



HAL
open science

Tracing the sources of suspended sediment and particle-bound trace metal elements in an urban catchment coupling elemental and isotopic geochemistry, and fallout radionuclides

Claire Froger, Sophie Ayrault, O. Evrard, Gaël Monvoisin, Louise Bordier, Irène Lefèvre, Cecile Quantin

► To cite this version:

Claire Froger, Sophie Ayrault, O. Evrard, Gaël Monvoisin, Louise Bordier, et al.. Tracing the sources of suspended sediment and particle-bound trace metal elements in an urban catchment coupling elemental and isotopic geochemistry, and fallout radionuclides. *Environmental Science and Pollution Research*, 2018, 25 (28), pp.28667 - 28681. <10.1007/s11356-018-2892-3>. <hal-01890467>

HAL Id: hal-01890467

<https://hal.science/hal-01890467v1>

Submitted on 15 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

[Click here to view linked References](#)

1 Tracing the sources of suspended sediment and particle-bound trace metal elements in
2
3 an urban catchment coupling elemental and isotopic geochemistry, and fallout
4
5 radionuclides
6

7
8 Claire Froger^{1, 2}, Sophie Ayrault¹, Olivier Evrard¹, Gaël Monvoisin², Louise Bordier¹, Irène Lefèvre¹, Cécile
9
10 Quantin²
11

12
13 ¹ Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), CEA-CNRS-UVSQ, Université
14
15 Paris-Saclay, Gif-sur-Yvette, France
16

17 ² Géosciences Paris Sud (GEOPS), Université Paris-Sud, Université Paris-Saclay, Orsay, France
18
19
20
21
22

23 Abstract

25 The excessive supply of contaminants from urban areas to rivers during the last centuries has led to deleterious
26
27 impacts on aquatic ecosystems. The sources, the behavior and the dynamics of these contaminants must be
28
29 better understood in order to reduce this excessive anthropogenic pollution. Accordingly, the current research
30
31 investigated the particle-bound trace element (TE) contamination of the 900-km² Orge River (Seine basin,
32
33 France) and **the potential sources of these particles (agricultural or forest soils, channel banks, road deposited**
34
35 **sediments)**, through the analysis of multiple fallout radionuclides, elemental geochemistry and lead isotopic
36
37 composition on suspended particulate matter (SPM) collected during a hydrological year at four stations
38
39 following an increasing urbanization gradient (300 to 5000 inhab.km⁻²). Fallout radionuclide measurements
40
41 showed an increasing contribution of recently eroded particles from urban areas to the SPM in downstream
42
43 direction. However, this contribution varied depending on hydrological conditions. A greater contribution of
44
45 particles originating from urban areas was observed during low stage periods. On the contrary, the contribution
46
47 of agricultural soils and channel banks that are less enriched in contaminants and fallout radionuclides was
48
49 higher during seasonal floods, which explained the dilution of radionuclide contents in sediment transiting the
50
51 river during those events. **Trace element** contamination of SPM in Cu, Zn, Pb and Sb increased from moderate
52
53 to significant levels with urban pressure in downstream direction (with corresponding enrichment factors raising
54
55 from 2 to 6). In addition, Pb isotopic ratios indicated that the main source of Pb corresponded to the “urban”
56
57
58
59
60
61
62
63
64
65

signature found in road deposited sediments. The low variations in lead isotope ratios found in the SPM for contrasting hydrological conditions demonstrated the occurrence of a single source of Pb contamination. These results demonstrate the need to better manage urban runoff during both flood and low precipitation events to prevent the supply of diffuse particle-bound contamination to rivers draining urban areas.

Keywords

Road Deposited Sediment; lead isotopes; sediment fingerprinting; recent sediment; legacy contamination.

1. Introduction

Human activities have strongly disturbed river ecosystems across the world through the significant supply of contaminants including an excess of nutrients and trace elements (TE) to the rivers (Meybeck, 2001; Vörösmarty et al., 2010). When these inputs exceed a certain level, a better management of river pollution is required through the reduction of industrial and domestic discharges or the improvement of wastewater treatment (Middelkoop, 2000; Rabalais et al., 1996; Santschi et al., 2001). The Seine River Basin draining Paris Megacity provides an emblematic example of anthropogenic river basin that has been exposed to significant pollution levels for more than one century (Grosbois et al., 2006; Meybeck et al., 2016).

The temporal evolution of contamination levels in the Seine River basin was previously reconstructed through the calculation of pollutant budgets and fluxes, in particular for metals such as Cu, Zn, Cd and Pb (Thévenot et al., 2007). Another strategy to reconstruct the historical contamination of the basin consists in analyzing sediment cores collected in frequently flooded areas in alluvial plains. These investigations showed that particulate TE contamination in the Seine River reached a peak in the 1960s when the industrial development in the basin was maximal (Ayrault et al., 2012; Le Cloarec et al., 2011; Lorgeoux et al., 2016). Since 1980, a global decrease in TE contamination levels has been observed in sediment transiting the Seine River as a result of the deindustrialization of the region and the adoption of environmental protection laws (Meybeck et al., 2016). For instance, the French law on water resources in 1992 and the European Water Framework Directive in 2000 contributed to define target quality requirements at the catchment scale. However,

1 despite these efforts, particulate-bound TE concentrations remain at a high level nowadays (Horowitz et al.,
2 1999; Le Pape et al., 2012; Priadi et al., 2011b; Thévenot et al., 2007).
3

4 Accordingly, the current sources and pathways supplying particulate pollutants to the rivers draining the
5 Seine basin should be identified. Their respective contribution should be quantified to properly guide
6 management decisions to improve the water and sediment quality. To this end, sediment tracing or
7 fingerprinting techniques have been developed to identify the sources supplying material to the river through
8 the analysis of conservative physico-chemical properties in both sources and sediment (Haddadchi et al., 2013).
9 However, these methods have mostly been developed and applied in agricultural and rural catchments (Foucher
10 et al., 2015; Le Gall et al., 2017b; Wilkinson et al., 2013). The identification of sediment sources in an urban
11 basin as complex as the Seine River basin requires the inclusion of multiple specific sources of particles and
12 contamination such as waste water treatment plants and urban runoff.
13
14
15
16
17
18
19
20
21
22
23

24 The identification of contamination sources using geochemical tracers including TE concentrations
25 associated with their isotopic composition has been widely used from the late 1980s (Chen et al., 2009; Juillot
26 et al., 2011). In particular, lead isotopic ratios were shown to provide a powerful tool for identifying the lead
27 sources as this isotopic signature is specific of a given ore type and it was demonstrated to remain stable during
28 its transfer with particles in the environment (Gulson et al., 1994; Komárek et al., 2008; Vaasjoki and Gulson,
29 1985). In France, significant modifications of lead isotopic ratios measured in environmental samples such as
30 airborne particles or river sediments during the last several decades were attributed to changes in anthropogenic
31 inputs of lead (Cloquet et al. 2006; Carignan et al. 2005; Ayrault et al. 2012; Monna et al. 1995). For instance,
32 the increasing proportion of lead originating from the use of leaded gasoline was demonstrated in sediment
33 collected during the 1990s (Elbaz-Poulichet et al., 1986; Monna et al., 1997; Véron et al., 1999). Then, after the
34 ban of leaded gasoline in 2000, a rapid shift in isotopic signatures was found in sediment and indicated the quick
35 and strong reduction of gasoline contribution to the total lead contamination found in the environment (Ayrault
36 et al., 2012). Accordingly, lead isotopic ratios **was** measured in association with elemental geochemistry to trace
37 potential changes in contamination sources and magnitude in sediment transiting urban catchments (Le Pape et
38 al., 2013).
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56

57 Furthermore, the transfer times of sediment and their potential spatial variations within a catchment **was**
58 investigated to check whether sediment transiting the river has been recently eroded from the sources, or whether
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
it mainly consists of material that was stored in the channel before being resuspended. To this end, sediment fingerprinting techniques based on the measurement of fallout radionuclides (FRN) characterized by different half-lives (^{137}Cs , ^7Be and $^{210}\text{Pb}_{\text{xs}}$) have been increasingly used, although they were mainly applied in agricultural catchments (Evrard et al., 2010; Gellis et al., 2017; Le Gall et al., 2017a; Matisoff et al., 2002). These natural (^7Be , $T_{1/2}= 53$ d; and $^{210}\text{Pb}_{\text{xs}}$, $T_{1/2}= 22$ y) and artificial (^{137}Cs , $T_{1/2}= 30$ y) FRN are mainly supplied to the soils by wet fallout, and they then quickly and strongly bind to fine particles (Mabit et al., 2008). The input of natural radionuclides is continuous, whereas that of radiocesium was exclusively associated with the thermonuclear bomb testing in the 1950s-1960s and the Chernobyl accident, as the fallout following Fukushima accident was shown to be negligible in France (Evrard et al., 2012). Accordingly, ^{137}Cs is mainly used to discriminate between topsoil material exposed to the fallout, and subsurface material sheltered from the rainfall. In addition, the contrasting half-lives of ^7Be and ^{210}Pb are used to discriminate between material enriched in ^7Be , reflecting their recent exposition to rainfall, and sediment depleted in ^7Be , reflecting their longer storage in the river channel (Evrard et al., 2016, 2010; Matisoff et al., 2005). To the best of our knowledge, the current study would provide one of the first studies coupling the measurement of multiple fallout radionuclides with elemental/isotopic geochemistry in sediment transiting an urban river.

33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
To conduct the current research, one of the most contaminated (Ayrault et al., 2014; Le Pape et al., 2012) sub-catchments of the Seine River Basin (i.e., the Orge River) was selected as it shares most characteristics of the Seine River basin (67,000 km²) while covering a much smaller surface area (900 km²). Furthermore, the Orge River catchment is exposed to a strongly increasing urban pressure in downstream direction, associated with a change in land uses (dominance of cropland and forest in upper catchment parts vs. dominance of urban areas close to the outlet) providing an ideal case-study to investigate the relationship between land-use and contamination processes. Finally, wastewater collected in this catchment is mainly redirected to a single treatment plant located in a nearby catchment, reducing the number of potential sources of sediment to the river (i.e. topsoil, channel banks, urban runoff).

53
54
55
56
57
58
59
60
61
62
63
64
65
The objectives of the current research were to define the sources and the dynamics of particles transiting the Orge River using fallout radionuclides as well as to quantify the levels and the sources of particle-bound contaminants using elemental geochemistry and lead isotopic ratios. To meet this goal, river sampling was conducted in the Orge River catchment on various occasions to cover variations of hydrological conditions. The

1 implications of these results to improve our understanding of particle transfer in urban catchments and to guide
2 the management of contamination sources will finally be discussed.
3
4
5

6 2. Materials and methods 7

8 2.1. Study site 9

10 All samples were collected in the Orge River catchment, a sub-catchment of the Seine River Basin located 30km
11 south of Paris City (Fig. 1). Three sampling sites were selected on the main stem of the Orge River, whereas a
12 fourth site was located on its main tributary, the Yvette River. The proportion of urban areas strongly increases
13 in downstream direction, varying from 1% in upper catchment parts to 56% at the outlet (Table 1). This change
14 is reflected by the strong increase in population densities in the drainage areas (from 300 inhabitants per km²
15 at the most rural study site – Dourdan (“D”), to 5000 inh.km⁻² at Viry (“V”, nearby the outlet). Although
16 wastewater is mainly treated outside of the catchment, misconnections in the sewage network are widespread
17 especially at the outlet, with connection failures estimated to reach 20% (SAGE Orge-Yvette, 2011). Data on
18 impervious surfaces in France for 2012 were retrieved from the European database CORINE Land Cover on
19 land uses (Gallego et al., 2016) and used to calculate impervious surface proportions in a 2.5, 5 and 10 km radius
20 around stations and in the sub-catchments drained by each monitoring station.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

36 Finally, the geology of the catchment is characterized by Eocene formations including carbonate rocks, marls
37 and gypsum, and Oligocene formations dominated by Fontainebleau sands (Le Pape et al., 2012; Schneider,
38 2005). Agricultural soils consisted of Luvisols, urban soils mainly corresponded to Fluvisols and some Luvisols,
39 and forest soils to Planosols and Luvisols based on the FAO World Reference Base classification.
40
41
42
43
44
45
46
47

48 2.2. Hydrological conditions 49

50 Sampling was conducted during a hydrological year with seven campaigns organized from June 2015 to
51 December 2016. Water discharge at the upstream station in Dourdan (“D”) varied from 0.1 to 1.1 m³.s⁻¹ (annual
52 mean of 0.2 m³.s⁻¹ from May 2015 to December 2016). At the downstream station in Viry-Châtillon (“V”),
53 discharge ranged from 1.4 to 20.5 m³.s⁻¹ (mean 3.3 m³.s⁻¹). The discharge of the main tributary, i.e., the Yvette
54 River, varied from 0.7 to 12 m³.s⁻¹, with a mean of 1.8 m³.s⁻¹ (May 2015 –December 2016).
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Sampling campaigns were organized to cover the hydrological variations of the Orge River and their seasonality (Fig.2). Accordingly, two campaigns were conducted during low stage periods with discharge $< 2 \text{ m}^3 \cdot \text{s}^{-1}$ in June 2015 and August 2016 (Viry discharge records). Sampling during campaigns with discharge comprised between 3 and $4 \text{ m}^3 \cdot \text{s}^{-1}$ in Viry was conducted in January 2016 and November 2016. Finally, flood campaigns were organised in September 2015 and April 2016 with discharges varying between 6 and $10 \text{ m}^3 \cdot \text{s}^{-1}$ at the outlet.

Furthermore, sediment traps were deployed from November 22, 2016 to January 3, 2017 to compare instantaneous vs. longer term records of sediment characteristics and TE contamination.

Precipitation amounts were retrieved from national meteorological records (Météo France, www.meteofrance.com) based on daily rainfall measurements at two rain gauges, one situated in Dourdan and the second in Bretigny-sur-Orge at mid-distance between Egly and Viry-Châtillon (Fig. 1).

2.3. Sampling and geochemical analysis

2.3.1. River Sampling

Two types of samples were collected in the river: instantaneous samples of river water including dissolved and particulate phases, and integrative samples of suspended particulate matter collected during 4 to 5 days using sediment traps. **The choice of sampling procedures was guided by the requirement of a significant amount of material (several grams) for (conducting) radionuclide measurements, difficult to achieve through the filtering of river water and justified by the representativity of (sediment) material collected in traps as demonstrated in several studies (Gateuille et al., 2014; Priadi et al., 2011a).** Prior to the sampling, all the flasks and bottles were washed with HNO_3 5% and rinsed three times with ultrapure water. In the field, they were washed again several times before collecting the samples.

On the first day of each campaign, about 10 L of water were sampled at each site to collect instantaneous SPM and 1 L of additional water was sampled for analyzing the dissolved phase only. In Egly (“E”) additional samples were taken from a pipe discharging water directly into the river ($E_{\text{discharge}}$). During each campaign, sediment traps were deployed in the river approximately 30 cm under the surface water level and submerged using ballast to collect suspended particulate matter. These traps consisted of two PET bottles of 1 L with ten drills of 2 cm diameter at their base, tied together to increase SPM collection. Four to five days later, sediment

1 traps were collected and instantaneous river water samples were collected again. Physico-chemical parameters
2 (pH, conductivity and temperature) were recorded during each sampling campaign.
3
4
5

6 2.3.2. Particulate source sampling

7 Samples representative of the potential sediment sources were collected across the catchment (Fig. 1).
8

9
10 First, topsoil samples were taken from A and L horizons in forests (n=10), as well as in agricultural (n=5) and
11 urban (n=8) areas. Most of those samples were collected in June 2015, however three samples located in
12 Dourdan were collected in 2017. Second, the eroding face of the channel banks was sampled in Dourdan, Egly
13 and Yvette in August 2016, at a distance of ~50 cm from the top, the first 2 cm were removed before sampling
14 to avoid the collection of particles originating from topsoil erosion. Channel bank samples could not be taken
15 in the downstream section of the river as it is channelized. Third, Road Deposited Sediments (RDS), consisting
16 of a mixture of particles transported by urban runoff on impervious surfaces, were sampled by sweeping the
17 road with a plastic-made brush at Viry stations in November 2016. Finally, a deep loess-derived Luvisol sample
18 was collected at 135 cm depth in a trench dug under cropland on the Saclay Plateau, north of the Yvette River,
19 to provide the potential background contamination signature in the study area.
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36

37 2.3.3. Sample preparation

38 River water samples were filtered (<0.45 µm porosity), dissolved aliquots were partly acidified (HNO₃ 0.5 N)
39 for subsequent TE and cation analysis and the remaining water was stored for anion, silica and carbonate
40 analyses. Suspended particulate matter from sediment traps was centrifuged (2800 g) and freeze-dried.
41 Suspended particulate matter and RDS were sieved to 200 µm (Pratt and Lottermoser, 2007), and soil samples
42 to 2 mm.
43
44
45
46
47
48

49 Approximately 100 mg of finely crushed SPM was mineralized in Teflon beakers and heated by Digiprep block
50 (SCP Science). Three replicates were analyzed for each SPM sample collected in traps and for those
51 instantaneous SPM samples with sufficient material available. Standard errors associated with the
52 measurements were calculated from those analyses conducted on these three replicates.
53
54
55
56
57
58
59
60
61
62
63
64
65

1 A three-step digestion was performed with first 4 mL of HF (30%) and 2 mL HClO₄ (67%) left at ambient
2 temperature for 2h then heated at 150°C for 6 hours. The second digestion phase used 3.75 mL of HCl (30%)
3 and 1.25 mL of HNO₃ (67%), added and kept at ambient temperature for 8 hours before heating at 120°C during
4 3h20. Finally, the last part consisted of three successive evaporations for 1 hour at 110°C after addition of 1mL
5 of HNO₃ (67%). The final solutions were transferred to 50 mL Falcon® (polyethylene) tubes. Each digestion
6 included a geostandard (Lake Sediment SL1 AIEA) and a blank to control mineralization quality.
7
8
9
10
11
12
13
14

15 2.3.4. Geochemical analyses

16 2.3.4.1. Major elements

17 Major elements (Ca, Na, Mg, K, Al, Fe) were determined by Atomic Absorption Spectrometry in both
18 mineralized SPM and dissolved phases using a VARIAN AAS240FS instrument.
19
20
21
22
23
24

25 2.3.4.2. Trace element concentrations

26 Minor and trace element (V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl) contents of
27 mineralized particulate samples and acidified dissolved samples were measured using an Inductively Coupled
28 Plasma Quadrupole Mass Spectrometer (ICP-QMS, X-Series, CCT II & Thermoelectron, France). A standard
29 of river water (SRM 1640a, NIST, USA) was used to control ICP-QMS precision, and the correction of
30 instrumental drift was based on the deviation observed on internal standards (Re, Rh and In). To avoid
31 interferences, additional series of analyses were conducted using the Collision Cell Technology mode using gas
32 input (H₂ (7%) and He (93%)) in particular for elements such as Cr, Fe, Ni, Zn, As.
33
34
35
36
37
38
39
40
41
42
43
44
45
46

47 2.3.4.3. Lead isotope ratio determination

48 Lead isotope ratios (²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb) were measured in solutions of mineralized samples by HR-ICP-
49 MS (Thermo Element XR, single collector). Measurement settings were a dwell time of 10 ms, 420 sweeps, and
50 5 replicates per sample. A Pb reference material NIST NBS 981 was measured every three samples to control
51 instrument drift and mass bias. The 2σ-error average of isotopic ratios was 0.14%±0.06 (n = 60). The solutions
52 of mineralized sediment lake standard SL1 were measured with samples and presented values of 1.2177 ±
53
54
55
56
57
58
59
60
61
62
63
64
65

0.0035 in $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.0320 ± 0.0091 in $^{206}\text{Pb}/^{207}\text{Pb}$ ($n = 12$) in agreement with those reference values of 1.217 ± 0.008 in $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.037 ± 0.003 in $^{208}\text{Pb}/^{206}\text{Pb}$ (Farmer et al., 2002).

2.4. Radionuclide measurements

Radionuclides were measured on SPM from sediment traps, RDS and channel banks samples rapidly after sampling (< 21 days). Topsoil samples collected in 2015 were analyzed in February 2017, (unfortunately) after the full decay of ^7Be . In contrast, the 3 samples collected in May 2017 were analyzed within two weeks after sampling. The samples were placed in polyethylene containers and sealed airtight. The activities of ^7Be , ^{210}Pb and ^{137}Cs were quantified at 447.6 keV, 46.5 keV and 661.5 keV by gamma spectrometry using very low-background coaxial N and P type GeHP detectors (Ortec, Canberra) available at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette, France. The excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) contribution originating from atmospheric fallout was calculated by subtracting from the total ^{210}Pb activity, the supported activity determined by two ^{222}Ra daughters (^{214}Pb and ^{214}Bi) measured at 295.2 and 351.9 keV for ^{214}Pb and 609.3 keV for ^{214}Bi . Activities were all expressed in $\text{Bq}\cdot\text{kg}^{-1}$ and decay-corrected to the sampling date. Internal and certified International Atomic Energy Agency (IAEA) standard were used to verify counting efficiency and measurement reliability. The analytical errors were of ca. 10% for ^{137}Cs and ^{210}Pb and of 20% for ^7Be .

2.5. Calculation of residence time and the contribution of recently eroded particles

The residence time of particles in the river was estimated using the following equation (1) reported in Matisoff et al., (2005):

$$t = \frac{-1}{(\lambda_{7\text{Be}} - \lambda_{210\text{Pb}})} \ln\left(\frac{A}{B}\right) + \frac{1}{(\lambda_{7\text{Be}} - \lambda_{210\text{Pb}})} \ln\left(\frac{A_0}{B_0}\right) \quad (1)$$

Where $\lambda_{7\text{Be}}$ and $\lambda_{210\text{Pb}}$ are the decay constants of respectively ^7Be and ^{210}Pb in d^{-1} , A and B are ^7Be and $^{210}\text{Pb}_{\text{xs}}$ activities measured in SPM samples in $\text{Bq}\cdot\text{kg}^{-1}$ and A_0 and B_0 the ^7Be and $^{210}\text{Pb}_{\text{xs}}$ activities of recently eroded particles. In the current research, the reference value for the ratio A_0/B_0 was fixed to 3.3, which corresponds to that maximum ratio found in road deposited sediments collected at the Viry site.

The percentage of recently eroded particles was also calculated (Matisoff et al., 2005)(Eq. (2)):

$$\% \text{ of recently eroded sediment} = 100 \times \frac{(A/B)}{(A_0/B_0)} \quad (2)$$

The reference value for A_0/B_0 was identical to that used in Eq. (1).

Based on ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{xs}}$ activities measured in SPM, a two-end-member equation was used to calculate the contribution of “older particles” with low activities in ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{xs}}$ ($\text{Bq}\cdot\text{kg}^{-1}$) and “recently tagged particles” with high activities in ${}^7\text{Be}$ and ${}^{210}\text{Pb}_{\text{xs}}$. The system of equations is detailed as follows:

$${}^7\text{Be}_{\text{SPM}} = x {}^7\text{Be}_{\text{old particles}} + y {}^7\text{Be}_{\text{recent particles}} \quad (3)$$

$${}^{210}\text{Pb}_{\text{SPM}} = x {}^{210}\text{Pb}_{\text{xs old particles}} + y {}^{210}\text{Pb}_{\text{xs recent particles}} \quad (4)$$

Where x and y are the respective proportions of older particles and recently eroded particles, and their ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ activities ($\text{Bq}\cdot\text{kg}^{-1}$). Contributions are calculated with the function *Solver* in Excel using a system of two equations with a two-step resolution.

2.6. Statistical analysis

Statistical tests were conducted to compare geochemical and radionuclide results between defined groups of samples. First, the Shapiro-Wilk test was used to evaluate the normality of the sample distributions with a selected α value of 0.05 defining the p -value limit (Shapiro and Wilk, 1965). Following the result of Shapiro test, sample comparison was conducted using Student’s test (or t-test) to compare two groups of normal distribution datasets or ANOVA to compare more than two groups. For those data with non-normal distributions, Kruskal-Wallis test was performed (Siegel and Castellan, 1988). Those three tests were interpreted using an α value of 0.05.

3. Results and discussion

3.1. Sources of SPM and particle dynamics

3.1.1. Characterization of SPM sources

Concentrations in ${}^{137}\text{Cs}$ measured in SPM and in potential sediment sources are presented in Fig.3, along with the results of the corresponding statistical comparison.

Suspended particulate matter from the Orge and Yvette Rivers showed relatively stable ${}^{137}\text{Cs}$ activities of $3.5 \pm 1.4 \text{ Bq}\cdot\text{kg}^{-1}$, similar to those found in most particle sources (i.e. river banks, RDS, agricultural and urban soils), with the exception of forest soils having a median activity of $8.8 \text{ Bq}\cdot\text{kg}^{-1}$ and a maximum value of $36.3 \text{ Bq}\cdot\text{kg}^{-1}$ (Table S6). Statistical tests confirmed the significance of this difference, excluding forest soils as a potential

1 major source of particles in upper sections of the Orge River. This exclusion was corroborated by results found
2 for major elements, with a depletion in K, Na and Mg in forest soils compared to those concentrations found in
3 other potential sources (Fig. S1), supporting the conclusion that forest soils did not provide a major source of
4 particles in upper catchment parts. Moreover, RDS showed low ^{137}Cs activities (median 0.5 Bq.kg^{-1}), suggesting
5 that RDS did not provide a dominant source of particles. Channel banks collected along the Orge River showed
6 lower ^{137}Cs activities of $1.4 \pm 1.8 \text{ Bq.kg}$ than SPM, although they were not statistically different. Finally,
7 agricultural and urban soils showed a ^{137}Cs activity of $2.8 \pm 0.8 \text{ Bq.kg}^{-1}$ and $4.9 \pm 0.2 \text{ Bq.kg}^{-1}$ very similar to
8 those results found in SPM. Accordingly, channel banks, agricultural soils and urban soils could not be
9 discriminated based on their ^{137}Cs activities, both providing potential significant sources of sediment to the
10 river.

11 A progressive increase in ^7Be and $^{210}\text{Pb}_{\text{xs}}$ concentrations was measured in SPM collected in downstream
12 direction in the Orge River (Fig. 4a, for a plot of their spatial variations). In Dourdan, SPM signatures ranged
13 between 12 and 57 Bq.kg^{-1} for ^7Be and from 22 to 50 Bq.kg^{-1} for $^{210}\text{Pb}_{\text{xs}}$. In contrast, in Viry, SPM showed much
14 higher values varying from 113 to 406 Bq.kg^{-1} for ^7Be and from 56 to 171 Bq.kg^{-1} for $^{210}\text{Pb}_{\text{xs}}$. This increase in
15 radionuclide concentrations measured in SPM indicated the increased supply of recently eroded particles in
16 downstream direction. The suspended particulate matter signatures in ^7Be and $^{210}\text{Pb}_{\text{xs}}$ plot well along a mixing
17 line between two potential particle sources (Fig. 4): the first end-member corresponded to RDS with respective
18 maximum values in ^7Be and $^{210}\text{Pb}_{\text{xs}}$ up to 704 ± 40 and $387 \pm 8 \text{ Bq.kg}^{-1}$, whereas the second end-member could
19 not be selected between channel banks, agricultural soils and urban soils to identify the main source supplying
20 particles to the river. However, given the virtual absence of urban soils in upper catchment parts and their low
21 connectivity to the river network, it is very unlikely that they provided a potential major source of particles.

22 The strong affinity of radionuclides to the finest particle fractions including clays has been demonstrated in
23 numerous studies (Blake et al., 2009; Davies and Shaw, 1993; Matisoff et al., 2005), and corrections based on
24 Al or Th that are enriched in the clay fraction are sometimes applied for correcting the particle size effect
25 (Foucher et al., 2015; Sakaguchi et al., 2006). In the current research, similar Al contents were found in SPM
26 ($40 \pm 8 \text{ g.kg}^{-1}$) and agricultural soils ($38 \pm 11 \text{ g.kg}^{-1}$), and they did not significantly vary from those found in
27 RDS and river banks ($24 \pm 2 \text{ g.kg}^{-1}$ and $26 \pm 5 \text{ g.kg}^{-1}$ respectively). These results demonstrate that the increasing
28 ^7Be and $^{210}\text{Pb}_{\text{xs}}$ activities between soils and SPM/RDS (Fig. 4) were not related to a grain size effect, and that

1 these activities could be used for comparing particle sources and SPM. As grain size corrections may result in
2 a bias in source contribution calculations (Smith and Blake, 2014), particle size was not corrected in the current
3 research. During particle transfer, changes in radionuclide content could be caused by either a dilution of the
4 signal with particles depleted in ^7Be or by the radioactive decay during the transport. In the Orge River, the
5 constant positive relationship between ^7Be and $^{210}\text{Pb}_{\text{xs}}$ in SPM suggests that the dilution effect provides the main
6 factor explaining the difference between those sites located in upper or in lower catchment parts. If the ^7Be
7 significantly decayed during transport as a result of particle storage within the system, sediment would be
8 depleted in this radioisotope resulting in SPM signatures falling outside of the mixing line actually observed
9 (Fig. 4). The fast transfer of particles in the river system is further supported by the estimation of short SPM
10 residence times with a mean of 63 ± 30 days (18–140 days) (Table 2), with a significant decrease observed for
11 the particles transiting the river at Dourdan (91 ± 22 days) compared to those transported downstream at Viry
12 (41 ± 22 days).

13 In addition to spatial variation, radionuclide content in SPM also presented variations between low stage periods
14 (mean and low flow periods) and seasonal floods (high waters) (Fig. 4b). The changes in signatures of samples
15 collected during seasonal floods remained limited at all stations with variations from 54 to 192 Bq.kg⁻¹ in ^7Be
16 and 41 to 87 Bq.kg⁻¹ in $^{210}\text{Pb}_{\text{xs}}$. On the contrary, characteristics of SPM collected during low stage periods were
17 much more scattered, with signatures varying between 12 and 406 Bq.kg⁻¹ in ^7Be and 23 to 171 Bq.kg⁻¹ in
18 $^{210}\text{Pb}_{\text{xs}}$. During low stage periods, SPM radionuclide signatures in ^7Be and $^{210}\text{Pb}_{\text{xs}}$ increased strongly in
19 downstream direction, clearly reflecting the input of recently tagged particles from urban areas in lower
20 catchments parts. However, residence times estimated based the on $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$ ratios did not vary significantly
21 between seasonal floods and low stage periods for a given site (Table 2).

3.1.2. Proportion of recently eroded particles

22 According to the results showing a mixing line between ^7Be and $^{210}\text{Pb}_{\text{xs}}$ (Fig. 4), equations (3) and (4) were used
23 to estimate the contributions of particle sources. Accordingly, *older particles* were considered to originate from
24 agricultural soils or channel banks (both showing the same signature) whereas *recent particles* were assumed
25 to correspond to RDS. The mean ^7Be and $^{210}\text{Pb}_{\text{xs}}$ activities for *older particles* originating from agricultural soils

(n = 5, Table S5) and river banks (n = 3, Table S5) were 1 Bq.kg⁻¹ for ⁷Be and 4.0 Bq.kg⁻¹ for ²¹⁰Pb_{xs}. Considering the large range of radionuclide activities found in RDS samples, the mean contributions of *recent particles* were calculated from those results obtained with the highest RDS signature (i.e. 704 Bq.kg⁻¹ in ⁷Be and 387 Bq.kg⁻¹ in ²¹⁰Pb_{xs}), that closest to the SPM signatures (i.e. 323 Bq.kg⁻¹ in ⁷Be and 168 Bq.kg⁻¹ in ²¹⁰Pb_{xs}), and the median RDS signature (i.e. 412 Bq.kg⁻¹ in ⁷Be and 232 Bq.kg⁻¹ in ²¹⁰Pb_{xs}) (Table S7). The mean standard error for the three sets of calculated contributions was 10%, with an increase from Dourdan (4% ± 1) to Viry (17% ± 7). The comparison of the recently eroded particle contributions estimated from the mixing line model and those calculated with the literature model based on ⁷Be/²¹⁰Pb_{xs} ratios (see section 2.6 and Table S8) revealed a similar trend for both approaches (Figure 5). Overall, an increasing contribution of recently eroded particles was observed in downstream direction for both models, with proportions ranging from 3 to 71% (Fig.5a) for the mixing model and from 16 to 79% (Fig. 5b) for the ⁷Be/²¹⁰Pb_{xs} ratio model. The main difference between both models is that the mixing model takes into account variations in the hydrological regime (Fig. 5a), which is not the case for the ⁷Be/²¹⁰Pb_{xs} ratio model (Fig. 5b). For instance, higher contributions of recent particles were observed in Viry during low stage periods (i.e. campaigns of Jan. 2016, Nov. 2016, Dec. 2016, Jun. 2015 and Aug. 2016) with a median value of 57± 15%, compared to contributions during seasonal flood (i.e. Sept. 2015 and Apr. 2016) showing a median value of 28± 7%. Conversely, the ⁷Be/²¹⁰Pb_{xs} ratio model did not reveal any temporal differences in the contributions of recent particles. The different pattern observed for particles collected at Egly and Yvette sites showing higher recent particle contributions during seasonal floods, may reflect the current development of building activities which was shown to accelerate soil erosion and the supply of sediment to nearby rivers (Chin, 2006; Huon et al., 2017; Nelson and Booth, 2002). This hypothesis is supported by those lower residence times calculated for particles transiting the river at Egly and Yvette sites during seasonal floods (40 ± 11 days and 33 ± 2 days respectively) compared to those found during low stage periods (82 ± 23 days for Egly SPM and 47 ± 10 days for Yvette).

3.1.3. Impact of urban surfaces and precipitation regime on the contribution of recently tagged particles

The increasing urban pressure in downstream direction is demonstrated when comparing the proportions of urban surface areas found in a 2.5, 5 and 10 km radius from each sampling station (Table 3). Urban pressure is

1 the highest in Viry draining the entire Orge catchment. As impervious surface rates evolution is similar for the
2 three radius tested and comprised between 2.5 and 10 km, those values corresponding to the mid-distance of 5
3
4 km were retained for further analysis.
5
6
7

8 The relationship between the proportion of impervious surfaces and the contribution of recently tagged particles
9 varied with hydrological conditions (Fig. 6). During low stage periods, a positive relationship was observed
10 between both variables. However, contributions of recent particles showed larger variations at Viry compared
11 to those observed at D, E and Y with an increase between low flow periods (Jun 2015, Aug 2016) and average
12 flow periods (Jan 2016, Nov 2016 and Dec 2016). On the contrary, no relationship could be observed between
13 the contribution of recent particles and the impervious surface areas during seasonal floods. As streamflow in
14 the Orge River shows a rapid response to rainfall (Fig. 2), those contrasted particle transfer processes observed
15 for different hydrological regimes (i.e., low stage periods and seasonal floods) may be explained by different
16 timing in precipitations across the entire catchment and variations in land use patterns of each station (Table 4).
17 To explore this hypothesis, antecedent precipitation records were compared for the sequence of sampling
18 campaigns.
19
20
21
22
23
24
25
26
27
28
29
30
31
32

33 The amount of antecedent precipitation varied depending on hydrological regimes and locations, with low stage
34 periods occurring after very low mean precipitation records varying from 1 mm per day in upper catchments
35 parts and up 8 mm per day in downstream parts. On the contrary, seasonal floods were triggered by higher
36 rainfall varying between 5 and 12 mm per day (Table 4), suggesting variations in sediment dynamics depending
37 on the hydrological regime. During seasonal floods (i.e. in Sept. 2015 and Apr. 2016), high intensity rainfall
38 impacted differently upper and lower catchment parts. In upper parts mainly occupied by agricultural land,
39 rainfall generated extensive soil erosion and supplied recently eroded particles to the river, particularly in Egly,
40 resulting in low residence times of particles (Table 2, section 3.1.2). Moreover, the short and homogenous
41 residence times found for particles at Egly, Yvette and Viry during those flood events (Table 2) reflected the
42 occurrence of a clear connection between upstream and downstream river sections, explaining the steady
43 contribution of recent particles observed at these three sites. During low stage periods (i.e. Jun. 2015 and Aug.
44 2016), soil erosion was low in upper catchment parts (Fig. 6a) as reflected by the long residence times observed
45 in Dourdan during both campaigns and in Viry during the June 2015 campaign (Table 2). The contribution of
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 the recently eroded particles up to 45% observed in Viry in August 2018 could be due to the occurrence of a
2 storm that generated extensive urban runoff one week before the sampling (Fig. 2) whereas, in June 2015,
3
4 sampling was conducted after 2 weeks of dry weather explaining the lower contribution of 26% of recent
5
6 particles for this campaign. Finally, average flow periods (i.e., Jan. 2016, Nov. 2016 and Dec. 2016),
7
8 characterized by frequent although low-intensity rainfall events (Fig. 2, Table 4) showed an intermediary
9
10 behaviour. In upper parts, the low contribution of recent particles (Fig. 6) reflected low soil erosion, supported
11
12 by a longer residence time of particles (Table 2), whereas the highest contribution of recently eroded particles
13
14 (Fig. 6) was found in lower river sections at Viry, reflecting the higher contribution of urban runoff in this area.
15
16
17
18
19
20
21
22

23 3.2. Contamination sources and magnitude

24 3.2.1. Local background

25 The local background signature was determined by the current research for the Orge catchment (Table 5). The
26
27 comparison with the literature shows the similarity of these values with those estimated for the entire Seine
28
29 Basin background. The latter values were estimated based on the analysis of riverbed sediment samples
30
31 collected in 56 small rural, agricultural and forested catchments across the Seine River basin and two additional
32
33 riverbed sediment samples collected in an archeological site (aged of 5000 BP) in Bercy (Paris *intramuros*)
34
35 (Horowitz et al., 1999; Thévenot et al., 2002). These background values were used in numerous studies
36
37 investigating the metallic contamination of sediment transiting the Seine River (Le Cloarec et al., 2011;
38
39 Meybeck et al., 2007; Thévenot et al., 2007).
40
41
42

43 The values of 11, 74, 0.6, 18 and 10 mg.kg⁻¹ respectively in Cu, Zn, Sb, Pb and Co measured in the Luvisol of
44
45 the Orge River catchment are similar with both UCC values and the Seine River background. However, higher
46
47 values in Cr and Ni of 69 and 32 mg.kg⁻¹, found in the Orge River catchment, could indicate a contamination of
48
49 the Luvisol by agricultural fertilizers especially for Cr (Le Pape et al., 2012).
50
51
52
53

54 3.2.2. Contamination of suspended particulate matter and particle sources

55 Enrichment factors (EF) were calculated (Chester & Stoner 1973) based on trace element concentrations in
56
57 SPM, agricultural soils, river bank and RDS provided in the Supplementary Material (Tables S1 and S3 for
58
59 SPM, Table S5 for potential particle sources):
60
61
62
63
64
65

$$EF = \frac{[TE]_{SPM}/[Al]_{SPM}}{[TE]_{background}/[Al]_{background}} \quad (5)$$

1
2
3 With [TE] the trace element concentration and [Al] the aluminum concentration in in mg.kg⁻¹ measured in SPM
4
5 and in the local Orge geochemical background as defined in Table 5.
6

7 Trace element concentrations and EF calculated in SPM collected in the Orge River (Table S1 and 3) did not
8
9 show any significant temporal variation throughout seasons or for different hydrological regimes.
10

11 In contrast, spatial variations were significant and they showed that changes in EF in SPM followed two trends.
12

13 First, Cu, Zn, Sb, Pb showed increasing EF values in downstream direction, with values ranging from 3 to 9 for
14
15 Cu, 2 to 7 for Zn, 3 to 6 for Pb and 2 to 7 for Sb. Significance of the differences observed between sites was
16

17
18 verified with a Kruskal-Wallis test and conclusive for all four contaminants. According to the literature
19

20 (Sutherland, 2000; Szuszkiewicz et al., 2016), an EF lower than 2 indicates a minimal contamination, moderate
21

22 contamination corresponds to EF varying between 2 and 5 and significant contamination is observed when EF
23

24 exceed 5. Accordingly, SPM from the Orge River catchment appears to be moderately contaminated in Dourdan,
25

26
27 Egly, Yvette, whereas it is considered to be significantly contaminated in Viry for Cu, Zn, Sb and Pb.
28

29 Furthermore, a significant correlation was observed between Cu-Zn-Sb-Pb with $r^2 > 0.9$ (Table S10) suggesting
30

31 the supply of these four contaminants by a common source likely located in urban areas found in the lower
32

33
34 catchment parts. Second, Ni, Co and Cr showed stable EF values ~1 throughout time for all three contaminants,
35

36 which likely indicates that these elements are provided by the geochemical background, and no enrichment is
37

38
39 observed in downstream direction.
40

41 Agricultural soils showed EF in Pb, Cu, Zn of respectively 2,3 and 1, which were lower than those found in
42

43 particles transiting the Orge River at the most upstream site in Dourdan (Fig. 7). In contrast, a significant
44

45 contamination in Sb was observed in agricultural soils, with an EF exceeding 5. As a comparison, channel banks
46

47 showed a significant contamination in Pb with an EF of 6 (Table S5), and EF similar to those found in
48

49 agricultural soils for Cu, Zn and Sb. Finally, road deposited sediments presented very high EF, beyond the range
50

51 of those found in the Orge SPM (Fig. 7), of 19 ± 7 for Pb, 38 ± 13 for Cu, 20 ± 11 for Zn and 71 ± 34 for Sb
52

53 (Table S5). Despite those disparities, agricultural soils and river banks showed EF in Co and Cr similar to those
54

55 found in SPM values, whereas slightly higher values were observed for RDS samples being moderately
56

57 contaminated. Accordingly, contamination rates found in RDS were in agreement with those results based on
58

radionuclide concentrations and demonstrated that urban areas provide a significant source of contaminated particles.

3.2.3. Lead isotopic signature of SPM and potential sources

All the lead isotope ratios are reported in Figure 8 and in Supplementary Material (Tables S2 and S10).

Lead isotopic ratios measured in SPM varied between 1.1845 ± 0.0010 and 1.1525 ± 0.0077 for $^{206}\text{Pb}/^{207}\text{Pb}$, and from 2.0780 ± 0.0019 to 2.1143 ± 0.0071 for $^{208}\text{Pb}/^{206}\text{Pb}$. Lead isotopic signatures in SPM plotted along a single line in the three isotope space diagram (Fig. 8), which indicates that the SPM signature results from a simple binary mixing of two sources of lead: a “natural source” and an “urban source”. After the quick decrease of the gasoline contribution to the lead signature since 2000 (Ayrault et al., 2012; Le Pape et al., 2013), the results of the current research confirm that leaded gasoline is not a dominant contamination source any more in the sediment transiting the Orge River more than 15 years after the ban.

The local background measured in the current research (Table 4) provides relevant values to calculate the natural background contribution. These background values remain close to those estimated for the Seine River background (Elbaz-Poulichet et al., 1986). In contrast, RDS showed isotopic signatures similar to those found in municipal solid waste combustors (MSWC) samples collected in Paris and Sète (southern France). The characteristics of MSWC fly ashes are considered to provide an “urban lead signature” (Ayrault et al., 2012; Carignan et al., 2005; Cloquet et al., 2006; Monna et al., 1997). The similar values found for French MSWC and RDS collected in the Orge River catchment confirm the relevance of using the latter values to characterize “urban lead” contaminating SPM transiting the Orge River.

These values suggest that RDS provide the major source of lead contamination to SPM transiting downstream sections of the Orge River. This result corroborates the findings derived from radionuclide measurements (section 3.1.1). Finally, the lead isotopic compositions provide a tool to discriminate between agricultural soil and channel banks that were characterized by similar radionuclide activities. Agricultural soils were characterized by higher $^{206}\text{Pb}/^{207}\text{Pb}$ signatures (1.1811 ± 0.0003) compared to channel banks (1.1761 ± 0.0043 to 1.1582 ± 0.0024). Furthermore, lower $^{208}\text{Pb}/^{206}\text{Pb}$ ratios were found in an agricultural soil sample (2.0813 ± 0.0069) compared to channel banks (2.0940 ± 0.0057 to 2.1079 ± 0.0065). The signatures measured in the SPM

1 collected at the upstream site (Dourdan) were very close to that of agricultural soil (Fig. 8a), suggesting that
2 cropland provided the major source of particles supplied to upper sections of the Orge River.
3

4 Finally, lead isotopic compositions in SPM did not change significantly for various hydrological regimes (low
5 stage waters vs. seasonal floods), demonstrating the occurrence of a steady source of Pb contamination in the
6 Orge River catchment despite those variations in particle transfer dynamics illustrated by changes in
7 radionuclide signatures.
8
9
10
11
12

13 14 15 16 17 4. Conclusions 18 19 20

21 The current research demonstrated based on multiple fallout radionuclide measurements that road deposited
22 sediments (RDS) provided a significant source of particles transiting an urban river representative of those
23 tributaries found in the Seine River basin, France, and in similar regions of the world characterized by extensive
24 legacy contamination. RDS were also shown to supply a major source of particle-bound contamination to the
25 river based on the examination of lead isotopic signatures. Furthermore, fallout radionuclide signatures
26 indicated that the contribution of sediment supplied by urban runoff increased when larger urban surfaces were
27 drained, although variations were observed for contrasting hydrological regimes. This trend was mainly
28 observed during low stage periods with a dominant contribution of urban areas, whereas a homogenization in
29 SPM signatures was found during seasonal floods with higher contributions of agricultural soils and channel
30 banks. This research also demonstrated the interest of coupling measurements of fallout radionuclides,
31 elemental and isotopic geochemistry to trace both particle-bound contamination sources and sediment dynamics
32 in urban catchments. In the future, this type of sediment tracing techniques could usefully be applied to organic
33 pollutants such as polycyclic aromatic hydrocarbons (PAH). This would improve our understanding of their
34 complex transfer in the environment and guide the implementation of effective management measures in order
35 to reduce the deleterious impacts generated by the supply of both organic and inorganic contaminants to urban
36 rivers.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Acknowledgements

This research was financially supported by the Paris-Sud University (PhD grant), the "Initiative de Recherche Stratégique" ACE-ICSEN funded by the University Paris-Saclay and the Seine River research program PIREN-Seine.

References

- Audry, S., Schafer, J., Blanc, G., Bossy, C., Lavaux, G., 2004. Anthropogenic components of heavy metal (Cd, Zn, Cu, Pb) budgets in the Lot-Garonne fluvial system (France). *Appl. Geochemistry* 19, 769–786. <https://doi.org/10.1016/j.apgeochem.2003.10.002>
- Ayrault, S., Le Pape, P., Evrard, O., Priadi, C.R., Quantin, C., Bonté, P., Roy-Barman, M., 2014. Remanence of lead pollution in an urban river system: A multi-scale temporal and spatial study in the Seine River basin, France. *Environ. Sci. Pollut. Res.* 21, 4134–4148. <https://doi.org/10.1007/s11356-013-2240-6>
- Ayrault, S., Roy-Barman, M., Le Cloarec, M.F., Priadi, C.R., Bonté, P., Göpel, C., 2012. Lead contamination of the Seine River, France: Geochemical implications of a historical perspective. *Chemosphere* 87, 902–910. <https://doi.org/10.1016/j.chemosphere.2012.01.043>
- Blake, W.H., Wallbrink, P.J., Wilkinson, S.N., Humphreys, G.S., Doerr, S.H., Shakesby, R.A., Tomkins, K.M., 2009. Deriving hillslope sediment budgets in wildfire-affected forests using fallout radionuclide tracers. *Geomorphology* 104, 105–116. <https://doi.org/10.1016/j.geomorph.2008.08.004>
- Carignan, J., Libourel, G., Cloquet, C., Le Forestier, L., 2005. Lead isotopic composition of fly ash and flue gas residues from municipal solid waste combustors in France: Implications for atmospheric lead source tracing. *Environ. Sci. Technol.* 39, 2018–2024. <https://doi.org/10.1021/es048693x>
- Chen, J., Gaillardet, J., Louvat, P., Huon, S., 2009. Zn isotopes in the suspended load of the Seine River, France: Isotopic variations and source determination. *Geochim. Cosmochim. Acta* 73, 4060–4076. <https://doi.org/10.1016/J.GCA.2009.04.017>
- Chester, R., Stoner, J.H., 1973. Pb in Particulates from the Lower Atmosphere of the Eastern Atlantic. *Nature* 245, 27–28. <https://doi.org/10.1038/245027b0>
- Chin, A., 2006. Urban transformation of river landscapes in a global context. *Geomorphology* 79, 460–487. <https://doi.org/10.1016/j.geomorph.2006.06.033>
- Cloquet, C., Carignan, J., Libourel, G., 2006. Atmospheric pollutant dispersion around an urban area using trace metal concentrations and Pb isotopic compositions in epiphytic lichens. *Atmos. Environ.* 40, 574–587. <https://doi.org/10.1016/j.atmosenv.2005.09.073>
- Cloquet, C., Carignan, J., Libourel, G., Sterckeman, T., Perdrix, E., 2006. Tracing source pollution in soils using cadmium and lead isotopes. *Environ. Sci. Technol.* 40, 2525–2530. <https://doi.org/10.1021/es052232+>
- Davies, K.S., Shaw, G., 1993. Fixation of ¹³⁷Cs by soils and sediments in the Esk Estuary, Cumbria, UK. *Sci. Total Environ.* 132, 71–92. [https://doi.org/10.1016/0048-9697\(93\)90262-5](https://doi.org/10.1016/0048-9697(93)90262-5)
- Dumas, C., Ludwig, W., Aubert, D., Eyrolle, F., Raimbault, P., Gueneugues, A., Sotin, C., 2015. Riverine transfer of anthropogenic and natural trace metals to the Gulf of Lions (NW Mediterranean Sea). *Appl. Geochemistry* 58, 14–25. <https://doi.org/10.1016/j.apgeochem.2015.02.017>
- Elbaz-Poulichet, F., Holliger, P., Martin, J.M., Petit, D., 1986. Stable lead isotopes ratios in major french rivers and estuaries. *Sci. Total Environ.* 54, 61–76. [https://doi.org/10.1016/0048-9697\(86\)90256-1](https://doi.org/10.1016/0048-9697(86)90256-1)
- Evrard, O., Beek, P. Van, Gateuille, D., Pont, V., Lefèvre, I., Lansard, B., Bonté, P., 2012. Evidence of the radioactive fallout in France due to the Fukushima nuclear accident. *J. Environ. Radioact.* 114, 54–60. <https://doi.org/10.1016/j.jenvrad.2012.01.024>
- Evrard, O., Lacey, J.P., Huon, S., Lefèvre, I., Sengtaheuanghoung, O., Ribolzi, O., 2016. Combining multiple fallout radionuclides (¹³⁷Cs, ⁷Be, ²¹⁰Pbxs) to investigate temporal sediment source dynamics in tropical, ephemeral riverine systems. *J. Soils Sediments* 1130–1144. <https://doi.org/10.1007/s11368-015-1316-y>
- Evrard, O., Némery, J., Gratiot, N., Duvert, C., Ayrault, S., Lefèvre, I., Poulenard, J., Prat, C., Bonté, P., Esteves,

- 1 M., 2010. Sediment dynamics during the rainy season in tropical highland catchments of central Mexico
2 using fallout radionuclides. *Geomorphology* 124, 42–54. <https://doi.org/10.1016/j.geomorph.2010.08.007>
- 3 Farmer, J.G., Eades, L.J., Atkins, H., Chamberlain, D.F., 2002. Historical Trends in the Lead Isotopic
4 Composition of Archival Sphagnum Mosses from Scotland (1838–2000). *Environ. Sci. Technol.* 36, 152–
5 157. <https://doi.org/10.1021/es010156e>
- 6 Foucher, A., Laceby, P.J., Salvador-blanes, S., Evrard, O., Le, M., Lefèvre, I., Cerdan, O., Rajkumar, V.,
7 Desmet, M., 2015. Quantifying the dominant sources of sediment in a drained lowland agricultural
8 catchment: The application of a thorium-based particle size correction in sediment fingerprinting.
9 *Geomorphology* 250, 271–281. <https://doi.org/10.1016/j.geomorph.2015.09.007>
- 10 Gallego, J., Sannier, C., Pennec, A., 2016. Validation of Copernicus Land Monitoring Services and Area
11 Estimation . <https://doi.org/10.1481/icasVII.2016.g42b>
- 12 Gasperi, J., Gromaire, M.C., Kafi, M., Moilleron, R., Chebbo, G., 2010. Contributions of wastewater, runoff
13 and sewer deposit erosion to wet weather pollutant loads in combined sewer systems. *Water Res.* 44, 5875–
14 5886. <https://doi.org/10.1016/j.watres.2010.07.008>
- 15 Gateuille, D., Evrard, O., Lefevre, I., Moreau-Guigon, E., Alliot, F., Chevreuil, M., Mouchel, J.-M., 2014. Mass
16 balance and decontamination times of Polycyclic Aromatic Hydrocarbons in rural nested catchments of
17 an early industrialized region (Seine River basin, France). *Sci. Total Environ.* 470–471, 608–617.
18 <https://doi.org/10.1016/j.scitotenv.2013.10.009>
- 19 Gellis, A.C., Fuller, C.C., Van Metre, P.C., 2017. Sources and ages of fine-grained sediment to streams using
20 fallout radionuclides in the Midwestern United States. *J. Environ. Manage.* 194, 73–85.
21 <https://doi.org/10.1016/j.jenvman.2016.06.018>
- 22 Grosbois, C., Meybeck, M., Horowitz, A., Ficht, A., 2006. The spatial and temporal trends of Cd , Cu , Hg , Pb
23 and Zn in Seine River floodplain deposits (1994 – 2000). *Sci. Total Environ.* 356, 22–37.
24 <https://doi.org/10.1016/j.scitotenv.2005.01.049>
- 25 Gulson, B.L., Mizon, K.J., Law, A.J., Korsch, M.J., Davis, J.J., Howarth, D., 1994. Source and pathways of
26 lead in humans from the Broken Hill mining community - an alternative use of exploration methods. *Econ.*
27 *Geol.* 89, 889–908. <https://doi.org/10.1007/BF00149589>
- 28 Hjortenkrans, D.S.T.T., Bergbäck, B.G., Häggerud, A. V., 2007. Metal emissions from brake linings and tires:
29 Case studies of Stockholm, Sweden 1995/1998 and 2005. *Environ. Sci. Technol.* 41, 5224–5230.
30 <https://doi.org/10.1021/es070198o>
- 31 Horowitz, A.J., Meybeck, M., Idrak, Z., Biger, E., 1999. Variations in trace element geochemistry in the
32 Seine River Basin based on floodplain deposits and bed sediments. *Hydrol. Process.* 1340, 1329–1340.
33 [https://doi.org/10.1002/\(SICI\)1099-1085\(19990630\)13:9<1329::AID-HYP811>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1099-1085(19990630)13:9<1329::AID-HYP811>3.0.CO;2-H)
- 34 Horowitz, A.J., Stephens, V.C., 2008. The effects of land use on fluvial sediment chemistry for the conterminous
35 U.S. - Results from the first cycle of the NAWQA Program: Trace and major elements, phosphorus,
36 carbon, and sulfur. *Sci. Total Environ.* 400, 290–314. <https://doi.org/10.1016/j.scitotenv.2008.04.027>
- 37 Huon, S., Evrard, O., Gourdin, E., Lefèvre, I., Bariac, T., Reyss, J.-L., Henry des Tureaux, T.,
38 Sengtaheuanghoung, O., Ayrault, S., Ribolzi, O., 2017. Suspended sediment source and propagation
39 during monsoon events across nested sub-catchments with contrasted land uses in Laos. *J. Hydrol. Reg.*
40 *Stud.* 9, 69–84. <https://doi.org/10.1016/j.ejrh.2016.11.018>
- 41 Juillot, F., Maréchal, C., Morin, G., Jouvin, D., Cacaly, S., Telouk, P., Benedetti, M.F., Ildefonse, P., Sutton,
42 S., Guyot, F. Bois, Brown, G.E., 2011. Contrasting isotopic signatures between anthropogenic and
43 geogenic Zn and evidence for post-depositional fractionation processes in smelter-impacted soils from
44 Northern France. *Geochim. Cosmochim. Acta* 75, 2295–2308. <https://doi.org/10.1016/j.gca.2011.02.004>
- 45 Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: A
46 review. *Environ. Int.* 34, 562–577. <https://doi.org/10.1016/j.envint.2007.10.005>
- 47 Le Cloarec, M.F., Bonte, P.H., Lestel, L., Lefèvre, I., Ayrault, S., 2011. Sedimentary record of metal
48 contamination in the Seine River during the last century. *Phys. Chem. Earth* 36, 515–529.
49 <https://doi.org/10.1016/j.pce.2009.02.003>
- 50 Le Gall, M., Evrard, O., Dapigny, A., Tiecher, T., Zafar, M., Minella, J.P.G., Laceby, J.P., Ayrault, S., 2017a.
51 Tracing Sediment Sources in a Subtropical Agricultural Catchment of Southern Brazil Cultivated With
52 Conventional and Conservation Farming Practices. *L. Degrad. Dev.* 28, 1426–1436.
53 <https://doi.org/10.1002/ldr.2662>
- 54 Le Gall, M., Evrard, O., Foucher, A., Laceby, J.P., Salvador-Blanes, S., Manière, L., Lefèvre, I., Cerdan, O.,
55 Ayrault, S., 2017b. Investigating the temporal dynamics of suspended sediment during flood events with
56
57
58
59
60
61
62
63
64
65

- 7Be and 210Pbxs measurements in a drained lowland catchment. *Sci. Rep.* 7, 1–10.
<https://doi.org/10.1038/srep42099>
- Le Pape, P., Ayrault, S., Michelot, J.-L., Monvoisin, G., Noret, A., Quantin, C., 2013. Building an isotopic hydrogeochemical indicator of anthropogenic pressure on urban rivers. *Chem. Geol.* 344, 63–72.
<https://doi.org/10.1016/j.chemgeo.2013.02.018>
- Le Pape, P., Ayrault, S., Quantin, C., 2012. Trace element behavior and partition versus urbanization gradient in an urban river (Orge River, France). *J. Hydrol.* 472–473, 99–110.
<https://doi.org/10.1016/j.jhydrol.2012.09.042>
- Le Pape, P., Quantin, C., Morin, G., Jouvin, D., Kieffer, I., Proux, O., Ghanbaja, J., Ayrault, S., Le Pape, P., 2014. Zinc Speciation in the Suspended Particulate Matter of an Urban River (Orge, France): Influence of Seasonality and Urbanization Gradient. *Environ. Sci. Technol.* 48, 11901–11909.
<https://doi.org/10.1021/es500680x>
- Lorgeoux, C., Moilleron, R., Gasperi, J., Ayrault, S., Bonté, P., Lefèvre, I., Tassin, B., Bonté, P., Lefèvre, I., Tassin, B., 2016. Temporal trends of persistent organic pollutants in dated sediment cores: Chemical fingerprinting of the anthropogenic impacts in the Seine River basin, Paris. *Sci. Total Environ.* 541, 1355–1363. <https://doi.org/10.1016/j.scitotenv.2015.09.147>
- Matisoff, G., Bonniwell, E.C., Whiting, P.J., 2002. Radionuclides as Indicators of Sediment Transport in Agricultural Watersheds that Drain to Lake Erie. *J. Environ. Qual.* 31, 62.
<https://doi.org/10.2134/jeq2002.6200>
- Matisoff, G., Wilson, C.G., Whiting, P.J., 2005. The 7Be/210Pbxs ratio as an indicator of suspended sediment age or fraction new sediment in suspension. *Earth Surf. Process. Landforms* 30, 1191–1201.
<https://doi.org/10.1002/esp.1270>
- Meybeck, M., 2001. Global alteration of riverine geochemistry under human pressure, in: Ehlers, E and Krafft, T. (Ed.), *Understanding the Earth System: Compartments, Processes and Interactions*. Springer-Verlag Berlin, Heidelberg, Platz 3, D-14197 Berlin, Germany, pp. 97–113.
- Meybeck, M., Lestel, L., Bonté, P., Moilleron, R., Colin, J.L., Rousselot, O., Hervé, D., de Pontevès, C., Grosbois, C., Thévenot, D.R., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). *Sci. Total Environ.* 375, 204–231. <https://doi.org/10.1016/j.scitotenv.2006.12.017>
- Meybeck, M., Lestel, L., Carré, C., Bouleau, G., Garnier, J., Mouchel, J.M., 2016. Trajectories of river chemical quality issues over the Longue Durée: the Seine River (1900S–2010). *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-016-7124-0>
- Middelkoop, H., 2000. Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands. *Netherlands J. Geosci. - Geol. en Mijnb.* 79, 411–427. <https://doi.org/10.1017/S0016774600021910>
- Monna, F., Benothman, D., Luck, J., 1995. Pb isotopes and Pb, Zn and Cd concentrations in the rivers feeding a coastal pond (Thau, southern France): constraints on the origin(s) and flux(es) of metals. *Sci. Total Environ.* 166, 19–34. [https://doi.org/10.1016/0048-9697\(95\)04514-2](https://doi.org/10.1016/0048-9697(95)04514-2)
- Monna, F., Croudace, I.A.N.W., Cundy, A.B., Lewis, J.T., 1997. Pb Isotopic Composition of Airborne Particulate Material from France and the Southern United Kingdom: Implications for Pb Pollution Sources in Urban Areas. *Environ. Sci. Technol.* 31, 2277–2286. <https://doi.org/10.1021/es960870+>
- Nelson, E.J., Booth, D.B., 2002. Sediment sources in an urbanizing, mixed land-use watershed. *J. Hydrol.* 264, 51–68. [https://doi.org/10.1016/S0022-1694\(02\)00059-8](https://doi.org/10.1016/S0022-1694(02)00059-8)
- Ollivier, P., Radakovitch, O., Hamelin, B., 2011. Major and trace element partition and fluxes in the Rhône River. *Chem. Geol.* 285, 15–31. <https://doi.org/10.1016/j.chemgeo.2011.02.011>
- Pratt, C., Lottermoser, B.G., 2007. Mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments, Cairns, northern Australia. *Environ. Geol.* 52, 437–448.
<https://doi.org/10.1007/s00254-006-0471-2>
- Priadi, C., Ayrault, S., Pacini, S., Bonté, P., 2011a. Urbanization impact on metals mobility in riverine suspended sediment: Role of metal oxides. *Int. J. Environ. Sci. Technol.* 8, 1–18.
- Priadi, C., Bourgeault, A., Ayrault, S., Gourlay-Francé, C., Tusseau-Vuillemin, M.-H., Bonté, P., Mouchel, J.-M., 2011b. Spatio-temporal variability of solid, total dissolved and labile metal: passive vs. discrete sampling evaluation in river metal monitoring. *J. Environ. Monit.* 13, 1470.
<https://doi.org/10.1039/c0em00713g>
- Rabalais, N.N., Turner, R.E., Justić, D., Dortch, Q., Wiseman, W.J., Gupta, B.K. Sen, Justic, D., 1996. Nutrient Changes in the Mississippi River and System Responses on the Adjacent Continental Shelf. *Estuaries* 19,

386. <https://doi.org/10.2307/1352458>

- Roy, S., 1996. Utilisation des isotopes du plomb et du strontium comme traceurs des apports anthropiques et naturels dans les précipitations et les rivières du bassin de Paris. PhD thesis. Paris VII University.
- SAGE Orge-Yvette, 2011. Actualisation de l'état des lieux et du diagnostic.
- Sakaguchi, A., Yamamoto, M., Sasaki, K., Kashiwaya, K., 2006. Uranium and thorium isotope distribution in an offshore bottom sediment core of the Selenga Delta, Lake Baikal, Siberia. *J. Paleolimnol.* 35, 807–818. <https://doi.org/10.1007/s10933-005-5621-0>
- Santschi, P.H., Presley, B.J., Wade, T.L., Garcia-Romero, B., Baskaran, M., 2001. Historical contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. *Mar. Environ. Res.* 52, 51–79. [https://doi.org/10.1016/S0141-1136\(00\)00260-9](https://doi.org/10.1016/S0141-1136(00)00260-9)
- Schneider, V., 2005. Apports de l'hydrodynamique et de la géochimie à la caractérisation des nappes de l'Oligocène et de l'Eocène et à la reconnaissance de leurs relations actuelles et passées: origine de la dégradation de la nappe de l'Oligocène (sud-ouest du bassin de Paris). PhD Thesis. Paris-Sud University.
- Shapiro, S.S., Wilk, M.B., 1965. An Analysis of Variance Test for Normality (Complete Samples). *Biometrika* 52, 591. <https://doi.org/10.2307/2333709>
- Siegel, S., Castellan, N.J., 1988. Nonparametric statistics for the behavioral sciences, McGraw-Hill.
- Smith, H.G., Blake, W.H., 2014. Sediment fingerprinting in agricultural catchments: A critical re-examination of source discrimination and data corrections. *Geomorphology* 204, 177–191. <https://doi.org/10.1016/j.geomorph.2013.08.003>
- Sutherland, R. a., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol.* 39, 611–627. <https://doi.org/10.1007/s002540050473>
- Szuskiewicz, M., Łukasik, A., Magiera, T., Mendakiewicz, M., 2016. Combination of geo- pedo- and technogenic magnetic and geochemical signals in soil profiles – Diversification and its interpretation: A new approach. *Environ. Pollut.* 214, 464–477. <https://doi.org/10.1016/j.envpol.2016.04.044>
- Thévenot, D.R., Meybeck, M., Lestel, L., 2002. Métaux lourds : des bilans en mutation, Rapport de synthèse Piren-Seine 1998-2002.
- Thévenot, D.R., Moilleron, R., Lestel, L., Gromaire, M.C., Rocher, V., Cambier, P., Bonté, P., Colin, J.L., de Pontevès, C., Meybeck, M., 2007. Critical budget of metal sources and pathways in the Seine River basin (1994-2003) for Cd, Cr, Cu, Hg, Ni, Pb and Zn. *Sci. Total Environ.* 375, 180–203. <https://doi.org/10.1016/j.scitotenv.2006.12.008>
- Vaasjoki, M., Gulson, B.L., 1985. Evaluation of drilling priorities using lead isotopes at the Lady Loretta lead-zinc-silver deposit, Australia. *J. Geochemical Explor.* 24, 305–316. [https://doi.org/10.1016/0375-6742\(85\)90040-8](https://doi.org/10.1016/0375-6742(85)90040-8)
- Véron, A., Flament, P., Bertho, M.L., Alleman, L., Flegel, R., Hamelin, B., 1999. Isotopic evidence of pollutant lead sources in northwestern France. *Atmos. Environ.* 33, 3377–3388. [https://doi.org/10.1016/S1352-2310\(98\)00376-8](https://doi.org/10.1016/S1352-2310(98)00376-8)
- Viers, J., Dupré, B., Gaillardet, J., 2008. Chemical composition of suspended sediments in World Rivers : New insights from a new database. *Sci. Total Environ.* 407, 853–868. <https://doi.org/10.1016/j.scitotenv.2008.09.053>
- Von Uexküll, O., Skerfving, S., Doyle, R., Braungart, M., 2005. Antimony in brake pads-a carcinogenic component? *J. Clean. Prod.* 13, 19–31. <https://doi.org/10.1016/j.jclepro.2003.10.008>
- Vörösmarty, C.J., McIntyre, P.B., Gessner, M.O., Dudgeon, D., Prusevich, A., Green, P., Glidden, S., Bunn, S.E., Sullivan, C.A., Liermann, C.R., Davies, P.M., 2010. Global threats to human water security and river biodiversity. *Nature* 467, 555–561. <https://doi.org/10.1038/nature09440>
- Widory, D., Fiani, E., Le Moullec, Y., Gruson, S., Gayraud, O., 2004. Development of a method for characterising contributions of point sources to atmospheric emissions of particles using a multi-isotopic approach. Application to the urban area of Paris. BRGM Report.
- Wilkinson, S.N., Hancock, G.J., Bartley, R., Hawdon, A.A., Keen, R.J., 2013. Using sediment tracing to assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin, Australia. *Agric. Ecosyst. Environ.* 180, 90–102. <https://doi.org/10.1016/J.AGEE.2012.02.002>
- Wong, C.S.C., Li, X., Thornton, I., 2006. Urban environmental geochemistry of trace metals. *Environ. Pollut.* 142, 1–16. <https://doi.org/10.1016/j.envpol.2005.09.004>

1
2
3
4
5
6
7 Figure captions:
8
9

10 Figure 1 : Orge River catchment: location, land use characteristics and monitoring stations (Source of
11 the land use data: Corine Land Cover, 2012)
12
13

14 Figure 2 : River discharge and precipitation recorded in the Orge River catchment from May 2015 to
15 December 2016

16 Mean water discharge at Viry site (Red dotted line). Low flow campaigns (Orange): June 2015
17 (28/05/2015 - 03/06/2015) and August 2015 (24/08/2016 - 29/08/2016). Average flow campaigns
18 (Green): January 2016 (21/01/2016 – 25/01/2016), November 2016 (16/11/2016 – 22/11/2016) and
19 December 2016 (5/12 and 15/12/2016). High flow campaigns (Blue): September 2015 (16/09/2015 –
20 21/09/2015) and April 2016 (07/04/2016 – 11/04/2016). Flood campaign (Black): June 2016 (2, 3 and
21 6/06/2016).
22
23
24

25 Figure 3: ^{137}Cs contents in Bq.kg^{-1} for SPM collected at D, E, Y, V, as well as in potential sources
26 (channel bank, agricultural soil, forest soil and Road Deposited Sediment). Values characterized by the
27 same letter (a, b or c) are not significantly different at the $\alpha = 0.05$ level
28
29
30

31 Figure 4: ^7Be and $^{210}\text{Pb}_{\text{xs}}$ activities measured in SPM collected at the four river stations (**a: Spatial**
32 **variations**) during contrasted hydrological regimes (**b: Temporal variations**), as well as in RDS at the
33 outlet site Viry, and in potential sources (agricultural soils, **urban soils**, channel banks and forest soils)
34
35
36

37 **Figure 5: Contribution of recently eroded particles to the Orge River particles estimated with the linear**
38 **mixing model (a) and the $^7\text{Be}/^{210}\text{Pb}_{\text{xs}}$ ratio model (b) following the increasing urbanization gradient in**
39 **the catchment and for different hydrological regimes.**
40
41

42 Figure 6: Relationship between the proportion of recently tagged particles and of impervious surfaces in
43 a 5-km wide area around each monitoring station and for various hydrological regimes ((a) Low stage
44 periods: Janv.2016, Nov.2016, Dec.2016, Jun.2015, Aug.2016 and (b) Seasonal floods: Sept.2015,
45 Apr.2016).
46
47
48

49 Figure 7: Enrichment Factors in trace elements in Suspended Particulate Matter collected at the 4
50 monitoring stations in the Orge River **along with EF of agricultural soils (black dotted line), river bank**
51 **samples (black solid line), and RDS (black double dashed line)**. Blue **dashed** line: lower limit of moderate
52 contamination; Red **dashed** line: lower limit of the significant contamination level.
53
54
55

56 Figure 8: Lead isotopic signatures found in contrasted soil/sediment samples collected in the Orge River
57 catchment and in potential sources: (a) Lead isotopic signatures of French gasoline (Monna et al., 1997;
58 Roy, 1996); Industrial lead estimated from French Municipal Solid Waste Combustors from Sete and
59 Paris (Monna et al., 1997; Widory et al., 2004); Road Deposit from the Orge (this study); Suspended
60 Particulate Matter from the Orge River (this study); Local background (this study); Agricultural soil from
61
62
63
64
65

1 Dourdan (this study) and channel bank (this study). (b) SPM lead signatures obtained at each river
2 monitoring site (Dourdan (D): circle, Egly (E): inverted triangle, Yvette (Y): triangle, Viry (V): square)
3 and for contrasted hydrological regimes (seasonal floods (SF): orange, low stage periods (LSP): blue)
4
5
6
7
8
9

10 Table captions:

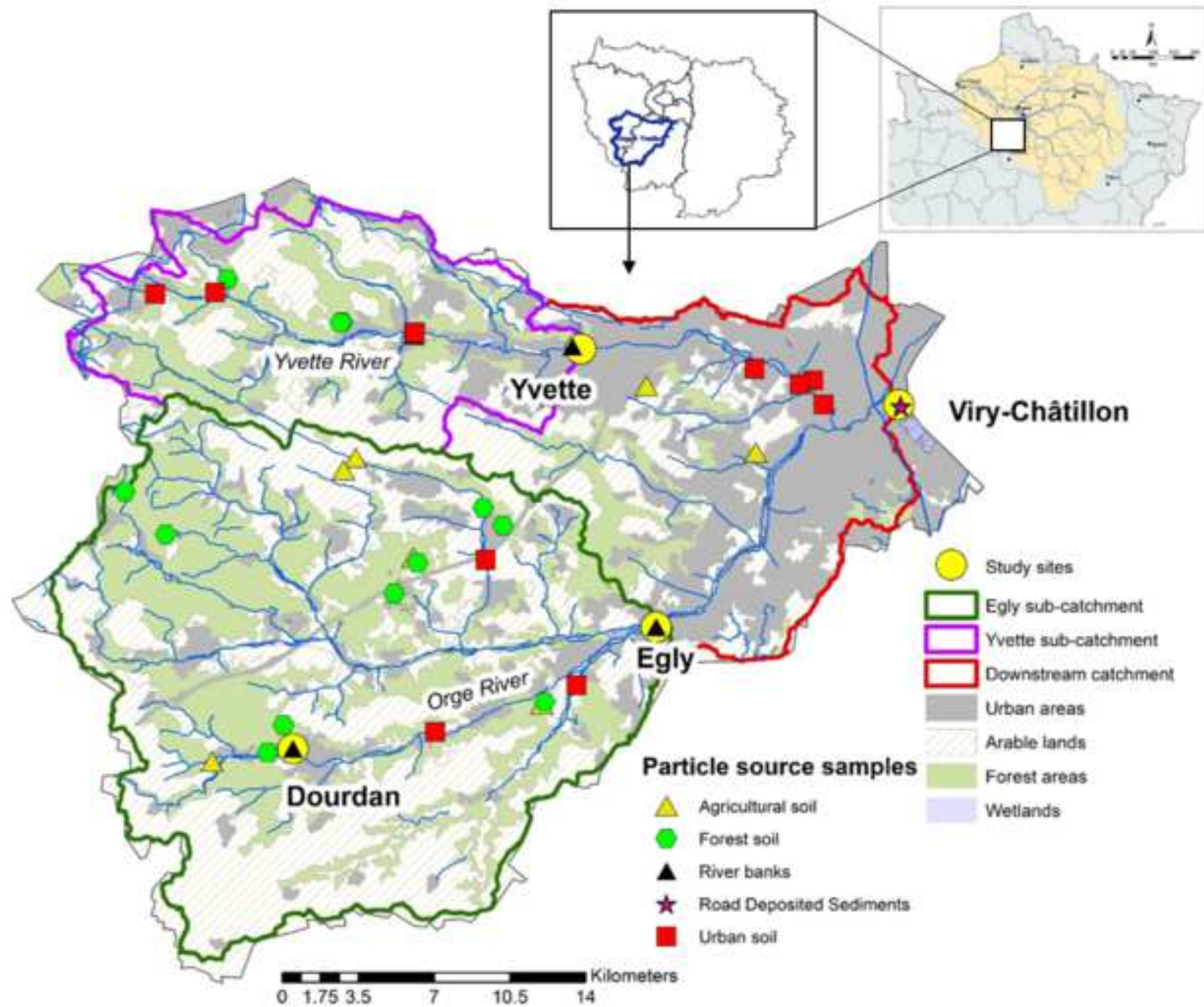
11
12 Table 1: Land use proportions and population densities in the Orge River sub-catchments drained by the
13 river monitoring sites
14

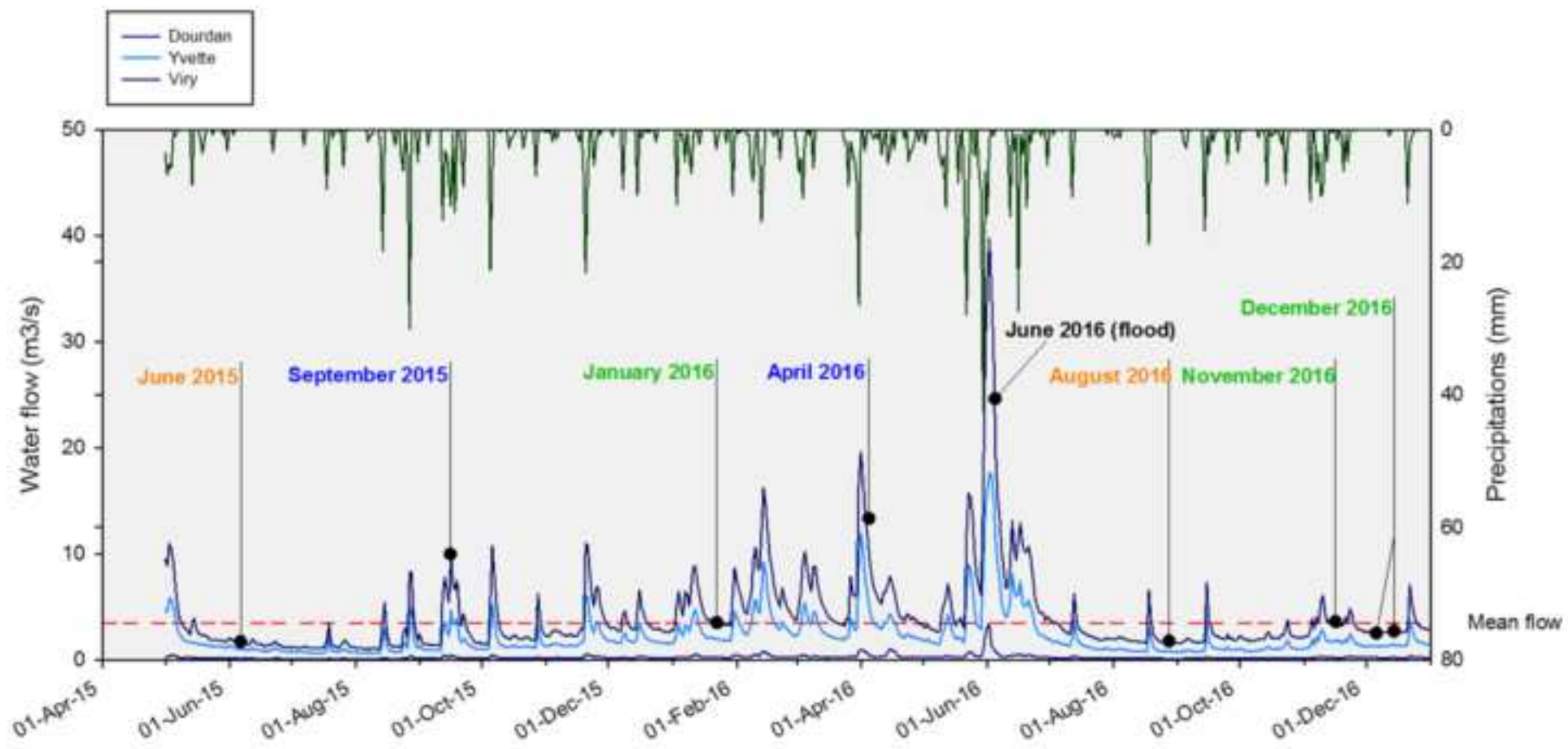
15
16 Table 2: Mean particle residence times and associated standard errors estimated for SPM samples
17 collected at each river station
18

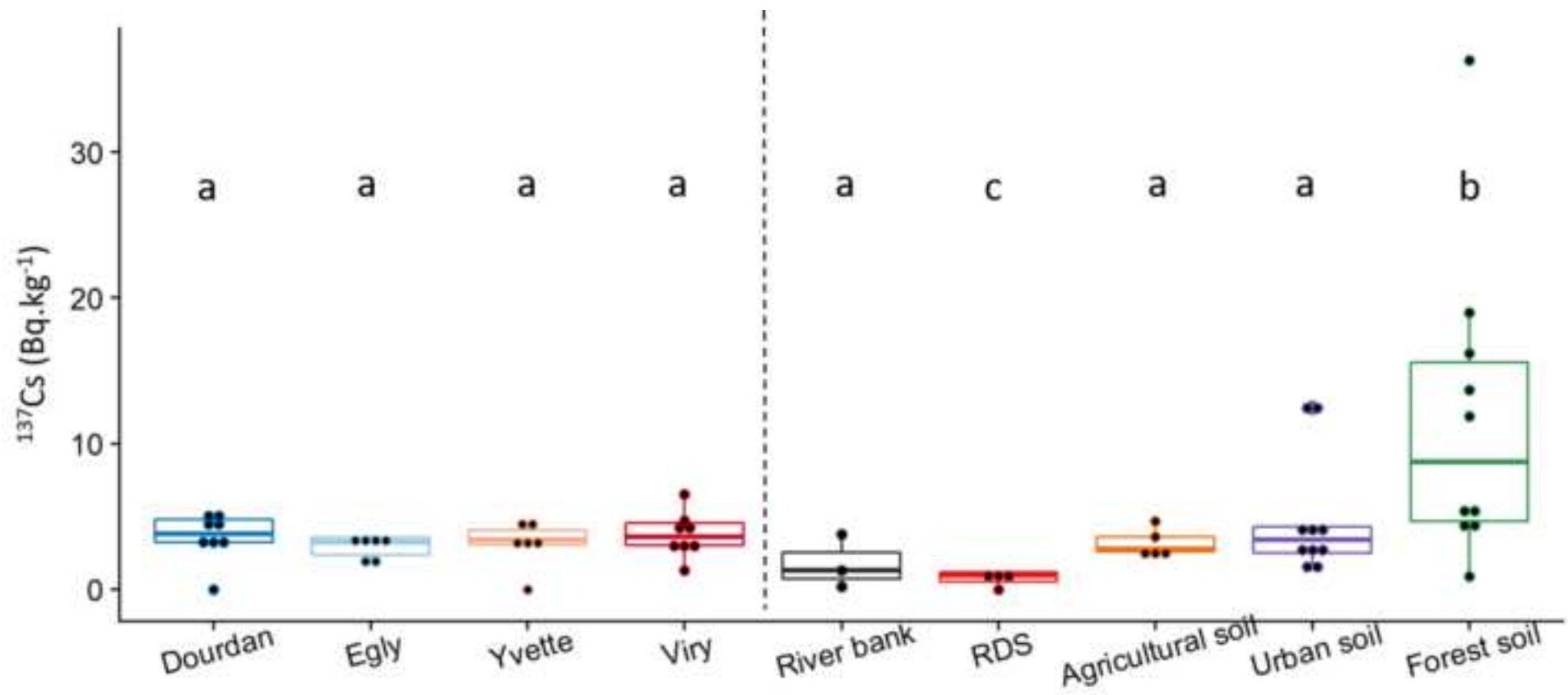
19
20
21 Table 3: Proportions of impervious surfaces in the area located in a 2.5, 5 and 10km radius from each
22 river monitoring station as well as in the drainage area of each station
23

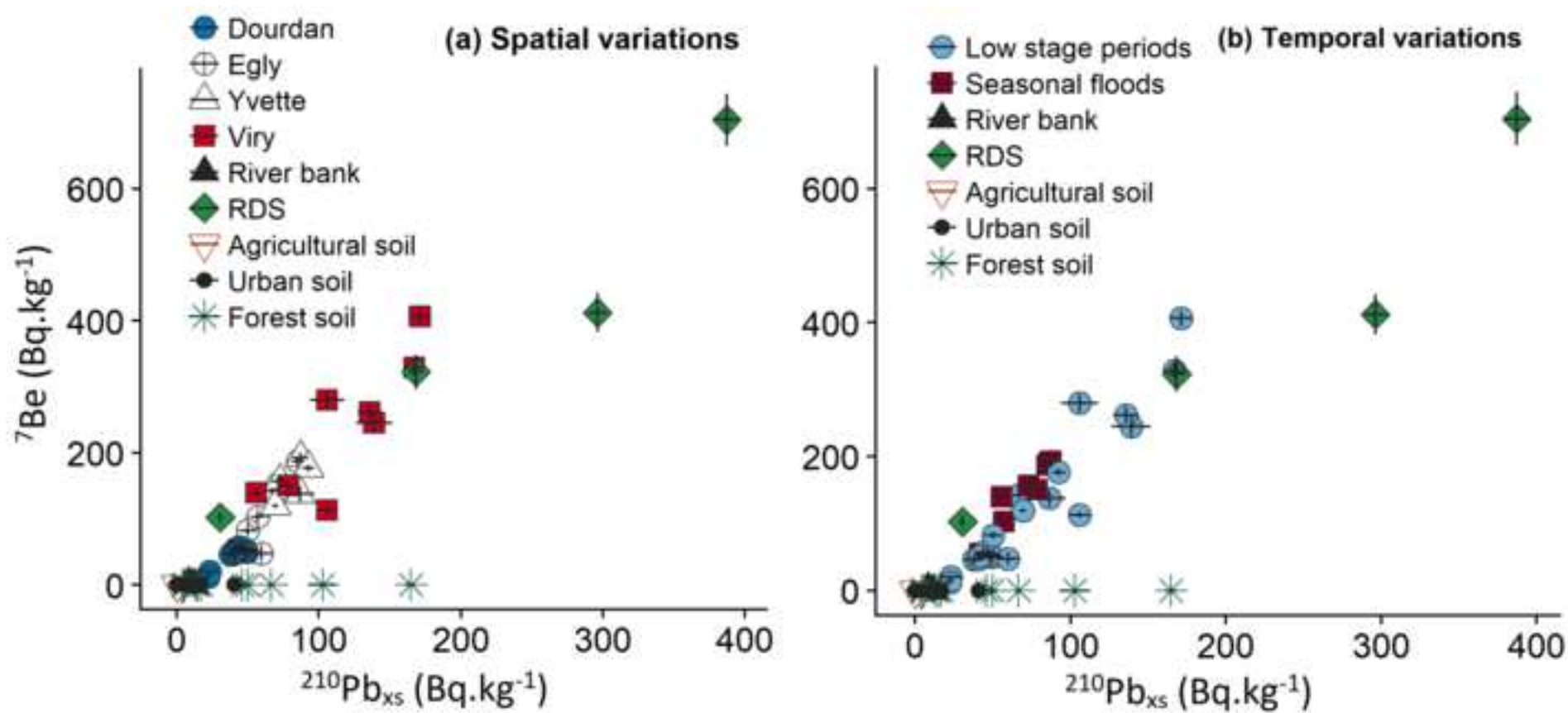
24
25 Table 4: Characteristics of antecedent precipitation recorded before sampling campaigns during the study
26 period in Dourdan (upstream part) and Bretigny-sur-Orge (downstream part), with water flow measured
27 at the outlet.
28

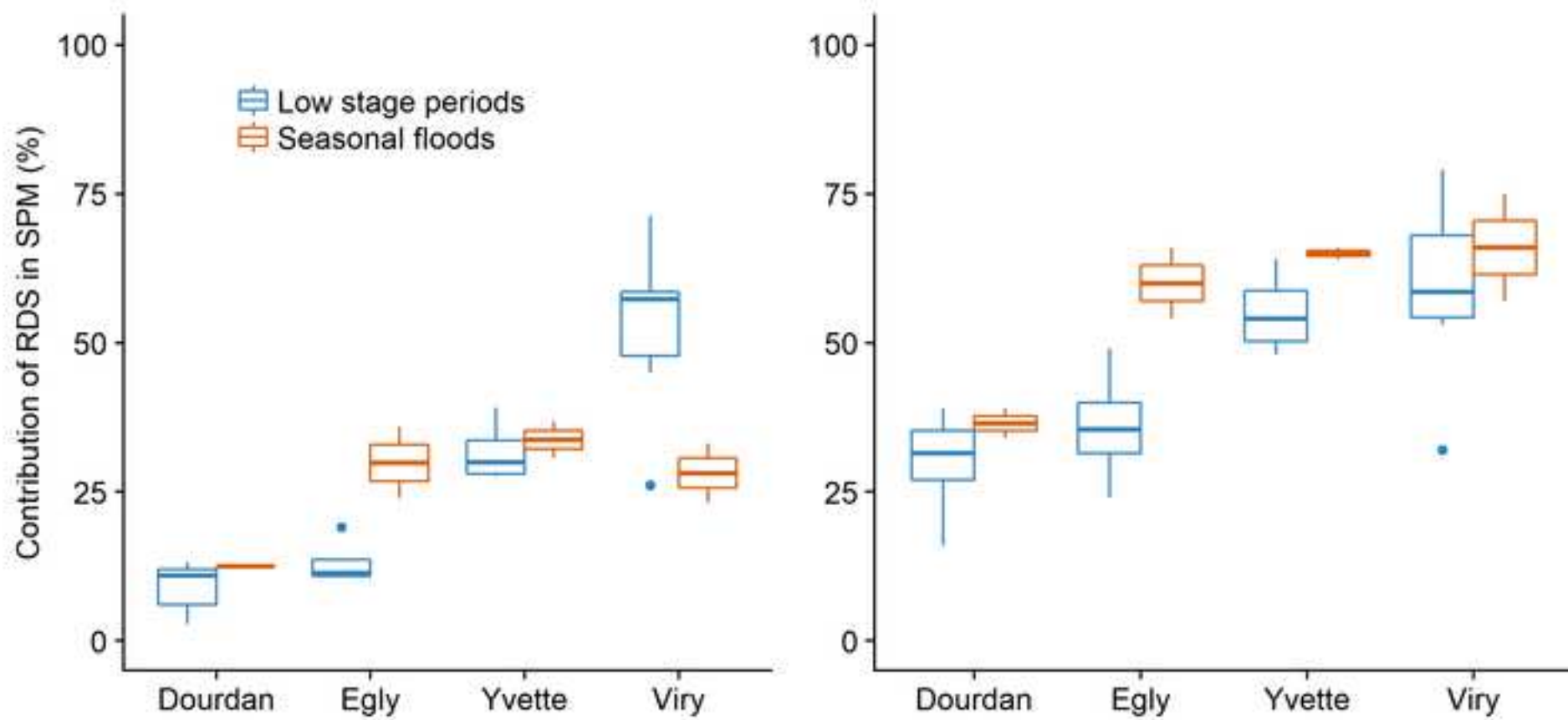
29
30 Table 5: Comparison of the metal background values defined for the Seine River (Thévenot et al., 2002)
31 for the Orge River (this study) and the Upper Continental Crust (Taylor and McLennan, 1995)
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

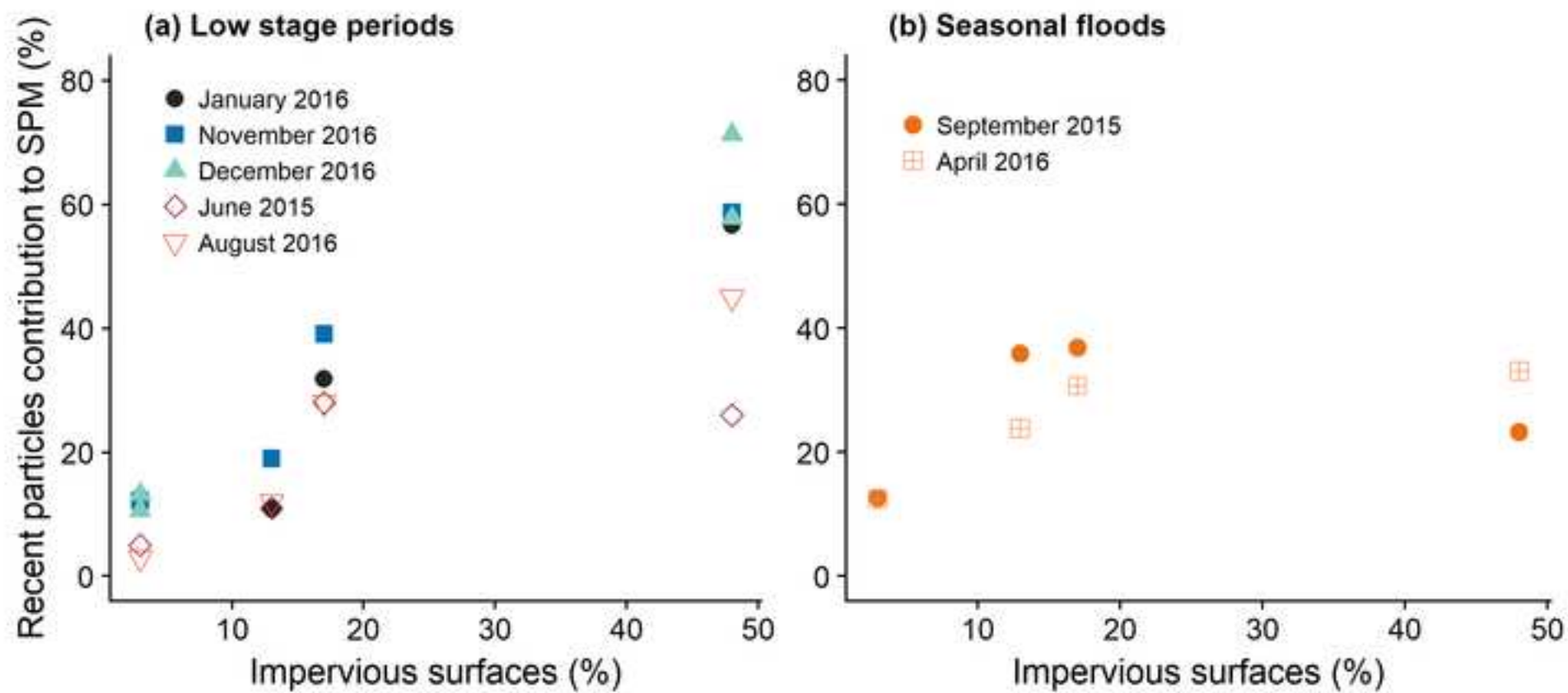


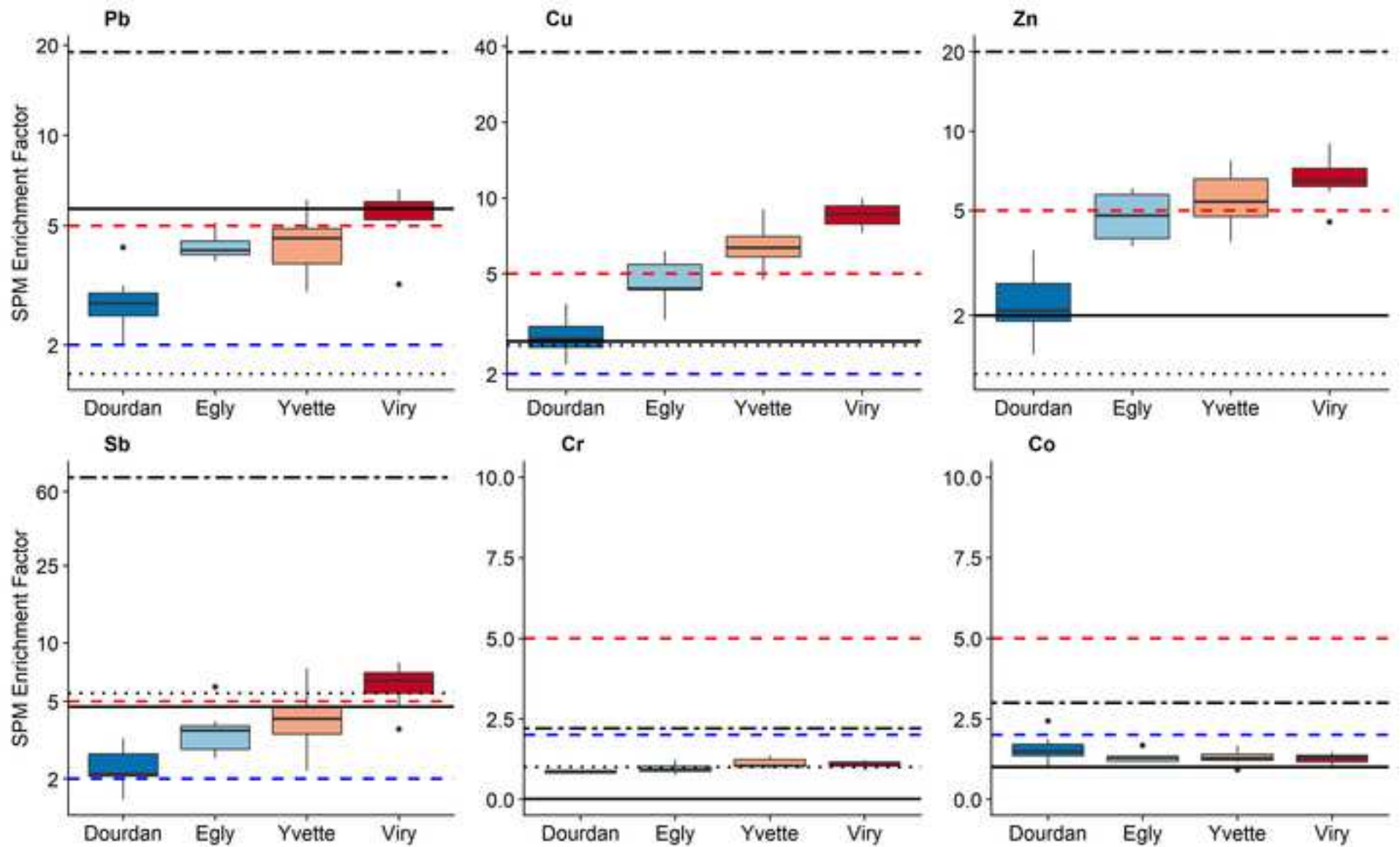












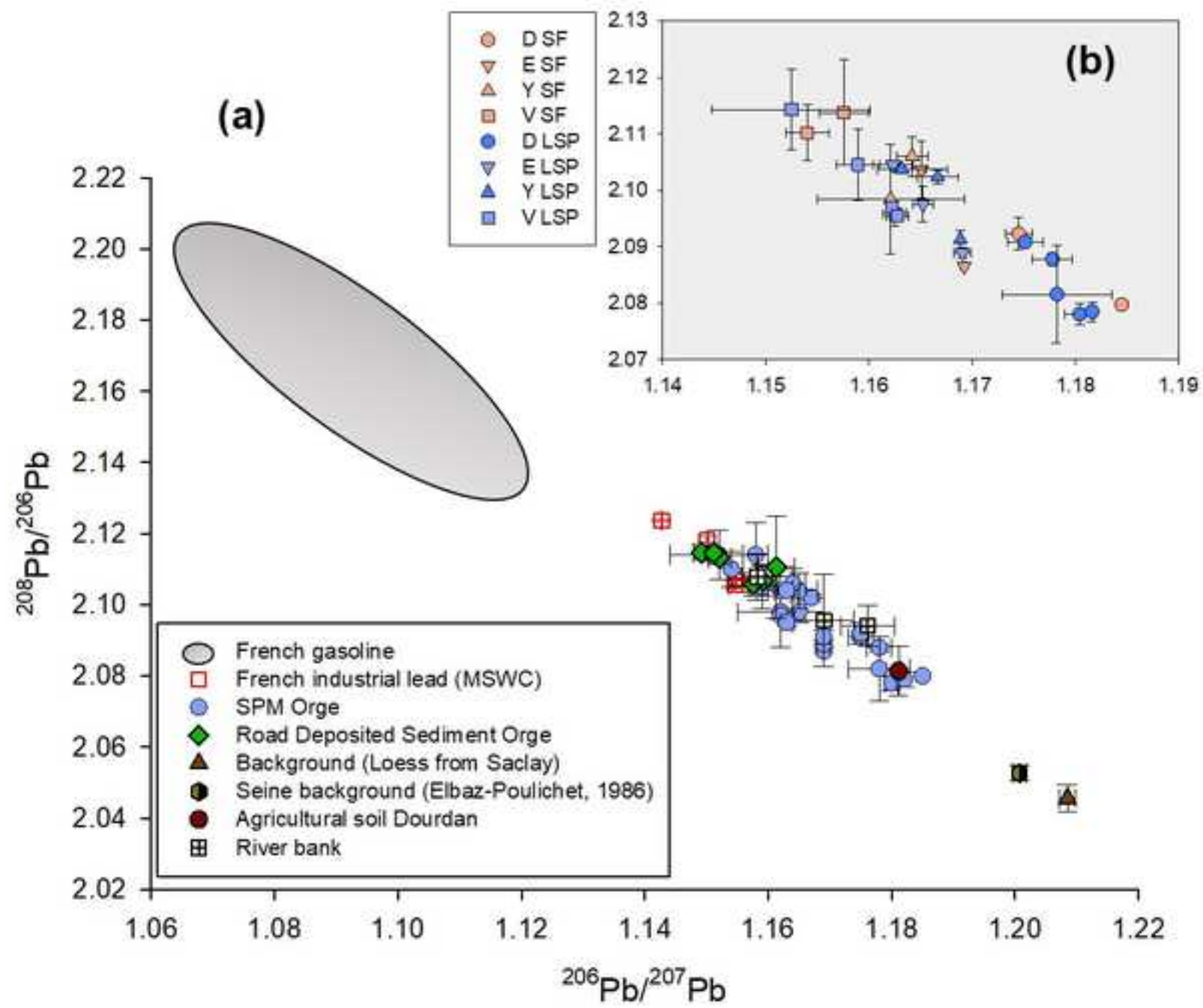


Table1

Sub-catchments	Dourdan	Egly	Yvette	Viry (outlet)
Urban areas (%)	1	11	20	56
Agricultural land (%)	86	49	42	33
Forests (%)	12	40	38	12
Population density (inhabitants.km⁻²)	300	1400	2100	5000

Table2

	June 2015	September 2015	January 2016	April 2016	August 2016	November 2016	December 2016	Mean value	SD
	Residence time (days)								
Dourdan	105	72	94	83	140	86	78	94	23
Egly	83	32	111	48	77	55	-	68	28
Yvette	35	32	57	34	51	43	-	42	10
Viry	88	22	49	43	18	26	41	41	22

Site	Impervious surfaces proportion (%)			
	2.5km	5km	10km	Sub-watershed
Dourdan	8	3	2	3
Egly	19	13	11	4
Yvette	25	17	15	9
Viry	52	48	43	12

Table4

	Water flow at the outlet ($\text{m}^3.\text{s}^{-1}$)	Antecedent precipitation during the 7 previous days (mm)		Mean precipitation per day ($\text{mm}.\text{d}^{-1}$)		Percentage of rainy days during the 2 weeks prior to sampling (rainfall amount > 2 mm)	
		Dourdan	Bretigny-sur-Orge	Dourdan	Bretigny-sur-Orge	Dourdan	Bretigny-sur-Orge
September 2015	6.5	58.7	22.8	12	6	33	33
April 2016	6.0	24.4	33.8	5	7	25	25
June 2015	1.9	1.4	1.4	0	1	0	0
August 2016	1.7	5.2	24.5	1	8	8	17
January 2016	3.5	1.4	1.8	0	1	25	25
November 2016	3.5	5	15.3	1	3	50	50
December 2016	3.1	6	2.4	1	0	17	4

Table5

	Cr	Co	Ni	Cu	Zn mg.kg⁻¹	Sb	Pb	Al
Luvisol (Saclay plateau soil)	69	10	31	11	74	0.6	18	49700
Seine background^{a, b}	40	9	16	15	60	0.8	20	33000
Upper Continental Crust^c	35	10	20	25	71	0.2	20	80400

^a: Thévenot et al. 2002; ^b: Le Cloarec et al. 2011; ^c: Taylor & McLennan 1995



[Click here to access/download](#)

Supplementary Material

[Supplementary_Froger_et_al_revised_VF.docx](#)

