 27 µg/kg (Babut et al., 2012). At ΣPCB_I of 10 µg/kg, 75% of fish from 3 cyprinid species from 3 sites in the Rhône River along a contamination gradient would match the regulatory threshold when applying the statistical model developed by Lopes et al. (2011). We therefore consider ΣPCB_I of 10 and 27 µg/kg as potential targets (Fig. 4a).

At some sites the ΣPCB_I concentration in the most recently deposited sediments are less than the lower target of 10 µg/kg, at others the ΣPCB_I concentration is between the two targets, and at some sites ΣPCB_I concentration exceeds the upper target of 27 µg/kg (Supplementary information Table S1). At sites ETL and MTE, ΣPCB_I concentrations at the sediment surface (top of the core) already are below the lower target value and are still decreasing (Desmet et al., 2012). At site CPX

the concentration in the most recently deposited sediment is just below the 10 μg/kg target, and at site TBR it is between the two targets. However, concentrations at site TBR are relatively constant before and after a brief peak in concentration around 2008 (Supplementary information Fig. S5). Similarly, at site BRE there is no trend in concentrations in recently deposited sediment (Desmet et al., 2012): although ΣPCB_I was less than the 27 μg/kg target in 2003–04, ΣPCB_I increased to 55.12 μg/kg in 2008. This increase is related either to the same event as the maximum at TBR (consistent with the similarity in PCB profiles, as indicated by the clustering) or to the modification of the sediment deposition pattern at BRE (Supplementary information Fig. S6). At site ARS, the concentration at the top of the core is near the 27 μg/kg target, and concentrations have been decreasing since 1996 (Supplementary information Table S1). The same pattern occurs at site GEC, with the exception of a high outlier in 1999. Following the approach described in Van Metre et al. (1998), we fit an exponential decay model to data from sites ARS and GEC from 1996 or 1998 to 2012 (Supplementary information Figs. S12 and S13). On the basis of these models, the concentrations at the sediment surface might reach 27 μg/kg ΣPCB_I in ~2014–2015 at ARS and ~2020 at GEC. The more ambitious target of 10 μg/kg might not be achieved before ~2045 at ARS and ~2030 at GEC. The apparent lack of logic in this second prediction (given that GEC is downstream of ARS) reflects the lack of data at concentrations between the two targets, which hinders a prediction at this sensitivity, and the considerable scatter in the data. The scatter likely arises from the fact that PCB concentrations at these sites are controlled by hydro-sedimentary processes (mechanisms of deposition) and by several areas where PCBs might be stored in the deposited sediments, i.e., the Rhône River and its tributaries.

5. Conclusion

Sediment cores from the Rhône River, from Lake Geneva to near the Mediterranean Sea, provide a historical record of PCB inputs. The ^{137}Cs peak associated with the Chernobyl accident identified in almost all of the cores provides a robust date marker. Large variability in PCB trends and congener mixtures within these cores indicates that a complex combination of sources and transport and (or) deposition patterns affect the PCB distribution. There are, however, some broad patterns in these data. Much higher PCB_I concentrations downstream from Lyon than upstream indicate that greater Lyon and some tributaries to the lower Rhône River currently (2013) are the principle sources of PCBs to the river. Rapid decreases in PCB concentrations that occurred between the mid-1980s and about 2000 have slowed, and it likely will take a decade or more before PCB concentrations in sediment are consistent with regulatory limits for fish consumption.

Conflict of interest

We declare no conflict of interest. Funding agencies had no role in the study design; in the collection, analysis, or interpretation of data; in the writing of the report; nor in the decision to submit the article for publication.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2014.01.026. These data include Google map of the most important areas described in this article.

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