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Spatial and Temporal Trends in PCBs in Sediment along the Lower Rhône River, France

Marc Desmet [a], Brice Mourier[b], Barbara J. Mahler [c], Peter C. Van Metre [c], Gwenaëlle Roux [b], Henri Persat [d], Irène Lefèvre [e], Annie Peretti[f], Emmanuel Chapron[g], Anaëlle Simonneau[g], Cécile Miège[f], and Marc Babut [f]

[a] UMR CNRS 6113 - ISTO, Université François Rabelais, Parc de Grandmont, 37200 Tours, France

[b] Université Lyon 1, UMR 5023 Ecologie des Hydrosystèmes Naturels et Anthropisés, ENTPE, CNRS, 3, Rue Maurice Audin, 69518 Vaulx-en-Velin, France

[c] U.S. Geological Survey - 1505 Ferguson Lane, Austin, TX, USA 78754

[d]Université de Lyon, UMR 5023 Ecologie des Hydrosystèmes Naturels et Anthropisés, Université Lyon 1, ENTPE, CNRS, 5 rue Raphaël Dubois, 69221 Villeurbanne, France

[e]UMR 8212 - LSCE, Bât. 12, avenue de la Terrasse, F-91198 Gif-sur-Yvette Cedex, France

[f] Irstea - UR MALY, 3 bis Quai Chauveau – CP220, F-69336 Lyon, France

[g]UMR CNRS 6113 - ISTO, Université d'Orléans, Campus Géosciences, 1A rue de la Férollerie, F-45071 Orléans, France

marc.desmet@univ-tours.fr
brice.mourier@entpe.fr
bjmahler@usgs.gov
pcvanmet@usgs.gov
gwenaelle.roux@entpe.fr
persat@biomserv.univ-lyon1.fr
Irene.Lefevre@lsce.ipsl.fr
royannie@gmail.com
emmanuel.chapron@univ-orleans.fr
anaelle.simonneau@univ-orleans.fr

cecile.miege@irstea.fr
marc.babut@irstea.fr

Corresponding author: Barbara Mahler

U.S. Geological Survey

1505 Ferguson Lane

Austin, TX 78754 USA

Tel: 001-512-927-3566

Fax: 001-512-927-3590

e-mail address: bjmahler@usgs.gov

Abstract
Despite increasingly strict control of polychlorinated biphenyl (PCB) releases in France since the mid-1970s, PCB contamination of fish recently has emerged as a major concern in the lower Rhône River basin. We measured PCB concentrations in Rhône sediment to evaluate the effects of PCB releases from major urban and industrial areas, sediment redistribution by large floods, and regulatory controls on PCB trends from 1970 to present. Profiles of PCBs (the sum of seven indicator PCB congeners) were reconstructed from sediment cores collected from an off-river rural reference site and from three depositional areas along the Rhône upstream and downstream from the city of Lyon, France. Core chronology was determined from radionuclide profiles and flood deposits. PCB concentrations increased progressively in the downstream direction, and reached a maximum concentration in 1991 of 281 μg/kg at the most downstream site. At the rural reference site and at the upstream Rhône site, PCB concentrations peaked in the 1970s (maximum concentration of 13 and 78 μg/kg, respectively) and have decreased exponentially since then. PCB concentrations in the middle and downstream cores were elevated into the early 1990s, decreased very rapidly until 2000, and since then have remained relatively stable. Congener profiles for three time windows (1965-80, 1986-93, and 2000–08) were similar in the three sediment cores from the Rhône and different from those at the rural reference site. The results indicate that permitted discharges from a hazardous-waste treatment facility upstream from Lyon might have contributed to high concentrations into the 1980-90s, but that industrial discharges from the greater Lyon area and tributaries to the Rhône near Lyon have had a greater contribution since the 1990s. There is little indication that PCB concentration in sediments downstream from Lyon will decrease over at least the short term.

Key words

Polychlorinated biphenyl (PCB); sediment core; Rhône River; trend

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the French or U.S. Governments.

1. Introduction

High levels of polychlorinated biphenyls (PCBs) have been measured repeatedly in sediment and fish in the Rhône River, particularly downstream from the city of Lyon (Babut et al., 2009;

Santiago et al., 1994), the largest city in the basin (metropolitan area population of 1.7 million) and the third largest in France. PCBs are ubiquitous environmental contaminants because of their extensive use from the 1930s to the 1980s and their environmental persistence (U.S. Environmental Protection Agency, 2004, 2011). In France, PCB use was banned in 1975 for open systems (e.g., pesticides, coatings) and in 1986 for 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). Since 2005, however, concern for human exposure to PCBs through fish consumption has risen greatly as sampling continues to identify streams in the Rhône basin with PCB-contaminated fish. Currently, commercial fishing and consumption of selected species of fish are banned as a result of PCB contamination in the main channels of the Rhône and Saône Rivers (the largest tributary to the Rhône) from upstream from Lyon to the Mediterranean Sea, and there are full bans of all fish species along reaches of numerous tributaries (Eaufrance, 2011). All of these bans have been imposed since 2005 and most were imposed since 2009, including one in 2011, on the basis of new or continued identification of fish with elevated concentrations of PCBs (Saônor.fr, 2011; Agence national de sécurité sanitaire, 2011).

PCBs are strongly hydrophobic and sediments therefore are the primary reservoir of PCBs in aquatic systems (Wong et al., 2001). Most mechanistic studies of food webs consider sediment ingestion as a major exposure route for PCBs for aquatic biota (e.g., Gewurtz et al., 2009; Morrison et al., 1997). Lopes et al. (2011) demonstrated that PCB concentrations in fish in the Rhône near Lyon were significantly related to PCB concentrations in Rhône bed sediment.

Using a statistical model, Babut et al. (2011) determined that the maximum PCB_I (sum of concentrations of seven indicator PCBs (Royal Order, 2000); non-detections treated as zeros) in sediment that corresponds to an acceptable PCB level in 90% of Rhône River fish is 5.9 μg/kg, a concentration well below concentrations of PCBs reported historically (1989) for the Rhône (Santiago et al., 1994). Knowledge of long-term trends in PCBs might contribute greatly to an improved understanding of long-term risks and of management options in the basin. Long-term data sets (e.g., 20-30 y) for PCBs in water, sediment, and fish, however, are not available for most large rivers, including the Rhône. Sedimentary archives such as sediment cores have been used to reconstruct PCB trends in many systems (e.g., Alcock et al., 1993; Eisenreich et al., 1989; Grimalt et al., 2004; Van Metre and Mahler, 2005), but because sediment-core reconstructions require long-term depositional settings (e.g., lakes), with the exception of a few studies in large fluvial reservoirs (Rosen and Van Metre, 2010; Van Metre et al., 1997), river deltas (Mai et al., 2005), and oxbow lakes (Bábek et al., 2008), this approach is rarely attempted in rivers.

In terms of mean annual discharge, the Rhône River is the second largest river in France and the third largest river in Europe (Pekarova et al., 2006). The mean daily discharge in the Rhône just downstream from the confluence with the Saône is 1,040 m^3/s (1966 to 2009) (Le Rhône à Ternay, streamflow-gauging station V3130020 (http://www.hydro.eaufrance.fr/)) (fig. 1; SI fig. S-1). The watershed of the Rhône is largely mountainous and covers 97,800 km^2 with marked climatic and geological heterogeneity (Desmet et al., 2005). The Rhône is a complex hydrologic system and several factors contribute to the distribution of sediment contamination, including:

(i) multiple tributaries and complicated watershed morphology, (ii) urban areas and industrial zones providing historical and current potential sources of contamination, (iii) extensive anthropogenic modification of the hydrology, and (iv) frequent flooding and sediment-flushing events that redistribute sediment. Since the Second World War, flow and sediment transport in the Rhône have been affected by construction of numerous dams (18 in France between Lake Geneva and the Mediterranean Sea) accompanied by structures for navigation, dike construction, and channel dredging (Andre and Lascombe, 1988; Pont et al., 2002). Accumulation of sediment behind the dams has led to periodic "flushing" (releases of impounded water) to clear sediment deposits, carried out approximately triennially from 1965 to 2003.

There are numerous potential sources of PCBs to the Rhône and its tributaries. These include industrial facilities with probable historical PCB discharges, PCB-contaminated sites and soils, and reported PCB spills (Robin des Bois, 2011). A synoptic survey of suspended sediments in the Rhône in 1989 found that PCB concentrations were much higher downstream from Lyon than upstream (Santiago et al., 1994), which the authors attributed to urban nonpoint sources and to inputs from the heavily industrialized zone downstream from Lyon. Major tributaries also might contribute to PCBs in the Rhône: the Bourbre, the Saône, and the Gier Rivers (fig. 1) all have partial or full commercial fishing and fish consumption bans as a result of PCB contamination (Eaufrance, 2011). A hazardous-waste treatment facility about 40 km upstream from Lyon (fig. 1) also has been identified as a potential PCB source (Babut et al., 2009; Santiago et al., 1994). This hazardous-waste treatment facility is one of two PCB incineration

facilities in France and is authorized to release small amounts of PCBs into the Rhône (Eaufrance, 2011).

Concerns about PCB contamination in the Rhône basin are prompting major sampling efforts to characterize PCB occurrence, identify sources, and understand trends (Eaufrance, 2011). As one of these efforts, the study presented here evaluated trends in PCBs in Rhône River sediments in the area of Lyon relative to land use, river-management practices, and restrictions on PCB releases. Recent (20–50 y) trends in PCBs in sediment were evaluated on the basis of sediment cores collected from depositional zones adjacent to the channel of the Rhône upstream and downstream from the PCB treatment facility.

2. Methods

2.1. Sampling locations

Sediment-core collection sites were chosen to evaluate the upstream-downstream distribution and temporal trends of PCB contaminated sediment and to assess the potential effects of the PCB treatment facility, the city of Lyon, and major industrial areas in the watershed on the sediment quality of the Rhône (fig. 1). Sediment cores were collected during May to July 2008 at three sites from 90 km upstream from Lyon to 40 km downstream (in upstream to downstream order, followed by their short names: La Morte, MTE; Crépieux-la-Pape, CPX; and Ile du Beurre, BRE), and in 2010 at a rural reference site in the interior of the Rhône basin (Lake

Paladru, PAL). Additional site information, maps, and aerial photos are provided in Supporting Information.

2.2 Core collection and sediment description

Sediment cores were collected with a UWITEC® gravity corer fitted with a 1.20-m long, 63-mm diameter plastic barrel with a core catcher at the bottom. Using an extended rod, the corer was pushed gently into the sediments from a boat. Multiple cores were collected at sites MTE, CPX, and BRE and one core was collected at site PAL. The cores ranged in length from 52 to 112 cm. At the laboratory, cores were sub-sampled at a 1-cm interval with the exception of the core from site PAL, which was sampled at a 0.5-cm interval. For PAL and MTE cores, sub-samples from one core were analyzed for PCBs, total organic carbon (TOC), grain-size distribution, and radionuclides. At sites CPX and BRE, sub-samples from one core (herein the primary core) were analyzed for PCBs, TOC, and grain-size distribution and samples from a second core (herein the radionuclide core) were analyzed for grain-size distribution and radionuclides. Grain-size distribution was 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 (g/cm^3) was determined as the difference between wet and dry mass divided by the volume of the container. High-resolution 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. Grain-size mean, mode, sorting, and skewness were

computed. Cumulative volumetric percentages of sand (>63 μm), silt (4-63 μm), and clay (<4 μm) were determined for each depth interval.

2.3 Analytical methods

Sediment-core samples were analyzed for radionuclides at the Laboratoire des sciences du climat et de l'environnement, Gif sur Yvette, France. Following drying, sub-samples from each core were analyzed for radionuclides by counting for at least 24 hours using gamma spectrometry. Gamma emissions were detected with a germanium detector and used to quantify ^{226}Ra, ^{210}Pb, and ^{137}Cs (Pinglot and Pourchet, 1995).

Samples were prepared for measurement of total 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. Total organic carbon was analyzed by high-temperature combustion (1,250°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, Orleans, France (www.eurofins.fr). PCBs were extracted in accordance with the certified method QMA 504-192 (DIN ENISO/IEC 17025:2000) (http://www.graie.org/osr/IMG/pdf/RS2_web.pdf). In brief, 5 g of dried, homogenized sediment were extracted for a minimum of 8 hours with toluene/acetone (90/10 v/v) in a Soxhlet apparatus. After addition of PCB-155 as an internal standard, the sample

extract underwent a clean-up step using gel permeation chromatography. Clean-up consisted of sequential passes through silica, aluminium oxide, Florisil, and active carbon columns. The sample extract was analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) in selected ion monitoring (SIM) mode. For the seven indicator PCBs, quantification limits ranged from 0.042 μg/kg (PCBs 118 and 180) to 0.146 μg/kg (PCB 153). Laboratory quality control consisted of periodic analysis of blanks and certified reference materials. Analytical results for environmental samples were not blank-corrected.

Eighteen PCB congeners were quantified (SI table S-1). Interpretations herein are based on the sum of the seven so-called indicator PCBs (PCB_I): International Union of Pure and Applied Chemistry (IUPAC) numbers 28, 52, 101, 118, 138, 153, and 180, the sum of which is commonly used in European national legislation to ensure food safety (Royal Order, 2000). These congeners are generally considered persistent and are thought to be good markers for human exposure to PCBs through ingestion (Wingfors et al., 2006)

2.4. Age dating of sediment

The date of deposition of sediment intervals within each core (SI figs. S-6 to S-9) was estimated on the basis of radionuclide profiles and, for Rhône sediment cores, on correlation of changes in grain-size distribution in the sediment cores to the timing of major floods and to major changes in river hydrology. The ^{137}Cs profile was used to determine one or two age-date markers in each core. ^{137}Cs was released into the atmosphere by nuclear weapons testing from

1952 to 1963 (Beck and Helfer, 1990). In 1986, the accident at the Chernobyl nuclear power plant in Ukraine resulted in relatively large releases of ^{137}Cs, and about 79% of the total fallout occurred over Europe (Anspaugh et al., 1988). Two date-depth markers thus can be identified in European sediment cores: the weapons testing peak in 1963 and the Chernobyl peak in 1986. The radionuclide ^{210}Pb was not used as a primary age-dating tool because the riverine setting of the Rhône coring sites leads to violation of the principle assumptions of ^{210}Pb dating models (Appleby and Oldfield, 1992). However, the ^{210}Pb profiles provided some corroboration of the dating and the chronological integrity of the cores. The occurrence of floods and associated changes in grain-size distribution in the cores provided support for the ^{137}Cs dating, provided additional depth-date markers at site CPX, and were the basis for correlating the primary and radionuclide cores at sites CPX and BRE for the purposes of age-dating (SI figs. S-8 and S-9). Dates were assigned to intervals in the cores between date markers assuming a constant sediment mass accumulation rate (MAR; g/cm^2-yr) between the date markers.

3. Results

3.1 Sediment age-dating

Primary date markers used to estimate sediment deposition dates in the cores were the date of site construction or of connection to the Rhône (sites CPX and BRE), peaks in ^{137}Cs, and changes in grain-size distribution corresponding to major flood events (SI figs. S-6 to S-9). A large or

sudden increase in grain size (i.e., a sudden decrease in the percentage of fine-grained fraction of material, i.e., less than 63 microns diameter, herein referred to as fines) followed by a gradual increase in the percentage of fines was assumed to be the result of a flood event, although only a few very pronounced changes in grain size were used as date markers in cores. At the two sites where radionuclides and PCBs were analyzed in separate cores (sites CPX and BRE), the cores were correlated for dating purposes on the basis of changes in grain size. Age dates for each sediment sub-sampling interval were based on assumption of a constant sediment MAR between date markers.

Age dates for core PAL were based on two distinct peaks in ^{137}Cs at depths of 8-8.5 and 3.5-4 cm (SI fig. S-6), interpreted as corresponding to nuclear-weapons testing (1963) and the Chernobyl accident (1986). The MAR during 1964–86 was 0.30 g/cm^2-yr, and during 1986–2010 was 0.27 g/cm^2-yr. Use of the ^{137}Cs peaks for age dating resulted in slightly older dates (about 2 y for most intervals) than those estimated using the ^{210}Pb constant-flux, constant-supply model (Appleby and Oldfield, 1992), but because the ^{137}Cs peaks were so marked, this age-dating approach was preferred.

Age dates for core MTE were based on a ^{137}Cs peak at 25-26 cm interpreted as the Chernobyl accident and a rise in ^{137}Cs at the bottom of the core interpreted as being associated with the weapons-testing peak in 1963 (SI fig. S-7). The Chernobyl peak is well defined, but the weapons-testing peak is indicated only by an increase to a maximum at the bottom of the core. The deepest sample in the core has a ^{137}Cs activity about 5 times greater than do samples in the

middle of the core, but the ^{137}Cs peak may have been at a depth deeper than that sampled by the core. The MAR during 1964–1986 was computed as 1.1 g/cm^2-yr, and during 1986–2008 as 0.48 g/cm^2-yr. The decrease in sedimentation rate after 1986 might have resulted from the construction of the dam at Champagneux in 1984 upstream from site MTE (fig. 1).

For site CPX, age dates for the radionuclide core (CPX 08-02) were estimated on the basis of the ^{137}Cs profile and on variations in grain size that were matched with floods (SI fig. S-8). A single pronounced ^{137}Cs peak at 85-86 cm was interpreted as resulting from the Chernobyl accident. A ^{137}Cs peak corresponding to nuclear weapons testing was not expected because the site was not formed until the early 1980s. Episodic large decreases in percentage of fines between about 57 and 77 cm in the core, reaching minima of about 20% (80% sand), were interpreted as corresponding to three large floods in the early 1990s (SI fig. S-1). More modest decreases in percentage of fines occurred in the upper part of the core, the largest of which was from 14 to 19 cm and was interpreted as corresponding to floods in 2001 and 2002. These date markers indicate an MAR of 2.3 g/cm^2-yr during the 1980s, 5.0 g/cm^2-yr during the early 1990s flooding, and 1.8 g/cm^2-yr after the 2001-2002 flooding. No major floods have occurred on the Rhône in the reach investigated since 2002 (SI fig. S-1). The river has been building a natural levee at the mouth of the site CPX quarry since the quarry was abandoned (SI fig. S-4), consistent with the observed decrease in MAR and increase in fines over time. The interval near the bottom of the radionuclide core with a dip in percentage of fines (to 22%) is dated as 1983.9, coinciding with a large flood in 1983. The primary core (CPX 08-01) was correlated to the radionuclide core (CPX 08-02) using grain-size distribution (measured in both cores), specifically by matching the thick

sequence of sand deposits that occurred in both cores at about 70-cm depth and a series of maxima and minima in percent fines that occurred in the upper 40-45 cm of the cores (SI fig. S-8).

For site BRE, age dates for the radionuclide core (BRE 08-03) were based on a ^{137}Cs peak at 53 cm depth and the pronounced change in grain-size distribution at 70-cm depth (SI fig. S-9). The ^{137}Cs peak was interpreted as corresponding to the Chernobyl accident. The change in grain-size distribution at 70 cm was interpreted as corresponding to removal of debris in 1984 that established a connection to the Rhône at the upper end of the side channel where the BRE core was collected. The MAR during 1986–2008 was computed as 3.1 g/cm^2-yr and the MAR from 1984–1986 was computed as 7.1 g/cm^2-yr. The higher MAR from 1984–1986 might be caused by the channel-clearing operations in 1984. Prior to 1984, the BRE site was not directly connected to the Rhône, the sediments were uniformly fine-grained, and no date markers were evident in either core. The primary core (BRE 08-01) was correlated to the radionuclide core (BRE 08-03) using grain-size distribution, specifically by matching the rapid transition from the thick sequence of silt and clay deposits deep in the cores to coarser and much more variable sequences above (SI fig. S-9). PCBs were detected to the bottom of the primary core (deepest sample at 104–105 cm), but the samples from before 1984 to the bottom of the core are not presented here because they are assumed to represent sediment originating elsewhere than the Rhône.

3.2 Recent trends in PCBs

PCB_l concentration profiles at the four sites differ both in timing and magnitude of peak concentrations (fig. 2; SI Table 1). In general, PCB_l concentrations at the rural (PAL) and upstream (MTE) reference sites peaked in the 1970s and decrease to present. Although PCB_l concentrations for the 1970s are not known at the downstream sites (CPX and BRE), at these sites there are large peaks in PCB concentrations in about 1990, followed by a rapid decrease in concentration in the early 1990s; PCB concentrations have remained relatively stable since the mid-1990s (fig. 2). Peak and current PCB_l concentrations are lowest at the PAL rural reference lake site and increase in the Rhône in a downstream direction.

PCB_l concentrations in sediment deposited at site PAL peaked in 1976 at a concentration of 13 μg/kg (fig. 2). Concentrations decreased rapidly from 1976 to 1985 before leveling off for about 10 years, then decreased steadily from 1998 to 2.2 μg/kg at the top of the core (2010). Organic carbon-normalized concentrations (PCB_l/TOC) were used to determine rates of change in concentrations (fig. 3); the normalization was done to exclude variations associated with the textural properties of the particles and enable between-site comparison. An exponential curve fit to PCB_l/TOC from the peak to present (r^2=0.90) indicates a half-life ($t_{1/2}$) of 12.6 years. The half-life determined here is not a rate of chemical decay but rather is a measure of the rate of change in PCB inputs to the coring site. The decrease in PCB_l from 1998 to 2008 is more rapid and linear than the long-term trend, with a $t_{1/2}$ of 6.2 y (r^2=0.94). The reason for a change in the rate of decrease in about 1998 is not known, but might be related to sediment dilution caused by anthropogenic activities in the watershed, such as construction, that mobilized deeper, uncontaminated sediment.

At site MTE, PCB_l concentrations are elevated and variable in sediment deposited during the 1960s and 1970s, and the maximum concentration of 78 μg/kg is 6 times higher than at the PAL reference site (fig. 2). Carbon-normalized PCB_l concentration decreases exponentially from 1964 to the top of core MTE (2008), with a half-life of 8.5 years (r^2=0.87) (fig. 3). The concentration in the most recently deposited sediment is 3.5 μ g/kg. The decrease in PCB_l since 2001 is slightly more rapid than for the whole period of the core, with a $t_{1/2}$ for this 8-year period of 6.4 years (r^2=0.99).

In contrast to PCB_l profiles at sites PAL and MTE, concentrations at site CPX are elevated and variable in the early 1990s, followed by a very rapid decrease in the mid-1990s and relatively stable concentration since (fig. 2). Maximum PCB_l concentrations (72 to 84 μg/kg) occur in sediment deposited during 1991–93. Since the decrease in the mid-1990s, PCB_l concentration varies around a central tendency of 15 μg/kg to the top of the core. Concentrations in Rhône sediment along this reach of the river prior to 1990 are not known. Although there is no significant trend in PCB_l concentrations from about 1993 to the top of the core in 2008 (Kendall's tau test of correlation, p=0.13), there are two brief increases followed by longer (~6-y) decreases within this time period (fig. 2). The rate of decrease from 2003 to 2008 following the small increase in 2003 is virtually identical to that of the longer-term rate of change during 1991–2000 ($t_{1/2}$ of 2.4 and 2.5 y, respectively; fig. 3). The minimum PCB_l concentration (8.9 μg/kg) occurs in the most recently deposited sediment.

Similar to the profile from site CPX, PCB_I concentrations at site BRE are elevated into the early 1990s then decrease rapidly (fig. 2). Concentrations reach a maximum of 282 μg/kg in 1991, about 3 times higher than that at site CPX, then decrease to concentrations that vary between 20 and 55 μg/kg. Also similar to site CPX, the sediment core does not record concentrations in Rhône sediments prior to the early 1980s. There was no significant change in concentrations of PCB_I from 2001 to 2008 (fig. 3).

3.3 PCBI congener profiles

Profiles of the seven indicator PCBs at the three Rhône sites were constructed for three time windows chosen to reflect periods of peak concentrations at site MTE (1965–1980) and at sites CPX and BRE (1986–93) and recent concentrations (2000-08) (fig. 4). The profiles represent the mean proportion of each congener contributing to PCB_I for the samples in the time window. Core profiles for the time windows were relatively similar at the three sites (fig. 4). In all cases, PCB 153 made up the highest proportion (typically 25–30%) and PCB 28 made up the lowest proportion (typically <5%) of PCB_I. Profiles for site PAL, however, differ somewhat from those at the other three sites in that proportions of the less chlorinated congeners (PCBs 52, 101, 118) are more elevated and those of the more chlorinated congeners (PCBs 153 and 180) are less elevated (fig. 4), consistent with preferential volatilization and atmospheric transport of the less chlorinated congeners (Wania and Mackay, 1993). In contrast, the profiles for sites MTE, CPX, and BRE fall within nearly identical ranges. Similar differences between the profiles for the 1986–93 and 2000–08 time windows at sites CPX and BRE (lower proportions of PCB 28 and higher proportions PCB 138 during the 2000-08 time window) and slightly higher proportions of

PCB 180 relative to those at sites PAL and MTE suggest that sites CPX and BRE might have one or more PCB_l sources that changed over time and(or) are different from those at sites PAL and MTE. The differences, however, are relatively subtle, and a thorough forensic analysis of PCB profiles would entail use of a much larger suite of congeners.

4. Discussion

The use of sedimentary archives to reconstruct contaminant trends has a long history (Davis, 1980). With the exception of studies using cores from reservoirs (e.g., Callender and Robbins, 1993; Van Metre et al., 1997), however, the approach is rarely applied to riverine settings because of the requirement that sediments remain undisturbed at the timescale of interest, often decades. The reservoirs created by dams on the Rhône were flushed approximately triennially (1965–2003) to remove deposited sediment, and therefore are assumed to be unsuitable for coring. However, in a large river system such as the Rhône, sediment may accumulate over long periods in settings other than reservoirs. Here we have located three such sites that are demonstrated, on the basis of their radionuclide profiles, to have accumulated sediment over about 25-50 years. Two of the sites (MTE and BRE) are in abandoned channels (oxbows) of the Rhône that remain connected to the main channel and one site (CPX) is in an abandoned sand and gravel quarry that is open to an active channel of the Rhône. Compared with cores from undisturbed natural lakes, the age dating of the riverine cores is not ideal, as indicated by the comparison of radionuclide profiles at site PAL to those at the other three sites (SI figs. S-6 to S-9). We contend, however, that because the dating is

constrained by known date markers, it is adequate for the reconstruction of recent (25-50 y) PCB concentration trends, and that this reconstruction provides a valuable perspective where historical data do not exist.

4.1 Differences in trends among sites and implications for sources

PCB trends vary considerably among the sites sampled here (fig. 2). The temporal trends at the rural (PAL) reference lake site and upstream (MTE) Rhône reference site are similar to those of global PCB emissions (Breivik et al., 2002) and widely reported patterns in PCB contamination, with the highest concentrations coinciding with maximum use and environmental release in the 1960s and 1970s and systematic decreases since (e.g., Eisenreich et al., 1989; Van Metre et al., 1997; Van Metre and Mahler, 2005; Jung et al., 2008; Iozza et al., 2008). The marked decreases in PCBs at these two sites beginning in the late 1970s are consistent with the interdiction of PCB use in open systems in France in 1975 (Journal Officiel, 1975).

The two sites downstream from Lyon (CPX and BRE) had high and variable concentrations in the late 1980s and early 1990s followed by rapid decreases into the mid-1990s, after which they remained relatively stable (fig. 2). The shape of the PCB profiles at sites CPX and BRE differ from the monotonic downward trend recorded at sites PAL and MTE from the mid-1980s on and are inconsistent with widely reported downward trends in PCBs beginning in the 1970s (e.g., Van Metre et al., 1998; Iozza et al., 2008). The rapid decreases in PCBs at sites CPX and BRE following peak concentrations in about 1990 indicate point-source releases likely occurred contemporaneous with those peaks. PCB_l concentrations at sites CPX and BRE decreased by

75% or more in the early to mid-1990s, and remained low thereafter (with the exception of one questionable sample collected from a depth of 36.5 cm in ~1997 at site BRE [fig. 2, SI table S-1]). Such a sudden and substantial decrease in the 1990s, 15 or more years after peak use, would be expected only if a relatively large source had been recently discontinued. Although flooding in the early 1990s might have played a role in variations in PCB concentrations at these two sites, it had little apparent effect at site MTE upstream, and subsequent floods in 2001 and 2002 did not cause substantial changes in concentration at either of sites CPX or MTE. Although the trends are anomalous relative to those at many sites, industrial releases of PCBs might have resulted in a later initiation of downward trends following regulation of production and use. Elevated concentrations of PCBs into the 1990s were reported for a sediment core from Lake Maggiore in northern Italy, which has a heavily industrialized and densely populated watershed (Guzzella et al., 2008), and a lack of a downward trend was reported for PCBs in sediment cores from an oxbow in the Morava River (Czech Republic), the basin of which has historical industrial land use (Bábek et al., 2008). One limitation to this interpretation, which is a consequence of the difficulty in finding long-term depositional sites in a river system, is that the cores of Rhône sediment do not extend back in time to the 1960s and 1970s. It therefore is not known if the concentrations in the Rhône in and downstream from Lyon were even greater before the 1980s.

There at least two potential PCB sources in the reach of the Rhône between sites MTE and CPX. The first is the Bourbre River (fig. 1), for which an elevated sediment PCB_l concentration (~200 μg/kg) in a sediment sample collected in 1997 was reported (Babut and Miège, 2007), and

which currently has a ban on fish consumption (Eaufrance, 2011). The watershed of the Bourbre includes several semi-industrial towns. A second potential PCB source is the hazardous-waste treatment facility upstream from Lyon (fig. 1). Because PCBs are treated and disposed of at this facility, its regulation is different from that of PCB use in France. It is not known how actual discharges from the hazardous-waste treatment facility compared to permitted limits from 1987–97, but the magnitude and timing of the permitted limits from 1987 to present is consistent with temporal trends in PCBs at sites CPX and BRE. The hazardous-waste treatment facility began operating in 1985, but PCB releases were not regulated until 1987; the first limit established in 1987 was 1.5 kg/d, which was reduced to 500 g/d in 1992, 200 g/d in 1995, and to 10 g/d in 2007 (Préfecture de la Région Rhône-Alpes, 2007). Actual releases, not reported until 1997, are very low (2-8 g/d in 1997 reduced to 0.17 g/d in 2010) (Fruget et al., 2010). An additional consideration is the construction of the dam at Villebois in 1986, downstream from site MTE and upstream from the hazardous-waste treatment facility and the confluence of the Rhône and Bourbre Rivers (fig. 1). The dam could have trapped relatively uncontaminated sediment from upstream, resulting in less dilution of sediment-associated PCB sources in the Rhône downstream after 1986.

Releases of PCBs to the Rhône upstream from site CPX, however, cannot fully explain the trends observed at site BRE, which indicates some unknown source in the city of Lyon or the adjacent industrial corridors. Mean PCB_l concentrations during 1990–1993 in the BRE core were 165 μg/kg, about 3 times greater than those for the same period in the CPX core (59 μg/kg). Also, recent trends between sites CPX and BRE differ: There is a systematic decrease at site CPX

since 2003 but an increase at site BRE since 2006 (fig. 2). The watershed of the Rhône at site BRE is much larger than at site CPX, as it is downstream from the confluence with the Saône and other tributaries (fig. 1), thus, considerable dilution of a point source upstream from site CPX is expected at site BRE. Mean flow in the Rhône 2 km upstream from the confluence with the Saône is 593 $m^3.s^{-1}$ (Le Rhône à Lyon (Perrache), station V3000015) compared with 1,040 $m^3.s^{-1}$ in the Rhône downstream from Lyon at Ternay (station V3130020) (http://www.hydro.eaufrance.fr/). The substantial increase in PCB_l concentrations during 1986–1993 in the downstream direction and the difference in recent trends can only be explained by additional PCB sources in the intervening reach. Potential sources include the city of Lyon, the industrial corridor downstream from Lyon, and the Saône and Gier River watersheds (fig. 1), consistent with sources evoked by Santiago et al. (1994).

4.2 Hydrologic controls on PCB concentrations

Sediment flushing events and floods likely have some effect on PCB distribution and trends in the Rhône watershed. Possible effects of the triennial flushing events are evident at site MTE, where episodic increases in PCBs (fig. 2) and organic carbon (not shown) from 1965 to the mid-1980s occur at intervals similar to those of the flushing events. Effects of major floods are evident at site CPX: A large decrease in percentage of fines in about 1990, assumed to be caused by the 1990 flood, corresponds to a sharp decrease in PCB_l concentration, followed by a large increase in the fine fraction, from 20 to 80% (SI fig. S-8), and a correspondingly large increase in PCB_l concentration, from 18.8 to 83.5 μg/kg (fig. 2, SI table 1). This pattern appears

to repeat to a lesser degree with the 1992 and 1993 floods (decrease in grain size and PCB_I concentrations, although grain-size data are not available for several intervals in this part of the core). The large increase in PCB_I concentrations following the return to finer sediment size, however, does not recur, possibly because a localized source was eliminated. Smaller shifts in grain size and PCB_I concentration after 1994 appear to be related, but the relation between the two is inconsistent.

4.3 Spatial and temporal PCB concentrations in sediment and implications for fish consumption

Sediment cores from multiple locations in a river system can indicate spatial and temporal variations in contamination (Callender and Rice, 2000). Concentrations of PCBs in sediments in the Rhône increase substantially in the downstream direction as the river passes through industrial and urban areas for all time windows analyzed (fig. 5). The median PCB_I concentration during 1986–1993 was 9 times higher at site BRE than at site MTE, and from 2000–2008 was 6 times higher. Temporally, the decrease in PCB_I concentration from one time window to the next is approximately proportional between sites (fig. 5). The relevance of these spatial and temporal patterns from the standpoint of fish contamination is reflected in PCB_I concentrations in bream (*Abramis brama*) (Babut et al., 2011), which follow a similar upstream-downstream pattern (fig. 5). The fish were collected in 2008 at sites MTE and BRE, and at a third site, the Grand Large, which is in another channel of the Rhône a few kilometers from site CPX and a similar distance upstream from Lyon (fig. 1). PCB_I concentrations are similar in surface sediments from Grand Large (median 18.5 μg/kg) (Babut et al., 2011) and recent

sediments (past 10 y) in the CPX core (median 13.7 μg/kg). The consistent relation between recent sediment and fish concentrations and the temporal trends in sediment concentrations indicate that PCB concentrations in fish 20 to 40 years ago likely were much higher than they are now.

Long-term downward trends in PCB concentrations at reference sites PAL and MTE and rapid decreases after highs in the early 1990s at sites CPX and BRE indicate that regulatory changes likely have contributed to a reduction in PCB contamination in the Rhône. Decreases in PCB concentrations at the downstream sites, however, appear to have slowed or stopped in the past ~15 years, and current concentrations (2011) are above the concentration of 5.9 μg/kg identified by Babut et al. (2011) as the maximum sediment concentration corresponding to acceptable concentrations in 90% of fish. The results of this study indicate that PCB contamination in the lower Rhône basin is likely to remain of concern for years to come.

Acknowledgements

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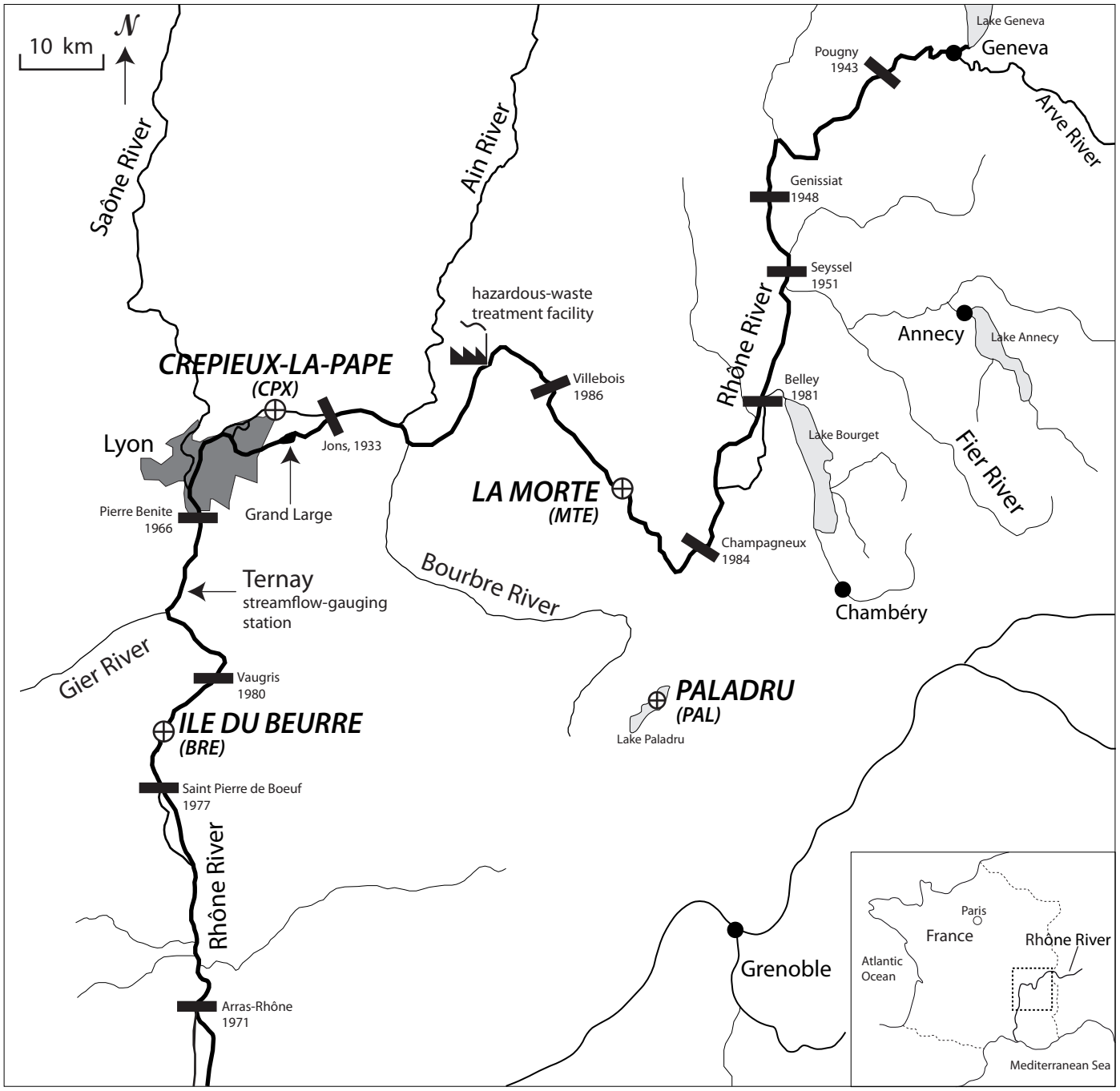

Figure 1. Map of the study area, Rhône basin, France.

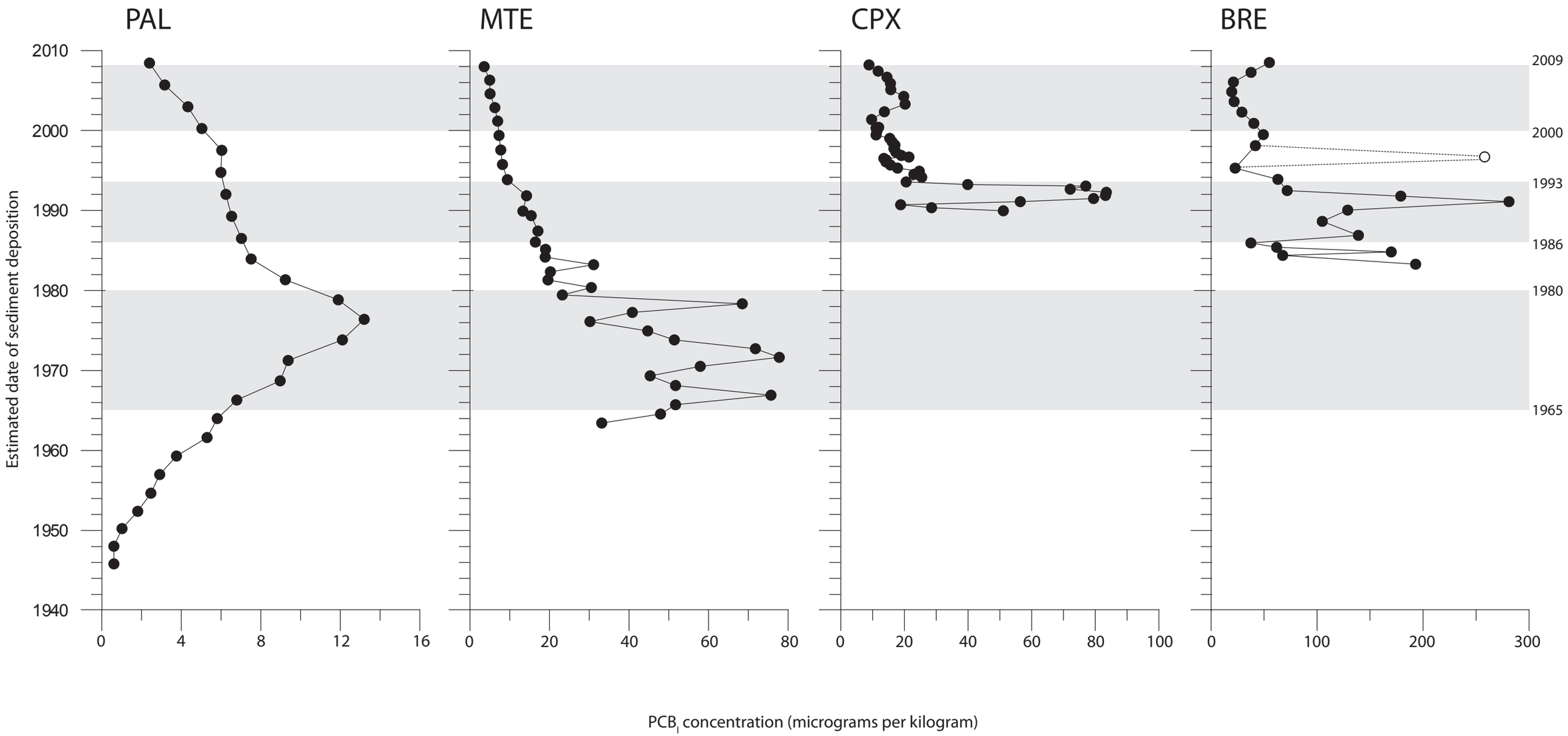

Figure 2. Profiles of the sum of the seven indicator PCBs (PCB$_l$) in sediment cores collected from Lake Paladru (PAL), La Morte (MTE), Crépieux-la-Pape (CPE), and Ile du Beurre (BRE), Rhône basin, France. Time windows used in additional analyses and interpretation are indicated in grey. A questionable data point for core BRE (open symbol) was not included in the analysis.

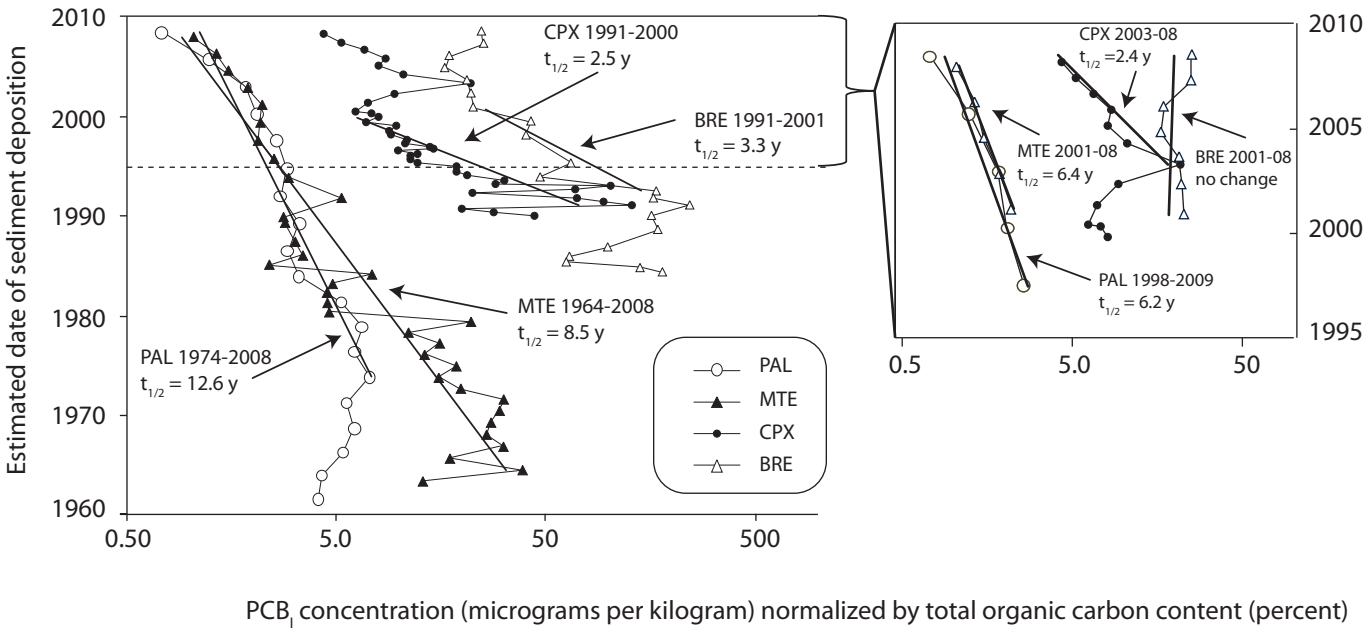

Figure 3. Rates of decrease of PCB_l (the sum of concentrations of seven indicator PCB) normalized by total organic carbon content for sediment cores from Lake Paladru (PAL), La Morte (MTE), Crépieux (CPX), and Ile du Beurre (BRE). Half-lives ($t_{1/2}$) were computed from an exponential fit for the dates indicated. Inset, right, shows half-lives for recent dates.

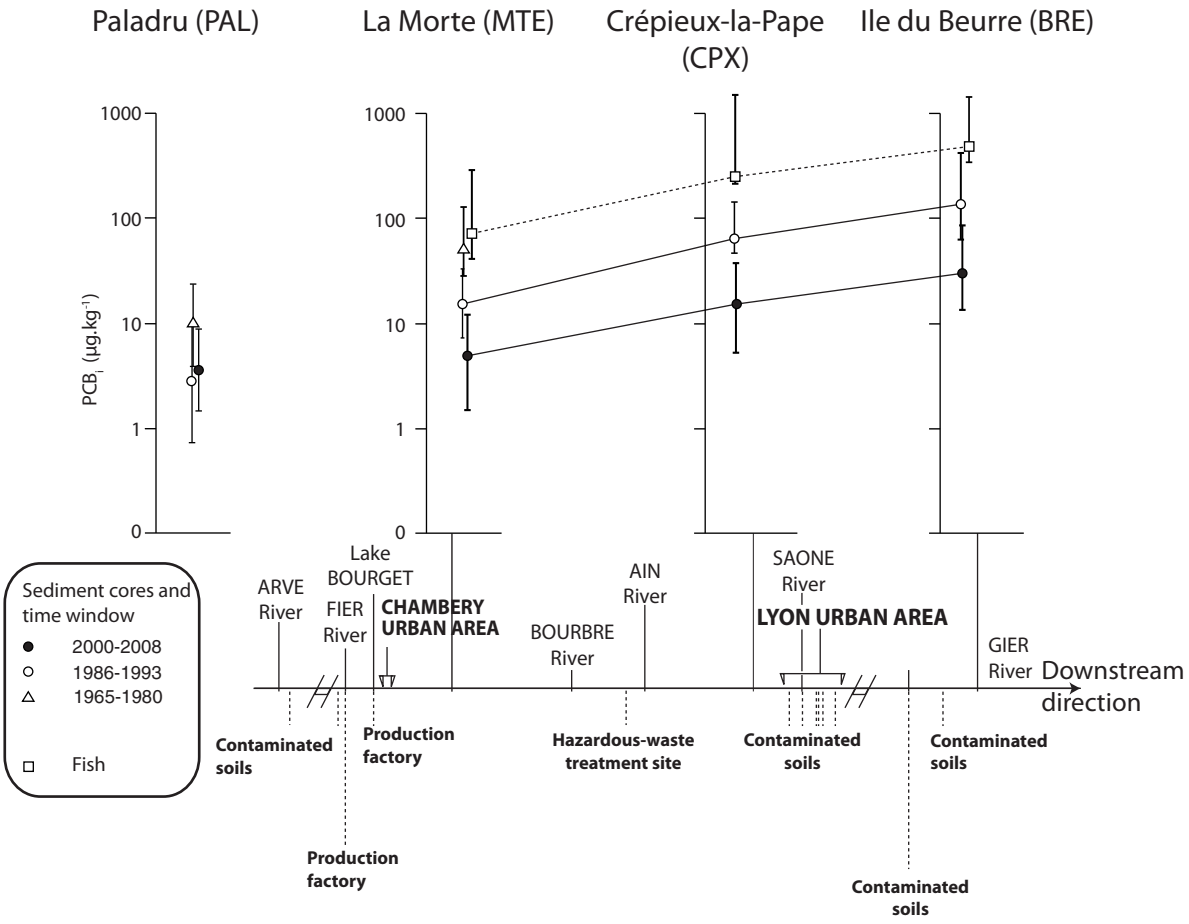

Figure 5. Mean and range of PCB_I concentrations in sediment cores from the Rhône River for three time windows and concentrations measured in fish (bream) in 2008 (Babut et al., 2011). Also shown are locations of two urban areas relative to the main stem of the Rhône and confluences with major tributaries (fig. 1), and locations of known or suspected PCB sources (Robin des Bois, 2011).

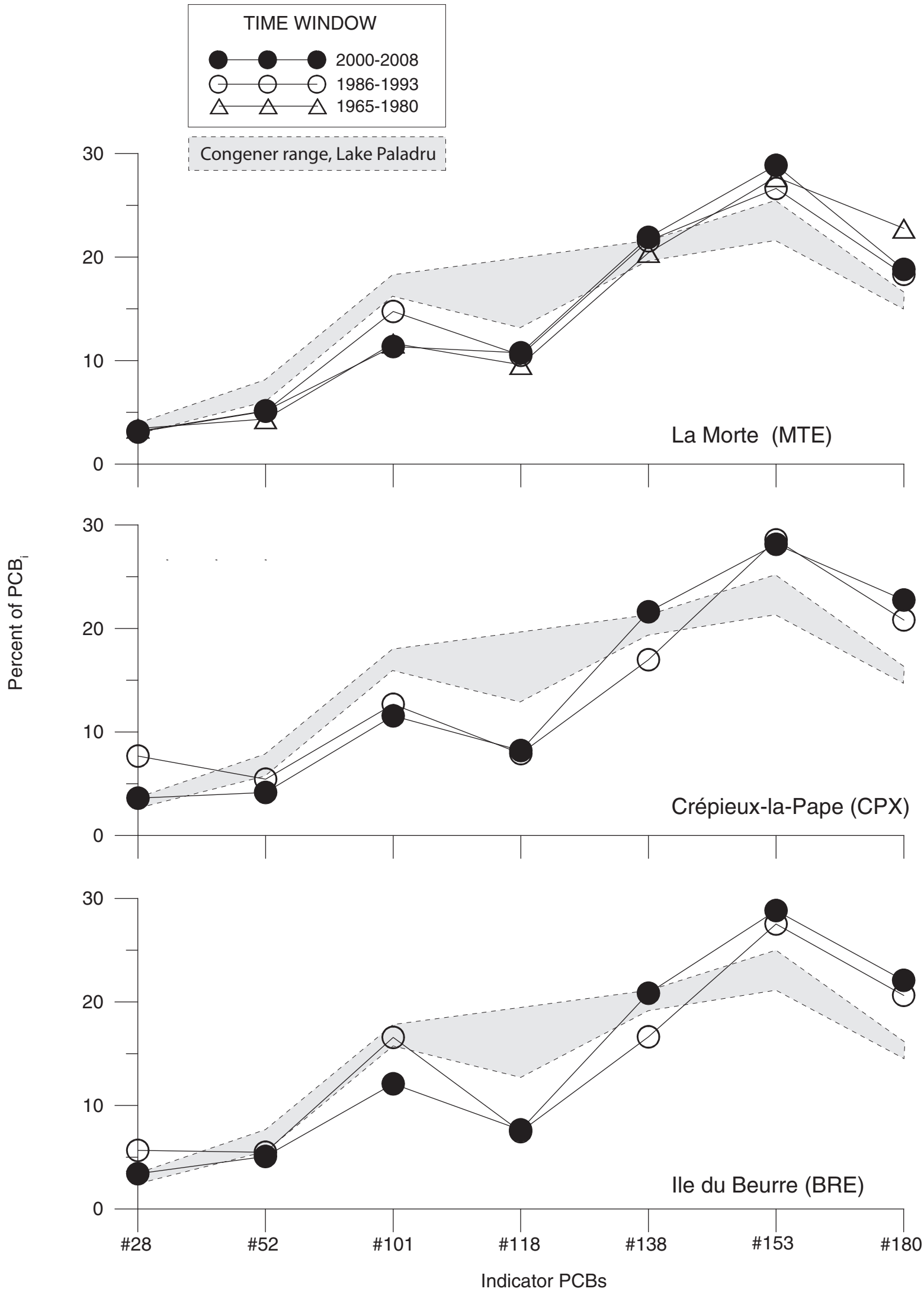

Figure 4. Profiles of the seven indicator PCBs at the three sediment coring sites along the Rhône River, France, for three time windows. Each congener is expressed as its proportional contribution the sum (PCB_i). The grey area indicates the range of profiles for the rural reference site Lake Paladru.

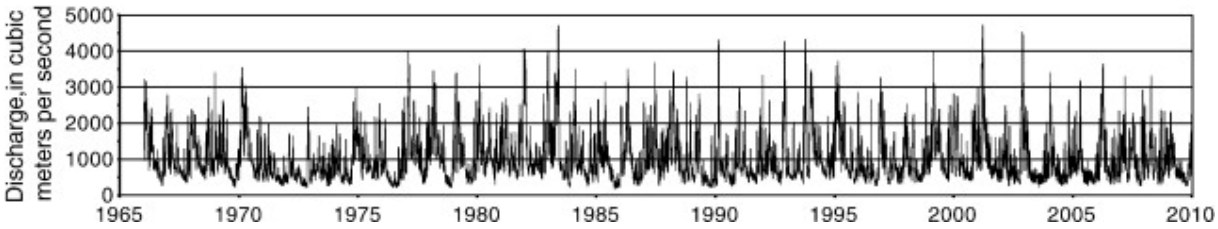

Fig. S-1. Rhône River daily mean discharge, as measured at the streamflow-gaging station at Ternay, near the city of Lyon

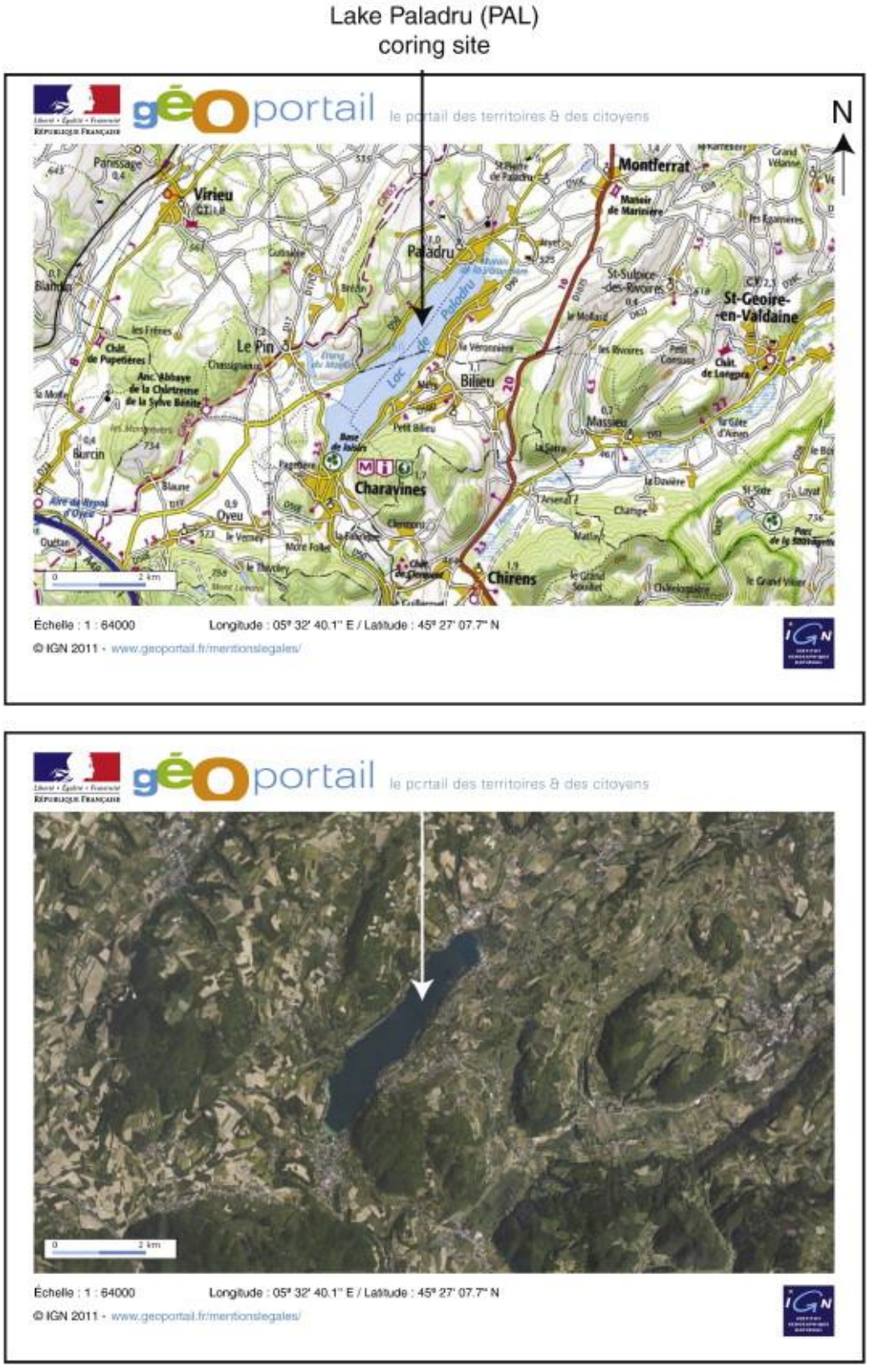

Fig. S-2. Map and aerial image of the coring site on Lake Paladru (PAL). Lake Paladru, a rural reference site, is in the east-central part of the Rhône basin (Fig. 1, full text). Land use in the watershed of Lake Paladru is agricultural with several small villages. Loading of PCBs to Lake Paladru is assumed to be mostly from long range atmospheric deposition.

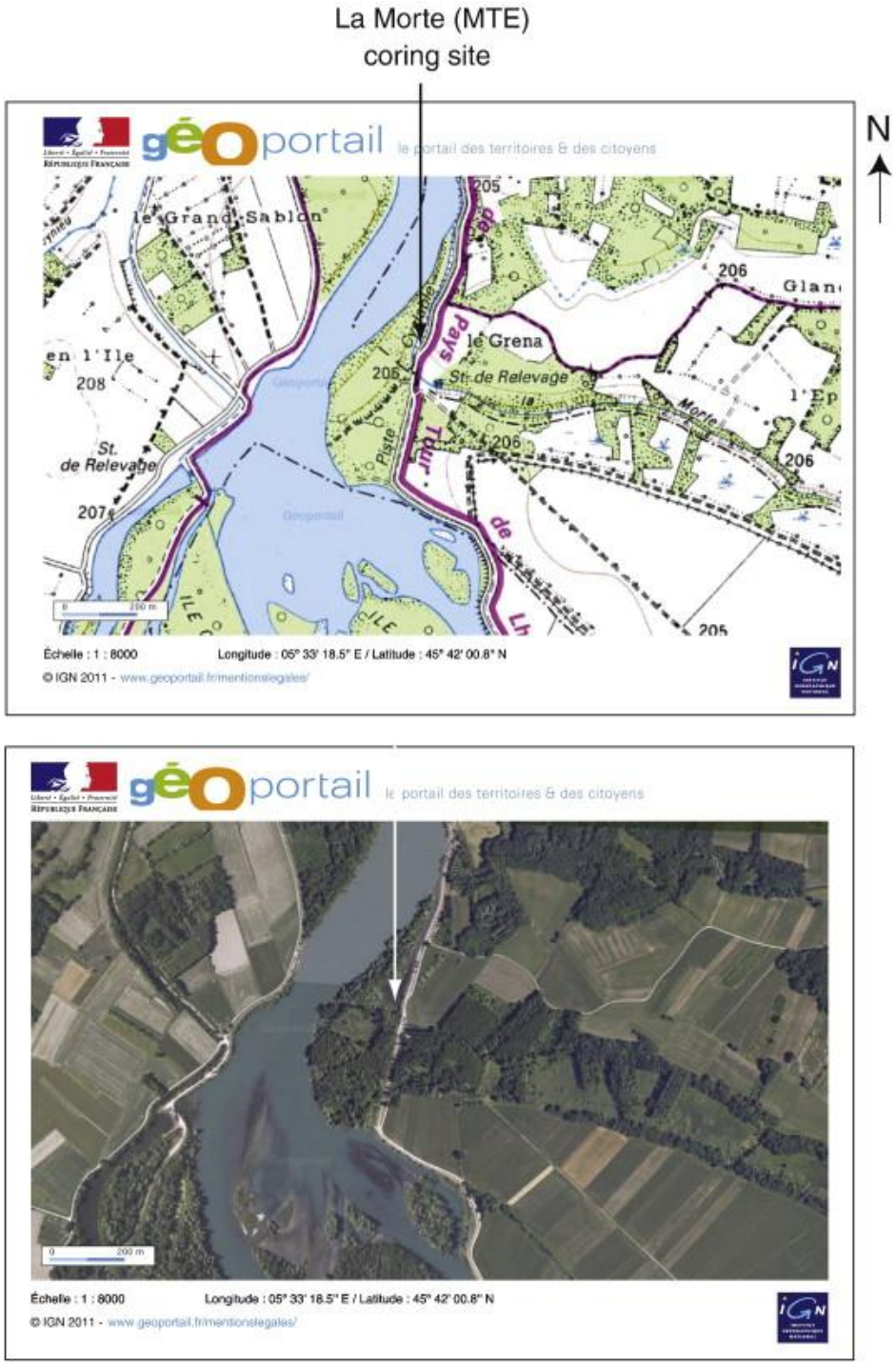

Fig. S-3. Map and aerial image of the coring site at La Morte (MTE). La Morte is the most upstream of the three coring sites on the Rhône River (Fig. 1, full text). It is located in a pond at the downstream end of a cutoff meander of the Rhône, which is open to the river at its downstream end. La Morte is in a relatively non-industrialized part of the Rhône basin upstream from the hazardous-waste treatment facility and Lyon. It was chosen to represent reference concentrations for the lower Rhône basin (i.e., downstream from Lake Geneva). There are, however, urban and industrial areas in the upper Rhône valley in Switzerland (upstream from Lake Geneva) and smaller urban areas and a few historical contamination sites between Lake Geneva and La Morte that might affect PCB concentrations at La Morte (Robin des Bois, 2011).

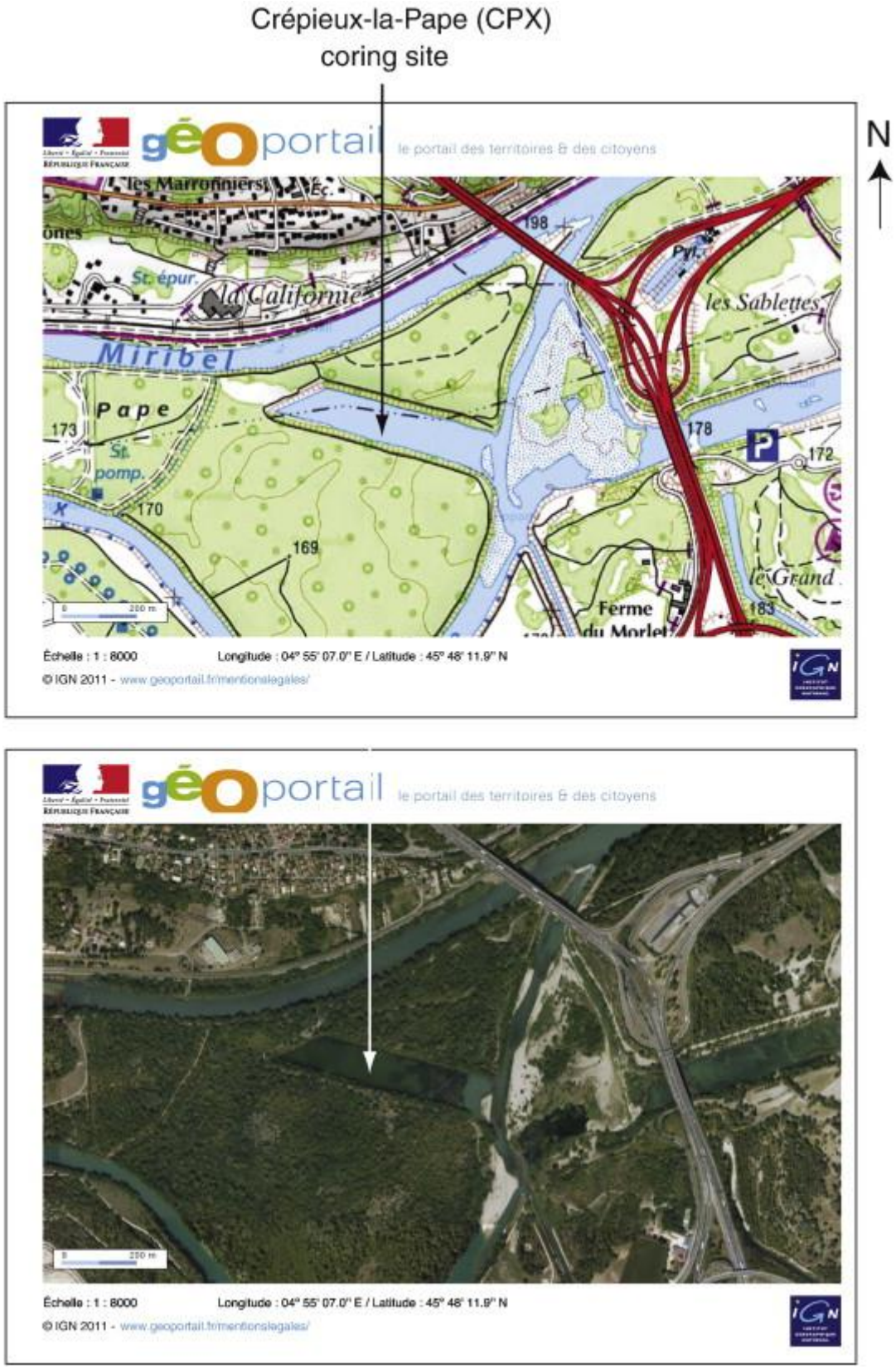

Fig. S-4. Map and aerial image of the coring site at Crépieux-la-Pape (CPX). The site is a former gravel quarry adjacent to the old channel of the Rhône River. It was formed at the beginning of the 1980s by dredging of alluvial deposits. The harbor-shaped feature left by quarrying is about 3 m deep at the center. Since quarrying ended in the early 1980s, flood deposits have formed a submerged levee that

may have progressively limited entry of coarser material to the quarry. Site CPX is in the greater Lyon urban area, 3 km upstream from central Lyon (Fig. 1, full text), and sediment quality of CPX thus is assumed to represent the effects of PCB inputs from a hazardous-waste treatment facility, smaller cities between Lyon and La Morte, the Bourbre River, and non-point emissions from the northern part of greater Lyon.

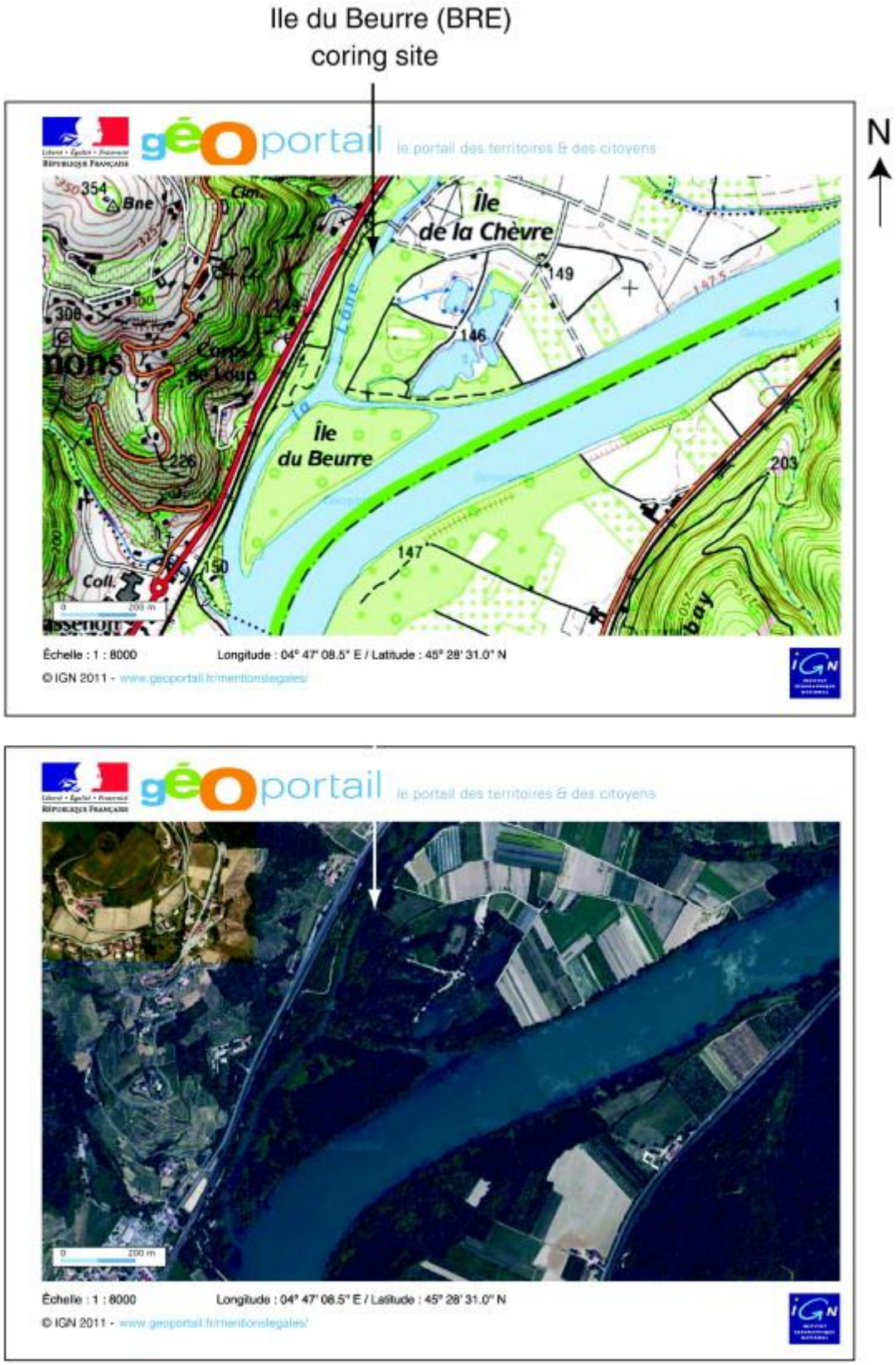

Fig. S-5. Map and aerial image of the coring site at Ile du Beurre (BRE). The site is in a small side channel in a forested wetland adjacent to the Rhône River, 40 km downstream from Lyon (Fig. 1, full text). This site was chosen because of its location downstream from Lyon and the industrial corridor that extends from south of Lyon to the confluence with the Gier River, which, like the Bourbre River,

has a full fish consumption ban as a result of PCB contamination (Eaufrance, 2011). Before 1977, the side channel was not connected to the Rhône River. In 1977, construction of the dam at Saint Pierre de Boeuf downstream from lle Beurre raised the water level in the river to that of the side channel, and in 1984 a debris dam separating the side channel and the Rhône was removed, allowing connection between the two water bodies (Eric Doutriaux, Départment du Patrimoine Fluvial, Pôle Hydraulique et Environnement, Compagnie Nationale du Rhône, 2011, written communication).

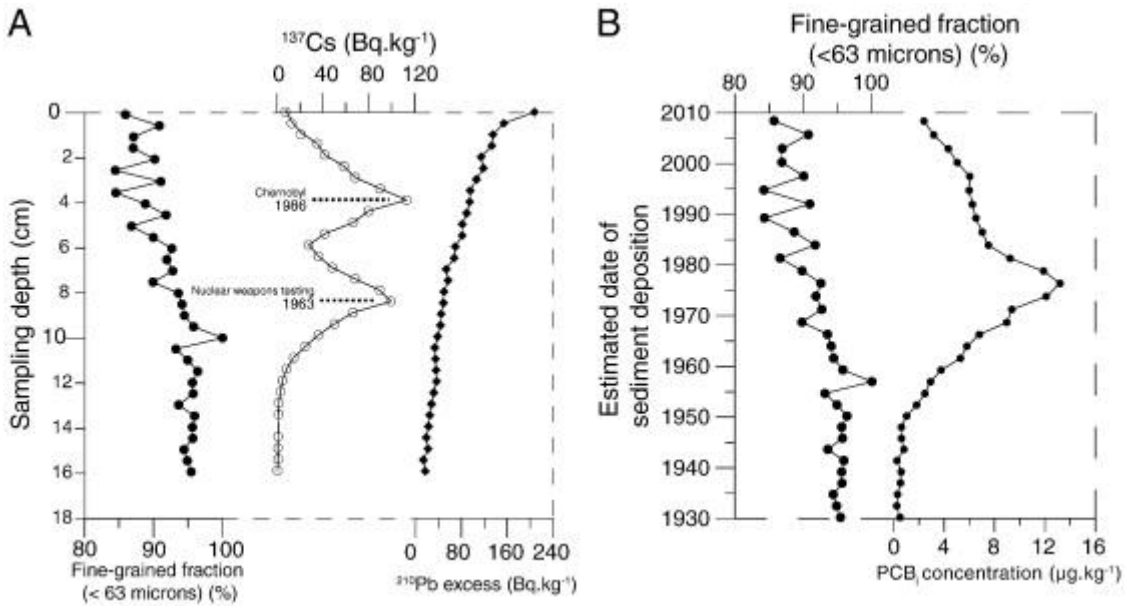

Fig. S-6. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for a sediment core from Lake Paladru (PAL), Rhône basin, France.

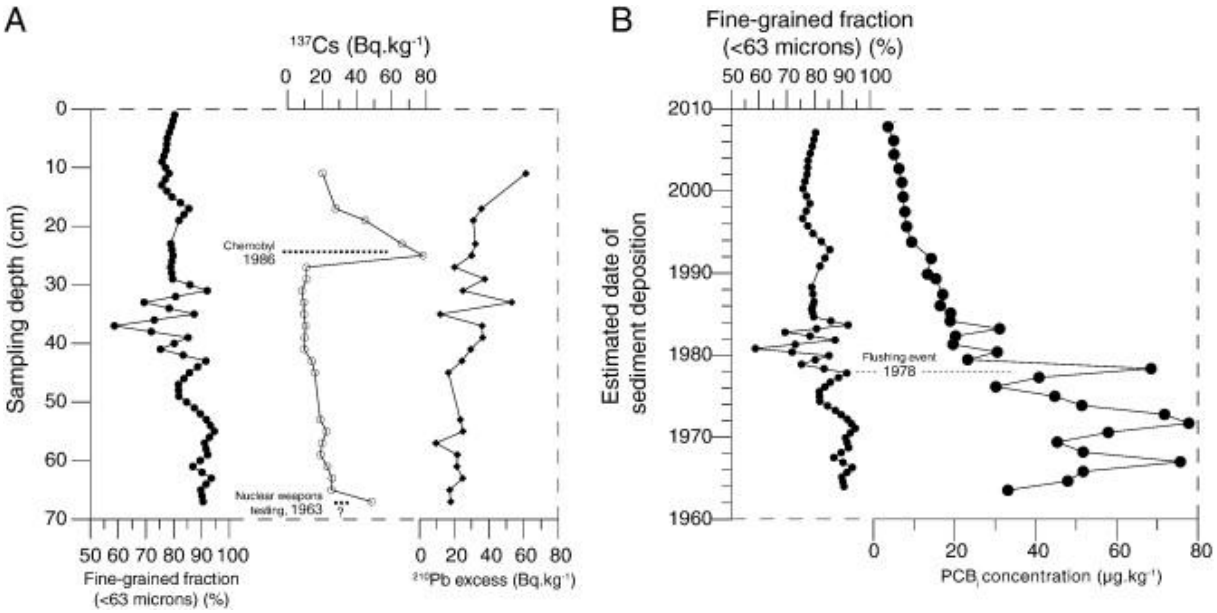

Fig. S-7. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for the sediment core from La Morte (MTE), Rhône basin, France.

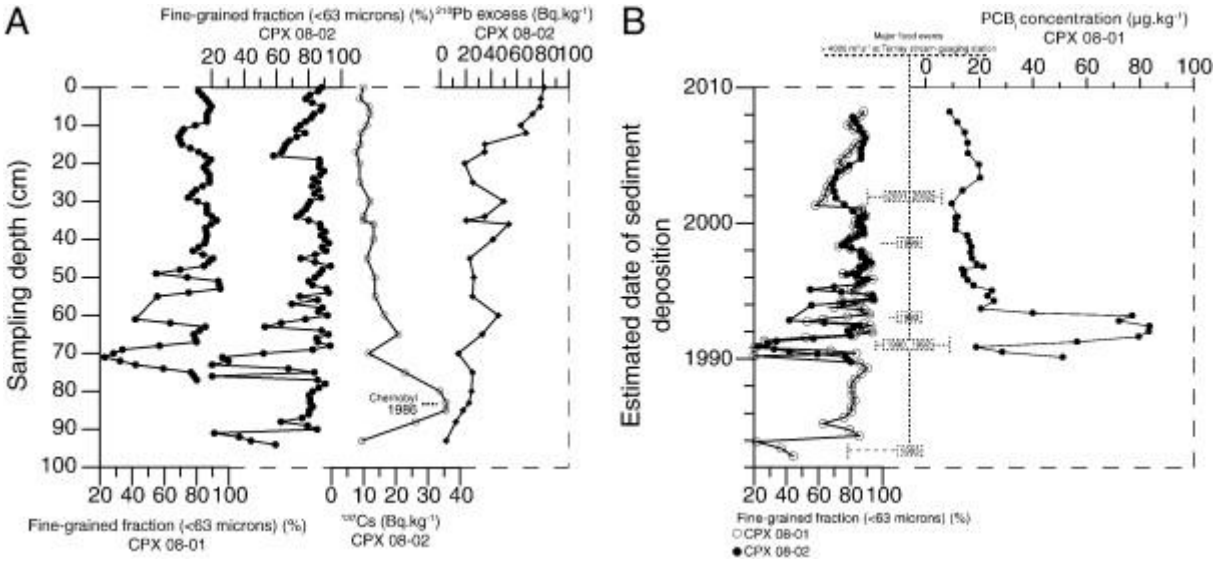

Fig. S-8. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for primary (CPX 08-01) and radionuclide (CPX 08-02) sediment cores from Crépieux-la-Pape (CPX), Rhône basin, France.

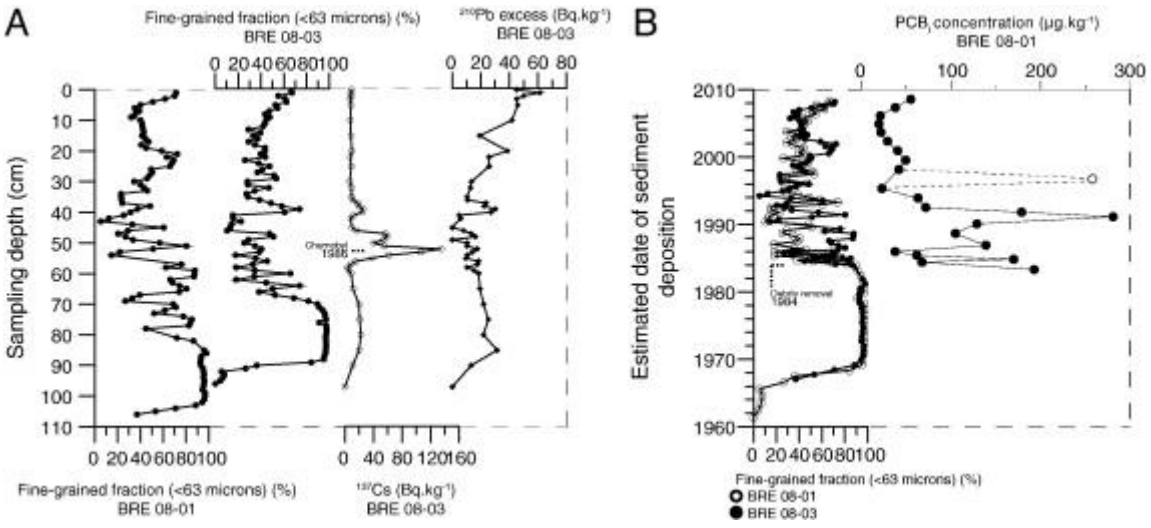

Fig. S-9. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for primary (BRE 08-01) and radionuclide (BRE 08-03) cores from Ile du Beurre (BRE), Rhône basin, France.

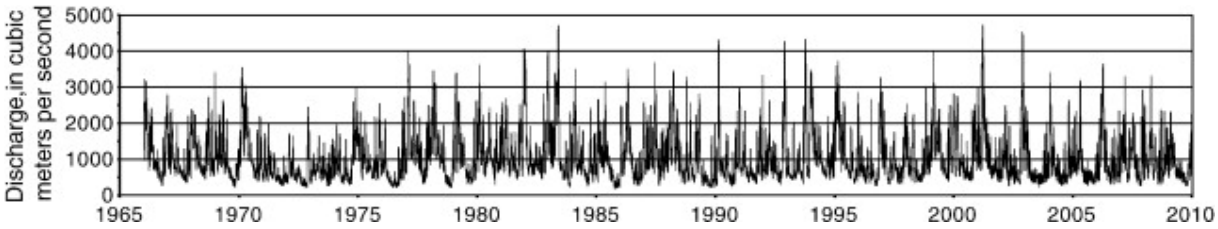

Fig. S-1. Rhône River daily mean discharge, as measured at the streamflow-gaging station at Ternay, near the city of Lyon

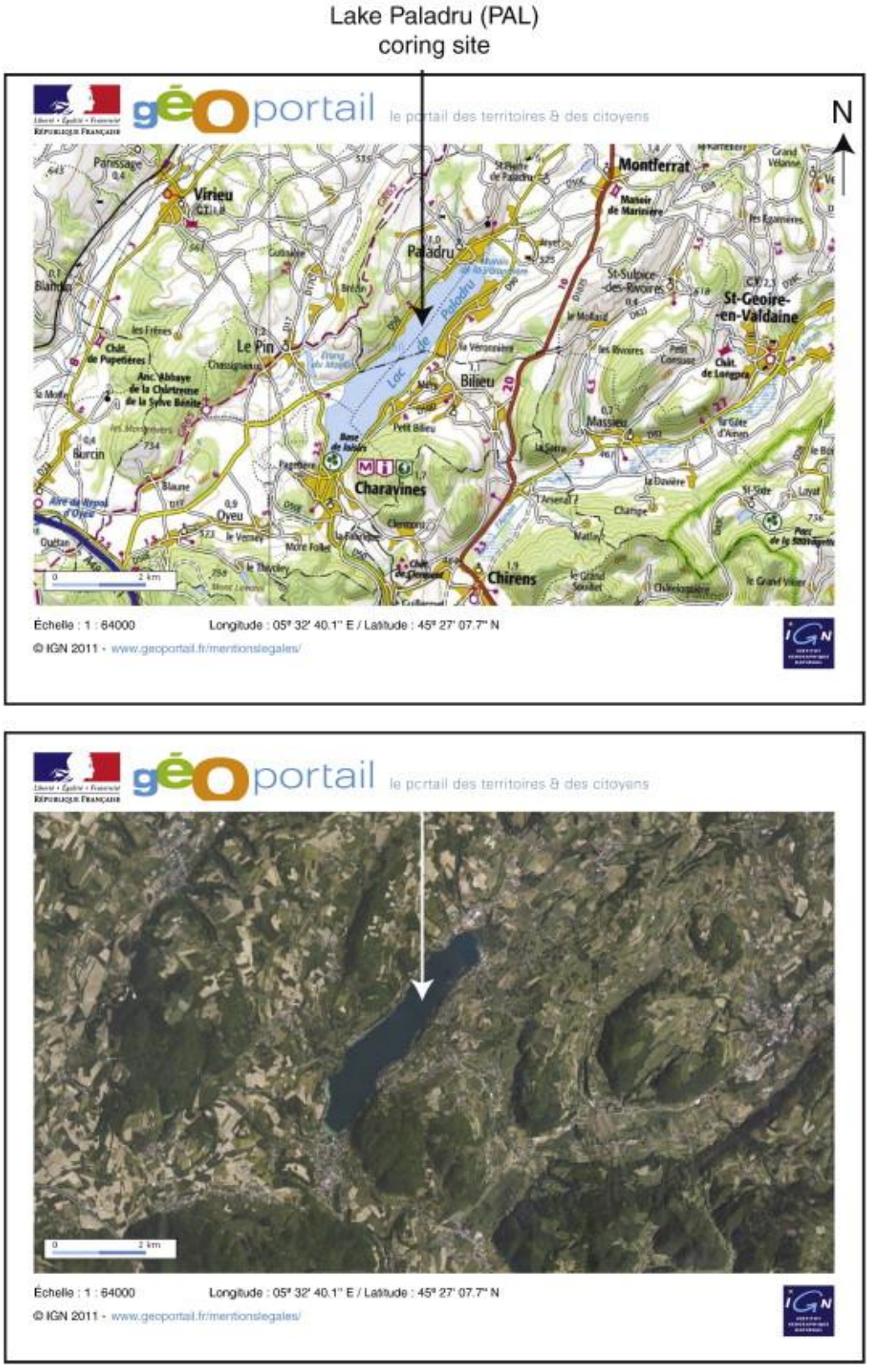

Fig. S-2. Map and aerial image of the coring site on Lake Paladru (PAL). Lake Paladru, a rural reference site, is in the east-central part of the Rhône basin (Fig. 1, full text). Land use in the watershed of Lake Paladru is agricultural with several small villages. Loading of PCBs to Lake Paladru is assumed to be mostly from long range atmospheric deposition.

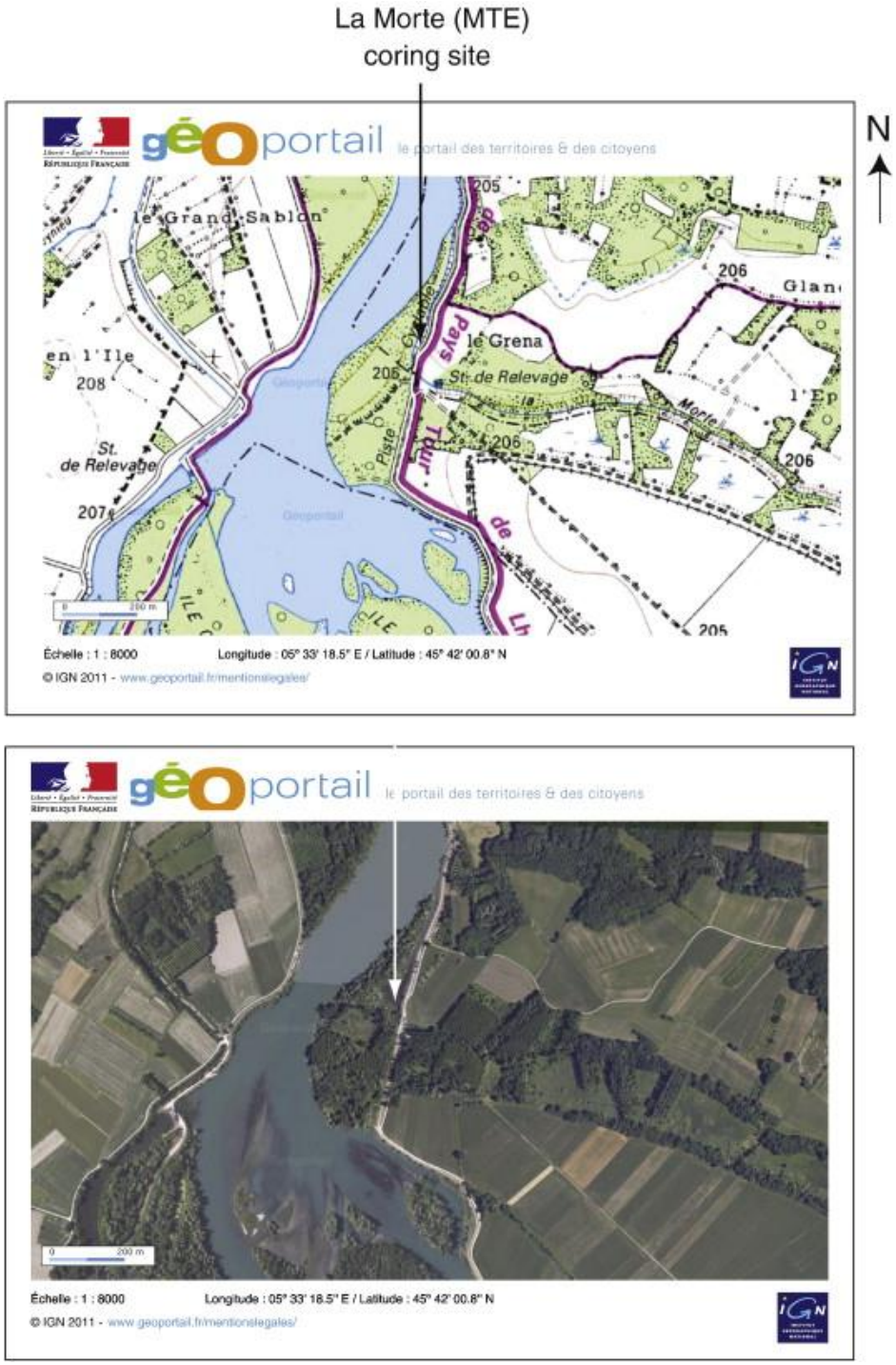

Fig. S-3. Map and aerial image of the coring site at La Morte (MTE). La Morte is the most upstream of the three coring sites on the Rhône River (Fig. 1, full text). It is located in a pond at the downstream end of a cutoff meander of the Rhône, which is open to the river at its downstream end. La Morte is in a relatively non-industrialized part of the Rhône basin upstream from the hazardous-waste treatment facility and Lyon. It was chosen to represent reference concentrations for the lower Rhône basin (i.e., downstream from Lake Geneva). There are, however, urban and industrial areas in the upper Rhône valley in Switzerland (upstream from Lake Geneva) and smaller urban areas and a few historical contamination sites between Lake Geneva and La Morte that might affect PCB concentrations at La Morte (Robin des Bois, 2011).

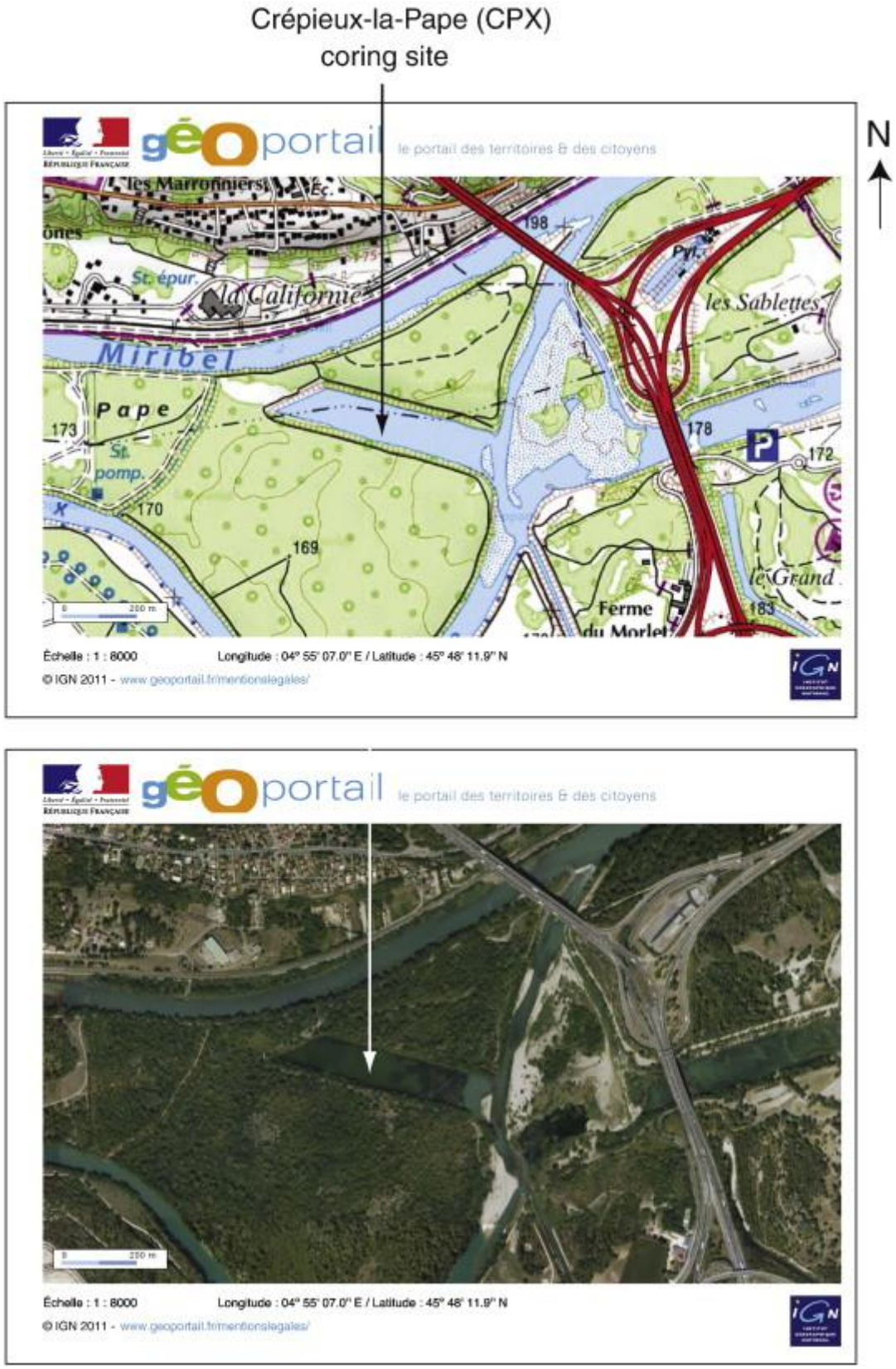

Fig. S-4. Map and aerial image of the coring site at Crépieux-la-Pape (CPX). The site is a former gravel quarry adjacent to the old channel of the Rhône River. It was formed at the beginning of the 1980s by dredging of alluvial deposits. The harbor-shaped feature left by quarrying is about 3 m deep at the center. Since quarrying ended in the early 1980s, flood deposits have formed a submerged levee that

may have progressively limited entry of coarser material to the quarry. Site CPX is in the greater Lyon urban area, 3 km upstream from central Lyon (Fig. 1, full text), and sediment quality of CPX thus is assumed to represent the effects of PCB inputs from a hazardous-waste treatment facility, smaller cities between Lyon and La Morte, the Bourbre River, and non-point emissions from the northern part of greater Lyon.

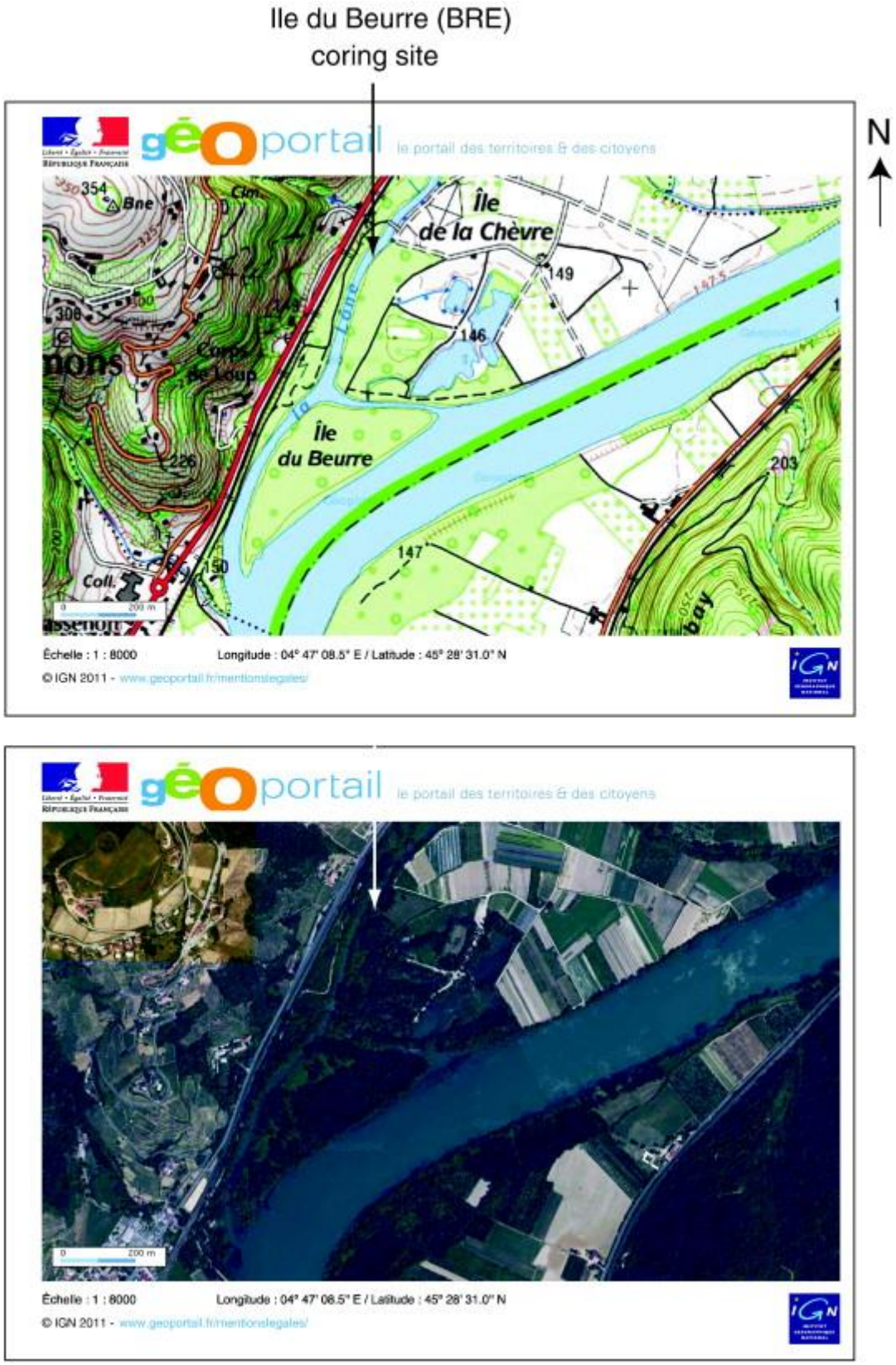

Fig. S-5. Map and aerial image of the coring site at Ile du Beurre (BRE). The site is in a small side channel in a forested wetland adjacent to the Rhône River, 40 km downstream from Lyon (Fig. 1, full text). This site was chosen because of its location downstream from Lyon and the industrial corridor that extends from south of Lyon to the confluence with the Gier River, which, like the Bourbre River,

has a full fish consumption ban as a result of PCB contamination (Eaufrance, 2011). Before 1977, the side channel was not connected to the Rhône River. In 1977, construction of the dam at Saint Pierre de Boeuf downstream from lle Beurre raised the water level in the river to that of the side channel, and in 1984 a debris dam separating the side channel and the Rhône was removed, allowing connection between the two water bodies (Eric Doutriaux, Départment du Patrimoine Fluvial, Pôle Hydraulique et Environnement, Compagnie Nationale du Rhône, 2011, written communication).

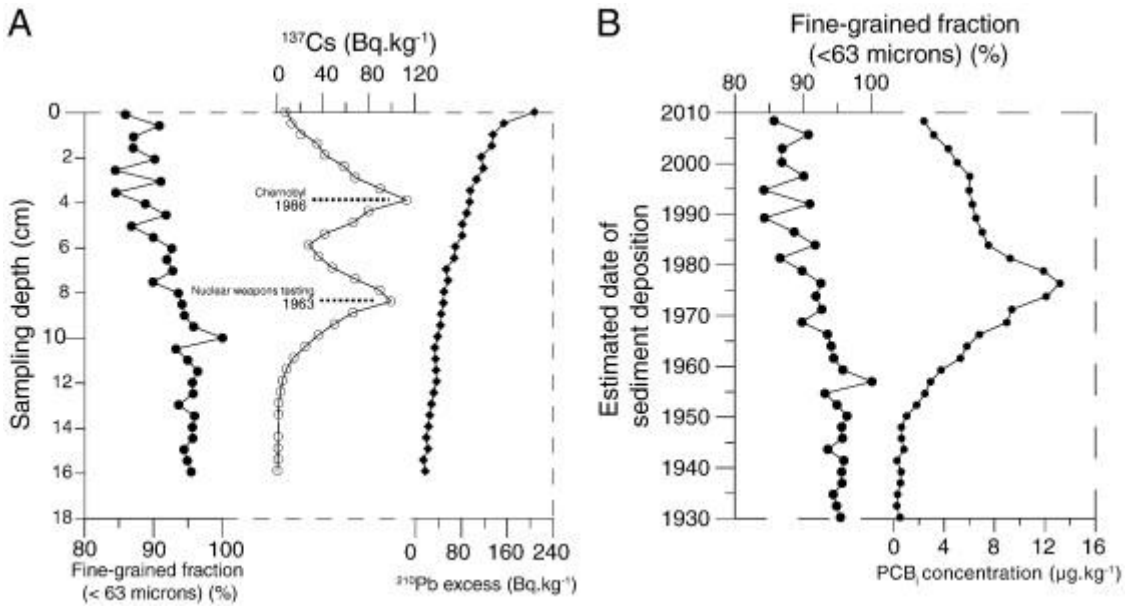

Fig. S-6. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for a sediment core from Lake Paladru (PAL), Rhône basin, France.

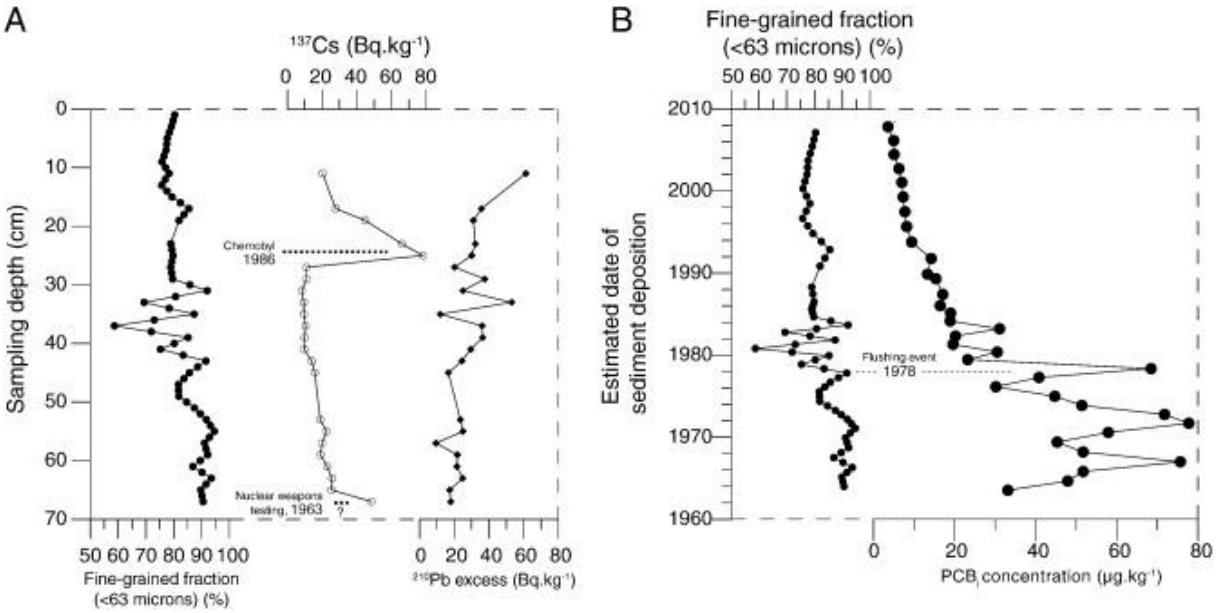

Fig. S-7. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for the sediment core from La Morte (MTE), Rhône basin, France.

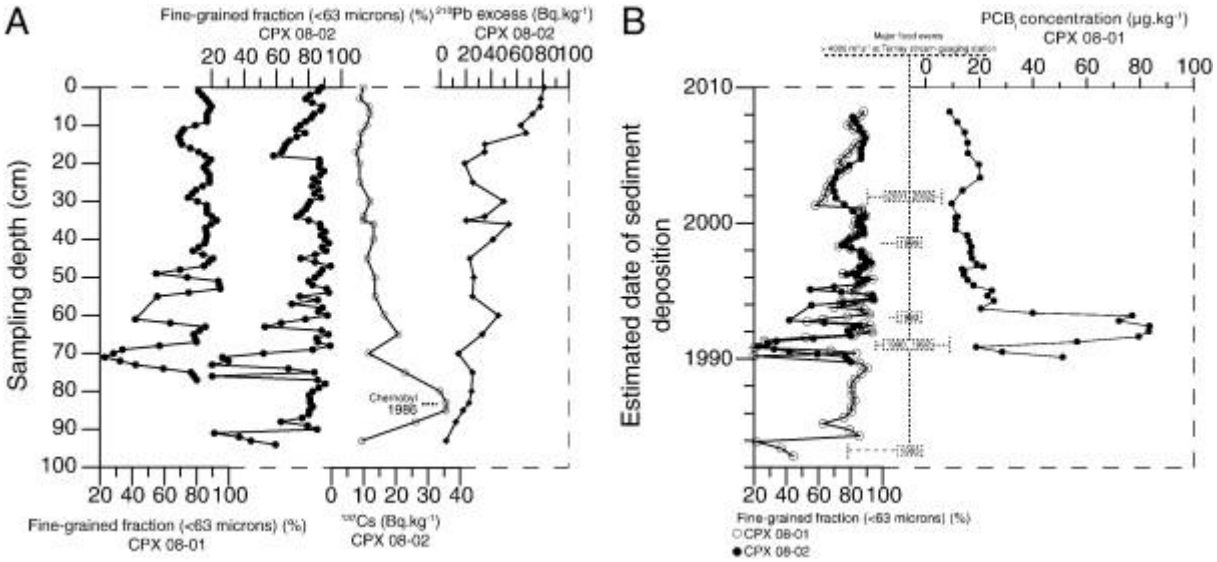

Fig. S-8. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for primary (CPX 08-01) and radionuclide (CPX 08-02) sediment cores from Crépieux-la-Pape (CPX), Rhône basin, France.

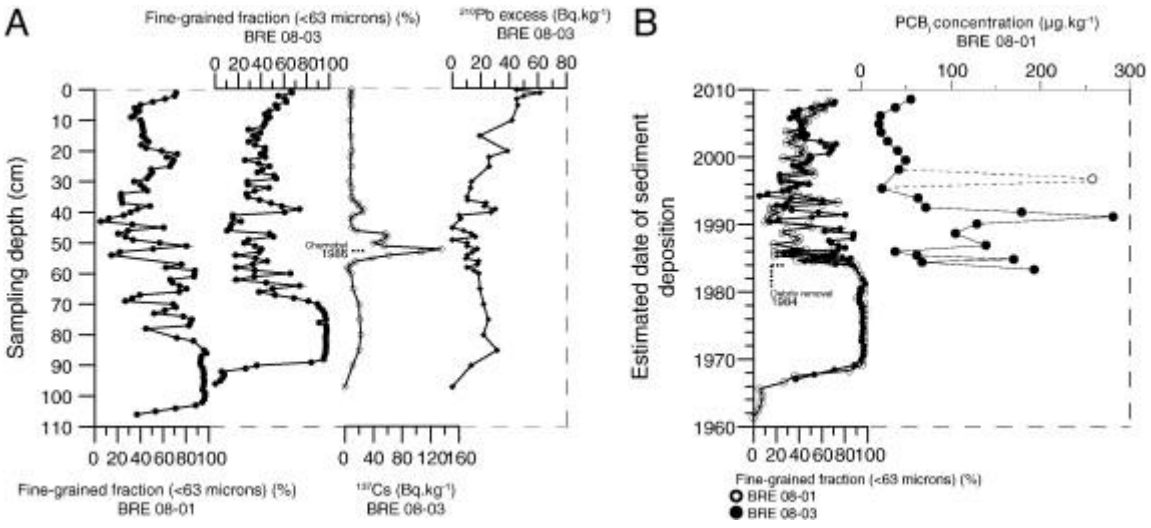

Fig. S-9. Grain size and radionuclide data by depth (A) and grain size and PCB_I profiles by date (B) for primary (BRE 08-01) and radionuclide (BRE 08-03) cores from Ile du Beurre (BRE), Rhône basin, France.