Innovative combination of tracing methods to differentiate between legacy and contemporary PAH sources in the atmosphere-soil-river continuum in an urban catchment (Orge River, France)

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Claire Froger[*,1,2], Sophie Ayrault[1], Johnny Gasperi[3], Emilie Caupos[3], Gaël Monvoisin[2], Olivier Evrard[1], Cécile Quantin[2]

*Corresponding author: c

laire.froger@lsce.ipsl.fr

Phone: +33 169824357

Address: Bat. 714, CEA – Orme les Merisiers, 91198, Gif-sur-Yvette, France

[1] Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), CEA-CNRS-UVSQ, Université Paris-Saclay, 91198 Gif-sur-Yvette, France

[2] Géosciences Paris Sud (GEOPS), Université Paris-Sud – CNRS- Université Paris-Saclay, 91400 Orsay, France

[3] Laboratoire Eau Environnement et Systèmes Urbains (LEESU), Université Paris-Est Créteil, UMR MA 102- Agro ParisTech, 94010 Créteil, France

Abstract

Polycyclic aromatic hydrocarbons (PAH) have been released by human activities during more than a century, contaminating the entire atmosphere – soil – river continuum. Due to their ubiquity in the environment and their potential severe biological impacts, PAH became priority pollutants and were targeted by environmental public agencies. To better manage PAH pollution, it is necessary to identify unambiguously the sources and pathways of those compounds at the catchment scale, and to evaluate the persistence of historical PAH pollution in the environment especially in those urban contexts concentrating multiple PAH sources. Accordingly, the current research monitored the contamination in atmospheric fallout, soils and rivers of a 950-km^2 catchment (Orge River) characterized by an increasing urban gradient in downstream direction, and located in the Seine River basin characterized by a high level of PAH legacy contamination. A combination of various approaches was used, including the widely used PAH diagnostic ratios, together with innovative methods such as PAH correlations and sediment fingerprinting using fallout radionuclides to clearly identify both the origin of PAH and their main PAH pathways to the river. The results demonstrated the persistence of legacy PAH contamination in the catchment, responsible for the signature of the suspended particulate matter currently transiting in the Orge River. They underlined the conservation of PAH through the soil – river continuum. Finally, urban runoff was demonstrated to provide the main PAH source to the river in the densely urbanized area by both PAH correlations and sediment fingerprinting. These results were used to model PAH concentrations in those particles supplied from urban areas to the river.

Keywords: PAH ratios, urban runoff, legacy contamination, sediment fingerprinting

1. Introduction

Human activities have led to deleterious impacts on aquatic ecosystems as a result of the discharge of numerous contaminants into the environment. Among these harmful substances,

polycyclic aromatic hydrocarbons (PAHs) released by the incomplete combustion or the pyrolysis of organic matter have been listed as priority pollutants by environmental state agencies since the 1970s due to their adverse effects on health (Grimmer, 1985). Accordingly, policies and regulations have been implemented to improve the river quality and to control further contaminant releases. In Europe, the Water Framework Directive (WFD, Directive 2000/60/EC) fixes the target concentrations for multiple contaminants in water bodies, in order to improve their chemical quality. In France, numerous river basins including the Seine River basin exceed the target concentrations with values reaching up to 20 $mg.kg^{-1}$ in the particulate fraction (Fernandes et al., 1997), threatening the achievement of the good chemical status. Accordingly, the identification of those sources supplying PAH contamination to rivers is required to improve the current management of water bodies. As PAH contamination is widespread in Western Europe because of the continuous atmospheric releases of these substances since 1850 (Fernández et al., 2000), it is particularly important to determine whether the high levels of contamination observed nowadays in rivers are mainly explained by the remobilization of legacy pollution or by the current releases of these substances.

Several tracing approaches have been developed during the last several decades to identify the main sources of PAH in the environment (Budzinski et al., 1997; Gateuille et al., 2014b; Yunker et al., 2002). The most frequent technique corresponds to the calculation of diagnostic molecular ratios. This approach is based on the use and combination of ratios between different PAH, as the contribution of specific molecules is characteristic of a given source type, typically the combustion of either biomass (coal, wood, grass), or that of crude oil and fossil fuel (Ravindra et al., 2008). The combination of two ratios is generally used to discriminate PAH according to their pyrogenic, petrogenic or mixed origin (Kavouras et al., 2001; Tobiszewski and Namieśnik, 2012). However, several studies pointed out the sensitivity of those ratios to environmental processes such as oxidation and photo-oxidation

leading to the preferential degradation of some PAH, therefore modifying the related ratios (Biache et al., 2014; Zhang et al., 2005). Moreover, as these ratios are not specific to a particular source, their interpretation remains limited and insufficient in complex urban catchments where the identification of well-localized sources is required. Other approaches involve statistical analyses such as principal component analysis (PCA), hierarchical cluster analysis (HCA) or modelling techniques like the positive matrix factorization (PMF) to identify sources (Motelay-Massei et al., 2003; Sofowote et al., 2011; Xu et al., 2016). Those statistical analyses take into account all the PAH molecules measured when processing the datasets, with the particularity for PCA and HCA to cluster PAH molecules or samples sharing similar characteristics. The PMF models are more complex and their results provide theoretical PAH profiles of the sources with their respective contribution, which can then be compared to the potential sources of PAH. Although statistical approaches may be powerful, caution must be taken when interpreting their outputs, as they strongly depend on data quality and quantity, and do not consider the multiple processes that may affect the fate of PAH in the environment (biodegradation, oxidation…). Finally, nitro and oxy-PAHs, which are commonly investigated because of their mutagenicity (Umbuzeiro et al., 2008), appeared to provide powerful tracers of some anthropogenic sources such as diesel combustion (Anyanwu and Semple, 2015; Keyte et al., 2016). However, their measurement requires further analytical developments, currently limiting their widespread use as diagnostic tracers.

In addition, the identification of PAH sources is challenging as their contribution may vary throughout time (Garban et al., 2002; Harrison et al., 1996). The impact of multiple local sources (household heating, vehicular emissions, industrial emissions), combined with long-range emissions or the remobilization of legacy pollution could complicate the identification of those sources (Haugland et al., 2008; Schifman and Boving, 2015). As a consequence, few studies have investigated the pathways of PAH in the atmosphere – soil – river continuum

(Gateuille et al., 2014a; Gocht et al., 2007; A. Motelay-Massei et al., 2007). The objective of the current research was to identify the PAH sources and pathways in an urban catchment and to differentiate between legacy and current PAH sources, through the investigation of PAH contamination in the atmosphere, the soil and the river during a hydrological year. To achieve this goal, the Orge River catchment was selected as it is representative of urbanized catchments (Froger et al., 2018) and located in an early industrialized region. Source identification using PAH diagnostic ratios was combined with new approaches such as PAH correlations and the measurement of fallout radionuclides used for sediment fingerprinting to better discriminate both sources and pathways of particle-bound PAH in the atmosphere, the soils and the river.

2. Material and methods

2.1. Study site

All river water, atmospheric and road sediments samples were collected in the Orge River catchment, which is located 30 km south of Paris City and drains into the Seine River (Figure 1; see Froger et al., 2018). Four sampling sites were selected based on their urbanization rate and previous work on the catchment (Le Pape et al., 2012): three were located on the main stem of the Orge River, whereas a fourth site was located on its main tributary, the Yvette River. The proportion of urban areas strongly increases in downstream direction, varying from 1% in upper catchment parts to 56% at the outlet. This change is reflected by the evolution of the population densities in the drainage areas (from 300 inhabitants per km^{-2} at the most rural study site – Dourdan ("D"), to 5,000 $inh.km^{-2}$ at Viry ("V", nearby the outlet). The geology of the catchment is characterized by Eocene formations including carbonate rocks, marls and gypsum, and Oligocene formations dominated by Fontainebleau sands (Le Pape et al., 2012).

In addition to river water and sediment samples, four road deposited sediments (RDS) were collected at the most urbanized site in Viry, nearby the local river sampling site, and samples of atmospheric fallout were collected on the roof of a building at Orsay.

2.2. Hydrological conditions

River water sampling was conducted during a hydrological year with the organization of five campaigns from January to December 2016. Daily water discharge at the outlet varied throughout the year from 1.6 to 39.5 $m^3.s^{-1}$ with a mean value of 3.5 $m^3.s^{-1}$. The sampling campaigns were organized to be representative of those hydrological conditions observed throughout the year in the Orge River (Figure 2). Accordingly, one campaign was organized during the low flow period (< 2 $m^3.s^{-1}$ at the outlet, August 2016), three campaigns occurred when the water flow was comprised between 2 and 5 $m^3.s^{-1}$ (January, November and December 2016) and one campaign was conducted during a flood (water flow exceeding 5 $m^3.s^{-1}$; April 2016). Sampling was also conducted during the extreme flood of June 2016 with a peak discharge of 39.5 $m^3.s^{-1}$ recorded at the outlet.

2.3. Sampling and PAH analysis

2.3.1. River, atmospheric deposition and road deposited sediment sampling

Punctual samples of river water (n = 32) were collected in the middle section of the river at 20 – 30 cm depth using 2-L brown glass bottles preliminary washed with detergent (TFD4) and grilled at 500°C (Bressy et al., 2012). The extraction protocol was rapidly conducted on the samples on the same day as the sampling. In addition, sediment traps composed of metal bottles submerged in the river (20 – 30 cm depth) were deployed during 4 to 5 days to collect suspended particulate matter (SPM) by sedimentation for a longer period (n = 22). Suspended

149 particulate matter recovered from the traps were decanted, the supernatant was removed and
150 the suspended solid was freeze-dried (Gateuille et al., 2014a). After the flood of June 2016,
151 floodplain sediments were collected overbank in Dourdan, Egly, Yvette and Viry after the
152 flood recession.

153 Samples of total atmospheric deposition were collected in Orsay, near the Yvette River
154 monitoring site, from the February 1^{rst}, 2016 to March 30, 2017 (Figure 1). Two funnels with
155 21 and 28 cm diameters were installed and connected to brown glass bottle collectors.
156 Atmospheric fallout samples (n = 26) were collected after variable periods, the median
157 duration between successive sample collections was 16 days.

158 Finally, four RDS were sampled on the road bordering the river sampling site at Viry. The
159 samples were freeze-dried and sieved to 200 µm as PAH are considered to be mainly
160 associated with the fine particle fraction (Pratt and Lottermoser, 2007) and the size of
161 particles washed during runoff is mainly under 300 µm (El-Mufleh et al., 2011; Revitt et al.,
162 2014; Roger et al., 1998).

163

164 ### 2.3.2. Sample preparation

165 The analytical protocol has been detailed in previous studies (Bressy et al., 2012; Froger et al.,
166 2019; Lorgeoux et al., 2016). In brief, instantaneous samples of river water and atmospheric
167 fallout were filtered just after sampling, first on quartz filters GF/D (porosity of 2.7 µm) then
168 on GF/F (porosity 0.47 µm) preliminarily grilled at 500°C. Filters were then freeze-dried.
169 Following filtration, extraction was done on a solid phase siliceous cartridge C18 (6 mL and
170 2000 mg). Solid sample extraction (atmospheric particles, river SPM and RDS) was
171 performed using a microwave assisted extraction (Microwave 3000, Anton Paar). Samples
172 were introduced in close bottles with a mixture of dichloromethane and methanol, heated at

100°C during 10 minutes (Lorgeoux et al., 2016). A sample of a certified material (i.e. a lake sediment standard, NIST 1944) was also extracted in the same sequence to validate the analytical method. To avoid interferences during the analysis, the purifications of all extracted samples were performed using silica gel columns (2.1 g of silica gel) to separate the different compound families using various solvent mixtures. Before extraction, an internal standard containing 6 deuterated PAH (naphthalene-D8, acenaphtheneD10, phenanthreneD10, pyreneD12, chryseneD12 and peryleneD12) was added to each sample, for both dissolved and particulate fractions.

2.3.3. PAH analysis

PAH concentrations in the dissolved and particulate phases (i.e. SPM) of river water samples and atmospheric fallout, and in the road deposited sediments were measured by gas chromatography coupled with a mass spectrometer (GC-MS, column RTX5SIL-MS (Restek, 60 m, 0.25 mm ID, 0.25 µm df)) used in SIM mode. Helium was the vector gas and the injection volume was 1 µL, the samples were heated at 330°C for 6 minutes before measurement. PAH were quantified using internal standards. The following PAH were measured: fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flh), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IndP), dibenzo(a,h)anthracene (DbahA) and benzo(g,h,i)perylene (BghiP). The results were expressed as the sum of 13PAHs (∑13PAHs). QA and QC were detailed in the supplementary material of Froger et al. (2019). Results found for naphthalene, acenaphtylene and acenaphtene were not considered in the current research, as these compounds are too volatile to be correctly quantified with the protocol used in this study.

197

198 2.3.4. Modeling the PAH profile of urban particles

199 Fallout radionuclide concentrations measured in the Orge River SPM were reported in a
200 previous paper (Froger et al., 2018) and showed a linear increase in ^{7}Be and $^{210}Pb_{xs}$ activities
201 in SPM collected in downstream direction (Fig. S2). This finding was interpreted as reflecting
202 the increasing supply of recently eroded particles supplied by urban areas to the river through
203 urban runoff (RDS source; see Froger et al., 2018 for hypothesis development). Moreover, the
204 linear trend suggested that agricultural soils depleted in both ^{7}Be and $^{210}Pb_{xs}$ provided the
205 main source of particles transiting the river in upper catchment parts. Based on these results, a
206 two end-member equation (Eqs. 1 and 2) was established to estimate the respective
207 proportions of particles supplied by agricultural land (P_{AP}, in %) and those delivered by urban
208 areas (P_{UP}, in %) to those SPM transiting the Orge River at each monitoring site.

209 $$^{7}Be_{SPM} = P_{AP}\ ^{7}Be_{old\ particles} + P_{UP}\ ^{7}Be_{recent\ particles} \quad \text{Eq. 1}$$

210 $$^{210}Pb_{xs\ SPM} = P_{AP}\ ^{210}Pb_{xs\ old\ particles} + P_{UP}\ ^{210}Pb_{xs\ recent\ particles} \quad \text{Eq. 2}$$

211 These proportions were applied to PAH concentrations to estimate the PAH concentrations of
212 the recent particles, which will be referred to as theoretical urban particles (TUP) (PAH_{TUP}).
213 In this model, PAH conservation was assumed during their transfer from the source to the
214 sampling site. All the calculations were conducted using the solver module of the Excel
215 software to find the solution to an equation system with multiple conditions, involving an
216 iterative process to converge to the most accurate result. To calculate the final PAH
217 concentrations of theoretical urban particles, each SPM sample *j* was modelled to correspond
218 to a mixture of agricultural particles and TUP ($MPAH_{SPM,,i,j}$) (Eq. 3).

219 $$[MPAH]_{SPM,i,j} = (P_{AP,j}[\mathrm{PAH}]_{i,AP} + P_{UP,j}[\mathrm{PAH}]_{i,j\ TUP}) \quad \text{Eq. 3}$$

$$e_j = \sum_{i=1}^{13} \frac{[MPAH]_{SPM,i,j} - [PAH]_{SPM,i,j}}{[PAH]_{SPM,i,j}} \quad \text{Eq. 4}$$

With $MPAH_{SPM,i,j}$ the modeled concentration of the PAH molecule *i* in the SPM sample *j*; $P_{AP,j}$ and $P_{UP,j}$ the proportions (in %) of particles originating from agricultural soils and from urban areas in the SPM sample *j* calculated based on the fallout radionuclide results; $[PAH]_{i,AP}$ the concentration of the PAH molecule *i* in particles originating from agricultural soils reported by Gasperi et al., (2016); $[PAH]_{i,j,TUP}$ the modeled concentration of the PAH molecule *i* in theoretical urban particles contained in the SPM sample *j*, which is the unknown value that will be estimated. This estimation is thus the result of iterations minimizing *e* (Eq. 4), the sum of the differences between the modeled PAH concentrations in SPM ($MPAH_{SPM,i,j}$) and the measured PAH concentrations ($PAH_{SPM,i,j}$).

The final PAH concentrations profile (Eq. 5) and the associated standard errors in the theoretical urban particles were calculated as the mean value of the $[PAH]_{i,j,TUP}$ estimated from each SPM sample *j*.

$$[PAH]_{i,TUP} = \sum_{j=1}^{n} \frac{[PAH]i,j,TUP}{n} \quad \text{Eq. 5}$$

3. Results and discussion

3.1. PAH contamination levels and variations in sediment

The concentrations of PAH in the atmospheric fallout and river SPM have been detailed in Froger et al., (2019). No temporal tendency in PAH variations was observed in atmospheric fallout particles, characterized by ∑13PAH concentrations varying from 5 to 93 $\mu g.g^{-1}$. On the contrary, SPM contamination of the Orge River ranged from 1.1 to 45.2 $\mu g.g^{-1}$ (∑13PAH) with an increase in PAH concentrations when moving in downstream direction, from a median value of 3.3 $\mu g.g^{-1}$ in Dourdan to 8.5 $\mu g.g^{-1}$ in Viry (∑13PAH). In addition, the

proportions of 4 rings and 5-6 rings PAH amounted to respectively 43% and 44% of the total PAH content, with only 11% of the total provided by the 3 rings PAH. Similar increasing trends in downstream direction were observed for all compounds (Kruskal-Wallis test, $p<0.05$) although the lowest *p-value* (i.e. 0.0002) was obtained for 4 PAHs indicating their larger spatial variability. The concentrations of 4 rings PAH increased from 1.1 to 3.9 $\mu g.g^{-1}$ (median concentrations) from Dourdan to Viry, those of 5-6 rings PAH raised from 1.3 to 3.6 $\mu g.g^{-1}$ whereas the increase was more limited for 3 rings PAH concentrations (from 0.4 to 0.8 $\mu g.g^{-1}$; Fig. S1).

Moreover, PAH concentrations in road deposited sediments ranged from 5.6 to 15.6 $\mu g.g^{-1}$ ($\sum$13PAH) with respective proportions of 4 (45 %) and 5-6 rings (41%) PAH similar to those found in river SPM. The PAH contents in RDS were similar to those measured in road sediments studied by Brown and Peake (2006), although in the lower range of others studies (Aryal et al., 2005; Murakami et al., 2005)

3.2. Tracing sources using Molecular Ratios

The four most frequently used molecular diagnostic ratios, i.e. Flh/(Flh + Py), BaA/(BaA + Chry), IndP/(IndP + BghiP) and Phe/(Phe + Ant) (e.g. Ravindra et al., 2008), were investigated in this study (Figure 3). Signatures of particulate samples from the Orge catchment, SPM, atmospheric particles, RDS and flood sediments, were compared (Figure 3). As molecular diagnostic ratios found in the Orge River SPM did not vary in downstream direction (see Table S2), they were considered as a single group despite their collection at 4 different sites. Those PAH ratios from the Orge catchment were compared with the PAH signatures derived from the compilation of literature data (Table 1), including potential sources of particulate-bound PAH corresponding to soil samples (Gaspéri et al., 2018) and runoff particles collected in the densely urbanized catchment of Sucy (south-east of Paris) (Gasperi et al., 2018 (Report)). The latter were selected as Sucy catchment presents similar

268 characteristics to those found at Viry site, in terms of drainage surface and urbanization rate.
269 The signature of legacy PAH contamination was also reconstructed based on the analysis of
270 successive layers from a sediment core collected in the alluvial plain of the Seine River
271 (Lorgeoux et al., 2016), which recorded PAH concentrations from the early 1950s to 2004.
272 Evolution of PAH concentrations showed a drastic increase from 1950 to 1963 before a
273 decrease between 1963 and 1970 and then a stabilization after 1970. Accordingly, those
274 values were divided into two periods: '1950 – 1963' and '1970 – 2004'.

275

276 The combination of Ind/(IndP + BghiP) with Flh/(Flh + Py) ratios (Figure 3a) indicated a
277 PAH origin at the boundary between fossil fuel and coal/wood combustion for all particulate
278 samples, except for soils. The molecular ratio of IndP/(IndP + BghiP) (Figure 3a) remained
279 very stable and similar in atmospheric particles, SPM, RDS, Seine River sediments and runoff
280 particles. These constant signatures in very different sample types is supported by Schwientek
281 et al., (2013) study demonstrating similar PAH patterns in river SPM throughout the
282 catchments. In addition, the results of previous studies showing the stability of PAH with a
283 high molecular weight (HMW) in various environmental conditions compared to that of
284 lighter PAH corroborate the conclusion of the current study (Biache et al., 2014; Zhang et al.,
285 2005). In contrast, soil samples showed very heterogeneous signatures, which were not related
286 to changes in spatial location or land use. This scattered pattern of values found in soils for
287 this ratio could be explained by the low concentrations, close to the detection limits, of IndP
288 and BghiP found in these samples, resulting in the higher variability of the ratio. Compared to
289 Ind/(IndP + BghiP), the Flh/(Flh + Py) ratio showed the occurrence of differences between the
290 signature of atmospheric particles and that of SPM suggesting a stronger contribution of fossil
291 fuel combustion in atmospheric particles than in SPM. The large range of values found in the
292 signatures of the Orge SPM, with Flh/(Flh + Py) ratios varying from 0.4 to 0.8 was likely

related to the sampling period (Kruskal Wallis test, $p<0.05$), as the highest ratios were found in the samples collected in November 2016 (median value of 0.62 for all sites), whereas the lowest values were found in January 2016 (median value of 0.52). The reason for these temporal variations could not be determined as both campaigns were characterized by similar hydrological and meteorological conditions.

When combining the BaA/(BaA + Chry) and the Flh/(Flh + Py) ratios (Fig. 3b), two trends could be highlighted: the first one includes atmospheric particles together with RDS and part of the runoff particles, while the second trend integrates Orge SPM and flood sediments, soil samples, and Seine River sediments. Diagnostic ratios indicated that PAH from the first group originated from the fossil fuel combustion, whereas the second group signatures reflected the occurrence of mixed sources and biomass combustion. This could be due to point-based sources of fossil fuel combustion for atmospheric and road particles (Ravindra et al., 2006), whereas river sediments may cumulate PAH inputs from multiple sources. Finally, the temporal variations observed for the Flh/(Flh + Py) ratio of SPM were not found for the BaA/(BaA + Chry) ratio.

The combination of Phe/(Ant + Phe) with Flh/(Flh + Py) ratios, however, underlined a different pattern (Fig. 3c), and most samples (including Orge SPM, RDS, atmospheric particles and soil samples) were shown to match the signatures of crude oil and fossil fuel combustion. Nevertheless, the Phe/(Ant + Phe) ratio was shown to be the most sensitive to environmental processes such as biodegradation and abiotic oxidation inducing the occurrence of significant modifications of source signatures (Alam et al., 2013; Katsoyiannis and Breivik, 2014). The observed petrogenic signature may therefore be attributed to the preferential degradation of anthracene, particularly sensitive to oxidation, which resulted in increased ratio values (Biache et al., 2014; Zhang et al., 2005).

Among the explored molecular ratios, the combination of Flh/(Flh + Py) and BaA/(BaA + Chry) (Fig. 3b) provided the most explicit insights into the sources of PAH in the Orge River catchment. On the one hand, PAH found in atmospheric particles and RDS were mainly supplied by the fossil fuel combustion, and their signatures matched those of runoff particles. On the other hand, PAH found in the Orge SPM reflected a fossil fuel and biomass combustion origin, and showed PAH signatures similar to those of soil samples and Seine River sediments. Nevertheless, the contradictions in sources identified by the PAH ratios underlined the caution needed when using these approaches to define PAH sources. Moreover, molecular diagnostic ratios did not reflect the increase in PAH concentrations observed in the Orge SPM from up to downstream sites and therefore provided no additional insight into the source of PAH inputs originating from those urban areas located downstream.

3.3. PAH correlation

Correlations between PAH have been used in several studies as a complement to PAH ratios for conducting PAHs source identification (Bertrand et al., 2015; Soclo et al., 2000). In the current research, SPM PAH concentrations for several 4 to 6 rings PAH showed a significant correlation with a coefficient above 0.9 (Table S1). For instance, Chry, Flt and BaA displayed correlation coefficients comprised between 0.90 and 0.97. Higher molecular weight PAH with 5 and 6 rings (BaP, IndP, DbahA, BghiP) also showed high intercorrelation with coefficients from 0.93 to 0.99. Interestingly, 4 rings PAHs appeared to better represent PAH inputs from urban areas in the lower section of the Orge River as shown by the increase of PAH concentrations in SPM with the urbanization gradient (see section 3.1, Fig. S1). Accordingly, correlations between Chry, Flt and BaA were tested between all the different types of samples (including SPM, flood sediments, atmospheric particles and RDS), and the potential sources of river particles (soils and urban runoff particles), along with the Seine River sediment

providing the signature of legacy contamination (Figure 4). As the range of PAH concentrations found in these samples was particularly large, the graph providing this comparison was plotted in log scale.

Overall, the correlations between Chry, Flt and BaA showed the occurrence of two trends, one composed of atmospheric particles and the second including the rest of the samples (Orge SPM, flood sediments, soil samples, runoff particles and Seine River sediments). Road deposited sediments appeared to be either included in the first (Figure 4a) or the second group depending on the PAH compounds considered (Figure 4b and 4c).

The similarities between soil and river samples (including sediments and SPM) highlighted by Chry, Flt and BaA correlations suggest an identical source and the conservation of those 4 rings PAH during their transfer. For instance, the alignment observed for the Orge SPM and the Seine River sediments indicated the conservation of the correlation between current Orge SPM and past Seine River SPM, despite the significant differences in their PAH concentrations. Moreover, particles transported during the flood of June 2016 and deposited on banks during the overflow have been identified as old particles, long-term stored in the Orge catchment and remobilized by high water flow (Le Gall et al., 2018). Those floodplain sediments appeared to present a PAH signature similar to the Seine River sediments (Figure 4). Therefore, those observations suggest that the current PAH contamination in the Orge River may reflect the global PAH accumulation over the catchment during more than a century of industrial activities (Lorgeoux et al., 2016; Pacyna et al., 2003). The signatures of runoff particles were also aligned with those of river particles and soil samples (Figure 4), although not with that of atmospheric particles. Those results tend to exclude atmospheric deposition as providing the major PAH primary source for runoff particles suggesting PAH released on urban surfaces as the main supply of PAH during runoff (Blanchard et al., 2001). In addition, the similarity between older sediments signature and those of current runoff also

supports the hypothesis of a long-term persistence of PAH in the river basin, characterized by the widespread and extensive contamination of soil samples, current Orge River SPM, and urban runoff particles as demonstrated by their PAH signature identical to that of legacy contamination (i.e. Seine River sediments).

The conservation of PAH signature over time and during the transfer of particles between the soils and the river observed here could be partly explained by a stabilization process occurring in soils during their aging, known to be responsible for the persistence of PAH in the environment (Biache et al., 2011), associated with their low degradation in the river. Depending on the soil characteristics (structure, organic matter content, microorganisms, etc.), PAH could be sequestered and stabilized in the soil reducing their availability (Cébron et al., 2013; Chung and Alexander, 2002), which could be explained by their strong sorption onto organic particles (Ghosh et al., 2003; Yang et al., 2008). Once stabilized in soil particles, the PAH might be less sensitive to degradation during erosion processes, explaining the similar signature found in both river and soil particles. In the river, oxidation processes may also affect PAH depending on the water composition (Miller and Zepp, 1979; Xia et al., 2009), physico-chemical conditions and microbial activity (Quantin et al., 2005). Nonetheless, studies showed that natural oxidation in water might be less important than expected based on the results of laboratory experiments because of the occurrence of multiple external factors such as variations in organic matter type and amount, microbial competition… (Fasnacht and Blough, 2002; Ge et al., 2016), reducing PAH degradation in rivers. Finally, the conservation of the PAH signature may also be explained by the similar degradation of the molecules in soils and sediments leading to a homogeneous signature of the contamination at the scale of the critical zone.

In contrast to river sediment and soil signatures, atmospheric particles showed a different pattern, with the occurrence of very variable signatures differing from those in river, soil and

runoff samples (Figure 4). This discrepancy suggests that the direct atmospheric contamination does not provide a major source of PAH for river particles, soil particles and urban runoff particles in the Orge River catchment, suggesting the dominance of the legacy contamination. Moreover, the atmospheric contamination was shown to be mainly related to the current PAH production in the atmosphere, such as vehicular emissions (Keyte et al., 2016; Oda et al., 2001) or household heating (Motelay-Massei et al., 2007) which could explain the variability of atmospheric particle signatures. In addition, 4 rings signatures of atmospheric particles might be modified by the occurrence of processes such as photo-oxidation or chemical oxidation in the atmosphere (Suess, 1976). For instance, the presence of reactive molecules (O_2, NO_x, SO_2) may lead to a degradation of PAH (Finlayson-Pitts, 1997; Nikolaou et al., 1984). Multiple factors may also influence PAH degradation in the atmosphere such as the particle composition, especially the presence of soot particles suggested to protect PAH from photo-degradation (Zelenyuk et al., 2012), or the humidity level and the sunlight intensity (Ringuet et al., 2012). This susceptibility of PAH bound to atmospheric particles to various degradation processes combined with the potential source variability may explain the very scattered pattern of the atmospheric sample signatures compared to the stable pattern found in river sediment and soil samples.

Finally, RDS signatures showed a depletion in the BaA content (Figure 4b and c, and Figure 3b), differentiating them from those urban runoff particles collected directly in separate storm sewers in Sucy. This depletion of BaA in RDS may be related to the higher sensitivity of BaA to changes in environmental conditions (temperature, availability of reactive compounds) compared to Chry and Flt and its faster degradation rate (Beyer et al., 2003; Butler and Crossley, 1981). As runoff and erosion are known to be particle-size selective, stormflow may have led to the preferential deposition of coarser particles on the road in Viry (i.e. RDS) whereas smaller particles (<100 µm) have been washed away by rainfall (Andral et al., 1999;

417 Owens et al., 2011). These particles were then likely highly exposed to photo-degradation,
418 which may explain the specific decrease in BaA concentrations in RDS collected on the road,
419 further illustrating the great caution required when using BaA as a potential source indicator.

420 The relative conservation of particulate-bound Chr and Flt between soils, urban runoff
421 particles, and river sediment suggests the potential of the Chr - Flt correlation to trace the
422 sources of PAH contamination in the study area. Accordingly, this correlation was tested
423 comparing the values found in the Orge River SPM collected at the different monitoring sites,
424 with those of the potential sources and including soil samples, RDS and urban runoff particles
425 (Figure 5). The correlation between Chr and Flt reflects the increasing PAH input in
426 downstream direction and identifies RDS and urban runoff particles as the potential ultimate
427 sources of particulate PAH contamination to SPM provided by urban areas.

428

429 ### 3.4. Radionuclide model to investigate PAH sources from urban areas

430 The estimated PAH contents in theoretical urban particles (TUP) were finally compared to
431 those PAH concentrations found in RDS and runoff particles (Figure 6).

432 The modelled concentrations of PAH in TUP appeared to be similar to those of both RDS and
433 runoff particles collected from storm sewers (Figure 6). This observation confirmed the
434 conclusion derived from PAH correlations (Figure 5) that those latter particles as provide the
435 major source of PAH transferred to the river from urban surfaces. Therefore, the combination
436 of sediment fingerprinting approach (i.e. radionuclides) with PAH signatures was shown to
437 provide consistent results and underlined urban runoff as the main source of PAH transiting in
438 the Orge catchment.

439 The model results also indicated that PAH concentrations in TUP were more similar to those
440 found in urban runoff particles from storm sewers compared to RDS (Figure 6). This suggests

441 that urban runoff particles collected from these sewers provide a better surrogate of the
442 ultimate source of contaminated urban particles supplied to the river. This further confirms
443 that the PAH composition of RDS might have been affected during their storage on the road
444 and might also be influenced by the sampling method. The depletion in BaA concentrations in
445 RDS supports the hypothesis of degradation processes, especially photo-degradation
446 occurring during RDS storage on the road (Marquès et al., 2017; Xu et al., 2013). In addition
447 to degradation processes, particle size sorting might also explain the lower PAH content
448 found in RDS, as the finest particles enriched in PAH might have been directly supplied to the
449 river by runoff (Aryal et al., 2005), while the coarser particles may have deposited on the
450 road, explaining their lower PAH content. These differences should therefore be considered in
451 future studies considering RDS as potential sources of contaminants in the rivers.

452 In the current research, fallout radionuclides were used to identify and predict the contribution
453 of contrasted PAH sources in the Orge River catchment. However, these results should be
454 interpreted with caution, given the potentially high reactivity of PAH molecules, and their
455 variations depending on their sources and the environmental conditions prevailing in the study
456 site. The transfer time of particles from urban surfaces to the river appears to be crucial, as it
457 may affect to a large extent the PAH degradation rate. In the Orge River system, the fast
458 transfer of particles once they have been supplied to the river (Froger et al., 2018) likely
459 reduces the potential degradation of particulate PAHs in the river because of the absence of
460 sediment storage in the channel in downstream sections of the river. This specific context
461 likely explains the good match observed between the modelled signature of TUP and that of
462 urban runoff particles collected in storm sewers. However, these results may likely not be
463 directly extrapolated to other potential study sites, as the concentration of several PAH may
464 decrease with increasing storage time of sediment in the river channel. Furthermore,
465 additional exposition to PAH sources like vehicle exhaust fumes may explain the higher

contamination levels observed in particles stored on urban surfaces (Bomboi and Hernández, 1991; Markiewicz et al., 2017). Moreover, the duration and the intensity of precipitation must also be considered when modeling the contamination behavior, as PAH concentrations in urban runoff tend to increase during storms (Blanchard et al., 2001). Nevertheless, the model based on radionuclide measurements to calculate theoretical PAH profiles of urban particles provided promising results: similar approaches could be used as a potential useful tool for characterizing contaminant dynamics and identifying their carrying phases.

4. Conclusions

The current research demonstrated first the persistence of PAH legacy contamination in the catchment and the conservation of those compounds in the soil-river continuum, as PAH diagnostic ratio and PAH correlations showed identical signatures for current Orge River SPM, Seine River basin soils and historical sediments from the Seine River. Atmospheric particles appeared to present another signature indicating a different PAH source and pattern for those samples. Finally, the combination of PAH signature with sediment fingerprinting approach using radionuclides to model PAH concentrations of particles transferred to the river from urban surfaces gave promising results, pointing runoff particles as the main PAH source in urban area. This model also underlined discrepancies between road deposited sediments collected on the road and runoff particles collected from stormsewers showing the need to consider these potential differences when assessing PAH sources in urban catchment.

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Figures and table captions:

Figure 1 : The Orge River catchment - land uses pattern, location of river sampling site and rain water collector (A: location of Seine River basin in Northern France, B: location of the Orge River catchment in the Ile de France Region around Mega Paris City)

Figure 2 : Water discharge of the Orge and Yvette rivers at the sampling sites and timing of the sampling campaigns

Figure 3 : Molecular diagnostic ratios of river SPM, atmospheric particles, flood sediments and RDS from the Orge River catchment along with the corresponding signatures of soils (Gaspéri et al., 2018), runoff particles (Gasperi et al., 2017), and Seine River sediment (Lorgeoux et al., 2016)

Figure 4 : Correlation between fluoranthene, chrysene and benzo(a)anthracene in Log10 displaying Orge River SPM, atmospheric particles, RDS and flood sediments along with soil samples (Gaspéri et al., 2018)*, runoff particles* (Gasperi et al., 2017)*, Seine River sediments* (Lorgeoux et al., 2016)

Figure 5 : Chrysene and fluoranthene content for the Orge River SPM displayed by sampling site, compared to the values found in the potential sources, including RDS samples, soil samples (Gasperi et al., 2016) and urban runoff particles from the Sucy site (Gasperi et al., 2017)

Figure 6 : PAH concentrations of modeled theoretical urban particles along with those of (urban) runoff particles and road deposited sediments

Table 1 : Literature data compiled to trace PAH contamination in the Orge River catchment (see detailed dataset in Table S6)

Table 1

	Description	Significance	Reference
Soil samples	Samples from the soil surface collected in 2009 – 2010 across the Seine River basin (n = 32)	Potential source of particulate-bound PAH	(Gaspéri et al., 2018)
Runoff particles	Particles collected in 2011 – 2012 from a storm sewer in Sucy catchment	Potential source of particulate-bound PAH from urban areas	(Gasperi et al., 2017)
Seine River sediments	Samples from a sediment core collected in the floodplain of the Seine River in 2008	Legacy contamination signature: 1950 – 1963: maximum PAH contamination 1970 – 2004: stabilized contamination	(Lorgeoux et al., 2016)

Figure 1

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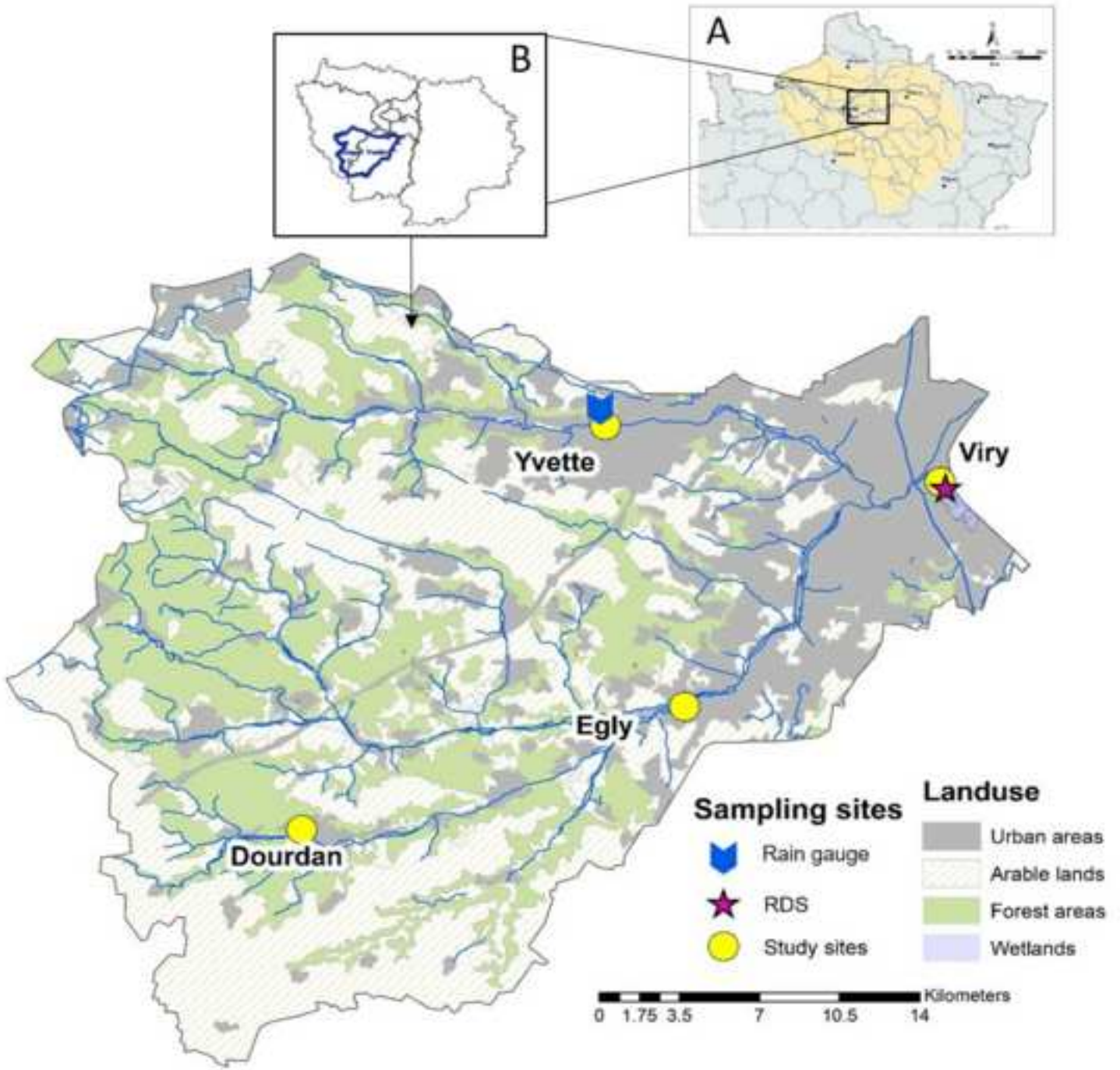

Figure 2

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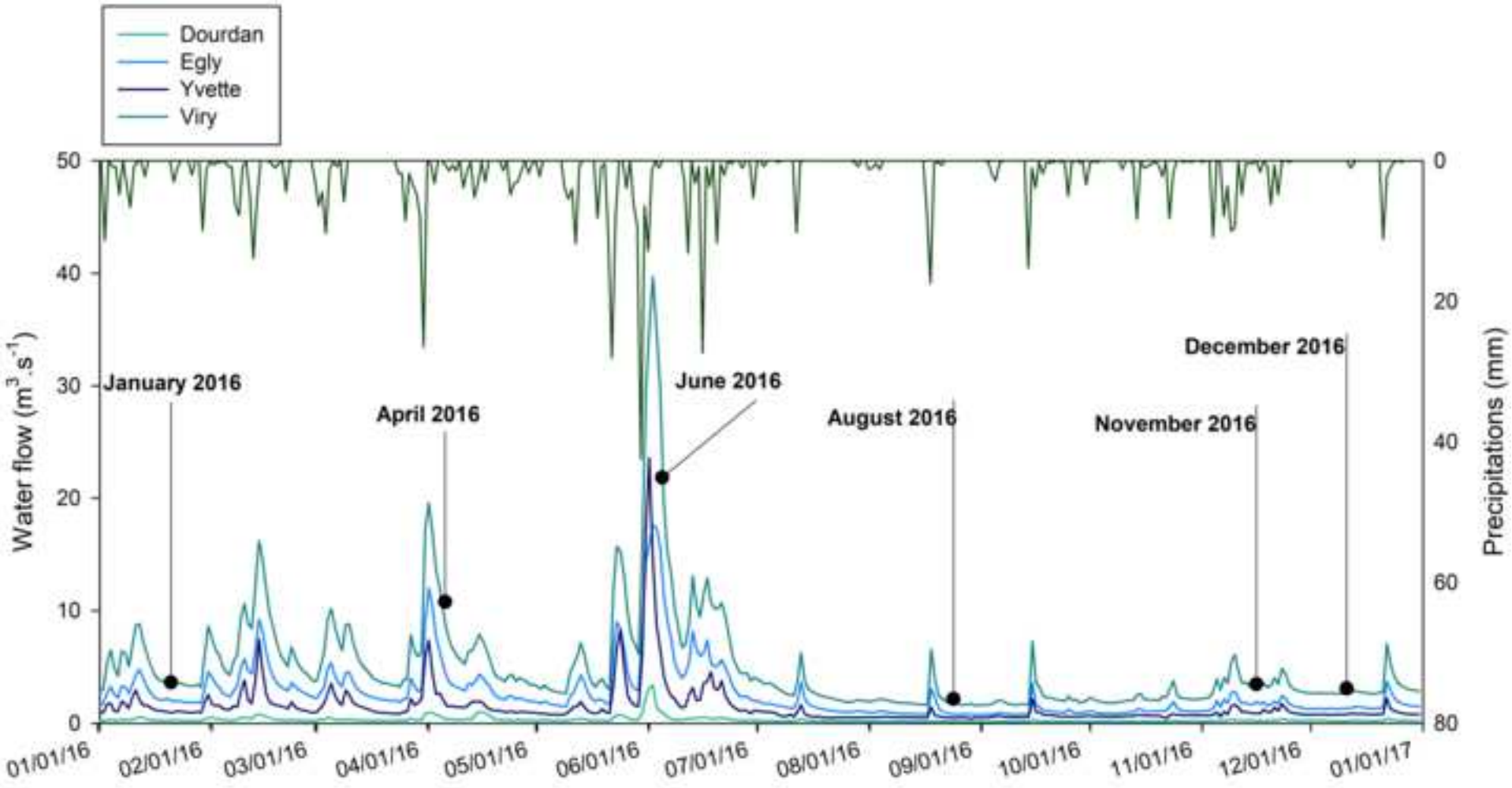

Figure 3

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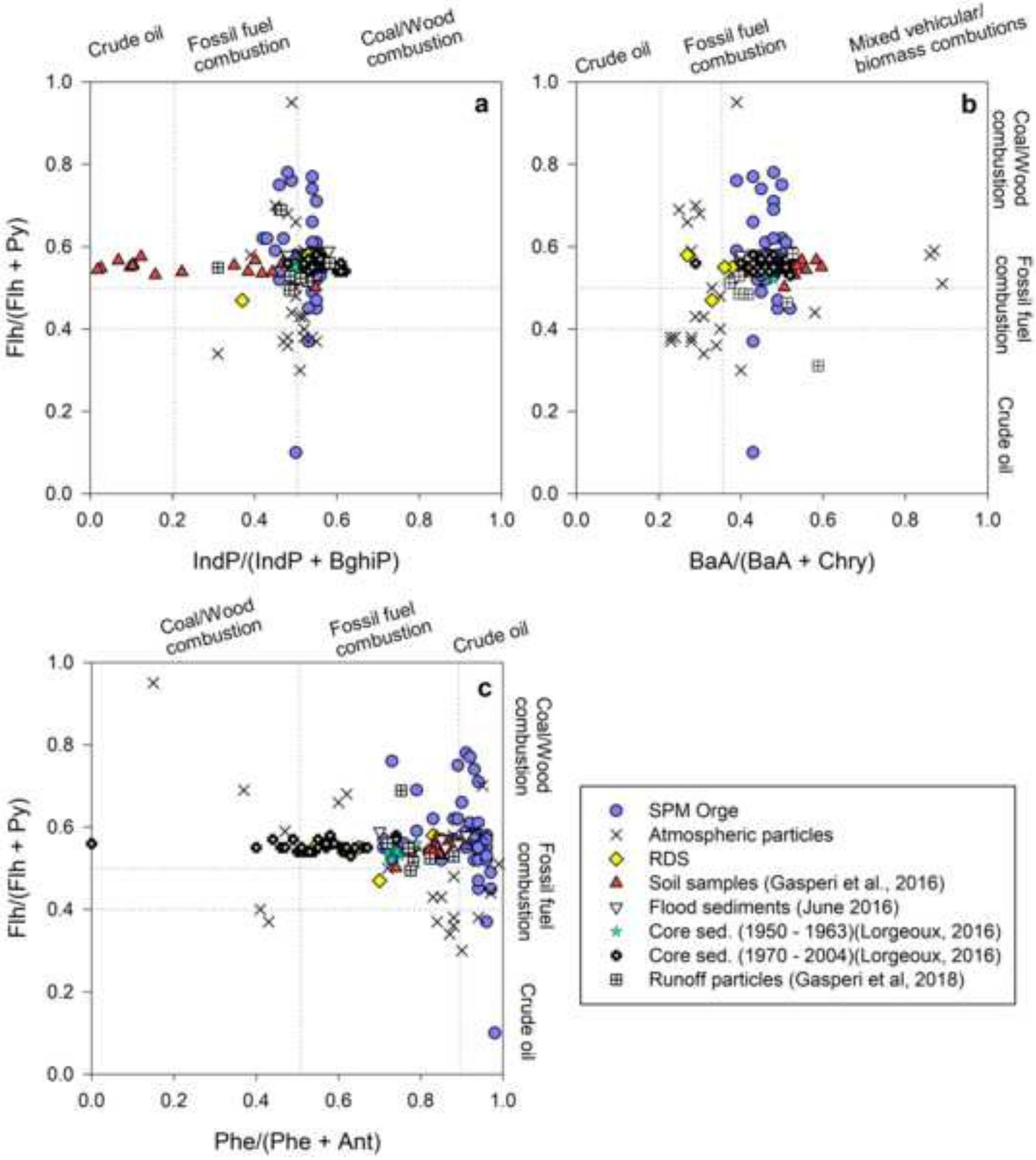

Figure 4

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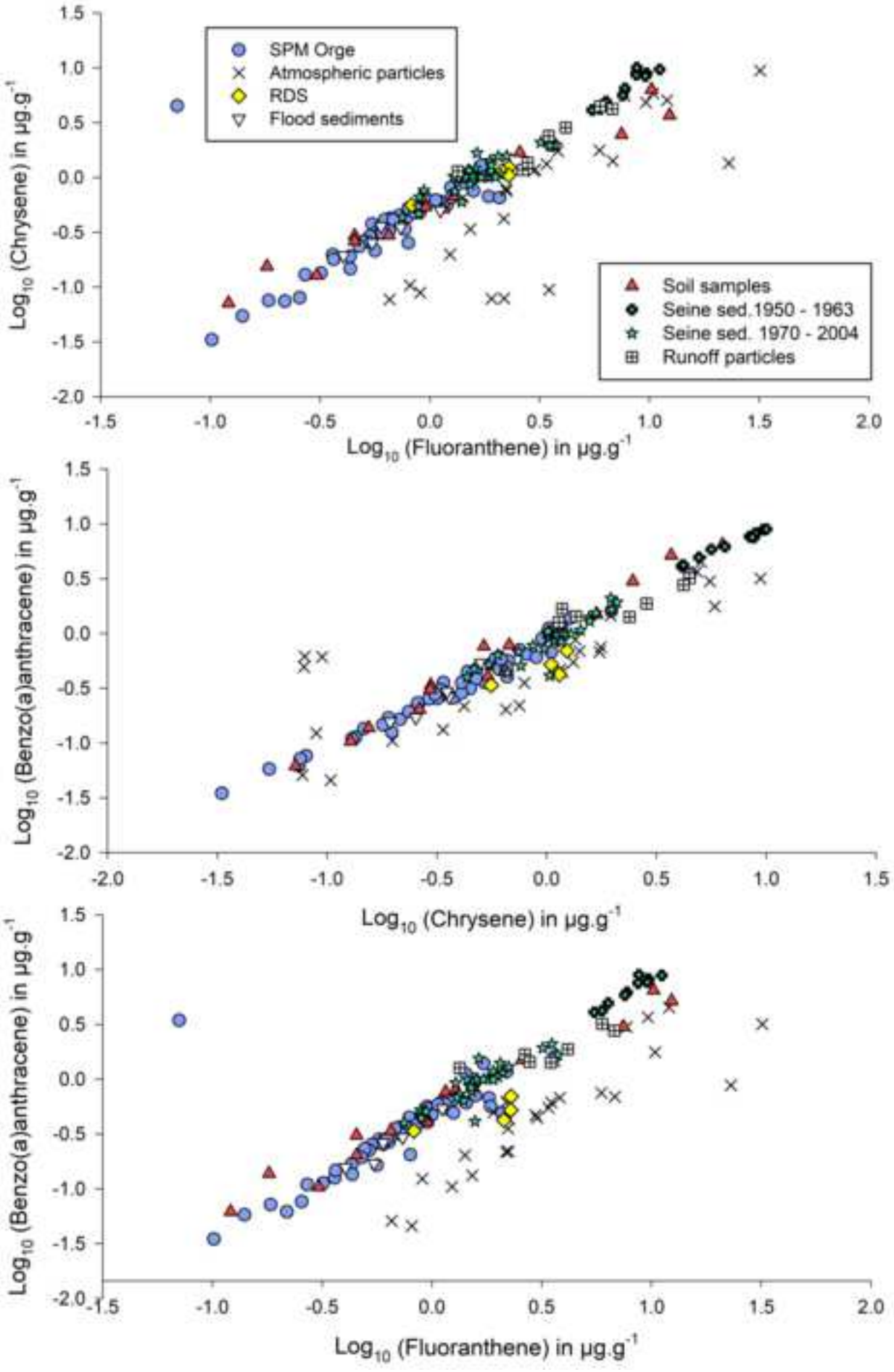

Figure 5

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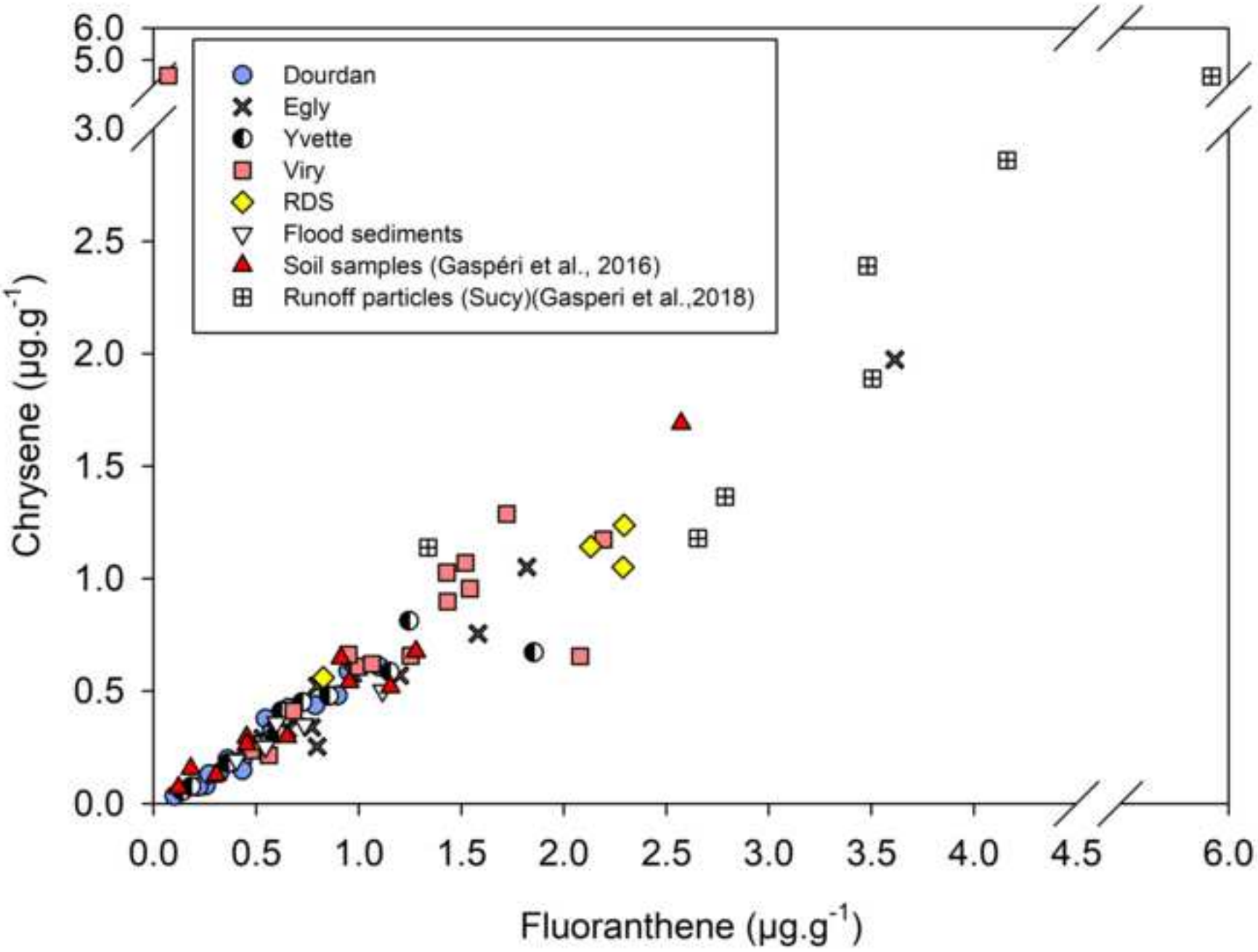

Figure 6

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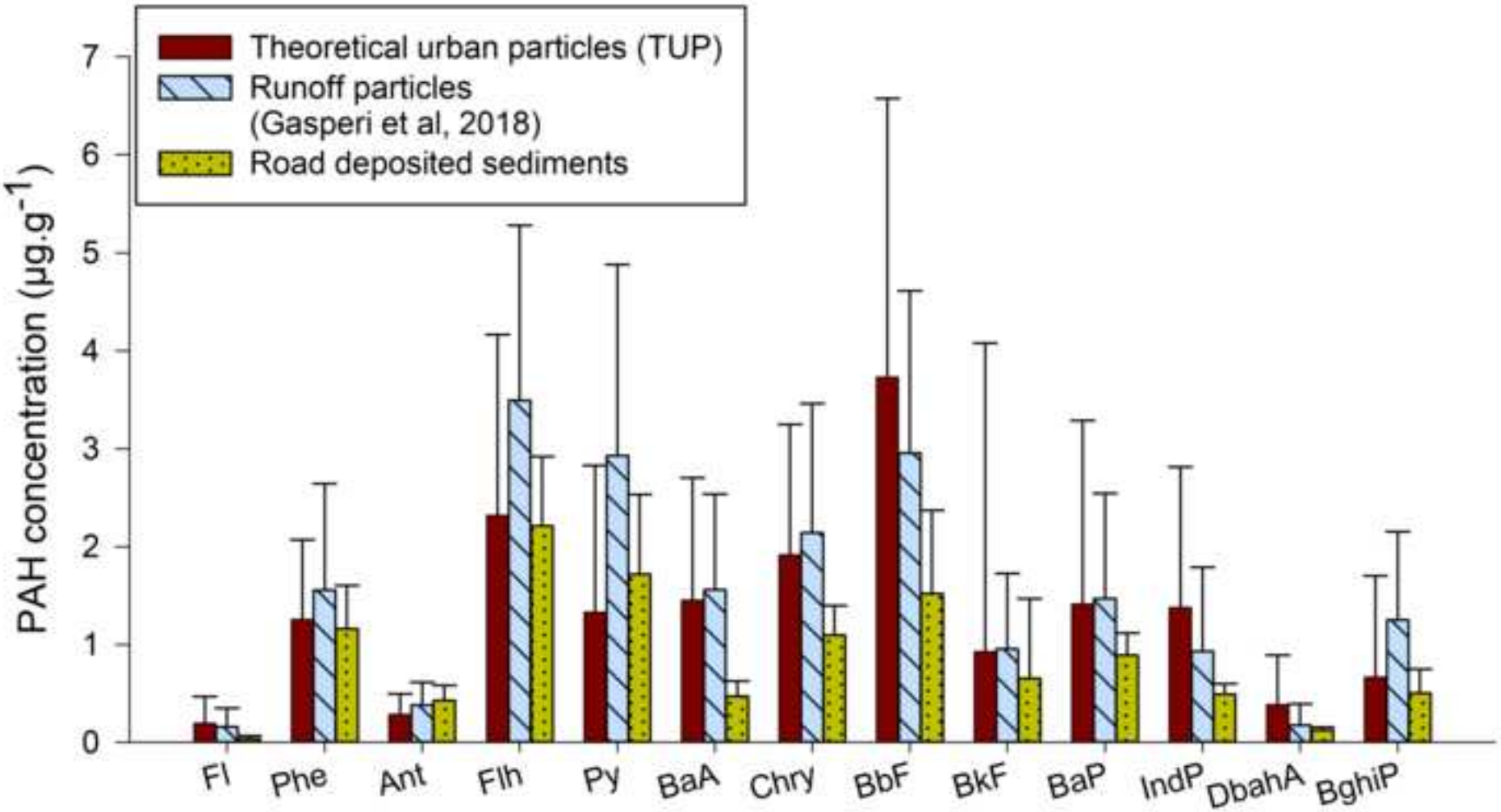

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