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Mass balance and decontamination times of Polycyclic Aromatic Hydrocarbons in rural nested catchments of an early industrialized region (Seine River basin, France)

D. Gateuille, O. Evrard, Irene Lefevre, Elodie Moreau-Guigon, Fabrice Alliot, Marc Chevreuil, Jean-Marie Mouchel

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1 **Mass balance and decontamination times of**
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3 **Polycyclic Aromatic Hydrocarbons in rural nested**
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6 **catchments of an early industrialized region (Seine**
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9 **River basin, France)**

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12 David Gateuille^{1,2*}, Olivier Evrard¹, Irène Lefevre¹, Elodie Moreau-Guigon²,

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14 Fabrice Alliot², Marc Chevreuil², Jean-Marie Mouchel²

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18
19 ¹ Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Unité Mixte
20
21 de Recherche 8212 (CEA-CNRS-UVSQ/IPSL), Gif-sur-Yvette, France

22
23 ² Structure et fonctionnement des systèmes hydriques continentaux (Sisyphe),
24
25 Unité mixte de Recherche 7619 (UPMC-CNRS-EPHE), Paris, France

26
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28 * david.gateuille@lsce.ipsl.fr
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33 **Abstract** Accumulation of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and their
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35 subsequent release in rivers constitute a major environmental and public health problem in
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37 industrialized countries. In the Seine River basin (France), some PAHs exceed the target
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39 concentrations, and the objectives of good chemical status required by the European Water Framework
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41 Directive might not to be achieved. This investigation was conducted in an upstream subcatchment
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43 where atmospheric fallout (n=42), soil (n=33), river water (n=26) and sediment (n=101) samples were
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45 collected during one entire hydrological year. PAH concentrations in atmospheric fallout appeared to
46
47 vary seasonally and to depend on the distance to urban areas. They varied between 60 ng.L⁻¹ (in a
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49 remote site during autumn) and 2380 ng.L⁻¹ (in a built-up area during winter). PAH stocks in soil of
50
51 the catchment were estimated based on land use, as mean PAH concentrations varied between 110
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53 ng.g⁻¹ under woodland and 2120 ng.g⁻¹ in built-up areas. They ranged from 12 to 220 kg.km². PAH
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55 contamination in the aqueous phase of rivers remained homogeneous across the catchment (72±38
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26 ng.L⁻¹). In contrast, contamination of suspended solid was heterogeneous depending on hydrological
27 conditions and population density in the drainage area. Moreover, PAH concentrations appeared to be
28 higher in sediment (230-9210 ng.g⁻¹) than in the nearby soils. Annual mass balance calculation
29 conducted at the catchment scale showed that current PAH losses were mainly due to **dissipation**
30 **(biodegradation, photo-oxidation and volatilization) within the catchments** (about 80%) whereas
31 exports due to soil erosion and riverine transport appeared to be of minor importance. Based on the
32 calculated fluxes, PAHs appeared to have long **decontamination** times in soils (40 to 1850 years)
33 thereby compromising the achievement of legislative targets. **Overall, the study highlighted the major**
34 **role of legacy contamination that supplied the bulk of PAHs that are still found nowadays in the**
35 **environment.**

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37
38 **Keywords** Contamination; Polycyclic Aromatic Hydrocarbons (PAHs); catchment; transfers; Seine
39 River; **decontamination** time.

40 41 **1. Introduction**

42 Reducing environmental contamination constitutes a major challenge for industrialized and
43 developing countries. Certain contaminants such as Polycyclic Aromatic Hydrocarbons (PAHs), a
44 large family of organic substances that are mainly released by the incomplete combustion of organic
45 matter (**OM**), are problematic because of their high toxicity and their known carcinogenic properties
46 for animals and humans (Rocher et al., 2006; Srogi, 2007). This public health **and environmental**
47 imperative is reinforced by **European** law. In the European Union, the Water Framework Directive
48 (WFD; Directive 2000/60/EC) requires that the member state water bodies reach good ecological and
49 chemical status by 2015, 2021 or 2027 (**see Suppl. Mat., section 1**). PAH contamination is widespread
50 in Western Europe (Nam et al., 2008), and this issue is particularly emblematic in the Seine River
51 basin where **high PAH** concentrations are being measured in sediment or water (Ollivon et al., 1995;

52 Gasperi et al., 2009) in more than 50% of water bodies, thereby compromising the achievement of the
1
2 53 good chemical status (AESN, 2010).
3

4 54 Although emissions have decreased during the last decades in Western Europe (Pacyna et al.,
5
6 55 2003), a large amount of PAHs have been released into the atmosphere for the last two centuries
7
8 56 (Fernández et al., 2000). In these regions, the current release of these compounds is **mainly** associated
9
10 57 with household heating and road traffic (Baek et al., 1991; Pacyna et al., 2003). Depending on their
11
12 58 volatility, PAHs delivered to the atmosphere exist in free vapor form or in association with
13
14 59 atmospheric particles (Lohmann & Lammel, 2004; Galarneau et al., 2006) and the gas/particle
15
16 60 partition is a critical parameter to understand their deposition on soils, vegetation or impervious
17
18 61 surfaces (Demircioglu et al., 2011; Simonich et Hites, 1994).
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22 62 Once deposited **onto** the ground, PAHs tend to be sorbed by the **organic matter** (Soares et al.,
23
24 63 2013). Several degradation and transport processes may take place in soils such as microbial activities,
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26 64 humification, volatilization, chemical and photo-oxidation. The rates of the degradation processes
27
28 65 depend on the conditions (O₂, temperature, pH, etc.) under which they occur, and PAH half-life in the
29
30 66 environment is generally reported to vary between a few days and several years (Aprill et al., 1990). In
31
32 67 addition to those degradation losses, PAHs may also be leached from impervious surfaces (**Krein and**
33
34 68 **Schorer, 2000; Bomboi and Hernandez, 1991**), or removed from soils through the erosion of particles
35
36 69 **to which they are bound** (Zheng et al., 2012). At the catchment scale, fluxes of PAHs **bound to the**
37
38 70 **suspended solid** (SS) mainly depend on sedimentary dynamics with main export of PAHs occurring
39
40 71 during floods (Mourhi et al., 2008; Conaway et al., 2012).
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44 72 In recent years, studies dealing with PAHs have grown in number but most of them were
45
46 73 restricted to the measurement of **PAH concentrations** in one of the different compartments of the
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48 74 environment (air, soil, sediment, water, vegetation) (e.g. **Blanchard et al., 2007; Van Metre et al.,**
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50 75 **2008; Gasperi et al., 2009; Villanneau et al., 2013**). In this context, there remains a lack of knowledge
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52 76 about the transfers between environmental compartments and, consequently, about the persistence of
53
54 77 these compounds in the environment. To our knowledge, there have been few attempts in the literature
55
56 78 to draw up a total PAH budget calculated at the catchment scale (**Bressy et al., 2012; Motelay-Massei**
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58 79 **et al., 2007**). Due to the spatial distribution of human activities, PAH contamination may be very
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80 heterogeneous within catchments. Furthermore, the wide range of sources emitting PAHs complicates
81 the complete understanding of transfers of these compounds in the environment. In order to better
82 constrain them, differences in their chemical signatures and in the relative abundance of the distinct
83 compounds may be used to better understand their origin and pathways in the environment (Guo,
84 2003; Soclo et al., 2000; Yunker et al., 2002). [More importantly, so far and to our knowledge, the
85 relative contribution of dissipation \(biodegradation, photo-oxidation and volatilization\) and
86 hydrosedimentary processes to PAH losses at the catchment scale has not been quantified.](#)

87 By monitoring PAH concentrations in different compartments along a network of nested
88 subcatchments (draining areas from 4.7 km² to 12,192 km²) for an entire hydrological year, this study
89 aims at addressing this knowledge gap and at providing a better understanding of PAH transfer
90 pathways at the catchment scale. To this end, (1) PAH concentrations were measured in the different
91 compartments of a catchment, (2) the stocks were quantified, (3) the dynamics of PAHs were assessed
92 in space and time and (4) the [decontamination](#) times of PAHs in soils were estimated by calculating a
93 mass balance and by quantifying the relative contribution of [dissipation](#) and hydrosedimentary
94 processes to PAH losses in the catchment. Overall, this [study may](#) be representative of the
95 contaminant concentrations and the processes involved in their transfer in lowland rural catchments of
96 early industrialized countries. The results of this study provide new insights on PAH transfers in the
97 environment, which will have significant implications for the potential achieving of water/sediment
98 quality guidelines required by the [European Union](#).

100 **2. Materials and methods**

101 Details on analysis methods, stocks and mass balance calculations, as well as estimation of
102 uncertainties are provided in the supplementary material.

103 **2.1. Study site**

104 In this study, we conducted a nested approach by installing sediment traps along a [network of
105 nested subcatchments within](#) the 104-km² Orgeval catchment. [The network was completed by a set of
106 traps along the Grand Morin River, further downstream of the Orgeval catchment outlet.](#) The Orgeval

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107 catchment is located 70 km eastward from Paris City (Fig. 1). Climate is semi-oceanic. Mean annual
108 rainfall measured since 1963 amounts to 646 mm, but the 12-month study period was drier than the
109 average with 540 mm. The prevailing winds blow mainly from the southwest and the west, or from the
110 northeast. Monthly mean temperature ranges from 0.6 °C (January) up to 18 °C (August), and the
111 annual mean temperature is about 11 °C. The Orgeval catchment is dominated by cropland and
112 grassland (covering 82% of the total surface), the rest of the surface being occupied by woodland
113 (17%) and built-up areas (including roads, <1%). However, the catchment is likely to be influenced by
114 major urban areas as potential atmospheric inputs from Paris conurbation may be expected (Blanchard
115 et al., 2007). About 90 % of the cultivated area is tile drained. The catchment is characterized by
116 gentle slopes (2.5%) with a mean altitude of 148 m.

118 2.2. Monitoring of hydrological and meteorological parameters

119 Hydrological and meteorological parameters have been monitored by IRSTEA (Institut
120 national de Recherche en Science et Technologies pour l'Environnement et l'Agriculture) since 1963
121 in the Orgeval catchment (Tallec, 2012). SS and surface water sampling sites were located close to
122 existing gauging stations. Flows were measured using ultrasonic flow sensors. Automatic samplers
123 collected 500 mL of water daily. Determination of SS concentrations in water was made by filtering
124 every 2-day composite samples on borosilicate glass microfiber filters with a 0.7-µm porosity
125 (Whatman ® GF / F). Rainfall depth was measured at 3 stations across the catchment, located close to
126 C1, C2 and T2* sampling sites.

128 2.3. Sampling

129 In order to better understand the pathways of PAHs at the catchment scale, atmospheric
130 fallout, soil, river water and suspended sediment samples have been collected in several locations
131 inside the nested subcatchments for 7 to 12 months. Sampling sites are shown in Fig. 2, most stations
132 were located within the Orgeval catchment, but additional river stations were installed along the
133 downstream Grand Morin and Marne Rivers to better investigate the spatial changes of PAH

134 [contamination in river water and sediment](#). Input fluxes from the atmosphere were estimated by
1 measuring the total concentration of PAHs in [atmospheric fallout \(n=42\)](#) and rainfall [depth](#) in the
2 135 catchment from June 2011 to April 2012. Three 0.06 m² and one 0.36 m² collectors have been installed
3 136 across the catchment to collect [the total](#) deposition and to document the spatial variability of
4 137 atmospheric fallout (Fig. 2). The 0.36-m² collector was placed on the highest point, i.e. the Butte de
5 138 Doue [C2] (180 m altitude). The 3 others collectors were respectively situated at Boissy-le-Châtel
6 139 [C3] ([garden in a small town](#)), Melarchez [C1] ([rural grassland](#)) and Chantemerle [C4] (organic
7 140 cropland). Samples were collected every two weeks to limit contaminant volatilization (Gladkte et al.,
8 141 2012; Ollivon et al., 2002). Samples were taken back to the laboratory inside 1-L liter glass bottles
9 142 placed in an ice box at 4°C. The extraction protocol was carried out within the week that followed
10 143 sampling.
11 144

145 Soils [samples \(n=33\) were collected at](#) several sites selected in order to cover the entire range of land
146 uses observed in the catchment (i.e., intensive [farming](#) [S1] and organic cropland [field](#) [S4], grassland
147 [S2], woodland [S5] and urban soils [S3]). At each site, 10 subsamples of surface material (top 8 cm)
148 were collected and mixed to provide a homogeneous sample from which 3 aliquots were taken. Coarse
149 organic fragments were removed from the surface layer. Soils were sampled at a minimum distance of
150 50 m from the closest road to avoid short range PAH deposition and to be representative of the entire
151 plot of land. Once collected, samples were placed in glass recipients over ice, and carried back to the
152 laboratory to be freeze-dried.

153 Finally, PAH concentrations in [aqueous phase \(n=26\)](#) and suspended sediment (SS) ([n=101](#))
154 were measured. Suspended sediment samples were collected at 9 nested stations between 30 March
155 2011 and 10 April 2012. Metallic cylindrical traps submerged into the water were used to collect
156 monthly SS. [After collection](#), samples were [kept at 4°C for 24h](#) to allow decantation. After this period,
157 the supernatant was removed and decanted solids were freeze-dried. Filtrations carried out on
158 supernatant showed that more than 99% of suspended sediment were [recovered](#) during decantation.
159 [Suspended sediment](#) sample collection was carried out [at 9 stations](#): Upstream Melarchez [T1] (4.2
160 km²), Melarchez [T2] (5.9 km²), La Loge [T2*] (6.4 km²), Les Avenelles [T3] (46 km²), Le Theil [T4]
161 (104 km²), Coubertin [T5] (721 km²), Montry [T6] (1206 km²), Condé-Ste-Libiaire [T6*] (10,946

162 km²) and Trilbardou [T7] (12,192 km²). Figure 3 illustrates the main characteristics (i.e. air
163 temperature, rainfall and river discharge) that prevailed during and between the successive fieldwork
164 campaigns.

2.4. Determination of PAHs

167 After extraction and purification, PAHs were analyzed by gas chromatography (Agilent GC
168 system 7890A) coupled with a mass spectrometer (Agilent 5975C inert XL MSD). MS signal
169 acquisition was performed in Selected Ion Monitoring (SIM) mode. Thirteen US EPA PAHs could be
170 determined: Acenaphtylene (ACY), Acenaphtene (ACE), Fluorene (FLU), Phenanthrene (PHE),
171 Anthracene (ANT), Fluoranthene (FTH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR),
172 Benzo(b)fluoranthene + Benzo(k)fluoranthene (BbF+BkF), Benzo(a)pyrene (BaP), and
173 Benzo(g,h,i)perylene (BghiP). Organic carbon was measured using a CHN Elemental Analyzer to
174 determine the carbon weight percentage in soil samples after carbonate removal.

2.5. Stock, mass balance and decontamination time calculations

Stock calculation

178 PAH stocks in soils of four upstream catchments were calculated based on land use (farmland,
179 woodland or built-up areas) using the following equation (Eq. 1). Areas covered by each land use in
180 the catchment were determined using the CORINE Land Cover 2006 database.

$$St = \sum_{i=1}^3 1350 \times U_i \times D_i \times C_i \quad (1)$$

182 Where St (g) is the PAH stock in the catchment. U_i is the area (m²) of the catchment under the i^{th} land
183 use and D_i (m) is the corresponding soil contaminated layer depth. Observed ploughing depth within
184 the Orgeval catchment vary between 0.10 and 0.40 m. Consequently, thickness of contaminated soils
185 was estimated to be equal to the mean ploughing depth (0.25 m) in arable fields and to the sampling
186 depth (0.08 m) in areas under other land uses, thereby neglecting a potential PAH transfer to the
187 deeper layers. The latter assumption is supported by previous results (Krauss et al., 2000) showing that
188 PAH concentration in soils decreased rapidly with depth under woodland. Doick et al. (2005) reported

189 that PAH contamination in soils under cropland was homogenous in the ploughed layer, and that it
190 rapidly decreased below. C_i (g.kg^{-1}) is the mean value of PAH concentration in samples collected in
191 soils under the i^{th} land use and 1350 (kg.m^{-3}) is the estimated bulk density of dry soil (McGrath and
192 Lane, 1989).

194 Mass balance calculation

195 Mass balance calculations were performed in four upstream subcatchments based on an
196 estimation of daily fluxes between 11 April 2011 and 10 April 2012. These catchments were chosen
197 because their limited size allowed a good estimation of incoming fluxes, and direct urban releases
198 were considered to be negligible as built-up areas occupied only a small proportion ($< 0.2\%$) of the
199 catchment surface (Eq. 2).

$$200 \quad \Phi_{at.fallout} = \Phi_{riv.export} + \Phi_{dissipation} + \Delta St \quad (2)$$

201 Where $\Phi_{at.fallout}$ is the atmospheric fallout (g.yr^{-1}) and it was hypothesized to represent the total
202 incoming fluxes. Under this assumption, PAH supply by local sources (especially roads) was
203 neglected. $\Phi_{riv.export}$ is the flux of PAHs exported (g.yr^{-1}) by the river in both particulate and aqueous
204 phases. ΔSt was the stock variation (g.yr^{-1}) calculated between the beginning (February 2011) and the
205 end (March 2012) of the sampling period. A dissipation term $\Phi_{dissipation}$, corresponding to the losses of
206 PAHs (g.yr^{-1}) within the catchment (mainly biodegradation, photo-oxidation and volatilization), was
207 added to close the mass balance and to decipher the difference measured between input and export
208 fluxes that could not be explained by the stock variation.

210 Decontamination times

211 According to the WHO (1998), the half-life of PAHs in soils can vary from a few days for the
212 lightest compounds up to several years for the heaviest ones. In this study, decontamination times
213 were calculated in each catchment by dividing the estimated stocks accumulated in soils by the sum of
214 the annual riverine export fluxes, in both stream water and suspended solid, and the estimated annual
215 dissipation (Eq. 3).

1 216
$$DT = \frac{St}{\Phi_{riv.export} + \Phi_{dissipation}} \quad (3)$$

2
3
4 217 Where DT is the decontamination time (year), St is the PAH stocks in soils, $\Phi_{riv.export}$ is the annual
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6 218 riverine export and $\Phi_{dissipation}$ is the annual losses in the catchment. These decontamination times are
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8 219 equivalent to the time required to remove all PAHs from soil when hypothesizing that there is no
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10 220 additional PAH supply.

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12 222 Uncertainties

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15 223 In this study, some uncertainties were related to the hypotheses made to close the mass
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17 224 balance calculation. First, we assumed that the wet and dry deposition of PAHs represented the total
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19 225 atmospheric input therefore neglecting the gaseous exchange (both deposition and volatilization). Few
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21 226 studies compared the order of magnitude of gaseous exchanges and the contribution of dry and wet
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23 227 deposition (Demircioglu et al., 2011; Park et al., 2001). However, gaseous exchange values were not
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25 228 directly measured but estimated based on models and the studies were conducted in specific
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27 229 environmental conditions (i.e. high PAH atmospheric concentration and a low soil contamination). It
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29 230 appeared that gaseous exchanges could be responsible for a significant fraction of the air-soil transfer,
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31 231 especially for low molecular weight PAHs. Based on the results reported by Demircioglu et al.
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33 232 (2011)), an order of magnitude of the gaseous exchange had been estimated and the influence of this
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35 233 hypothesis on the calculated decontamination times is discussed below (section 3.6). Secondly, due to
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37 234 the contamination heterogeneity within the plots, uncertainties might also have arisen from the stock
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39 235 variation calculation as change in mean concentration could have been detected only if higher than
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41 236 10%. Mass balance calculations were therefore carried out by assuming that there was no change in
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43 237 PAH stocks. This assumption is discussed below (section 3.5) based on historical trends of
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45 238 atmospheric deposition.

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47 239 Uncertainties may also arise from the flux measurements and they can be quantified (see
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49 240 Suppl. Mat., section 5). Overall, uncertainties on the SS flux, the aqueous riverine export of PAHs and
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51 241 the atmospheric input were respectively below 16, 11 and 5 % (except for T2* where uncertainties on
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53 242 aqueous export reached 35%).

3. Results and discussion

3.1. Atmospheric fallout

Fallout of PAHs in the Orgeval catchment was quantified (n=42) and results are reported in Table 1. Although there were some local differences in atmospheric fallout, time-averaged concentration in rainwater (295 ng.L⁻¹, SD: 40 ng.L⁻¹) remained uniform across the catchment with the exception of the collector located in the built-up area [C3] where periods with higher contamination were observed. This spatial homogeneity suggested that a significant fraction of the contamination originated from regional sources located outside of the catchment. The mean estimated deposition flux (157 µg.m⁻² . yr⁻¹) was of the same order of magnitude as previously reported by Motelay-Massei et al. (2007) (70 µg.m⁻² .yr⁻¹) and Blanchard et al. (2007) (78 µg.m⁻² .yr⁻¹) in other rural areas of the Seine River basin. In contrast to this rather good spatial homogeneity, large temporal variations in fallout were observed. Maximal incoming fluxes were measured during the first intense rainfall event of the cold period in early December and during the cold spell of February. The temporal trends observed at the 4 study sites were very similar and showed a significant increase in PAH atmospheric fallout during winter (p<0.001; Mann-Whitney test). Such a rise in winter was reported in other studies, and it may be related to the increase in use of household heating (Bozlaker et al., 2008; Motelay-Massei et al., 2003). Individual heating devices using fossil fuels are known to be a major source of PAHs in urban areas (Orasche et al., 2012). Moreover, low temperatures lead to a shift in the gas/particle distribution of PAHs (Kaupp et MacLachlan, 1999; Liu et al., 2013) and concentrations of PAHs bound to particles are therefore usually higher in winter (Galarneau et al., 2006).

3.2. Soils

The total PAH concentrations were measured in soils (n = 33) from plots under different land uses (Table 2). The highest contamination was observed in Boissy-le-Châtel town (S3) with a mean concentration in PAHs of 2120 ± 1590 ng.g⁻¹ (n = 8). Surprisingly, PAH concentrations in soils from this small town (3110 inhab. in 2010) were in the same order of magnitude as reported from more industrialized parts of the Seine River basin (450-5650 ng.g⁻¹) (Motelay-Massei et al., 2004). In

270 contrast, the most contaminated rural areas displayed PAH concentrations that were about 5 times
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2 271 lower ($395 \pm 190 \text{ ng.g}^{-1}$ at the S1 conventional farming site), and the difference was even 20-fold
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4 272 lower at the less contaminated sites ($120 \pm 30 \text{ ng.g}^{-1}$ at S2 and $110 \pm 20 \text{ ng.g}^{-1}$ at S5). The high
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6 273 variability of PAH concentration observed at S3 urban site suggested a highly significant influence of
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8 274 soil disturbance as well as very local pollutant sources.

10
11 275 PAH concentrations measured under conventional (S1) and organic farming cropland (S4, 250
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13 276 $\pm 20 \text{ ng.g}^{-1}$) were two- to threefold higher than the ones measured under grassland (S2) and woodland
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15 277 (S5). Cropland was not amended with sewage sludge so that the difference may be explained by the
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17 278 direct pollution generated by the use of agricultural machinery for farming operations (Phoungthong et
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19 279 al., 2013). This may also explain the high variability of PAH concentrations observed within the
20
21 280 cultivated plot as ploughing operations may lead to short-scale redistribution of surface particles
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23 281 (Chartin et al., 2013). Finally, the strong similarity of PAH concentrations measured in soils collected
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25 282 under forests and grassland (110 ng.g^{-1}) suggested that they corresponded to the regional
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27 283 contamination background signal supplied by atmospheric inputs alone.

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29 284 Additional information about sources was provided by calculating several diagnostic PAH
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31 285 ratios (see Suppl. Mat. Table F). The different ratios provided consistent results in all the samples, and
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33 286 showed that PAH contamination in the Orgeval catchment mainly originated from pyrolytic sources
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35 287 (Yunker et al., 2002; Hu et al., 2012). Some statistical differences were detected between soils under
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37 288 different land use types especially for the PHE/(ANT+PHE) ratio for which values were significantly
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39 289 lower ($p < 0.001$) in urban and agricultural soils (0.72 ± 0.05) compared to other land uses ($0.83 \pm$
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41 290 0.02). This difference highlights a larger contribution of residential heating sources to urban soil
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43 291 contamination whereas the higher values found in agricultural soils may be due to a stronger influence
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45 292 of petroleum combustion sources (Sicre et al., 1987). When calculating the FLH/(FLH+PYR) ratio,
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47 293 values appeared to be significantly higher ($p < 0.001$) under conventional farming ($0.56 \pm 0.01 \%$ at
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49 294 S1) than under other land uses ($0.54 \pm 0.01 \%$). This may be due to the contribution of an additional
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51 295 petrogenic source in cropland.

52
53 296 Measurement of PAH concentrations in soils under different land uses allowed to estimate the
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55 297 PAH stocks in the subcatchments. The largest stocks (220 kg.km^{-2}) were found in the vicinity of built-

298 up areas where local emission sources are concentrated. The stocks estimated in cropland were lower
299 on average [than in built-up areas, even though](#) they remained of the same order of magnitude (130
300 kg.km⁻²). This may be explained by mechanical burying of contaminants during ploughing ([Wild et
301 al., 1990](#)). Indeed, PAHs found in deep horizons [may be](#) partially protected from soil erosion and the
302 changes in physico-chemical parameters (absence of light, lower nutrient content, etc.) may limit their
303 biodegradation ([Levanon et al., 1994](#)). In contrast, surface horizons with high organic matter content
304 under woodland and grassland may prevent PAH from migration in the soil (Krauss et al., 2000). In
305 this context, PAHs are [likely](#) trapped in layers where the highest biodegradation rates are observed.
306 This might explain the limited stocks estimated under grassland and woodland.

307 This result demonstrates the relevance of considering land use to provide quantitative
308 estimations of the stocks accumulated within the subcatchments. This shows the strong effect of local
309 urban sources, even in small towns, and the impact of agricultural activities on soil contamination.

311 3.3. Surface waters

312 Although PAHs are preferentially found in the particulate phase, the aqueous phase may play
313 an important role in PAH transfers across catchments characterized by low sediment yields.

314 Concentrations of PAHs measured in the aqueous phase at 5 sampling sites are shown in [Table 3](#). The
315 mean value of PAH contamination in all samples was 72 ± 38 ng.L⁻¹. No spatial trend could be [found](#)
316 along the upstream/downstream transect [and no statistical difference was detected between the low](#)
317 [stage and the flood periods. The present results allowed to quantify the order of magnitude of the PAH](#)
318 [fluxes transported in the aqueous phase \(3.9 - 6.9 g.km⁻².yr⁻¹\)](#).

319 3.4. Suspended Solid

320 PAH concentrations measured in SS during the study period are reported in [Table 4 \(see](#)
321 [Suppl. Mat. Table G\)](#). The contamination in SS was very high and mean concentrations systematically
322 exceeded 1000 ng.g⁻¹, except at one upstream station (T2*) that mainly drains a forested area ($230 \pm$
323 260 ng.g⁻¹). During the low stage period, the lowest concentrations were measured at the sampling
324 sites located in the uppermost parts of the catchment, T1 (2330 ± 590 ng.g⁻¹), T2 (1090 ± 310 ng.g⁻¹)

325 and T2* draining respectively 4.2, 5.9 and 6.4 km², which can be explained by the virtual absence of
326 built-up areas in these subcatchments. However, on a regional scale, these concentrations cannot be
327 considered as low since they are of the same order of magnitude than those measured in estuarine
328 sediment from other French rivers (1000 to 2000 ng.g⁻¹) (Bouloubassi and Saliot, 1991; Budzinski et
329 al., 1997; Ollivon et al., 1995) where the impact of industrialisation is obvious. This result shows the
330 importance of PAH contamination in this rural catchment.

331 Generally, the concentrations increased in downstream direction with the progressively higher
332 density of population living in the catchment. A strong relationship (Fig. 4: $r^2 = 0.55$; $p < 0.05$) was
333 found between PAH concentrations in SS and density of population in the drainage areas. However,
334 there were some local differences that did not follow an upstream-downstream gradient. For example,
335 lower levels were observed during low flow period at T2 and T4 (3460 ± 985 ng.g⁻¹) than at upstream
336 stations (respectively [T1] and [T3] (4530 ± 1890 ng.g⁻¹)). This may be explained by the occurrence of
337 different physical processes such as particles size sorting or different dominant soil erosion processes
338 in those river sections. At T2, bank erosion was observed whereas surface soil erosion dominated at
339 T1. Bank erosion leads to the input of particles from deeper soil horizons that were assumed to be less
340 contaminated than surface layers. Therefore, upstream sediment was likely diluted with less
341 contaminated SS at this station. At T4, the dilution of contaminated SS may be due to the input of
342 sediment coming from the western part of the catchment, in which population density is about two-
343 fold lower. The maximum time-averaged concentration was observed during the low water period at
344 T5 (9205 ± 3770 ng.g⁻¹) just downstream of Coulommiers in the Grand Morin River, the largest urban
345 area in the study site (i.e., 14,544 inhabitants in 2010). Although the PAH concentrations were lower
346 at T6 than at T5, they remained higher than the ones measured at T6* (3001 ± 560 ng.g⁻¹) and T7
347 (2940 ± 370 ng.g⁻¹). This might be explained by the fact that the Grand Morin River catchment
348 (drained at T5 and T6) is more contaminated than most upstream parts of the Marne River catchment
349 (drained at T6*). This is consistent with the higher population density observed in the Grand Morin
350 River catchment than in the rest of the area.

351 During the flood period, the upstream-downstream gradient (mean of $1970 - 8280$ ng.g⁻¹) in
352 PAH contamination was much more obvious. Values at T1, T2* and T5 are not available for this

353 period because high water velocity carried away the SS traps. For all other stations with the exception
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2 354 of T3, an increase in PAH concentrations was observed during floods compared to the low stage
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4 355 period. However, this difference was only significant for T2, T6 and T7 ($p < 0.05$). The contribution of
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6 356 the Grand Morin River catchment (drained at T6) to the contamination of the Marne River sediment
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8 357 (drained at T7) was also detected during the flood period and it may be explained by the
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11 358 proportionally larger contribution of the Grand Morin tributary to the total sedimentary flux conveyed
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13 359 by the Marne.

360 Two hypotheses can be made to explain the much higher PAH concentrations measured in SS
16
17 361 than in soils. First, both the erosion and the transportation processes may lead to changes in the
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19 362 physico-chemical properties of the particles (Koiter et al, 2013; Zheng et al., 2012). Indeed, PAH
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21 363 concentrations were assumed to be higher in upper layers of the soils, and surface erosion would lead
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23 364 to preferential erosion of contaminated particles and to higher PAH levels in sediment (Krauss et al.,
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25 365 2000). This was supported by a significant increase in (OC) contents observed from soils (mean: 1.71
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27 366 ± 0.64 %) to sediments (mean: 4.93 ± 1.48 %) even though it remained lower than the rise measured in
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29 367 PAH concentrations. In the same way, size sorting of the particles may occur during transportation
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31 368 (Motha et al., 2002), therefore leading to a change in PAH concentration as pollutants may
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33 369 preferentially be bound to different size fractions (Kukkoken et Landrum, 1996; Piérard et al., 1996;
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35 370 Wang et al., 2001). Second, supplementary sources (e.g. urban waste) or more contaminated areas
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37 371 (e.g. roadside area) that were not integrated in the initial sampling scheme may supply additional PAH
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39 372 loads to the rivers and result in enrichment of SS in PAHs within the river. However, none of these
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41 373 hypotheses allowed explaining all the spatial and the temporal changes observed during our study.
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43 374 Those variations are likely to be driven by a combination of processes and further investigation is
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45 375 required to investigate their relative contribution. Using fingerprinting methods based on radionuclides
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47 376 may provide information about the sources and the residence times of particles within catchments and
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49 377 rivers, and about their relation with PAH concentration in sediment (Evrard et al., 2010).
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3.5. Annual mass balances of PAHs at the catchment scales

Mass balance calculations are synthesized in Table 5. Although atmospheric fallout of PAHs was larger in winter, there was a supply of PAHs throughout the year. In contrast, exports of PAHs in the aqueous and particulate phases were only significant during the flood period as $79 \pm 13\%$ of the total riverine PAH fluxes were exported during flood period (125 days). The mass balance of PAHs indicates that PAH inputs were higher than riverine outputs within all investigated subcatchments during the study period. However, the study period was characterized by a lower cumulative annual rainfall amount (540 mm) than the long-term average records (648 mm). The return period of the largest observed flood (in early January) was about 7 months. Consequently, the mass balance calculated in this study is likely to be representative of the behaviour of PAHs during dry years. Except at La Loge (T2*), particle-bound PAHs represented more than 70% of the total amount of PAHs exported by rivers during the sampling period. This highlights the importance of sediment-borne transfers in the riverine export of contaminants with low water solubility. Particle-bound PAH fluxes were relatively low at T2* despite a sediment yield similar to the one observed in other subcatchments (Table 5). Although highly variable, PAH concentrations in SS collected at this station appeared to be systematically lower than at the other stations. This difference between T2* and the other sampling sites may be explained by the fact that woodland covered 67% of the catchment surface draining to this station or by the occurrence of different erosion processes in this area. Additional fingerprinting investigations are ongoing to better discriminate the SS sources and outline the dominant erosion processes prevailing in the different subcatchments. Annual PAH loads exported by the river at T4 reached 3.2 kg, i.e. $0.03 \text{ kg.km}^{-2}.\text{yr}^{-1}$. In contrast, Motelay-Massei et al. (2006) reported much higher fluxes in an urban catchment of the downstream part of the Seine River basin ($5.2 \text{ kg.km}^{-2}.\text{yr}^{-1}$).

Quantifying biodegradation, photo-chemical oxidation and volatilization rates of PAHs in the field at a scale which is consistent with our study may be difficult, and most of the studies dealing with these processes were conducted either in laboratory or at the small plot scale (Johnsen et al., 2005; Wild et al., 1991). Mass balance calculation was carried out assuming that there was no change in

406 PAH stocks in soils (Table 5) as no significant variation in PAH concentrations in soils was detected
1 during our study ($\Delta St = 0$ in Eq. (2)). Therefore, dissipation was computed as the difference between
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3 measured atmospheric input and riverine exports. The dissipation within the catchments (mainly
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5 degradation and volatilization processes) therefore appeared to be the main process of PAH removal
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7 from soils, thereby supporting previous results: e.g. Wild and Jones (1995) stated that biodegradation
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9 and photo-oxidation as the main PAH removal processes in the environment. Those losses were found
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11 to be higher in T2* subcatchment where forests cover 67% of the drainage area. Indeed, material rich
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13 in fulvic acids can result in higher rates of contaminant degradation (Bogan and Sullivan, 2003). Even
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15 though they represent the main PAH removal fluxes in the investigated catchments, the dissipation
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17 rates (cumulating all loss processes) calculated at the scale of the Orgeval catchment and
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19 subcatchments remained much lower than degradation rates reported in the literature suggesting that
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21 PAH dissipation processes may be lower than expected when examined at a catchment scale. Several
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23 explanations may be put forward to explain this difference. First, experimental parameters may
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25 strongly differ depending on the local environmental conditions (Shuttleworth and Cerniglia, 1995)
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27 and degradation process may be reduced by chemical or physical conditions in the soil, such as
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29 temperature, pH, moisture, or aeration (Bogan and Sullivan, 2003; Kästner et al, 1998). Then, several
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31 processes may limit PAH degradation such as bacteria consortium competitions, limited
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33 bioavailability and toxicity (Haritash and Kaushic, 2009; Nzila, 2013). Long-term storage in soils may
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35 also prevent PAHs from degradation as aging and sequestration are more likely to occur at those
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37 timescales (Mahmoudi et al. 2013). Our results on dissipation revealed that the measured annual PAH
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39 input (and output) only represents a small proportion (< 0.5%) of the total estimated stocks
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41 accumulated in the catchment, which is in agreement with our observation regarding the stock extent.
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43 However, low changes in PAH stocks at a catchment scale cannot be precisely assessed without long
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45 term monitoring results, and only very high dissipation rates could have been assessed from a
46 429
47 detectable drop in PAH concentrations in soils during this study.
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51 An estimation of stocks in soils cumulated throughout the years was carried out based on
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53 historical deposition rates of atmospheric PAHs reported by Fernández et al. (2000). Their results were
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55 consistent with another work dealing with emissions (Pacyna et al., 2003) and showed that deposition
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434 rates in France increased from 1883-1890 to reach a peak in the 1960s and then decreased to the
435 current values. An order of magnitude of the PAH legacy stocks was calculated based on current
436 deposition rates and assuming that PAH fallout in the studied catchments followed the same temporal
437 trend (maximum of $1600 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in 1965). When hypothesizing that the PAH losses in the
438 catchment were proportional to the cumulated stock, the annual loss rate should reach a maximum of
439 about 0.5 % to match with the current stocks. Based on this value, PAH losses during our study should
440 have been twice higher ($360 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) than the one estimated ($157 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). Given the rough
441 hypothesis that was made, both values must be considered as similar. This result supports the
442 assumption that the yearly variations of PAH stock at the catchments scale are limited.

3.6. Estimation of decontamination times

445 Estimated decontamination times for all the compounds in the 4 subcatchments are reported in
446 Table 6. They appeared to be much higher (44 – 1850 yrs) compared to half-lives (< 10 yrs) reported
447 in the literature (e.g., WHO, 1998) and several assumptions have been suggested above to explain
448 these differences. Results suggested that heaviest PAHs have longer decontamination times in the
449 investigated catchments (550–1850 yrs), because they are strongly bound to particles and they may
450 therefore remain trapped in the soils. In contrast, the lightest compounds associated with
451 decontamination times estimated between 44 and 670 years may either be transferred faster to the
452 rivers or degraded.

453 In order to investigate the influence of the hypotheses we made on decontamination times, we
454 calculated 3 sets of DT for T2 sampling site as an example, following 3 scenarios (Table 6). The first
455 is the reference scenario (1), DT were calculated without taking into account the gaseous deposition
456 and using the hydrological parameters measured during the study period. In the second scenario (2),
457 the gaseous deposition was considered using the ratio between gaseous exchange and the total
458 deposition reported by Demircioglu et al. (2011). Consequently, mass balance calculations were
459 modified, resulting in an increase of the dissipation flux in the catchment. Finally, the third scenario
460 (3) investigated the impact of hydrology. Indeed, the study period was rather dry, and river discharge
461 and SS flux remained limited (Max. flow: $545 \text{ m}^3\cdot\text{s}^{-1}$). In this third scenario, the dissipation flux was

462 assumed to be equal to the one calculated in 2012, but riverine exports were calculated based on flow
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2 463 and SS concentrations measured in 1999 (Max. flow: 1800 m³.s⁻¹).
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4 464 Inclusion of gaseous exchanges in the calculation had a strong impact on decontamination
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6 465 times of light PAHs. Those decontamination times were much shorter for those compounds than
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8 466 according to the first scenario, but the effect on the heaviest PAHs was less significant. In contrast, the
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10 467 third scenario had a larger impact on the decontamination times of the heaviest compounds. The
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12 468 precise evaluation of atmospheric deposition of gaseous PAHs is a highly complex issue, therefore the
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14 469 main conclusion we can derive from scenario (2) is that depollution time for lightest PAHs may be
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16 470 shorter than estimated with the reference scenario (1). However, the conclusion obtained from the
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18 471 reference scenario remains robust with depollution times of the order of hundreds years rather than
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20 472 tens of years, which is of major concern regarding the attainment of WFD objectives. The effect of
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22 473 hydrology (scenario 3) does not significantly modify this conclusion as decontamination times
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24 474 calculated following 3 remained of the same order of magnitude.
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28 475 They also underline that the soils play a crucial role in buffering the transfer of PAHs at the
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30 476 catchment scale (Sehili and Lammel, 2007; Wild and Jones, 1995). The results also highlighted the
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32 477 important role played by legacy contamination that supplied the bulk of PAHs that are still found in
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34 478 the environment.
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40 480 **4. Conclusions**

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42 481 From a management perspective, any decontamination strategy should require both the
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44 482 decrease in PAH emissions and the optimization of biodegradation and oxidation processes. However,
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46 483 given the long decontamination times estimated in this study, the WFD concentration targets are
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48 484 unlikely to be reached for PAHs by 2015, 2022 or 2027. This is underlined by the weight of the legacy
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50 485 PAH contamination reflected by the dominant pyrolytic origin of PAHs found in soils and sediment.
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52 486 Although more investigations are required on PAH sources and their transfer processes in rivers,
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54 487 actions may be proposed to avoid the local release of highly contaminated material or wastewaters into
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56 488 rivers. Identification of the precise location of those sources and their isolation from the river network
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489 may limit their supply of PAHs to the river and alleviate the contamination peaks. In addition, as
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2 490 cropland plays a major role in PAH storage at the catchment scale, soil erosion control measures
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4 491 should be implemented in those areas to limit as much as possible their supply of contaminated
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6 492 material to the rivers. In future, a more detailed work on the discrimination of PAH sources is required
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8 493 to better constrain PAH pathways in the environment. In particular, the use of sediment fingerprinting
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10 494 methods could offer a solution to better quantify the processes responsible for the enrichment of PAHs
11
12 495 in sediment and to better constrain their transit times in rivers and catchments.
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15 496

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27
28 502 contribution No.
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33 504 **Figure captions**

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39 506 **Fig. 1** Location of the study sites in (a) France and (b) the Seine River basin.
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43 508 **Fig. 2** Location of the sampling sites and land use patterns (CORINE Land Cover 2006) within the
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45 509 Orgeval catchment and along the Grand Morin River and its junction with the Marne River.
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50 511 **Fig. 3** Hydrological and meteorological parameters measured at Boissy-le-Châtel (C3 – Rainfall and
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52 512 temperature) and at Le Theil (T4 – River flow).
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56 514 **Fig. 4** Relationship between the mean PAH concentrations measured as the SS sampling sites and the
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58 515 population density living within the corresponding drainage areas.
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1 **Table 1**

2 Concentrations of $\Sigma 13$ PAHs (ng.L^{-1}) measured in atmospheric fallout between 28 June 2011 and 21
 3 February 2012. Samples were considered to be collected during the cold period when mean
 4 temperature measured during the sampling period was below 10°C (i.e. from 8 December 2011 to 21
 5 February 2012).

Sampling Sites	n	Warm Period			Cold Period		
		Min	Max	Mean \pm SD	Min	Max	Mean \pm SD
C1	10	80	260	190 \pm 70	260	1275	620 \pm 420
C2	10	130	400	250 \pm 100	90	1270	615 \pm 460
C3	12	120	640	250 \pm 180	170	2380	740 \pm 760
C4	10	60	330	180 \pm 100	200	950	480 \pm 285

6

1 **Table 2**

2 Concentrations of $\sum 13$ PAHs (ng.g^{-1}) and organic carbon measured in soils between 22 February 2011
 3 and 3 April 2012 and corresponding estimated stocks.

Sampling Sites	n	Land Use	OC \pm SD (%)	Min	Max	Mean \pm SD	Stocks (kg.km^{-2})
S1	8	Intensive Cropland	1.15 \pm 0.22	190	760	395 \pm 190	130
S2	8	Grassland	1.54 \pm 0.45	60	160	120 \pm 30	12
S3	8	Built-up area	2.56 \pm 0.35	340	5305	2120 \pm 1590	220
S4	4	Organic cropland	1.44 \pm 0.35	230	270	250 \pm 20	80
S5	5	Woodland	2.18 \pm 0.38	90	150	110 \pm 20	12

4

1 **Table 3**2 Concentrations of $\Sigma 13$ PAHs (ng.L^{-1}) measured in surface waters between 5 October 2011 and 10

3 April 2012. Samples collected in January, February and March were considered as flood samples.

Sampling Sites	n	Low water period			Flood Period		
		Min	Max	Mean \pm SD	Min	Max	Mean \pm SD
T2	6	16	96	62 \pm 29	61	100	80 \pm 20
T3	6	15	93	62 \pm 33	33	135	68 \pm 47
T4	5	22	97	70 \pm 34	25	85	55 \pm 30
T6	5	33	167	112 \pm 57	67	73	70 \pm 3
T7	4	21	88	54 \pm 33	75	81	78 \pm 3

4

1 **Table 4**2 Concentrations of $\Sigma 13$ PAHs (ng.g^{-1}) measured in SS between 30 March 2011 and 10 April 2012.

Sampling Sites	n	Population density (inh.km^{-2})	Low water stage Period				Flood Period			
			OC (%)	Min	Max	Mean \pm SD	OC (%)	Min	Max	Mean \pm SD
T1	8	16.2	4.94 ± 1.07	1250	3390	2330 ± 590	-	-	-	-
T2	13	24.1	4.59 ± 1.09	675	1480	1090 ± 310	3.09 ± 0.80	1205	3030	1970 ± 710
T2*	8	18.0	3.73 ± 0.83	50	860	230 ± 260	-	-	-	-
T3	11	56.5	6.54 ± 1.12	2000	8110	4530 ± 1890	4.05 ± 1.80	2730	3760	3310 ± 430
T4	14	28.9	7.52 ± 1.98	2310	5250	3460 ± 985	5.83 ± 0.78	3055	4420	3800 ± 560
T5	8	68.8	4.39 ± 0.76	3980	14080	9205 ± 3770	-	-	-	-
T6	13	85.3	4.45 ± 1.37	3230	7400	4760 ± 1160	5.27 ± 0.14	5480	10690	8280 ± 2150
T6*	13	60.5	5.13 ± 0.71	2420	4060	3000 ± 560	5.14 ± 1.02	3000	4870	3935 ± 940
T7	13	64.7	4.73 ± 0.62	2340	3520	2940 ± 370	5.55 ± 0.60	5500	9600	7570 ± 1630

3

1 **Table 5**

2 Mass balances (g.yr^{-1}) of $\Sigma 13$ PAHs calculated over a year in the 4 upstream subcatchments and corresponding sediment yields. Fluxes and losses within the
 3 catchments are provided in g.year^{-1} . Percentages of the total export fluxes are provided between brackets and estimated decontamination times (DT) are in
 4 years.

Sampling Sites	Sediment yield ($\text{t.km}^{-2}.\text{yr}^{-1}$)	PAH stocks (kg)	Input fluxes	Aqueous exports	Particle-borne fluxes	Losses in the catchments	DT
T2	18.9	410	910	40 (4%)	160 (18%)	710 (78%)	450
T2*	6.68	240	1030	30 (3%)	20 (2%)	980 (95%)	230
T3	4.88	3430	7380	290 (4%)	770 (10%)	6320 (86%)	460
T4	7.38	7640	16,320	510 (3%)	3160 (19%)	12,650 (78%)	470

5

1 **Table 6**

2 Estimated decontamination times (DT; years) of the 13 PAHs in the 4 upstream subcatchments.

	ACY	ACE	FLU	PHE	ANT	FLH	PYR	BaA	CHR	BbF+BkF	BaP	BghiP
T2 (1)	200	220	160	80	320	630	460	1800	1130	1140	1610	1290
T2* (1)	100	170	90	40	140	310	230	850	550	510	700	630
T3 (1)	210	240	170	90	330	670	490	1840	1150	1080	1520	1310
T4 (1)	210	240	160	80	310	640	460	1850	1170	1100	1590	1340
T2 (2)	-	-	25	11	52	60	76	1020	310	990	1400	1090
T2 (3)	100	140	90	60	160	180	160	240	190	180	310	530

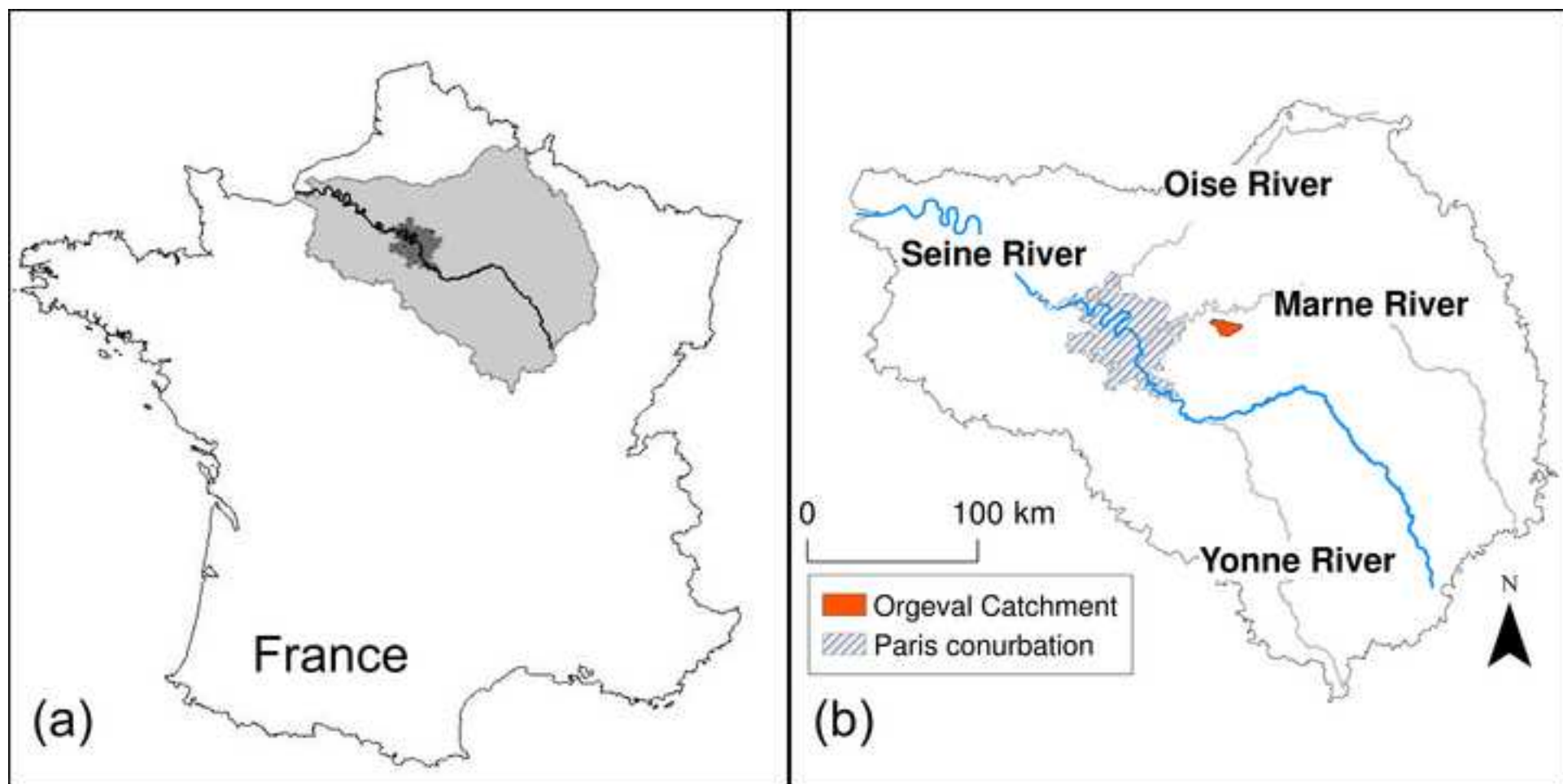
3 (1) DT calculated with the hydrological parameters measured in 2011-2012 (dry year) but gaseous deposition was not taken into account

4 (2) DT calculated with the hydrological parameters measured in 2011-2012 (dry year) and gaseous deposition was taken into account based on Demircioglu et
 5 al. (2011).

6 (3) DT calculated with the hydrological parameters measured in 1999 (wet year) but gaseous deposition was not taken into account

Figure

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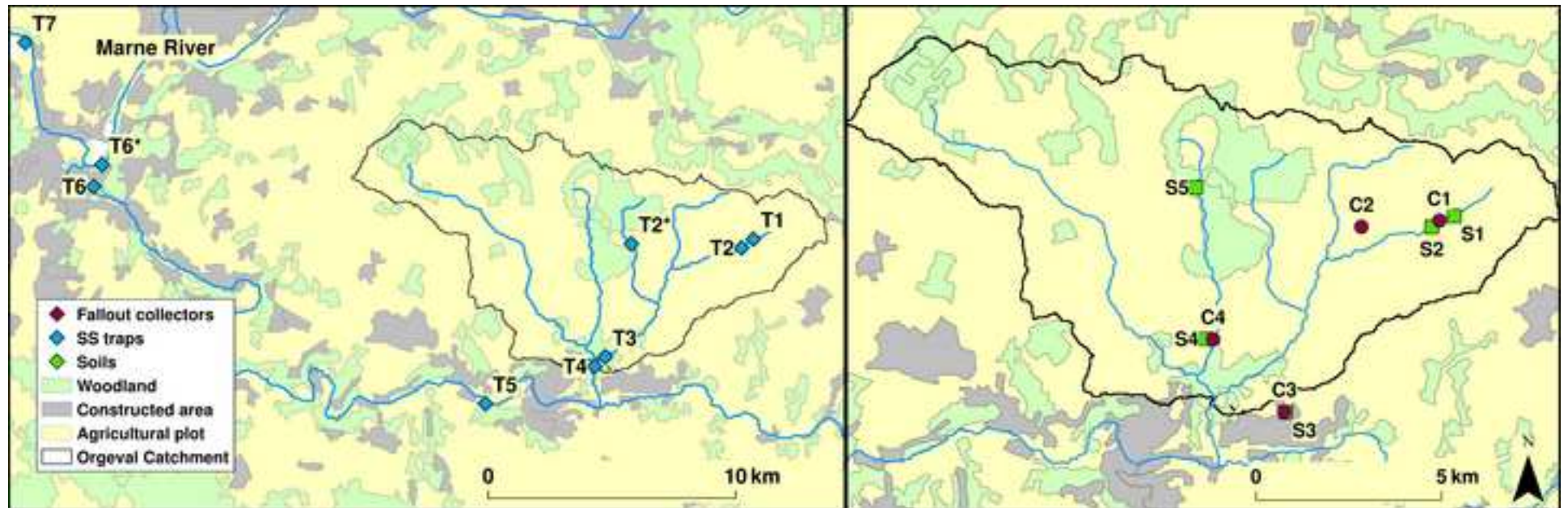


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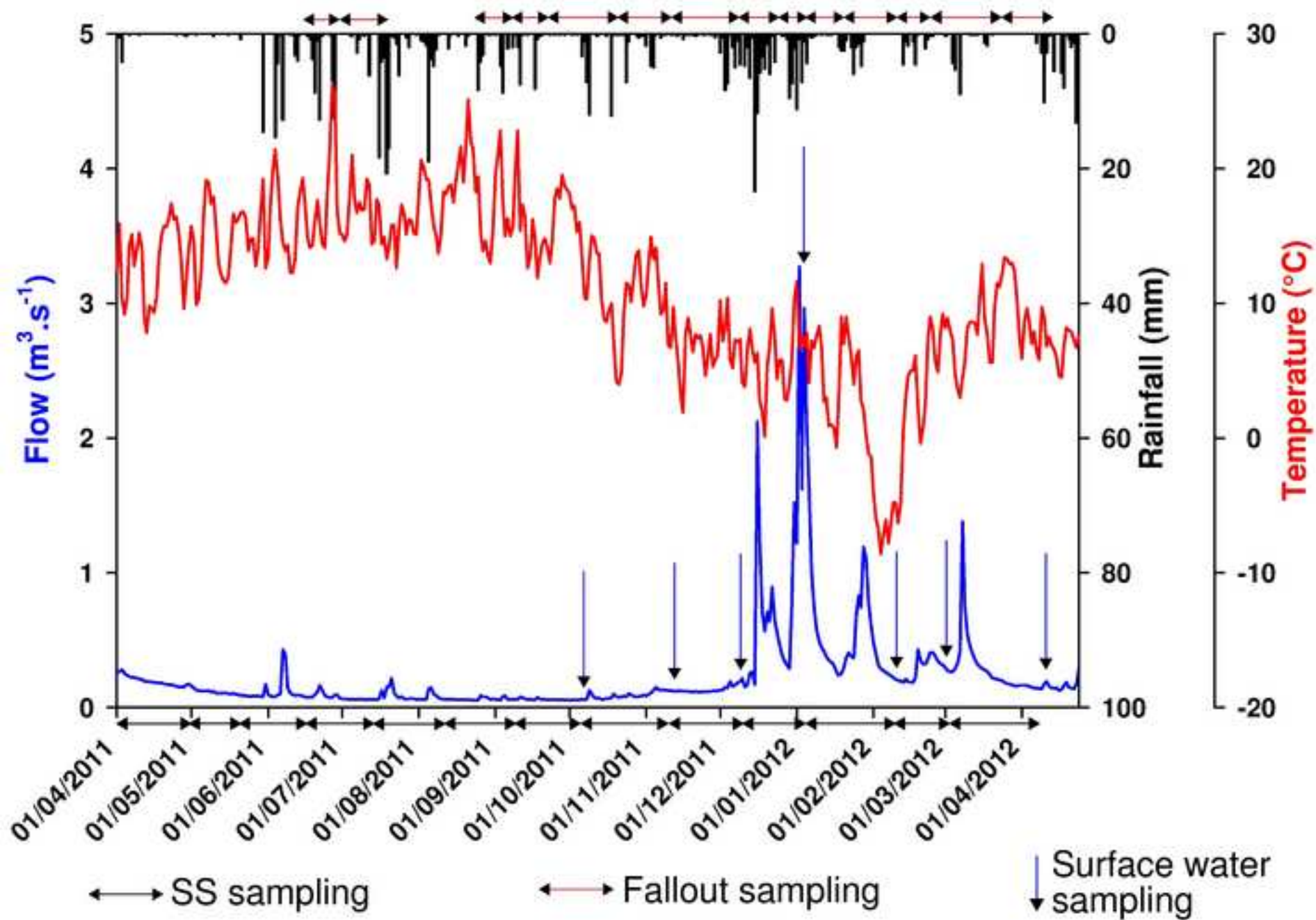
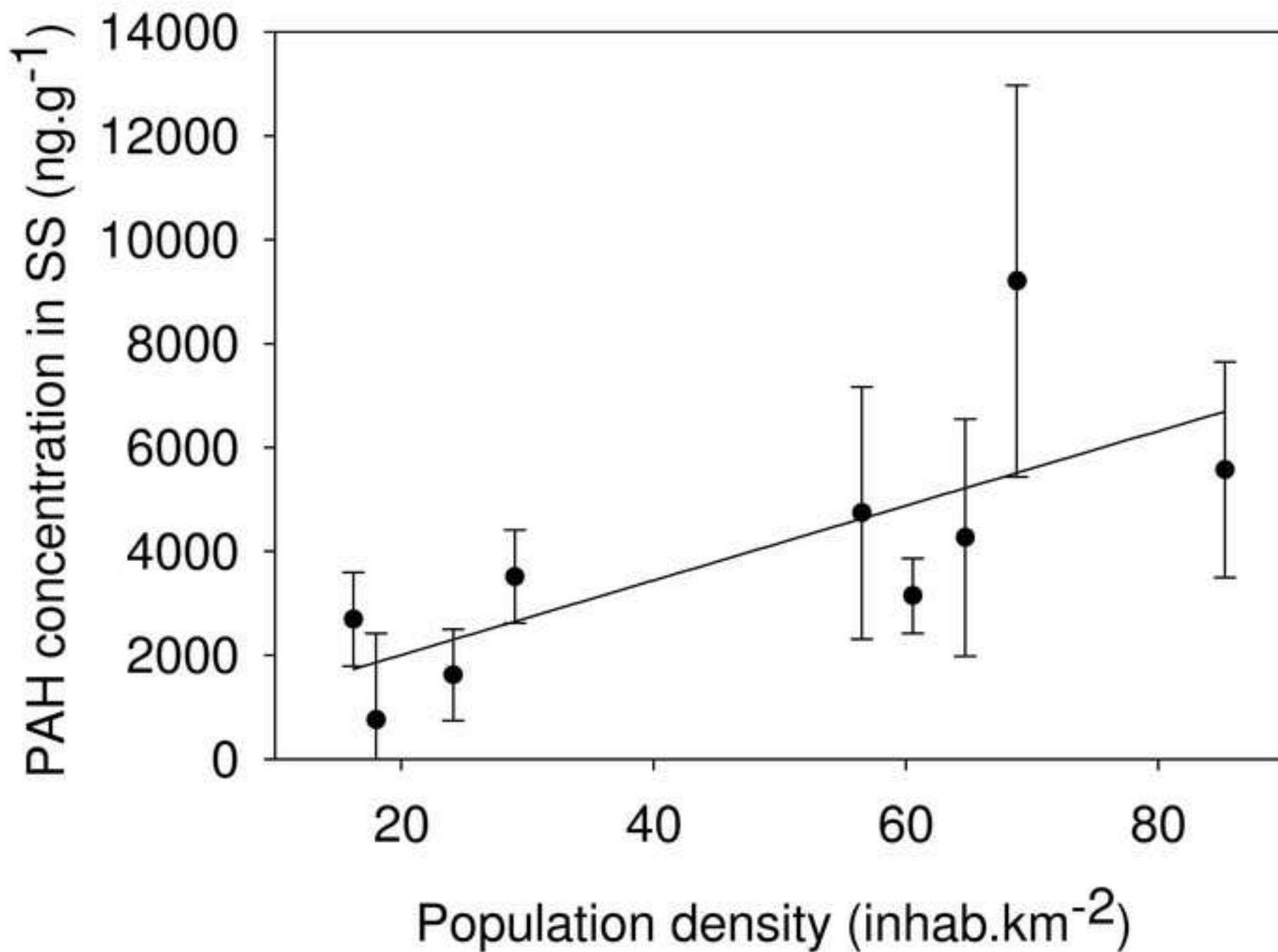


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