



## Storage and source of polycyclic aromatic hydrocarbons in sediments downstream of a major coal district in France



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### ABSTRACT

During the 20th century, the local economy of the Upper Loire Basin (ULB) was essentially based on industrial coal mining extraction. One of the major French coal districts with associated urban/industrial activities and numerous coking/gas plants were developed in the Ondaine-Furan subbasins, two tributaries of the upper Loire main stream. To determine the compositional assemblage, the level and the potential sources of contamination, the historical sedimentary chronicle of the 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs) has been investigated. PAH concentrations were determined using gas chromatography/mass spectrometry (GC/MS) in a dated core, sampled in the Villerest flood-control reservoir located downstream of the Ondaine-Furan corridor (OFC). The most contaminated sediments were deposited prior to 1983 ( $\Sigma 16\text{PAHs}$  ca. 4429–13,348 ng/g) and during flood events ( $\Sigma 16\text{PAHs}$  ca. 6380 ng/g – 1996 flood; 5360 ng/g – 2003 flood; 6075 ng/g – 2008 flood), especially in medium and high molecular weight PAHs. Among them, typical pyrogenic PAHs such as FLT, PYR, BbF and BaP were prevalent in most of the core samples. In addition, some PAHs last decade data is available from the Loire Bretagne Water Agency and were analyzed using high-performance liquid chromatography with postcolumn fluorescence derivatization (HPLC/FLD). These results confirm that the most highly contaminated sediments were found downstream of OFC ( $\Sigma 16\text{PAHs}$  ca. 2264–7460 ng/g). According to the observed molecular distribution, PAHs are originated largely from high-temperature pyrolytic processes. Major sources of pyrogenic PAHs have been emphasized by calculation of specific ratios and by comparison to reported data. Atmospheric deposition of urban and industrial areas, wood combustion and degraded coal tar derived from former factories of coking/gas plants seem to be the major pyrogenic sources. Specifically, particular solid transport conditions that can occur during major flood events lead us to emphasize weathering of former contamination sources, such as more preserved coal tar.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received particular attention because of their widespread accumulation in soils, sediments and waters and their associated toxic, carcinogenic and mutagenic risks (Lehr and Jerina, 1977; White, 1986; Zedeck, 1980). PAHs found in aquatic environments are generally strongly sorbed onto organic and inorganic suspended particles because of their

low water solubilities (Karcher, 1988). Thus, sediments are one of the most important PAH reservoirs (Landrum and Robbins, 1990; Readman et al., 1984). A vast number of publications reports the presence of PAHs in river sediment (Doong and Lin, 2004; Fernandes et al., 1997; Fu et al., 2011; Gocht et al., 2001; Ko et al., 2007; Xu et al., 2007), lakes (Choudhary and Routh, 2010; Grimalt et al., 2004; Guo et al., 2010, 2011; Jung et al., 2008) or marine environments (Pereira et al., 1996; Qiao et al., 2006; Soclo et al., 2000; Witt, 1995). Thus, the United States Environmental Protection Agency (U.S. EPA) has listed 16 of these PAHs on their priority-pollutant list.

PAHs may have different sources, which are primarily

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anthropogenic. The pyrogenic origin is one of the major sources of PAHs (Mc Elroy et al., 1989). More precisely, PAHs with four to six rings are generally formed through incomplete combustion of recent and fossil organic matter at high temperature during anthropogenic activities, such as burning of fossil-fuels, vehicular emissions, combustion processes of solid incineration plant and domestic heating (Dahle et al., 2003; Sanders et al., 2002; Yunker et al., 2002), but also during natural processes, such as forest and prairie fires (Lafamme and Hites, 1978). These pyrogenic PAHs can be dispersed over long distances in the atmosphere and then deposited by wet and dry deposition (Cranwell and Koul, 1989). In contrast, significant sources of PAHs with two or three rings derived from petrogenic contamination are offshore petroleum hydrocarbon production and/or petroleum exportation. A well-known approach to characterize the predominant sources of PAHs is the use of relative PAH ratios considering isomers formed by different processes (Yunker et al., 2002). These ratios are based on the relative thermodynamic stability of some PAH isomers. The thermodynamics of the pyrogenic and petrogenic formation of PAHs lead to the release of two different classes of isomers. The isomers called “kinetic” are mainly generated during combustion at elevated temperature and have a low relative stability. In contrast, “thermodynamic” isomers have higher relative stability and are produced at low temperatures during long duration processes such as diagenesis or catagenesis (Budzinski et al., 1997; Yunker et al., 2002).

Until now, historical records of PAH pollution were largely derived from lake and sea sediment core studies (Fernandez et al., 2000; Grimalt et al., 2004; Guo et al., 2006; Itoh et al., 2010; Jung et al., 2008; Xu et al., 2014), whereas results of similar investigations of European fluvial systems have been scarcely reported (Gocht et al., 2001; Ayrault et al., 2008; Micic et al., 2013). One of the main reasons for this lack is the difficulty of finding continuous and undisturbed records over several decades in industrialized basins. Then, no study has yet investigated the distribution and sources of PAHs in the Upper Loire Basin (ULB) bed sediments, although it includes one of the major French coal districts. Currently, few studies have also reported PAHs contamination from industrialized and urbanized regions associated to coke production in aquatic systems (Li et al., 1998; Gu et al., 2003; Christensen and Bzdusek, 2005). Then, the objectives of the present study are (i) to make an environmental assessment of the historical record of the Villerest flood-control reservoir to expand its potential for the reconstruction of the PAHs contamination over the last thirty years, (ii) to compare this contamination to some PAHs data obtained from a broader context of the ULB bed sediments (iii) to identify the possible sources of PAHs in order to understand the environmental quality of large fluvial systems close to coal districts.

## 2. Material and methods

### 2.1. Description of the study area

The sampling area is located in the upstream part of the Loire basin. The Loire river is the largest river in France (1012 km) and the upper section is 448 km long with a drainage area of 17,570 km<sup>2</sup> (15% of the total basin area). The coal district is located in the Ondaine-Furan corridor (OFC), two small tributaries of the upper Loire main stream (Fig. 1). It was in operation since the early 18th century up to the late 1980s. In the early 20th century, it became the 1st French coal producer (4.9 million tons/year in 1918; Barau, 2008). The local economy of the study area was thereby essentially based on this industrial coal mining extraction and led to the setting of over 70 coking and/or gas plants (Fig. 1). Furthermore,

related metallurgy activities, weapon, paper mill, smelting and glass plant industries were very active along the OFC.

### 2.2. Sampling site and sediment collection

Dhivert et al. (2015) sampled a previous core in the Villerest flood-control reservoir in 2010 (VIL2010) in order to determine the historical record of heavy metal contamination. A new core sampled in the same sedimentary reservoir in 2012 (VIL2012), allows us to provide information about recorded PAH contamination. The Villerest flood-control reservoir was built between 1976 and 1983 and is located downstream of the industrial and coal mining district (Fig. 1). Water filling operations occurred step by step between 1983 and 1984, and the dam has been in operation since then. It contains 128 mm<sup>3</sup> of water on average and is 36 km long, with a maximum depth of 60 m close to the dam. Three major flood events occurred over the entire upstream basin since the dam operating phase: in 1996 (972 m<sup>3</sup> s<sup>-1</sup>), in 2003 (1570 m<sup>3</sup> s<sup>-1</sup>) and in 2008 (1490 m<sup>3</sup> s<sup>-1</sup>).

The coring site (45°58'54"N, 4°02'15"E) was located 200 m upstream of the Villerest dam (Fig. 1) in the deepest zone of the reservoir. The VIL2012 core was sampled with a UWITEC gravity corer fitted with a 2-m-long and 90-mm-diameter plastic liner. Then, the 130-cm-long core was opened and described. The sampling resolution for organic analysis was chosen according to visual sedimentary description, with a layer thickness ranging from 2 to 6 cm. Overall, 26 slices were freeze-dried and crushed to homogenize prior to analysis.

In addition, some PAHs data is available from the Loire Bretagne Water Agency (LB Agency). In the study area, the LB Agency surveys the sediment quality of 19 stations over the 2005–2010 period and under the European Water Framework (Fig. 1 and Table 1). Bed sediments (0–5 cm) were collected in glass bottles, kept cold (5 °C) and transported to the CARSO laboratory (Lyon, France; [www.groupecarso.com](http://www.groupecarso.com)) for PAH analysis. PAHs concentration ranges of this survey could strengthen our spatial distribution substudy of organic contaminants in ULB sediments around our focused sediment core study.

### 2.3. Analytical protocol

#### 2.3.1. Grain size analysis

Particle size analysis was performed after a 1-min sonication step with a Malvern Mastersizer 3000 laser diffraction microgranulometer on each fresh 2-cm core slice (measurement range between 0.05 and 2000 μm). Grain-size median (D<sub>50</sub>) and cumulative volumetric percentages of clay (<2 μm), silt (<63 μm) and sand (>63 μm) were computed with the Gradistat spreadsheet (Blott and Pye, 2001) using the Folk and Ward geometric method (Folk and Ward, 1957).

#### 2.3.2. PAH analysis

PAHs were extracted using the pressurized liquid extraction (PLE) technique with an accelerated solvent extractor (ASE™ 350, ThermoScientific®). Extraction cells of 34 mL were used and filled with a mixture of 2.5 g of the sediment sample and diatomaceous earth (Sigma Aldrich®). Extractions were carried out with dichloromethane at 100 °C and 100 bars, 5 static cycles of 4 min and a rinse volume of 60%. Extracts were evaporated until dryness under a gentle stream of nitrogen and then reconstituted in 1 mL of dichloromethane. Benzo(a)pyrene D-12 (Sigma–Aldrich®) was then added to the samples as an internal standard. External calibration was performed with a commercial mixture of the 16 PAHs (at 2000 μg/mL each in dichloromethane, Restek®) and a calibration curve (8 standards, 0–250 ng/mL of each compound in

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