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# Remanence of lead pollution in an urban river system : a multi-scale temporal and spatial study in the Seine River basin, France

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1                   1                   **Remanence of Lead Pollution in an Urban River System:**  
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3                   2                   **A multi-scale temporal and spatial study in the Seine River basin,**  
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5                   3                   **France**  
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17 **Abstract**

18 Total lead (Pb) concentration and Pb isotopic ratio ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) were determined in 140  
19 samples from the Seine River basin (France), covering a period time from 1945 to 2011 and  
20 including bed sediments (bulk and size fractionated samples), suspended particulate matter  
21 (SPM), sediment cores, and combined sewer overflow (CSO) particulate matter to constrain the  
22 spatial and temporal variability of the lead sources at the scale of the contaminated Seine River  
23 basin. A focus on the Orge River sub-catchment, which exhibits a contrasted land-use pattern,  
24 allows documenting the relation between hydrodynamics, urbanization and contamination  
25 sources. The study reveals that the Pb contamination due to leaded gasoline that peaked in the  
26 1980s has a very limited impact in the river nowadays. In the upstream Seine River, the isotopic  
27 ratio analysis suggests a pervasive contamination which origin (coal combustion and/or gasoline  
28 lead) should be clarified. The current SPM contamination trend follows the  
29 urbanization/industrialization spatial trend. Downstream of Paris, the lead from historical use  
30 originating from the Rio Tinto mine, Spain ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1634 \pm 0.0001$ ) is the major Pb  
31 source. The analysis of the bed sediments (BS) (bulk and grain size fractionated) highlights the  
32 diversity of the anthropogenic lead sources in relation with the diversity of the human activities  
33 that occurred in this basin over the years. The “urban” source, defined by waste waters  
34 including the CSO samples ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.157 \pm 0.003$ ), results of a thorough mixing of leaded  
35 gasoline with “historical” lead over the years. Finally, a contamination mixing scheme related to  
36 hydrodynamics is proposed.

37 **Keywords:** suspended particulate matter, lead isotopes, sewer overflow, urban lead, sediment  
38 cores

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## 1. Introduction

Lead (Pb) is a problematic metallic contaminant in numerous river systems across the world (Kachur et al., 2003; Sun et al., 2011; Grosbois et al., 2012). Reconstructing the history of Pb contamination and quantifying the dynamics of Pb transport in river systems is important to design appropriate remediation policies and evaluate their environmental impact. The historical record of Pb contamination in river sediments may be accessed by dating and analyzing sediment cores collected within floodplains (Alfonso et al., 2001; Ayrault et al., 2012). In addition, the comparison of lead concentrations and lead isotopic ratios along the entire sediment sequence may provide powerful constraints on the evolution of natural and anthropogenic sources that supplied Pb to the river throughout time (Monna et al., 2000; Shoty et al., 1998). However, extrapolation of floodplain data to the whole river system is not straightforward because of several problems detailed hereafter. Fine particles that deposit in floodplains may differ in Pb concentration and isotopic composition from coarse bed sediment particles that may represent a large fraction of the river particulate flux (Horowitz and Elrick, 1987; Stone and Droppo, 1996). Moreover, fine particles collected in floodplains during a short time period (i.e., during high water stages) may not be representative of the average fine particles transported by the river. Therefore, the relevance and/or the impact of those potential biases must be evaluated to strengthen the understanding of Pb behavior in river systems. In the present study, we focus on the Seine River system (64,700 km<sup>2</sup>) which is highly impacted by Pb contamination (Meybeck et al., 2007, Ayrault et al., 2012). The Seine catchment is affected by very high anthropogenic pressures and is characterized by a very limited dilution of metallic contaminants due to the low suspended matter concentrations prevailing in the Seine River waters. As a consequence, the Seine Basin is structurally fragile and its river course, downstream of Paris megacity, has been and is still ranked among the world's most contaminated rivers (Meybeck et al., 2007). Indeed, cores collected within a floodplain located downstream of Paris revealed high levels of contamination (Pb up to 400 mg/kg) between 1920s and 1960s followed by a decrease in Pb

1 68 concentrations since 1960. In 2003, Pb concentrations ( $Pb \approx 50 \text{ mg/kg}$ ) were still significantly  
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3 69 above the estimated geochemical background ( $Pb \approx 20 \text{ mg/kg}$ , Thévenot et al., 2007). The  
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5 70 contribution of three main sources that may be used as « end-members » in mixing models  
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7 71 (Ayrault et al., 2012) has been previously identified based on the use of stable Pb isotopes ( a  
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9 72 full literature review can be found in Komarek et al., 2008). (1) The local natural background  
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11 73 signature ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.2007 \pm 0.0011$ ) was determined using a 8000 BP- $^{14}\text{C}$  dated sediment  
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13 74 (Elbaz-Poulichet et al., 1986). A very similar value ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.2035$ ) was obtained in an  
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15 75 undisturbed C soil horizon developed in loess deposits collected next to the Chateau de  
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17 76 Versailles gardens (Semlali et al., 2004). Those soils are widely found in the Seine River  
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19 77 watershed, particularly in its downstream part. (2) The lead from historical (hereafter called  
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21 78 “historical” Pb) originating from the Rio Tinto mine in Spain ( $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.1634 \pm 0.0001$ ;  
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23 79 Marcoux, 1998) that has accumulated in the Seine basin since the 19<sup>th</sup> century at least (Ayrault  
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25 80 et al., 2012). (3) Pb used in additives to gasoline ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.08 \pm 0.02$ ), that contain high  
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27 81 proportions of Australian lead from the Broken Hill mine ( $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.040 \pm 0.001$ ) ; this  
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29 82 latter signature was determined based on information from Octel Ltd at Paimboeuf, which was  
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31 83 the single provider of leaded additives for French gasoline (Véron et al., 1999). A fourth source  
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33 84 of lead to Parisian soils, coal combustion, has been evidenced by Semlali et al. (2004)  
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35 85 ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.183$ ) but was not detected by Ayrault et al. (2012) in the downstream core  
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37 86 sediments.  
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39 87 Over the years, mixing between “historical” and “gasoline” Pb have yielded a composite “urban”  
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41 88 Pb signature ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ ), as determined by analyzing waste water treatment  
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43 89 plant (WWTP) effluents collected in 2006 (Ayrault et al., 2012). Owing to this mixing, the  
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45 90 “urban” end-member is supposed to vary in both space and time, in particular because of the  
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47 91 prohibition of gasoline leaded additives in 2000. However, despite their sampling during  
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49 92 different campaigns and the different nature of the analyzed urban wastes (liquid/solid), the  
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51 93 WWTP signature did not significantly differ from the signature of the three major Parisian  
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53 94 municipal solid waste incinerators in 2001 ( $1.1550 \pm 0.0005$ ; Widory, 2004). It appeared  
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55 95 therefore necessary to constrain the evolution of the “urban” Pb signature at different scales  
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1 96 within the Seine River basin.  
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3 97 Previous work showed a significant decrease in the gasoline-originated lead contribution to the  
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5 98 Seine River sediment contamination from 1986 to 2003 due to the implementation of  
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7 99 regulations on the use of leaded gasoline additives and their subsequent ban in 2000 (Ayrault et  
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10 100 al., 2012). In this context, Pb found in the Seine River is dominated by a mixing between urban  
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12 101 lead (coinciding with high lead concentration) and natural lead (coinciding with low lead  
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14 102 concentration). Similar trends were observed in the very urbanized Orge River subcatchment  
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16 103 (1300 km<sup>2</sup>) (Le Pape et al., 2013).  
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18 104 Atmospheric Pb deposition across the Seine River basin was estimated to vary between 2000  
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20 105 (1994-2003; Thévenot et al., 2007) and 2900 t.y<sup>-1</sup> (1955-2004; Saby et al., 2006), whereas the  
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22 106 Pb emissions were estimated to 2700 t.y<sup>-1</sup> (1955 to 2004, considering that the Seine River basin  
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24 107 contributes to 30% of the total French emissions; Pacyna and Pacyna, 2000). In addition to the  
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26 108 Pb accumulation in soils, a large urban stock of Pb exists in the region. Thévenot et al. (2007)  
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28 109 constructed the Pb budget at the scale of the Seine River basin. They concluded that a huge  
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30 110 amount (594,000 t) of Pb has accumulated since centuries in Paris megacity because of its use in  
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32 111 roof covers, pipes, cables shielding, oxide containing glasses, etc. These stocks show different  
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34 112 environmental behaviors and lifetimes.  
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36 113 Pb-bearing soil particles may be delivered to the rivers during erosion events. The Seine River  
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38 114 basin is affected by low to moderate soil erosion rates, which is reflected by mean exports  
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40 115 estimated to 10 t.km<sup>2</sup>.y<sup>-1</sup> (Meybeck et al., 1998). The residence times of particles in soils are  
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42 116 long (5000–40,000 yrs depending on their location within the catchment). In contrast, the  
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44 117 residence time of the particles within the river is much shorter (180–500 days) Altogether, those  
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46 118 findings led us to investigate whether gasoline-originated lead could have been completely  
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48 119 washed out from the Seine River basin since their ban in 2000. The complete flush of the  
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50 120 gasoline-lead bearing particles would then provide an original and alternative method to  
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52 121 evaluate the sediment turnover of the river.  
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55 122 We propose to compile Pb elemental and isotopic data collected on different material types (i.e.  
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57 123 suspended particulate matter, riverbed sediment, overflow plain sediment) along a network of  
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1 124 nested stations to document the processes occurring at different temporal scales (flood, seasonal,  
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3 125 annual, decadal) and at two catchment scales: Seine (64,700 km<sup>2</sup>) vs. Orge (1300 km<sup>2</sup>).  
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5 126 However, owing to evident logistical and analytical constrains, it was not possible to conduct  
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7 127 such a detailed study compiling Pb data measured in all sediment types (suspended particulate  
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9 128 matter (SPM), bed sediment (BS)) and taking into account the different hydrological stages  
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11 129 throughout the year at the scale of the entire Seine River basin. We therefore focused a  
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13 130 significant part of the sampling effort on the Orge River basin (1300 km<sup>2</sup>), which drains into the  
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15 131 Seine River just upstream of Paris, because its land uses are characterized by a gradient of  
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17 132 increasing anthropogenic influence along its course, from headwaters dominated by forests and  
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19 133 cropland to its junction with the Seine River where its flows across densely inhabited areas (Le  
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21 134 Pape et al., 2012). Detailed investigation of the processes occurring in this catchment will  
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23 135 provide important insights on the role of river hydrodynamics and provide a way to better  
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25 136 constrain the relative contribution of pollution sources in space and time (Le Pape et al., 2013).  
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27 137 We will finally attempt to extrapolate the conclusions drawn from the Orge River study to the  
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29 138 entire Seine River basin.  
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## 32 140 **2. Materials and Methods**

### 33 141

### 34 142 **2.1. Study sites**

35 143 All sampling sites were located in the Seine River basin (Fig. 1), a sedimentary basin situated in  
36 144 the north of France, and flowing across the Greater Paris Region. This river drains an area of  
37 145 64,700 km<sup>2</sup> characterized by a mean population density of 215 inh./km<sup>2</sup>, and constitutes  
38 146 therefore an ideal example of highly urbanized basin as it accounts for 25% of French  
39 147 agriculture, 30% of the country's industry and 23% of its population. The Orge River  
40 148 subcatchment is located in the upper part of the Seine River basin, and drains an area of 1300  
41 149 km<sup>2</sup> with a population density ranging between 200 inh./km<sup>2</sup> in upper parts to 8000 inh./km<sup>2</sup>  
42 150 close to the junction with the Seine River.  
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### 52 151 **Figure 1**

### 53 152

### 54 153 **2.2. Sampling**

55 154 All the sample locations and collection periods are detailed in Table 1.  
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### 60 155 **Table 1**

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157 *2.2.1. Suspended sediment from the entire Seine River basin*

158 At the scale of the whole Seine River basin, the sampling scheme aimed to distinguish the  
159 impacts of two anthropogenic sources on the Seine River (Priadi et al., 2011a). The first source  
160 is diffuse and coincides with the area of Greater Paris itself, including the most densely  
161 urbanized area with more than 3700 inh./km<sup>2</sup>. Treated municipal wastewater from small  
162 treatment units and urban runoff are the major sources identified as supplying metal to the river  
163 in this area (Thévenot et al., 2007). The second source is point-based, and coincides with the  
164 Seine-Aval wastewater treatment plant (WWTP) treating around 1.7 million m<sup>3</sup> per day and  
165 located 30 km downstream of Paris. Therefore, the first sampling site was located at  
166 Marnay-sur-Seine, in upper parts of the Seine River catchment (Priadi et al. 2011b, and Fig.1).  
167 It was chosen as being representative of a site unaffected by the Greater Paris region where the  
168 population density is only 15-30 inhabitants/km<sup>2</sup>. The second site is located at Bougival, 40 km  
169 downstream of Paris city (Strahler order 7). It was chosen to study the impact of Greater Paris  
170 just upstream of the Seine-Aval WWTP effluent outflow. A third site, located 40 km further  
171 downstream, at Triel-sur-Seine, was selected to take the additional inputs of this WWTP into  
172 account. The Triel station is situated downstream of the junction between the Seine River and  
173 one of its major tributaries, the Oise River. SPM sampling was performed in sediment traps  
174 collected monthly from October 2008 to October 2009.

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179 *2.2.2. Riverbed sediment (BS) from the entire Seine River basin*

180 Riverbed sediments were collected in the framework of the National River Network (sampling  
181 operated by the Service Navigation de la Seine (SNS)) in 2007-2009, at a succession of sites  
182 within Paris as well as along the 10-km river section located just downstream of Paris.

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184 *2.2.3. Combined sewer overflow (CSO) sampling.*

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1 185 Details on the CSO sampling are given in Passerat et al. (2011). The CSO occurred in August  
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3 186 2008, during a summer storm that affected Paris. It lasted for 6 h (from 5:50 a.m. to 11:50 a.m.)  
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5 187 and resulted in the discharge of ca. 600,000 m<sup>3</sup> of untreated urban waste water into the Seine  
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7 188 River. Twelve successive samples were collected automatically in the CSO, each sample being  
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9 189 a time-proportional composite of the waters discharged during a 30-min period. The analyses of  
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11 190 each sample allowed to apportion the volume of domestic waste water and the runoff over the  
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13 191 CSO duration. In parallel, the plume impacted by the CSO was sampled four times during its  
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15 192 flow from the release point to a distance of 20 km.  
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#### 19 194 *2.2.4. Sediment sampling in the Orge subcatchment*

20 195 Sampling campaigns were performed in 2001 and in 2010/2011 along the Orge River, including  
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22 196 two of its tributaries, to exhibit spatio-temporal trends of urban contamination at the scale of  
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24 197 this small but densely populated catchment (Le Pape et al., 2012). Sampling sites were  
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26 198 selected to document the urbanization and land use gradients: upstream sites in forests and  
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28 199 agricultural areas “D” (for Dourdan) and “C” (for Saint Chéron), the sites “R” (for Rémarde)  
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30 200 and “E” (for Egly) considered to be under a slight urban influence, and the most urbanized  
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32 201 downstream sites “L” (for Longpont-sur-Orge), “Y” (for Yvette) and “V” (for Viry-Chatillon).  
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34 202 The bed sediments sampled in the Orge River (10 uppermost cm) during the 2010/2011  
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36 203 campaigns were frozen and quickly freeze-dried. For the third campaign (April 2011), 10 to 15  
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38 204 g of each bed sediment sample were sieved using deionized water and separated into three grain  
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40 205 size fractions: > 200 μm, 200 μm > X > 63 μm, and < 63 μm. Each recovered fraction  
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42 206 composed of water and sediment was then dried at 40°C in an oven. After drying, the mass of  
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44 207 each fraction was measured and compared to the initial mass of sediment sieved to calculate the  
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46 208 contribution (% mass) of each grain size in the samples.  
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48 209 Chemical and lead isotopes analyses were finally carried out on one crushed gram of each grain  
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50 210 size fraction, following the methods described in sections 2.3 and 2.4.  
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#### 51 212 *2.3. Elemental determination*

52 213 The Seine River and Orge River SPM and BS samples were totally digested according to the  
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54 214 procedures described in Priadi et al. (2011b) and Le Pape et al. (2012). In brief, the total  
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56 215 digestion step was conducted in PTFE closed flasks, on a digestion block (Digiprep, SCP  
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58 216 Science) by successive additions of concentrated ultra-pure acids (HCl, HNO<sub>3</sub>, HF, and HClO<sub>4</sub>).  
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1 217 The solutions were evaporated to dryness, retaken 3 times in 2 mL of HNO<sub>3</sub> and then diluted  
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3 218 with 50 mL of MilliQ water. The elemental content was analyzed by inductively coupled plasma  
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5 219 – mass spectrometry ICP-MS (XII CCT series, Thermo Electron), according to the procedures  
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7 220 referred to above. The Seine River cores samples analyses were described in Ayrault et al.  
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9 221 (2012). The data quality of the elemental concentration determination was controlled with the  
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11 222 reference material IAEA-SL-1 (lake sediment), provided by the International Atomic Energy  
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13 223 Agency, Vienna. The values obtained with this procedure were in good agreement with the  
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15 224 certified values. The uncertainties of the determination of Pb and Al concentrations discussed in  
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17 225 the present paper were 5% and 14%, respectively.  
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#### 22 227 **2.4. Lead isotopes ratio determination.**

23 228 Lead isotope ratios (<sup>208</sup>Pb/<sup>206</sup>Pb and <sup>206</sup>Pb/<sup>207</sup>Pb) were measured in the same solutions as for  
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25 229 elemental concentration determinations, after appropriate dilution, using a ICP-QMS (X Series,  
26  
27 230 ThermoElectron, France), following the procedure detailed in Ayrault et al. (2012). The  
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29 231 experimental conditions were three channels reading; dwell time of 30 ms; 100 sweeps; 5  
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31 232 replicates per sample. Mass bias and drift of the isotope ratios were corrected based on repeated  
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33 233 measurements of the Pb reference material NIST SRM-981 that was analyzed every three  
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35 234 samples. SRM-981 was also repeatedly analyzed as a sample to control the bracketing  
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37 235 correction. Certified values for the SRM-981 are <sup>206</sup>Pb/<sup>207</sup>Pb = 1.09333 ± 0.00039. The figure of  
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39 236 merits for the Seine River core samples and the Orge River SPM are in Ayrault et al. (2012) and  
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41 237 Le Pape et al. (2013), respectively. For the Orge River bulk and sieved BS analyses, the ratio  
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43 238 was <sup>206</sup>Pb/<sup>207</sup>Pb = 1.0933 ± 0.0025 (n=14). For the Seine River BS and trapped SPM analyses,  
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45 239 the measured ratio were <sup>206</sup>Pb/<sup>207</sup>Pb = 1.0933 ± 0.0018 (n=4) and <sup>206</sup>Pb/<sup>207</sup>Pb = 1.0929 ± 0.0027  
46  
47 240 (n=19), respectively.  
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#### 50 241 51 242 **2.5. Enrichment factor**

52 243 The lead concentrations in the SPM are expressed as an enrichment factor (EF) calculated in  
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54 244 reference to the local geochemical background and normalized by the SPM aluminum (Al)  
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56 245 contents with the following background concentrations: Pb = 20 mg/kg (Meybeck et al., 2004;  
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1 246 Thévenot et al., 2007) and background Al = 36 g/kg (Thévenot et al., 2007), (Eq. 1). The 20  
2 247 mg/kg value may be overestimated, due to the anthropogenic disturbance of the watershed and  
3  
4 248 the difficulty to sample pristine sediment. The systematic analysis of the various lithologies  
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6 249 found in the Seine River would be necessary to confirm the relevance of this value, as proposed  
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8 250 by Reimann and de Caritat (2005). Similar limitations could be drawn on Al background  
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10 251 concentration that may be underestimated in the upstream part of the catchment and particularly  
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12 252 in the crystalline Yonne River subcatchment, whereas it may be overestimated in the  
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14 253 downstream part of the catchment after the confluence with the Marne River draining  
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16 254 carbonate-rich substrates/rocks. The EF of the Bouafles sediment core were calculated using  
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18 255 scandium (Sc) instead of Al, considering the background value of Sc = 11 mg/kg (Ayrault et al.,  
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20 256 2010).  
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$$EF (Pb) = \frac{\frac{[measured Pb]}{[measured Al]}}{\frac{[background Pb]}{[background Al]}} \quad (\text{Eq. 1})$$

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### 34 260 **3. Results**

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#### 36 262 **3.1. Pb concentration**

37 263 In the Seine River, Pb concentration ranged from 75 to 282 mg/kg in the bed sediments (BS)  
38 264 (Table 2) and from 18 to 245 mg/kg in the SPM (Table 3). These concentrations remained  
39 265 generally consistent with those measured in the TR01 upstream core (40-90 mg/kg; Ayrault et  
40 266 al., 2012). The downstream cores B2 and M1 exhibited much higher concentrations in the SPM  
41 267 deposited prior to 1970 (up to 460 mg/kg). Overall, there is a Pb concentration gradient  
42 268 increasing from the upstream areas, i.e. with low urbanization/industrialisation and low Pb  
43 269 content, to the downstream areas, i.e. with high urbanization/industrialisation and high Pb  
44 270 concentration. Extremely high Pb concentrations are obtained in the CSO samples (Pb= 244-948  
45 271 mg/kg) and in the CSO plume generated in the Seine River (Pb= 175-407 mg/kg) (Table 4). The  
46 272 EF ranged from 1 in the less urbanized/industrialized area (Marnay) to 3-11 in most  
47 273 urbanized/industrialized area and to 4-22 in the “dirty water plume”. It even peaked up to  
48 274 54-105 in the CSO samples.  
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1 275  
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3 276 **Tables 2, 3 and 4**  
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6 278 The Pb content in the Orge River BS ranged from 15 to 83 mg/kg in the bulk bed sediments and  
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8 279 remained much lower than in the SPM collected at the same locations (Table 5). There was no  
9  
10 280 increase in the BS Pb concentration along the urbanization gradient. For SPM, the correlation  
11  
12 281 is only valid during high water periods. In the case of the size fractionated bed sediments of the  
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14 282 Orge River, the range of Pb concentration was somewhat larger (10 – 110 mg/kg), but remained  
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16 283 in the same order of magnitude.  
17

18 284  
19 285 **Table 5**  
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21 286  
22 287 **3.2.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio**

23 288 The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio measured in most of the Seine River (SPM and bed sediments) and Orge  
24  
25 289 River basins (bed sediments) ranged from 1.15 to 1.18. Only one sample of bed sediment  
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27 290 collected in the Seine River had a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio as low as  $1.138 \pm 0.002$ . In the Seine River,  
28  
29 291 there is a rough correlation between the degree of urbanization/industrialization of the area  
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31 292 sampled and the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio measured in the SPM and the bed sediments. Hence, the study  
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33 293 of Seine River SPM collected each month in sediment traps (2008-2009) showed an  
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35 294 upstream-downstream trend with a signature decreasing from  $1.175 \pm 0.003$  for the most  
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37 295 upstream site to  $^{206}\text{Pb}/^{207}\text{Pb} = 1.1627 \pm 0.0025$  (n=9 site T) in the most downstream section of  
38  
39 296 the Seine River. The signature of this site sampled over one hydrological year fits well with the  
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41 297 signature determined in the upper section of the cores, corresponding to sediment deposited in  
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43 298 2003. We can therefore conclude that the signature derived from the dated floodplain cores is  
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45 299 representative of the average annual signature of the SPM.  
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47 300 **Figure 2.**  
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51 302 In contrast, the study of the Seine River bed sediment showed variable signatures (from  
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53 303  $^{206}\text{Pb}/^{207}\text{Pb} = 1.138 \pm 0.003$  to  $1.165 \pm 0.002$ ) coupled to very variable lead contents. Among the  
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55 304 7 samples studied here, two sites have been sampled twice (yearly sampling during low  
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57 305 waterflow), exhibiting significant variation between samples (e.g., at site Sar,  $^{206}\text{Pb}/^{207}\text{Pb} =$   
58  
59 306  $1.163 \pm 0.002$  and  $1.158 \pm 0.003$ , in 2008 and 2009, respectively; Table 2). Above all, the bed  
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61 307 sediment collected at Colombes in August 2009 combines the highest lead content being and the  
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63 308 highest gasoline lead contribution to the isotopic ratio. After removing this point from further  
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65 309 analysis, the bed sediments collected between 2007 and 2009 at locations close to the Bougival

1 310 site had an average isotopic signature of  $^{206}\text{Pb}/^{207}\text{Pb} = 1.163 \pm 0.003$  (n=6), close to the trapped  
2 311 SPM at site B ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.161 \pm 0.002$ , n=8). This indicates that both SPM and bed  
3 312 sediment are associated with similar sources, but that bed sediment composition may be  
4 313 punctually affected by local releases or river hydrodynamic changes. SPM and riverbed  
5 314 sediment may be submitted to differential transport processes (Chon et al., 2012).  
6 315 In the Orge River, the lead signature of the BS remained close to that of the SPM. Surprisingly,  
7 316 BS collected during high waterflow exhibited a Pb signature close to the one of urban lead at all  
8 317 sites including the less urbanized one, whereas those collected during low waterflow were  
9 318 characterized by a dominance of the natural source signature (Fig. 3). The lead isotopic  
10 319 signature ( $^{206}\text{Pb}/^{207}\text{Pb}$ ) measured in SPM collected in 2010/2011 was significantly higher than  
11 320 the one measured in material sampled in 2001, and was closer to the natural lead signature. On  
12 321 the contrary, there was no significant difference in the isotopic signature of SPM collected under  
13 322 low and high waterflows (Fig. 3).  
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### 324 **Figure 3**

## 326 **4. Discussion**

### 328 ***4.1. Temporal variability of lead sources in the Seine River***

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330 During most of the 20<sup>th</sup> century, Pb found in the Seine sediments originated from the huge  
331 amount of this metal that has accumulated in Paris since the 19<sup>th</sup> century (in painting, roof single  
332 elements, ...) and coming ultimately from the Rio Tinto mine. At the end of the 20<sup>th</sup> century, the  
333 isotopic composition of the downstream sediment core showed that “gasoline” Pb supplied up  
334 to 20% of the Pb contained in the Seine River sediment, with a peak around 1986 (Ayrault et al.,  
335 2012). “Gasoline” Pb was over-represented in the Seine River sediments compared to other  
336 possible sources/stocks, most likely because it was emitted directly to the atmosphere and often  
337 deposited in urban areas where it was rapidly washed out towards the Seine River. Natural Pb in  
338 the Seine River basin has a distinct isotopic signature ( $^{206}\text{Pb}/^{207}\text{Pb}=1.2007$ ). We can therefore  
339 use Pb isotopes to determine the nature and contribution of the different Pb sources to the  
340 environment.

341 Mixing between Pb of different sources can be studied with diagrams representing the isotopic

ratio as a function of the inverse of the concentration, as a binary mixing produces a linear correlation (Ayrault et al., 2012).

We considered a sediment (s) constituted of 3 components: a natural component (n), an anthropogenic component (a) and a Pb-free component (d) that dilutes the two others. The sample mass, Pb concentration, Al concentration and Pb isotopic ratio are noted  $m$ ,  $Pb$ ,  $Al$  and  $R$ , respectively. Mixing equations are:

$$m_s = m_n + m_a + m_d \quad (\text{Eq. 2})$$

$$Al_s = \frac{(m_n Al_n + m_a Al_a + m_d Al_d)}{m_s} \quad (\text{Eq. 3})$$

$$Pb_s = \frac{(m_n Pb_n + m_a Pb_a + m_d Pb_d)}{(m_s)} \quad (\text{Eq. 4})$$

$$R_s = \frac{(m_n Pb_n R_n + m_a Pb_a R_a + m_d Pb_d R_d)}{C_s} \quad (\text{Eq. 5})$$

By definition,  $Pb_d = 0$ . In addition, we assume that  $Al_d = 0$  and  $Al_a = 0$

$$Al_s = \frac{m_n Al_n}{m_s} \quad (\text{Eq. 6})$$

$$Pb_s = \frac{(m_n Pb_n + m_a Pb_a)}{m_s} \quad (\text{Eq. 7})$$

$$R_s = \frac{(m_n Pb_n R_n + m_a Pb_a R_a)}{C_s} \quad (\text{Eq. 8})$$

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The EF calculation equation (Eq. 1) may then be written as:

$$EF = \frac{(Pb_s/Al_s)}{(Pb_n/Al_n)} = \frac{(m_n Pb_n + m_a Pb_a)/m_n Al_n}{(Pb_n/Al_n)} = 1 + \frac{m_a Pb_a}{m_n Pb_n} \quad (\text{Eq. 9})$$

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Dividing the numerator and denominator of Eq. 8 by  $m_n Pb_n$ , we obtain:

361

$$\begin{aligned} R_s &= \frac{\left(R_n + \frac{m_a Pb_a R_a}{m_n Pb_n}\right)}{1 + \frac{m_a Pb_a}{m_n Pb_n}} \\ &= \frac{R_n + (EF - 1)R_a}{EF} \\ &= R_a + (R_n - R_a) \frac{1}{EF} \quad (\text{Eq. 10}) \end{aligned}$$

Therefore, the mixing of the two Pb-bearing phases “natural” + “anthropogenic” diluted by

1 366 Pb-free materiel (e.g., quartz sand) produces a linear relationship between the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio  
2  
3 367 and  $1/\text{EF}$ . Suspended particles collected in 2008/2009 at sites M, B and T form a broad linear  
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5 368 array in a  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $1/\text{EF}$  diagram with the EF factor increasing ( $1/\text{EF}$  decreasing) from  
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7 369 weakly to highly urbanized and industrialized area (Fig. 2). It suggests a mixing between an  
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9 370 anthropogenic and a natural end-member.  
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11 371 The isotopic signature of the “natural” end member should be defined by the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio at  
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13 372  $\text{EF} = 1$ . It corresponds to the Marnay sediments, in which  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio is significantly below  
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15 373 the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ( $= 1.20$ ) of the natural end-member determined in the literature. This  
16  
17 374 difference might be due to locally different bedrocks or to pervasive contamination by gasoline  
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19 375 Pb or both. Only 20% of gasoline lead would be sufficient to shift the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the  
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21 376 Marnay sediment from 1.20 to 1.18. Such a small EF variation might not be significantly  
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23 377 resolvable considering the uncertainties on the natural background Pb level discussed above.  
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25 378 The anthropogenic end-member is best represented by the collected waters overflowing in the  
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27 379 Seine River during heavy rain events (noted CSO hereafter, for combined sewer overflow). This  
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29 380 material is made up of 27% of organic matter carried by urban waste waters, mixed with rain  
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31 381 waters. The high Pb EF of the CSO samples is consistent with the affinity of Pb for organic  
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33 382 matter (Balabane and van Oort, 2002, Pernet-Coudrier et al., 2011). Urban runoffs have been  
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35 383 shown to contain high Pb concentration, together with Zn and Cu (Gromaire-Mertz et al., 2001).  
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37 384 The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the CSO ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.1573 \pm 0.0025$ ) corresponds to the urban  
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39 385 signature determined by analyzing the WWTP effluent collected in 2006 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm$   
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41 386  $0.002$ , Ayrault et al., 2012). It represents a mixing between the historical Pb accumulated since  
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43 387 the 19<sup>th</sup> century and “gasoline” Pb. We note that the range of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio covered by CSO is  
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45 388 narrower than the range found in the Bouafles sediments throughout the 20<sup>th</sup> century (Fig. 2).  
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47 389 This suggests that Pb transported nowadays by the Seine River is produced by a thorough  
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49 390 mixing between historical and gasoline lead, mixing that displayed a steady signature over the  
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51 391 last decade. This implies that 20 years after the complete ban of leaded gasoline in France,  
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53 392 gasoline Pb still contributes to the Pb contamination in the Seine River.  
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55 393 There is a significant scattering of the CSO samples and of the different types of SPM data  
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1 394 below the urban-natural mixing line. This scattering is likely due to the involvement of punctual  
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3 395 sources in Paris *intra muros* that have not been completely homogenized. Nevertheless, the  
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5 396 observed scattering is generally smaller than the change in isotopic ratio observed in the Seine  
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7 397 River sediment during the 20th century and recorded in the B1 core.

8  
9 398 The isotopic signature of suspended particles collected in the river nearby the core sampling site  
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11 399 can be compared to top-core sediments. The upstream Seine River core TR01 samples (covering  
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13 400 the 1970–2002 period) are plotted on a mixing line between urban lead and natural lead (Ayrault  
14  
15 401 et al., 2012). The recent TR01 sample signature ( $1.175 \pm 0.003$  in 2001) is consistent with the  
16  
17 402 signature found in Marnay SPM. Unfortunately, Al or Sc was not measured on core TR01  
18  
19 403 samples, preventing calculation of the EF. For the 1994-2003 period, the downstream Seine  
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21 404 River core B1 samples are plotted on a mixing line between urban lead and natural lead (Fig. 2).  
22  
23 405 For the 1994-2003 period, the downstream Seine River core B1 samples are plotted on a mixing  
24  
25 406 line between urban lead and natural lead (Fig. 2) with a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of  $1.166 \pm 0.004$  in  
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27 407 2003, a signature on the high boundary (but not significantly different) of the downstream Seine  
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29 408 River sites Bougival and Triel (with comparable EF).

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32 409

#### 33 410 ***4.2. Temporal variability of lead sources in the Orge River***

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37 412 For the Orge River catchment, lead concentrations were found to be 2 to 6 times higher in SPM  
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39 413 than the natural local background (20 mg/kg) and to be a function of the urbanization density  
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41 414 (Le Pape et al., 2013) (Table 4, Fig. 3). The trends indicated a change in the lead contamination  
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43 415 origin during the last decade. Indeed, the lead fingerprints evolved from a three-end member  
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45 416 system (natural + urban + gasoline) to a two-end member one (natural + urban) (Fig. 3),  
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47 417 corresponding to the end of lead gasoline supply to the river (Le Pape et al., 2013). These results  
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49 418 highlighted the consequences of gasoline-lead ban in France (2000), as already observed in the  
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51 419 Seine River basin (Ayrault et al., 2012). The lack of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio lower than the urban  
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53 420 signature in the SPM of the Orge River, a small and partly channelized urban catchment, could  
54  
55 421 be explained by a faster turnover of sediments compared to one in the Seine River watershed  
56  
57 422 that presents depositional areas allowing transitory to long term storage of particles. In a  
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59 423  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $1/EF$  diagram, the 2010/2011 Orge SPM samples correspond to the same mixing  
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61 424 trend as the one observed at the Seine basin scale, with most samples falling slightly below the  
62  
63 425 urban-natural mixing line (Le Pape et al., 2013). The Orge SPM displays a larger scattering



1 426 below the urban-natural mixing line. During the high waterflow, the 2010/2011 SPM samples  
2 427 contamination displayed a clear upstream ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.177 \pm 0.002$ ) to downstream  
3 428 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.158 \pm 0.002$ ) trend matching the urbanization trend, suggesting a shift from a  
4 429 diffuse source of lead to an urban contamination. During low waterflow, no clear pattern  
5 430 appears in the upstream to downstream signature trend. This may be attributed to local urban  
6 431 runoff releases occurring during low waterflow periods, as shown in Le Pape et al. (2013).  
7 432 The behavior of the Orge River bed sediment is clearly different from that of the SPM.  
8 433 Whatever the hydrodynamics of the river, the upstream to downstream signature trend did not  
9 434 follow the urbanization gradient, with the most upstream, less urbanized, site “D” signature  
10 435 varying from  $^{206}\text{Pb}/^{207}\text{Pb} = 1.165 \pm 0.002$ ; 40.5 mg/kg to  $^{206}\text{Pb}/^{207}\text{Pb} = 1.150 \pm 0.002$ ; 70.9 mg/kg;  
11 436 lying between the “historical” and the “urban” end-members.  
12 437 In the Orge River, the ratio  $^{206}\text{Pb}/^{207}\text{Pb}$  is never higher than  $1.179 \pm 0.002$  (Pb=54.8±2.7 mg/kg,  
13 438 site D) at the most upstream, less urbanized, site. These  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios remain significantly  
14 439 below the natural  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio and similar to the recent TR01 upstream core sample  
15 440 signature ( $1.175 \pm 0.003$  in 2001). Their signature is also close to the one of material collected  
16 441 in upstream Seine River sections even though they contain a higher Pb concentration. It might  
17 442 suggest the implication of a pervasive contamination by an anthropogenic Pb source that is  
18 443 more radiogenic than the gasoline additives, at the scale of the Orge River watershed. Studying  
19 444 A horizons collected each year at Versailles (15 km from Paris, 20 km from the Orge River  
20 445 watershed) from 1929 to 2000, Semlali et al. (2004) demonstrated that more than half of the  
21 446 anthropogenic Pb present nowadays in the topsoil was deposited before 1928. It has an isotopic  
22 447 signature  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.18$  (the ratio in the 1929 soil is  $^{206}\text{Pb}/^{207}\text{Pb} = 1.183 \pm 0.001$ ) and it could be  
23 448 related to coal combustion, coal used in Europe having a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio very close to 1.18  
24 449 (Komarek et al., 2008; Chiarada et al., 2000; MacKinnon et al., 2011; Semlali et al., 2004). This  
25 450 is in agreement with other European studies that attributed the value of 1.18 to a “pre-gasoline”  
26 451 anthropogenic signature (Farmer et al., 2000; MacKinnon et al., 2011; Catinon et al., 2013). In a  
27 452 study dedicated to agricultural soils in the UK, MacKinnon et al. (2011) observed that despite  
28 453 the proximity to motorway and roads, non- gasoline Pb from historical, industrial and  
29 454 coal-burning emissions was the dominant component except for very limited areas located in the  
30 455 immediate vicinity of roads.  
31 456 Although Pb isotopic signature in soils seems to be significantly affected by coal combustion  
32 457 and industrial fallout during the 19<sup>th</sup> century, the Seine River SPM collected at downstream  
33 458 floodplain sites during most of the 20<sup>th</sup> century are largely dominated by the Rio Tinto signature  
34 459 (Ayrault et al., 2012) with no significant contribution of a “coal” signature. To document this  
35 460 apparent contradiction, a detailed study of the Pb concentration, isotopic signature and lability is

1 461 currently performed in the Orge River catchment, with a special attention paid to the different  
2 462 soil types and horizons. This scheme will be further extended to the entire Seine River basin.

### 3 463 4 464 **4.3. Lead-bearing particles in the river**

5 465  
6 466 The possible relationship between the grain size and the Pb isotopic signature was investigated  
7 467 using the Orge River sampling campaign Jan 2011 (high waterflow) bed sediment. For this  
8 468 campaign, the SPM signature exhibits a clear upstream to downstream trend. We assumed that  
9 469 SPM originate from the BS finest fractions through resuspension of the bed sediment as it  
10 470 represents the major contamination pathway of the water column (Chon et al., 2012). Except at  
11 471 the most urbanized site where BS can be sampled (Y) (where the three fractions display similar  
12 472 signatures), the analyses of the sieved fractions showed that the signature of the different grain  
13 473 size fractions varied randomly from one site to the next (Table 5, Fig. 4). The finest fraction  
14 474 (<63 µm) is the most contaminated one (up to 110 mg/kg at the most urbanized site Y).  
15 475 However, because the coarser fractions (> 63 µm and > 200 µm) provide the bulk of the total  
16 476 mass of the BS samples, these coarse fractions bear a significant part of the Pb content (up to 72%  
17 477 of Pb is recovered in the >200 µm fraction at site Y).

### 18 478 19 479 **Table 5, Figure 4**

20 480  
21 481 The comparison of the signature of SPM versus BS as a function of river hydrodynamics is  
22 482 given in Fig. 5. It tends to show that during low waterflow, SPM signature tends to be closer to  
23 483 the “natural” end-member than the BS signature, whereas during high waterflow, the SPM  
24 484 signature is on average closer to the urban end-member than the BS one. This clearly supports  
25 485 the hypothesis of a BS resuspension during high waterflow conditions.

### 26 486 27 487 **Figure 5**

28 488  
29 489 Lead  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio was also measured in “road deposit sediments” (RDS), corresponding to  
30 490 sediments sampled in a road gutter at a strongly urbanized site (8000 inh/km<sup>2</sup>). The result  
31 491 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.144 \pm 0.003$ , Table 4) revealed the remanence of leaded gasoline in this sample  
32 492 that is mainly composed of coarse grains (Le Pape et al., 2013). In the UK, RDS exhibited  
33 493 signatures ranging from 1.13 to 1.145 (2001 samples) and 1.14 to 1.17 (2010 samples) (Mac  
34 494 Kinnon et al., 2012). The persistent leaded gasoline pollution at places where urban dust  
35 495 accumulated over decades was progressively leached by runoff over long periods of time

1 496 contributing to the contamination of the bed sediment. Moreover, our results show that there is  
2  
3 497 no direct contamination of the SPM from the RDS. This is consistent with the results of Catinon  
4  
5 498 et al. (2013) showing that dust coarse fraction (200-2000  $\mu\text{m}$ ) trapped in an outdoor urban  
6  
7 499 building for 40 years have similarly conserved the memory of the gasoline lead contamination  
8  
9 500 ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.146 \pm 0.002$ ).

10  
11 501 SEM analysis of the lead-bearing particles in the Seine River bed sediment showed the presence  
12  
13 502 of coarse particles ( $> 50 \mu\text{m}$ , up to  $200 \mu\text{m}$ ) bearing Pb and evidencing an anthropogenic origin  
14  
15 503 (alloys, quartz particles covered with a thin layer of Pb; Priadi, unpublished results). The results  
16  
17 504 on the Orge River sediments analyses are similar (Le Pape et al., 2013), showing Pb-containing  
18  
19 505 paint chips ( $\# 20 \mu\text{m}$ ) whereas the finest particles (Pb-phosphates;  $\# 5 \mu\text{m}$ ) are provided by soil  
20  
21 506 erosion. Unfortunately, SEM analyses only do not permit to conclude on lead isotopic signature  
22  
23 507 in those particles.

24  
25 508 The lead contamination on coarse particles observed by SEM, and the isotopic signature  
26  
27 509 measured on the RDS, which mainly contained coarse particles outline a difference compared to  
28  
29 510 results of previous studies exhibiting that exogenous Pb is linked to very fine particles, such as  
30  
31 511 the clay fraction (Semlali et al., 2001; Sutherland et al., 2003). However, those studies were  
32  
33 512 investigating diffuse atmospheric contamination due to gasoline emissions, whereas urban rivers  
34  
35 513 receive water-transported anthropogenic Pb from different origins (gasoline, paints, alloys...).

36  
37 514 Sediment sieving to  $50 \mu\text{m}$  or  $63 \mu\text{m}$  conventionally performed in river contamination studies  
38  
39 515 may then lead to the loss of this coarse fraction, which seems to play an important role in both  
40  
41 516 the urban Orge River Pb transport and contamination. Further studies would be necessary to  
42  
43 517 evaluate if this observation is applicable to other urban with varying geological characteristics.  
44  
45 518

#### 40 519 ***4.4. Towards a river contamination mixing scheme.***

41 520

42  
43 521 Leaded gasoline additives have been significantly used from the 1950s, with a maximum of  
44  
45 522 emissions in 1971 (Ferrand et al., 1999). From 1970 to 1990, successive regulations reduced  
46  
47 523 lead concentration in gasoline. The leaded gasoline was progressively replaced with unleaded  
48  
49 524 gasoline from 1990 to 2000. Lead from gasoline was intensively emitted for 30 years, from  
50  
51 525 1960 to 1990 at a rate of 5000 to 12000 t per year (roughly 1500 to 3500 t per year for the Seine  
52  
53 526 River basin).

54  
55 527 Here, we compare the flux of “gasoline” Pb transported by the river to the flux of “gasoline” Pb  
56  
57 528 emitted over the Seine Basin in 1986, when the gasoline contribution was the highest in the  
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1 529 Seine River sediment. The flux of “gasoline” Pb transported by the Seine is given by:  
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4 530  $F_{\text{gasolinePb-river}} = f * Pb * F_{\text{particles}} = 26 \pm 7$  ton/y, where  $f$  is the fraction of Pb in the sediment derived  
5  
6 531 from gasoline ( $\approx 23 \pm 6\%$ ),  $Pb$  is the total concentration of Pb in the sediment ( $\approx 153 \pm 18$  mg/kg)  
7  
8 532 in 1986 downstream Paris and the Seine-Aval WWTP at the Muids and Bouafle sites (Ayrault et  
9  
10 533 al., 2012).  $F_{\text{particles}}$  is the annual flux of particles ( $\approx 750$  ton/y, Meybeck et al., 1998).  
11  
12 534 Assuming that the Seine River basin receives 25% (Saby et al., 2006) of the 7500 tons of  
13  
14 535 gasoline Pb emitted in France in 1986 (Ferrand et al., 1999), the emission flux  $F_{\text{gasolinePb-emission}}$  is  
15  
16 536 estimated to 1900 tons.  
17  
18 537 Hence, the river exports only 1.4% of the gasoline Pb deposited annually. It implies that most of  
19  
20 538 the gasoline Pb remains stored in the soils of the Seine River basin. Nevertheless, gasoline Pb is  
21  
22 539 removed much more efficiently than  $^{210}\text{Pb}$ , a natural Pb radionuclide supplied homogeneously  
23  
24 540 over the basin by rainfall, for which only 0.7% of the annual deposit reaches the estuary (Le  
25  
26 541 Cloarec et al., 2007). Indeed, natural  $^{210}\text{Pb}$  is deposited homogeneously over the whole Seine  
27  
28 542 River Basin, whereas gasoline Pb is mostly deposited around Paris (the bulk of gasoline fallout  
29  
30 543 occurred within a distance of 60-100 km from Paris, Saby, 2006). In this context, gasoline Pb  
31  
32 544 would have  $2.0 \pm 0.5$  times more chance to reach the river than  $^{210}\text{Pb}$ , due to the larger proportion  
33  
34 545 of impermeable surfaces directly connected to the river in Paris and in its close suburbs  
35  
36 546 compared to the rest of the basin.  
37  
38 547

### 40 548 **Figure 6**

41 549  
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43 550 This does not imply that lead from gasoline has been completely and definitely flushed from the  
44  
45 551 Seine River basin, even in urban areas. The fast decrease of leaded gasoline contribution to the  
46  
47 552 river contamination after the emissions stopped may be attributed to the fact that the leaded  
48  
49 553 gasoline was mainly emitted in the most urban areas and along the roads (MacKinnon et al.,  
50  
51 554 2011). Soil erosion affecting areas connected to the river network and runoff on urban surfaces  
52  
53 555 supply fine particles contaminated in Pb to the watercourses during heavy rainfall (Fig. 6).  
54  
55 556 However, because of the strong affinity of Pb for organic matter (e.g., Semlali et al., 2001,  
56  
57 557 Balabane et al., 2002) and the low erosion rates recorded in the Seine River basin, the residence  
58  
59 558 time of this contaminant in soils is very long (up to 10,000 years, Le Cloarec et al., 2007).  
60  
61 559 Together with the in-depth diffusion of Pb in soils (Bacon et al., 1996), this indicates that soil  
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1 560 may constitute a sink for atmospheric anthropogenic Pb which would therefore exert a low but  
2  
3 561 continuous pressure on the river water quality. When the river flows across the Paris megacity,  
4  
5 562 the huge amount of Pb accumulated in the city infrastructure (pipes, roofs, ...) imprints the  
6  
7 563 signature of the Rio Tinto ore (the “historical” Pb) on the sediment transiting in the downstream  
8  
9 564 sections of the river.

10 565

## 11 566 **5. Conclusions**

12 567

13  
14 568 This extensive study of the Pb composition in the river sediments allows to infer the spatial and  
15  
16 569 temporal variability of the anthropogenic Pb sources in the Seine River basin. In the upstream  
17  
18 570 part of basin, before the river flows across the Paris megacity, most of the current Pb river  
19  
20 571 contamination is supplied by soil erosion that stores anthropogenic contamination that has  
21  
22 572 accumulated since the 19<sup>th</sup> century. Further studies are needed to elucidate the origin of this  
23  
24 573 pervasive soil contamination. The large contamination depth associated with the long residence  
25  
26 574 time of the particles in the soil complicates the detection of any decontamination trend in the  
27  
28 575 basin soils at the decadal scale. To evaluate precisely this “background” contamination, a  
29  
30 576 detailed study of the natural concentration and isotopic signature of the different lithologies and  
31  
32 577 soil types present in the basin is required.

33  
34 578 In the downstream part of the river under strong urban influence, the contamination is mainly  
35  
36 579 due to the release of the so-called “urban” Pb whose signature results from a thorough mixing of  
37  
38 580 “historical” and “gasoline” Pb. Urban Pb exhibits a remarkably steady signature over time and  
39  
40 581 space, even though a progressive decrease in the gasoline contribution could have been expected  
41  
42 582 after the ban of leaded additives. It appears that, after the first flush of the gasoline Pb within the  
43  
44 583 decade that followed the ban, a significant part of the gasoline Pb emitted in the basin had  
45  
46 584 transformed into an “urban alloy”. Further studies coupling solid speciation tools and isotopic  
47  
48 585 studies at the scale of particles would help in characterizing the bearing phases and availability  
49  
50 586 of the urban lead.

51 587

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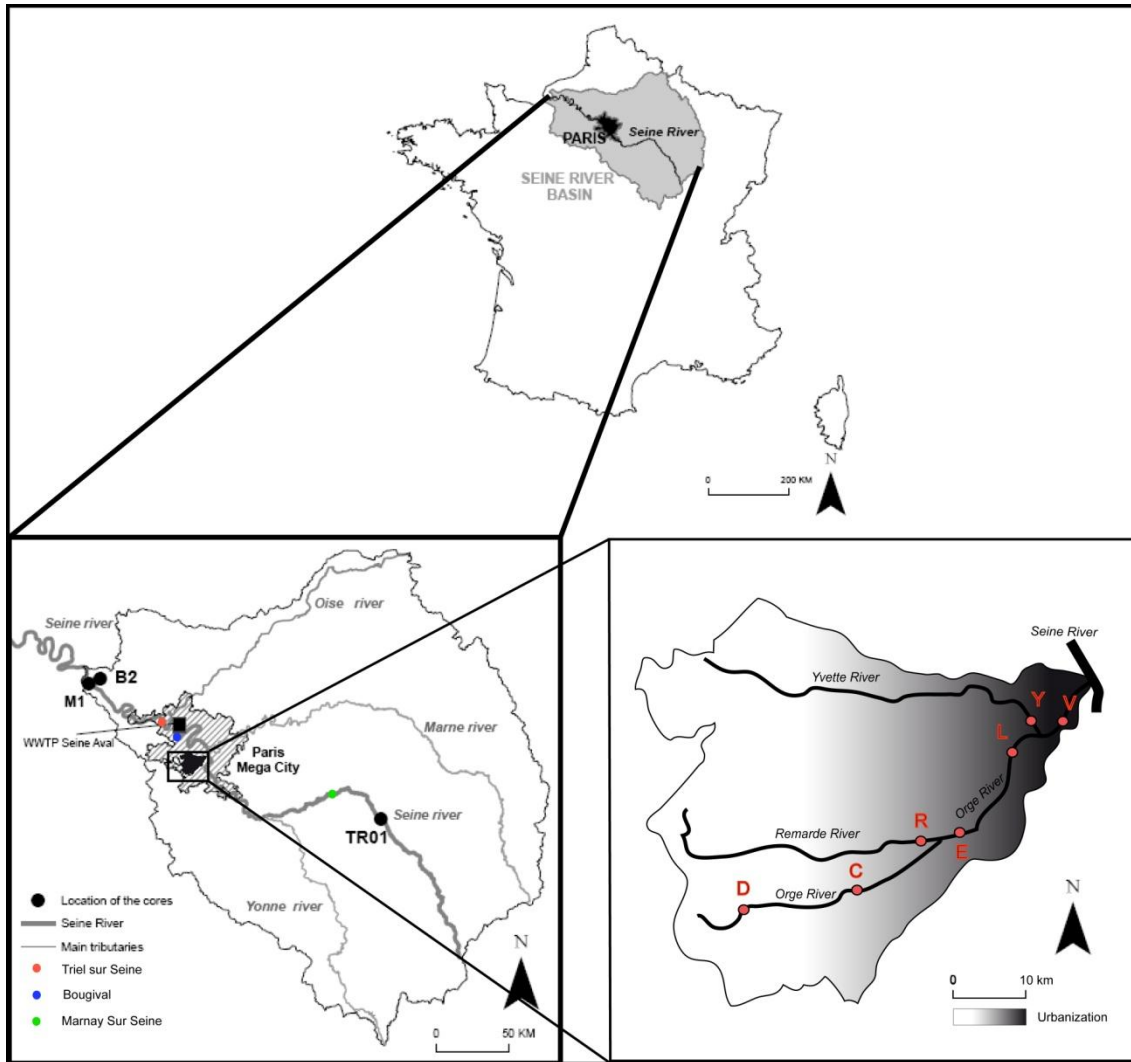
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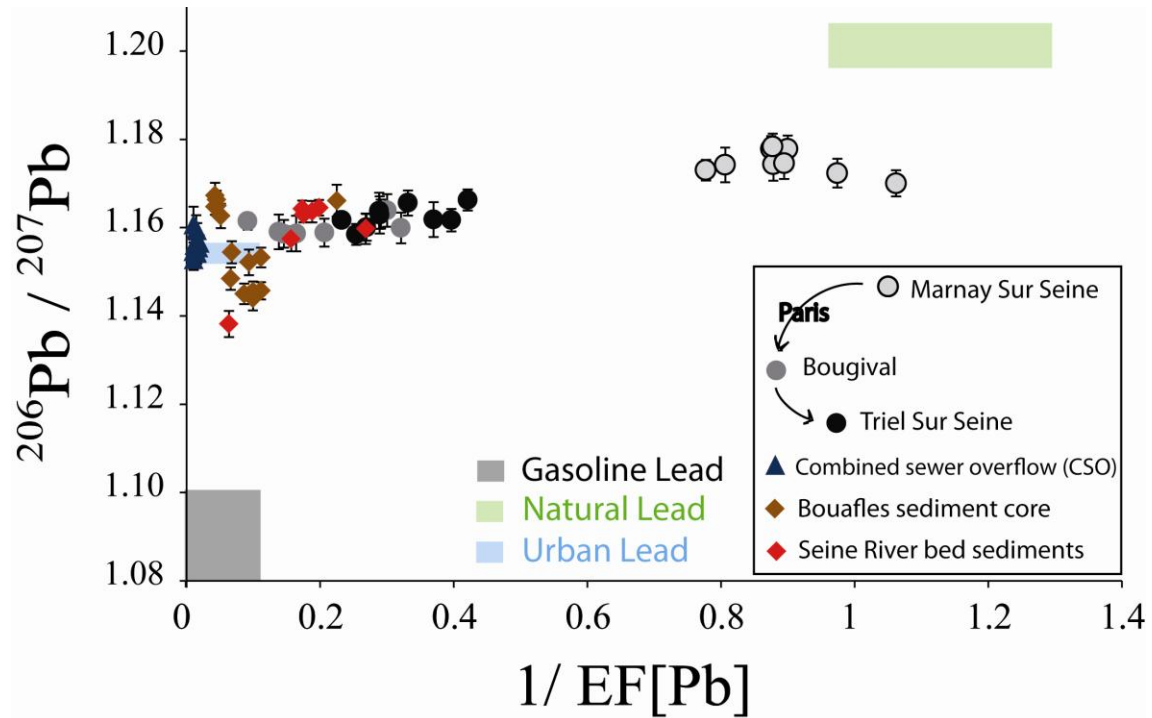
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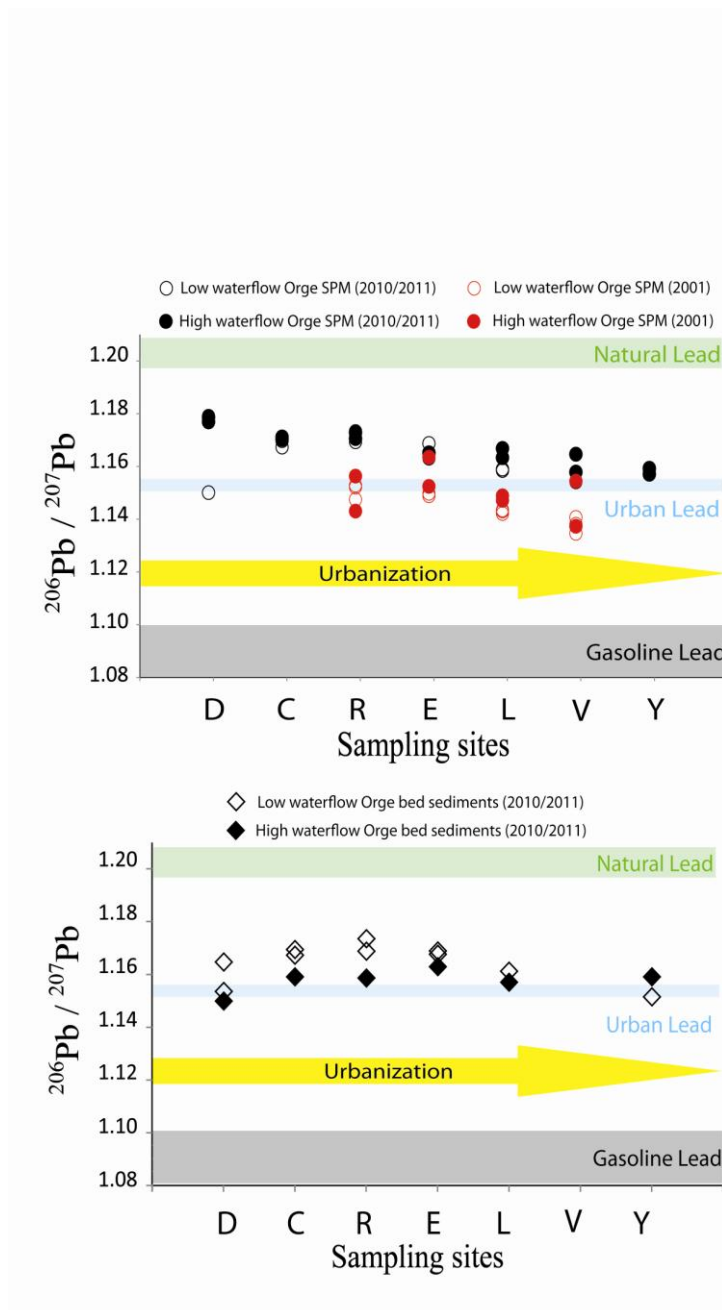
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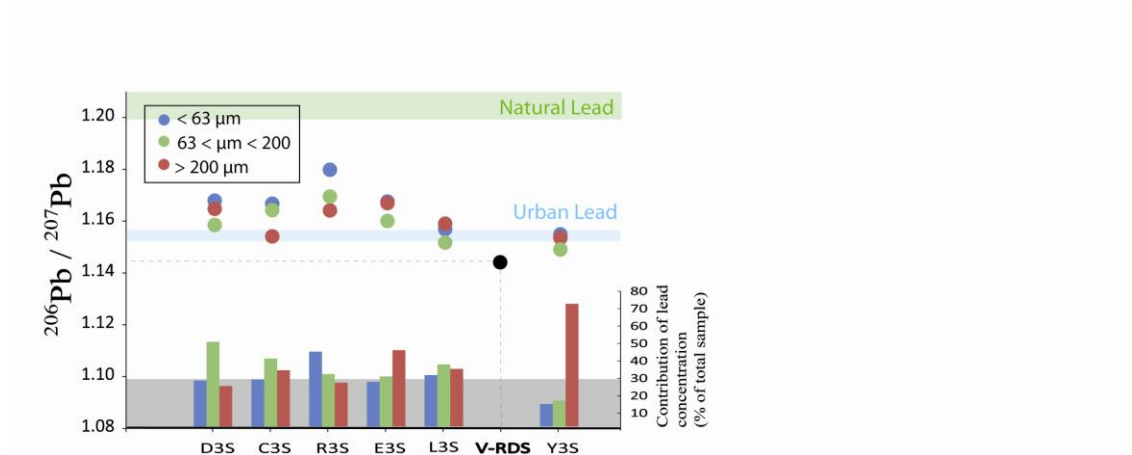
**Figure 1.** Location of the studied catchments. The Orge River catchment (900 km<sup>2</sup>) (down, right) is a sub-catchment of the Seine River basin (64,700 km<sup>2</sup>) (down, left). See Table 1 for the sampling sites labels.



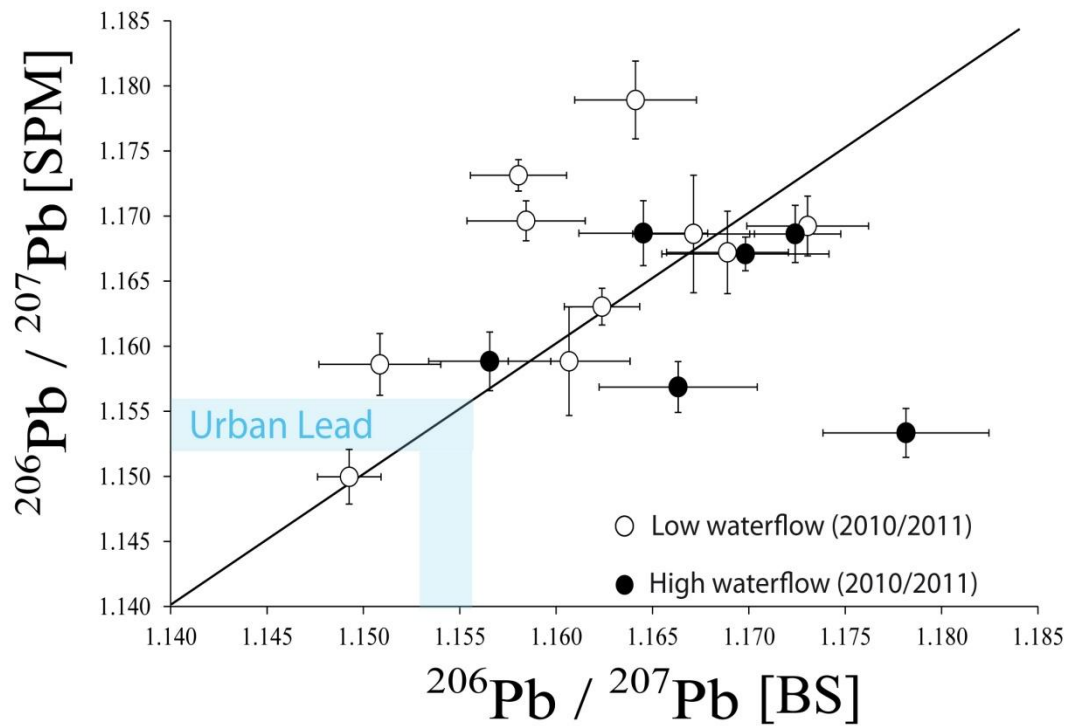
**Figure 2.** Isotopic Pb signature versus  $1/EF$ .  $EF$ : enrichment factor (see text). The colored arrays delimited end-member areas (blue for “urban” Pb, gray for “gasoline” Pb, green for “natural” Pb).



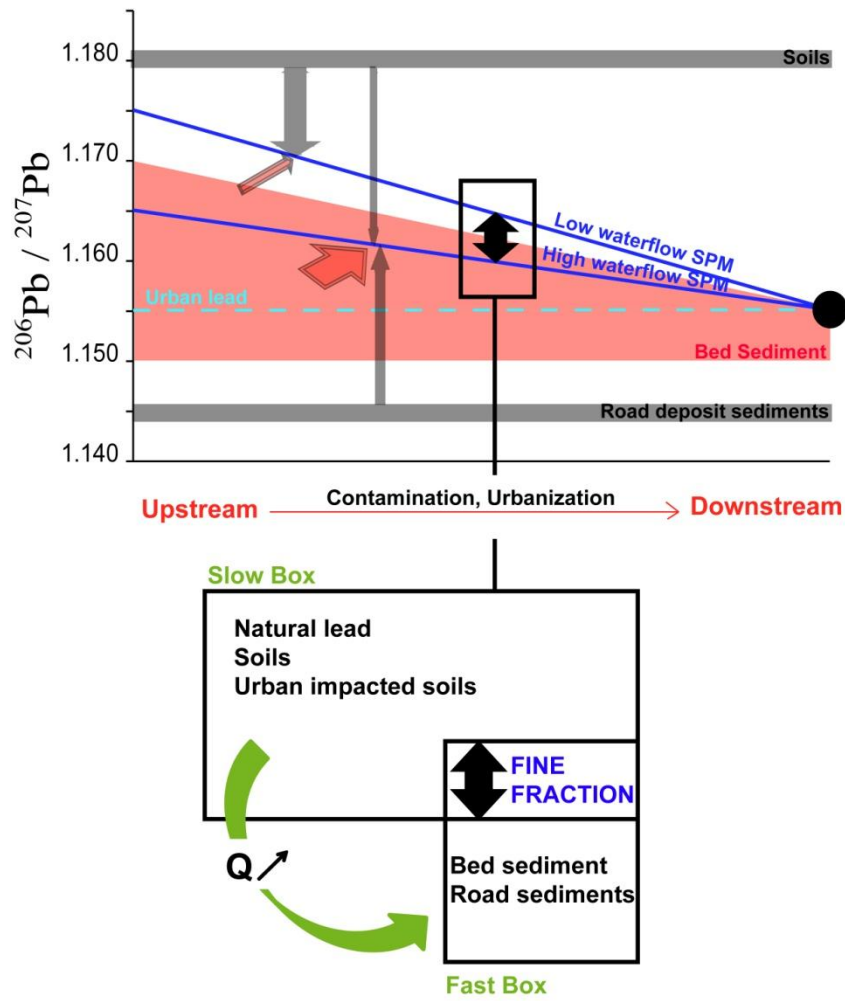
**Figure 3.** Isotopic Pb signature in suspended particle matter (SPM) (top) and bed sediments (BS) (down) of the Orge River. Open circles are for low water flow samplings. Closed circles are for high waterflow samplings. The symbol size matches the error amplitude.



**Figure 4.** Isotopic Pb signature of the sieved bed sediments of the Orge River. RDS: road-side sediment sampled at V site. See Table 1 for the sites label. The symbol size matches the error amplitude.



**Figure 5.** Isotopic Pb signature of the suspended particle matter (SPM) and bed sediments (BS) of the Orge River. Open circles are for low water flow samplings. Closed circles are for high waterflow samplings.



**Figure 6.** Scheme of the Pb contamination pathways along an urban river.

**Table 1.** Sample types, location and period of collection.

Site	Label	Lambert II coordinates		Sampling date
<b>Seine</b>				
Bed sediments (provided by SNS)				
Paris, Pt Tolbiac	Tol	595770	2427906	Sep 2007
Suresnes	Sur	592144	2429828	Sep 2007; Aug 2009
Sartrouville	Sar	586939	2438517	Jul 2008; Sep 2009
Colombes	Col	591484	2435843	Aug 2009
Clichy	Cli	598131	2434990	Aug 2009
Cores (Ayrault et al., 2012)				
Troyes	TR01	726238	2372883	Mar 1998
Muids	M1	525581	2470343	Apr 2003
Bouafles	B2	529698	2468611	Apr 2003
SPM (Priadi et al., 2011 a, b)				
Marnay-sur-Seine	M	690279	2391403	Dec 2008 - Sept 2009
Bougival	B	583671	2431778	Jan 2009 - Sept 2009
Triel-sur-Seine	T	575458	2442308	Dec 2008 - Aug 2009
Combined sewer overflow (Passerat et al., 2013)				
Clichy	CSO	598131	2434990	Aug 2008
<b>Orge (Le Pape et al., 2012 and 2013)</b>				
SPM and bed sediment				
Dourdan	D	575202	2392697	Jun 2010; Sep 2010; Jan 2011; Apr 2011
St Chéron	C	584428	2394522	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Rémarde	R	589402	2398180	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Egly	E	591912	2398466	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Longpont-sur-Orge	L	597093	2405080	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Yvette	Y	599432	2408855	Jun 2010; Sep 2010; Jan 2011; Apr 2011
Viry-Chatillon	V	603074	2408773	2001; Jun 2010; Sep 2010; Jan 2011; Apr 2011
Road side dust				
Viry-Chatillon	RDS	603074	2408773	Jan 2011



**Table 2.** Seine River bed sediment data. The three first letters correspond to the label of the sampling site (see Table 1), the two last figures refer to the sampling year (see Table 1). EF: enrichment factor (see text).

	$^{206}\text{Pb} / ^{207}\text{Pb} \pm 2s$	Al (mg/kg)	Pb (mg/kg)	EF
<b>Tol 07</b>	1.1645 $\pm$ 0.0019	30870 $\pm$ 4320	99.7 $\pm$ 5.0	5.8
<b>Sur 07</b>	1.1600 $\pm$ 0.0034	36145 $\pm$ 5060	75.2 $\pm$ 3.8	3.7
<b>Sar 08</b>	1.1632 $\pm$ 0.0017	29360 $\pm$ 4110	93.8 $\pm$ 4.7	5.8
<b>Sur 09</b>	1.1639 $\pm$ 0.0024	24885 $\pm$ 3485	74.0 $\pm$ 3.7	5.4
<b>Col 09</b>	1.1384 $\pm$ 0.0030	31580 $\pm$ 4420	281.7 $\pm$ 14.1	16.1
<b>Cli 09</b>	1.1647 $\pm$ 0.0018	33910 $\pm$ 4750	95.5 $\pm$ 4.8	5.1
<b>Sar 09</b>	1.1577 $\pm$ 0.0028	30370 $\pm$ 4252	108.5 $\pm$ 5.4	6.4

**Table 3.** Seine River trapped SPM. EF: enrichment factor (see text).

Sampling date	$^{206}\text{Pb} / ^{207}\text{Pb} \pm 2s$	Al (mg/kg)	Pb (mg/kg)	EF
<b>Marnay (M)</b>				
20/12/2008	1.1777 $\pm$ 0.0033	36954 $\pm$ 5174	23.5 $\pm$ 1.2	1.14
20/01/2009	1.1781 $\pm$ 0.0028	34735 $\pm$ 4863	22.1 $\pm$ 1.1	1.14
20/02/2009	1.1744 $\pm$ 0.0039	29556 $\pm$ 4138	20.4 $\pm$ 1.0	1.24
20/03/2009	1.1703 $\pm$ 0.0030	38998 $\pm$ 5460	20.4 $\pm$ 1.0	0.94
20/04/2009	1.1725 $\pm$ 0.0033	32687 $\pm$ 4576	18.7 $\pm$ 0.9	1.03
10/06/2009	1.1746 $\pm$ 0.0037	30757 $\pm$ 4306	19.5 $\pm$ 1.0	1.14
22/06/2009	1.1781 $\pm$ 0.0030	31796 $\pm$ 4451	19.7 $\pm$ 1.0	1.11
20/07/2009	1.1786 $\pm$ 0.0030	31552 $\pm$ 4417	20.0 $\pm$ 1.0	1.14
20/08/2009	1.1748 $\pm$ 0.0036	31723 $\pm$ 4441	19.7 $\pm$ 1.0	1.12
20/09/2009	1.1733 $\pm$ 0.0023	32090 $\pm$ 4493	23.0 $\pm$ 1.1	1.29
Median $\pm$ SD	1.1752 $\pm$ 0.0028		20.7 $\pm$ 1.6	
<b>Bougival (B)</b>				
20/01/2009	1.1591 0.0039	38862 5441	105.2 5.3	4.87
20/02/2009	1.1601 0.0042	54900 7686	95.4 4.8	3.13
20/03/2009	1.1633 0.0028	41725 5842	80.0 4.0	3.45
20/04/2009	1.1641 0.0024	46881 6563	87.1 4.4	3.34
10/06/2009	1.1617 0.0026	39883 5584	245.2 12.3	11.07
20/07/2009	1.1593 0.0041	43563 6099	176.7 8.8	7.30
20/08/2009	1.1588 0.0030	36609 5125	140.7 7.0	6.92
20/09/2009	1.1589 0.0024	43416 6078	148.0 7.4	6.14
Median $\pm$ SD	1.1607 0.0021		134.8 2.8	
<b>Triel (T)</b>				
20/12/2008	1.1621 0.0032	38909 5447	58.7 2.9	2.71
20/01/2009	1.1631 0.0035	42411 5938	81.8 4.1	3.47
20/02/2009	1.1658 0.0033	32886 4604	55.3 2.8	3.03
20/03/2009	1.1665 0.0037	38273 5358	50.7 2.5	2.38
20/04/2009	1.1619 0.0019	45352 6349	63.7 3.2	2.53
10/06/2009	1.1640 0.0040	43473 6086	84.1 4.2	3.48

22/06/2009	1.1603	0.0031	39913	5588	82.7	4.1	3.73
20/07/2009	1.1587	0.0040	40782	5709	89.6	4.5	3.96
20/08/2009	1.1619	0.0041	40981	5737	98.5	4.9	4.33
Median $\pm$ SD	1.1627	$\pm 0.0025$			75.8	$\pm 0.9$	

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**Table 4.** Combined sewer overflow (CSO) particulate matter composition. EF: enrichment factor (see text).

	$^{206}\text{Pb} / ^{207}\text{Pb} \pm 2s$	Al (mg/kg)	Pb (mg/kg)	EF
CSO-1	1.1568 $\pm$ 0.0017	461 $\pm$ 23	15442 $\pm$ 2162	53.8
CSO-2	1.1599 $\pm$ 0.0031	560 $\pm$ 28	13540 $\pm$ 1896	74.4
CSO-3	1.1531 $\pm$ 0.0024	801 $\pm$ 40	13641 $\pm$ 1910	105.7
CSO-4	1.1596 $\pm$ 0.0017	452 $\pm$ 23	12026 $\pm$ 1684	67.6
CSO-5	1.1559 $\pm$ 0.0018	515 $\pm$ 26	12517 $\pm$ 1752	74.1
CSO-6	1.1609 $\pm$ 0.0040	566 $\pm$ 28	9398 $\pm$ 1316	108.5
CSO-7	1.1571 $\pm$ 0.0026	478 $\pm$ 24	10881 $\pm$ 1523	79.0
CSO-8	1.1549 $\pm$ 0.0026	948 $\pm$ 47	15855 $\pm$ 2220	107.6
CSO-9	1.1557 $\pm$ 0.0024	588 $\pm$ 29	17547 $\pm$ 2457	60.3
CSO-10	1.1546 $\pm$ 0.0015	684 $\pm$ 34	17502 $\pm$ 2450	70.3
CSO-11	1.1545 $\pm$ 0.0024	656 $\pm$ 33	17056 $\pm$ 2388	69.2
CSO-12	1.1563 $\pm$ 0.0024	244 $\pm$ 12	4668 $\pm$ 654	94.0
Median $\pm$ SD	1.1573 $\pm$ 0.0025	579 $\pm$ 181		

**Table 5.** Orge River bulk and sieved bed sediments. EF: enrichment factor (see text).

	$^{206}\text{Pb} / ^{207}\text{Pb} \pm 2s$		Pb (mg/kg)		Mass %	Al (mg/kg)		EF
<b>D1S</b>	1.1497	$\pm 0.0016$	70.9	$\pm 3.5$	bulk	X		X
<b>C1S</b>	1.1589	0.0031	44.2	2.2	bulk	X		X
<b>R1S</b>	1.1585	0.0025	32.8	1.6	bulk	X		X
<b>E1S</b>	1.1628	0.0020	64.5	3.2	bulk	X		X
<b>D3S</b>	1.1534	0.0043	46.3	2.3	bulk	20055	$\pm 2808$	4.151
<b>C3S</b>	1.1671	0.0043	10.3	0.5	bulk	8598	1204	2.156
<b>R3S</b>	1.1687	0.0024	37.1	1.9	bulk	32736	4583	2.038
<b>E3S</b>	1.1687	0.0033	64.5	3.2	bulk	39955	5594	2.906
<b>L3S</b>	1.1569	0.0041	39.5	2.0	bulk	17535	2455	4.057
<b>Y3S</b>	1.1589	0.0032	72.2	3.6	bulk	12405	1737	10.483
<b>D3S&gt;200</b>	1.1586	0.0049	28.4	1.4	30.1	11913	1668	4.285
<b>C3S&gt;200</b>	1.1643	0.0032	11.3	0.6	39.7	8158	1142	2.493
<b>R3S&gt;200</b>	1.1696	0.0045	38.5	1.9	23.9	34433	4821	2.013
<b>E3S&gt;200</b>	1.1601	0.0025	69.1	3.5	41.5	44854	6279	2.773
<b>L3S&gt;200</b>	1.1518	0.0050	47.6	2.4	20.3	11819	1655	7.243
<b>Y3S&gt;200</b>	1.1492	0.0037	37.2	1.9	69.8	14431	2020	4.640
<b>63&lt;D3S&lt;200</b>	1.1648	0.0034	35.3	1.8	50.7	23282	3259	2.726
<b>63&lt;C3S&lt;200</b>	1.1542	0.0025	9.9	0.5	54.5	11060	1548	1.619
<b>63&lt;R3S&lt;200</b>	1.1642	0.0050	31.5	1.6	34.9	27727	3882	2.045
<b>63&lt;E3S&lt;200</b>	1.1670	0.0029	74.0	3.7	25.4	44198	6188	3.014
<b>63&lt;L3S&lt;200</b>	1.1591	0.0046	15.3	0.8	68.0	11367	1591	2.424
<b>63&lt;Y3S&lt;200</b>	1.1536	0.0040	21.1	1.1	25.9	10768	1508	3.535
<b>D3S&lt;63</b>	1.1680	0.0044	50.7	2.5	19.1	41577	5821	2.196
<b>C3S&lt;63</b>	1.1668	0.0042	64.7	3.2	5.8	37132	5198	3.138
<b>R3S&lt;63</b>	1.1799	0.0040	37.9	1.9	41.3	43537	6095	1.569
<b>E3S&lt;63</b>	1.1676	0.0044	50.8	2.5	33.1	40678	5695	2.248
<b>L3S&lt;63</b>	1.1570	0.0049	73.6	3.7	11.7	45155	6322	2.936
<b>Y3S&lt;63</b>	1.1550	0.0036	110.0	5.5	4.3	44335	6207	4.467
<b>D4S</b>	1.1646	0.0023	40.5	2.0	bulk	X		X
<b>C4S</b>	1.1693	0.0018	14.6	0.7	bulk	X		X
<b>R4S</b>	1.1735	0.0011	15.8	0.8	bulk	X		X
<b>E4S</b>	1.1676	0.0018	64.7	3.2	bulk	X		X
<b>L4S</b>	1.1611	0.0018	26.8	1.3	bulk	X		X
<b>Y4S</b>	1.1513	0.0025	30.4	1.5	bulk	X		X
<b>RDS</b>	1.1443	0.0028	35.6	1.8	bulk	X		X