



**HAL**  
open science

## Suspended Particulate Matter Collection Methods influence the Quantification of Polycyclic Aromatic Compounds in the River System

Fayez Abuhelou, Laurence Mansuy, Catherine Lorgeoux, Delphine Catteloin, Valéry Collin, Allan Bauer, Hussein Jaafar Kanbar, Renaud Gley, Luc Manceau, Fabien Thomas, et al.

► **To cite this version:**

Fayez Abuhelou, Laurence Mansuy, Catherine Lorgeoux, Delphine Catteloin, Valéry Collin, et al.. Suspended Particulate Matter Collection Methods influence the Quantification of Polycyclic Aromatic Compounds in the River System. *Environmental Science and Pollution Research*, 2017, 24 (28), pp.22717-22729. 10.1007/s11356-017-9840-5 . hal-01760448

**HAL Id: hal-01760448**

**<https://hal.univ-lorraine.fr/hal-01760448>**

Submitted on 6 Apr 2018

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

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

1 **Suspended Particulate Matter Collection Methods influence the Quantification of Polycyclic**  
2 **Aromatic Compounds in the River System**

3  
4 **Fayez Abuhelou<sup>1</sup>, Laurence Mansuy-Huault<sup>1</sup>, Catherine Lorgeoux<sup>2</sup>, Delphine Cattelain<sup>2</sup>, Valéry Collin<sup>1</sup>,**  
5 **Allan Bauer<sup>1</sup>, Hussein Jaafar Kanbar<sup>1</sup>, Renaud Gley<sup>1</sup>, Luc Manceau<sup>3</sup>, Fabien Thomas<sup>1</sup>, Emmanuelle**  
6 **Montargès-Pelletier<sup>1</sup>.**

7 <sup>1</sup> Laboratoire Interdisciplinaire des Environnements Continentaux, CNRS-Université de Lorraine-LTER-Zone  
8 Atelier Moselle, 54500 Vandœuvre-lès-Nancy, France.

9 <sup>2</sup> GeoRessources UMR 7359, CNRS-Université de Lorraine-CREGU, BP239, 54506 Vandœuvre-lès-Nancy, France.

10 <sup>3</sup> Laboratoire d'Observation des Territoires, Université de Lorraine, Ile du Saulcy, F-57045 Metz 01, France

11 <sup>a</sup>  
12 Université de Lorraine, LIEC, UMR7360, Vandœuvre-lès-Nancy 54506, France

13 <sup>b</sup>  
14 CNRS, LIEC, UMR7360, Vandœuvre-lès-Nancy 54506, France

15 <sup>c</sup>  
16 Université de Lorraine, CNRS, CREGU, GeoRessources lab, UMR7359, Vandœuvre-lès-Nancy 54506,  
17 France

18  
19  
20 **Corresponding author : L. Mansuy-Huault**

21 [laurence.huault@univ-lorraine.fr](mailto:laurence.huault@univ-lorraine.fr)

22 **Tel : +(33) 3 72 74 55 25**

23  
24  
25 **Abstract**

26 In this study, we compared the influence of two different collection methods, filtration (FT) and continuous flow  
27 field centrifugation (CFC) on the concentration and the distribution of polycyclic aromatic compounds (PACs) in  
28 suspended particulate matter (SPM) occurring in river waters. SPM samples were collected simultaneously with FT  
29 and CFC from a river during six sampling campaigns over two years, covering different hydrological contexts. SPM  
30 samples were analyzed to determine the concentration of PACs including 16 polycyclic aromatic hydrocarbons  
31 (PAHs), 11 oxygenated PACs (O-PACs) and 5 nitrogen PACs (N-PACs). Results showed significant differences  
32 between the two separation methods. In half of the sampling campaigns, PAC concentrations differed from a factor 2  
33 to 30 comparing FT and CFC collected SPMs. The PAC distributions were also affected by the separation method.  
34 FT-collected SPM were enriched in 2-3 ring PACs whereas CFC-collected SPM had PAC distributions dominated by  
35 medium to high molecular weight compounds typical of combustion processes. This could be explained by distinct  
36 cut-off threshold of the two separation methods and strongly suggested the retention of colloidal and/or fine matter  
37 on glass-fiber filters particularly enriched in low molecular PACs. These differences between FT and CFC were not  
38 systematic but rather enhanced by high water flow rates.

39

40 **Keywords:** Continuous Flow Centrifuge, Filtration, Polycyclic Aromatic Compounds, Suspended Particulate Matter.

41

## 42 **Introduction**

43 PACs constitute a wide group of organic micropollutants, ubiquitous in aquatic environments. They include the 16  
44 PAHs identified as priority pollutants by the United States Environmental Protection Agency due to their mutagenic  
45 and carcinogenic properties (Keith and Telliard 1979) (e.g. benzo(a)pyrene, benzo(a)anthracene, chrysene,  
46 benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(123-cd)pyrene and dibenzo(a,h)anthracene). PAHs  
47 originate from pyrolytic or petrogenic sources and are used as markers of combustion processes, fuel spills or tar-oil  
48 contaminations to trace inputs in the environment. Among PACs, oxygen (O-PACs) and nitrogen (N-PACs)  
49 containing polycyclic aromatic compounds are emitted from the same sources as PAHs but can also be the products  
50 of photochemical, chemical or microbial degradation of PAHs (Kochany and Maguire 1994; Bamford and Baker  
51 2003; Tsapakis and Stephanou 2007; Lundstedt et al. 2007 ; Biache et al. 2017). These polar PACs have recently  
52 received increasing attention in the monitoring of coking plant sites because of their toxicity. More soluble than their  
53 parent PAHs, their transfer from soil to river should be enhanced but reports on their occurrence in aquatic  
54 environments are scarce (Qiao et al. 2014; Siemers et al. 2015).

55 PACs enter the river systems through gas exchange at the air-water interface for the most volatile compounds, or  
56 associated to soot particles for the high molecular weight PACs, through atmospheric deposition and run-off or  
57 leaching of terrestrial surfaces (Cousins et al. 1999; Heemken et al. 2000; Countway et al. 2003; Gocht et al. 2007).  
58 These compounds partition among the entire water column, depending on their physical-chemical properties  
59 (solubility, vapor pressure, and sorption coefficient), and the hydrologic conditions in the river (Zhou et al. 1999).  
60 The low molecular weight PAHs are found in the dissolved phase whereas the high molecular PAHs are associated  
61 to particulate or colloidal matter (Foster et al. 2000; Countway et al. 2003). Although less studied than the sediments  
62 or the dissolved phase of the water column, the suspended particulate matter (SPM) plays a major role in the  
63 transport and fate of hydrophobic micropollutants in rivers and numerous studies focus on their characterization  
64 (Fernandes et al. 1997; Bianchi et al. 2007; Patrolecco et al. 2010; Maioli et al. 2011; Chiffre et al. 2015; Le Meur et  
65 al. 2017). In this perspective, the reliability of the process of sampling collection is a crucial prerequisite to ensure  
66 the quality of the analyses and the conclusions that can be drawn from their study.

67 Several methods are used to collect SPM from aquatic systems (e.g. Bates et al. 1983; Rossé et al. 2006; Ademollo et  
68 al. 2012). Sediment traps and field continuous flow centrifugation rely on the size and density properties of particles

69 to promote their separation from water, similarly to sedimentation occurring in natural systems. Both methods offer  
70 the advantage of extracting SPM from a large volume of water (several hundred liters) and then provide a large  
71 amount of SPM, statistically representative because it integrates a large time window of at least several hours.  
72 Filtration is the most widespread technique used for SPM collection since it is easy to handle on the field and in the  
73 lab. The separation is controlled by the pore size of the filters. It is generally performed on small volumes that  
74 represent only a snapshot of river water. Several studies have pointed out the advantages and drawbacks of the  
75 different techniques. The distribution of organic compounds between dissolved and particulate phases is strongly  
76 affected by the separation technique. An overestimate of organic compounds in the particulate phase can be observed  
77 when SPM are separated with filtration, assigned to the colloid clogging of the membrane during filtration but these  
78 differences seem to depend on the amounts of suspended solids, the organic matter content as well as the ionic  
79 strength in the river (Bates et al. 1983; Morrison and Benoit 2001; Rossé et al. 2006; Ademollo et al. 2012). Anyway,  
80 most of the studies focus on the total concentrations of organic compounds in SPM and seldom discuss the influence  
81 of the separation techniques on the distribution of organic compounds although these distributions are often used to  
82 trace their origin such as in the case of PAHs.

83 In that perspective, we analyzed the concentration and the distribution of PACs in SPM collected in a river affected  
84 for more than one century by intense industrial activities (iron ore mining and steel-making plants) and the associated  
85 urbanization. Two sampling methods were compared i.e. field continuous flow centrifugation (CFC) and filtration on  
86 glass-fiber filters (FT). The study covered different hydrological situations and several sampling sites where the two  
87 sampling methods were applied. Two groups of PACs were explored: 16 PAHs representing a group of hydrophobic  
88 compounds ( $3.3 < \log K_{ow} < 6.75$ ) and 11 oxygenated and 5 nitrogen PACs, which represent a class of meanly  
89 hydrophobic properties ( $2 < \log K_{ow} < 5.32$ ).

90

## 91 **Material and methods**

### 92 **Characteristics of sampling sites**

93 The Orne River is a left side tributary of the Moselle River, northeast of the Lorraine region, France (Fig 1). It is a  
94 small river (Strahler order 4), with an extended watershed area of 1,268 km<sup>2</sup>, covered by forest (26.5 %), agriculture

95 (67 %) and urban land (6 %). The Orne is 85.8 km long and flows from an altitude of 320 to 155 m asl. The monthly  
96 averaged flow fluctuates between 1.5 and 19 m<sup>3</sup> s<sup>-1</sup> with a mean flow of 8.1 m<sup>3</sup> s<sup>-1</sup> and maximum flow rates reaching  
97 at 170 m<sup>3</sup> s<sup>-1</sup>. This river has been highly impacted by iron ore extraction and steel-making industries during the whole  
98 20<sup>th</sup> century. Five different sampling sites were chosen based on criteria of representativeness and accessibility for  
99 the field continuous flow centrifuge in the lower part of the Orne river, on the last 23 km before the confluence with  
100 the Moselle River: Auboué (AUB), Homécourt (BARB), Joeuf (JOAB), Moyeuve-Grande (BETH) and Richemont  
101 (RICH). BETH site at Moyeuve-Grande is located at a dam that influences the river hydrology: the water depth  
102 ranges between 3 and 4 m while it is meanly 1 m at the other sites and the water speed (<0.5 m s<sup>-1</sup> at the dam) is 1.5  
103 to 5 times lower than at other sites.

#### 104 **SPM collection**

105 SPM were collected at six periods of time between May 2014 and May-June 2016 covering different hydrological  
106 situations (Table 1). The field continuous flow centrifugation (CFC) and filtration (FT) were applied to obtain  
107 SPM<sub>CFC</sub> and SPM<sub>FT</sub> respectively. Additionally, in May and June 2016, water samples from the inlet and outlet of the  
108 CFC were collected and filtered back in the laboratory, to obtain SPM<sub>FT In-CFC</sub> and SPM<sub>FT Out-CFC</sub>.

109 The CFC operation, as already mentioned by Le Meur et al. (2015), started with river water being pumped to the  
110 mobile CFC (CEPA Z-41 running at 20000 RPM, equivalent to 17.000×g), located 10-50 m beside the river. The  
111 CFC feeding flow rate was set to 600 L h<sup>-1</sup>. The cut-off threshold of the field centrifuge was shown to be close to 5  
112 µm by measuring the grain-size of waters at the outlet of the centrifuge. Depending on the campaign, the CFC was  
113 run between 1h30 and 3h in order to obtain representative samples in sufficient amounts (from several grams to 100  
114 g of dry matter). The SPM<sub>CFC</sub> was recovered from the Teflon plates covering the internal surface of the centrifuge  
115 bowl and transferred into glass bottles, transported to the lab in an ice-box to be immediately frozen, freeze-dried and  
116 stored at 4°C for further use.

117 Depending on the water turbidity, and in order to collect sufficient amount of SPM<sub>FT</sub> on filters, 7.5 L of water were  
118 collected in amber glass bottles and when necessary, additional 10 or 20 L were collected. All water samples were  
119 brought back to the lab and filtered within 24 h. To facilitate the filtration process, especially for high turbidity  
120 samples, waters were filtered sequentially on pre-weighted glass fiber filters, first on GFD (Whatman, 90 mm  
121 diameter, nominal pore size = 2.7 µm) followed by GFF (Whatman, 90 mm diameter, nominal pore size = 0.7 µm).

122 Filters were then wrapped in aluminum foil, frozen, freeze-dried and weighted individually, to  $\pm 0.01$  mg, and the  
123 SPM content on each filter in  $\text{mg L}^{-1}$  was determined as the difference between the filter weight before and after  
124 filtration process.

125

## 126 **Analytical methods**

### 127 *Global parameters and elemental content*

128 Water temperature, electric conductivity (EC) and turbidity were measured using a portable multiparameter device  
129 (Hach®). The Dissolved Organic Carbon (DOC) was measured with an automated total organic C analyzer (TOC-  
130 VCPH. Shimadzu, Japan) on filtered water (0.22  $\mu\text{m}$  syringe filters) stored in brown glass flasks at 4°C. The  
131 Particulate Organic Carbon (POC) was determined on the carbonate-free freeze-dried samples of  $\text{SPM}_{\text{CFC}}$  (1 M HCl;  
132 left to stand 1 h; shaken 0.5 h) and measured using a CS Leco SC144 DRPC analyzer and/or a CS Horiba  
133 EMIA320V2 analyzer at SARM-CRPG Laboratory. The grain size distribution of particles in raw waters (except for  
134 the campaign of May 2014) was determined using laser diffraction (Helos, Sympatec). The raw waters were  
135 introduced into the Sucell dispersing unit and were ultrasonicated for 20 seconds. Duplicate or triplicate  
136 measurements were performed to improve the measurement quality with and without ultrasound treatment. The  
137 particle size distribution was then represented as volumetric percentage as a function of particle diameter. In  
138 addition, the percentiles ( $D_i$ ) of the particles were calculated using Helos software.  $D_i$  is the  $i^{\text{th}}$  percentile, i.e. the  
139 particle diameter at which  $i$  % of the particles in the sample is smaller than  $D_i$  (in  $\mu\text{m}$ ).

### 140 *Sample treatment*

141 Up to 2 g of dry matter of  $\text{SPM}_{\text{CFC}}$  and from 0.06 to 1.4 g of dry matter  $\text{SPM}_{\text{FT}}$  were extracted with an Accelerated  
142 Solvent Extractor (Dionex® ASE350). ASE cells were filled with activated copper powder (to remove molecular  
143 sulphur) and sodium sulfate ( $\text{Na}_2\text{SO}_4$  to remove remaining water) and pre-extracted for cleaning. Samples were  
144 extracted at 130°C and 100 bars with dichloromethane (DCM) with two cycles of 5 min (Biache et al. 2008). After  
145 adjusting the volume at 5 mL, a 1 mL aliquot was taken out for clean-up step. It was spiked with external extraction  
146 standards (mixture of 6 deuterated compounds:  $[\text{}^2\text{H}_8]$ Dibenzofuran,  $[\text{}^2\text{H}_{10}]$ Fluorene,  $[\text{}^2\text{H}_{10}]$ Anthracene,

147 [<sup>2</sup>H<sub>8</sub>]Anthraquinone, [<sup>2</sup>H<sub>10</sub>]Fluoranthene, [<sup>2</sup>H<sub>12</sub>]Benzo[ghi]perylene) to control the loss during the sample  
148 preparation. The 1 mL aliquot was then evaporated to dryness using a gentle N<sub>2</sub> flow, diluted into 200 μL of hexane  
149 and transferred onto the top of a silica gel column pre-conditioned with hexane. The aliphatic fraction was eluted  
150 using 3.5 mL of hexane. PAC fraction was eluted with 2.5 mL of hexane/DCM (65/35; v/v) and 2.5 mL of  
151 methanol/DCM (50/50; v/v). The latter fraction was spiked with 20 μL at 12 μg mL<sup>-1</sup> of internal quantification  
152 standards (mixture of 8 deuterated compounds: [<sup>2</sup>H<sub>8</sub>]Naphthalene, [<sup>2</sup>H<sub>10</sub>]Acenaphthene, [<sup>2</sup>H<sub>10</sub>]Phenanthrene,  
153 [<sup>2</sup>H<sub>10</sub>]Pyrene, [<sup>2</sup>H<sub>12</sub>]Chrysene, [<sup>2</sup>H<sub>12</sub>]Perylene and [<sup>2</sup>H<sub>8</sub>]9H-fluorenone) before evaporation and the volume was  
154 adjusted to 100 μL with DCM. To improve the chromatographic resolution, the sample was derivatized by adding  
155 BSTFA in (1:1; v/v) and finally injected in 200 μL volume in the gas chromatograph–mass spectrometer (GC–MS).

### 156 *Analysis*

157 The instrument used was an Agilent 6890N gas chromatograph equipped with a DB 5-MS column (60 m × 0.25 mm  
158 i.d. × 0.25 μm film thickness) coupled with an Agilent 5973 mass selective detector operating in single ion  
159 monitoring mode. The molecules were detected with a quadrupole analyzer following ionization by electronic  
160 impact. The temperature program was the following: from 70°C to 130°C at 15°C min<sup>-1</sup>, then from 130°C to 315°C  
161 at 3°C min<sup>-1</sup> and then a 15 min hold at 315°C. 1 μL of sample was injected in splitless mode at 300°C. The carrier  
162 gas was helium at 1.4 mL min<sup>-1</sup> constant flow.

### 163 *Validation and quality control*

164 The quantitative analyses of PACs were carried out using internal calibration using specific family standard (refer to  
165 supporting information S1). For each quantified compound, the GC/MS was calibrated between 0.06 and 9.6 μg mL<sup>-1</sup>  
166 with 10 calibration levels. The calibration curves were drawn and satisfactory determination coefficients were  
167 obtained (r<sup>2</sup> >0.99). To verify the quantification, two calibration controls (lower and higher concentrations) were  
168 carried out every 6 samples and only a deviation lower than 20% was accepted. The limits of quantification (LOQ)  
169 for an extraction of 1 g of sample were between 0.06 and 0.12 μg g<sup>-1</sup> (refer to supporting information S1).  
170 Experimental and analytical blanks were also monitored regularly to assess external contamination.  
171 The whole analytical procedure was validated using reference materials (SRM 1941a, NIST) for PAHs. For O-PAC  
172 and N-PAC analysis, no commercial reference material was available. So the laboratory took part to an



173 intercomparison study on the analysis of O-PAC and N-PAC in contaminated soils (Lundstedt et al. 2014). The  
174 methodology was then adapted to sediment and SPM. The recoveries of external standards, added in each sample,  
175 were checked and the quantification was validated if it ranged between 60 and 125 % (refer to supporting  
176 information S2).

177

## 178 **Results**

### 179 *Sampling campaign characteristics*

180 The global parameters (Table 1) exhibited different hydrological situations in the successive sampling campaigns.  
181 May 2014 and October 2015 corresponded to the lowest flow conditions with a daily mean water discharge around  
182  $1.5 \text{ m}^3 \text{ s}^{-1}$  and rather high water temperature (13 to  $17^\circ\text{C}$ ). The turbidity and the SPM contents were respectively  
183 lower than 3 NTU and  $6 \text{ mg L}^{-1}$ . The water discharge in May 2015 ranged between 8 and  $21 \text{ m}^3 \text{ s}^{-1}$  with turbidity  
184 values around 30 NTU and SPM contents from 16 to  $54 \text{ mg L}^{-1}$ . Higher water discharges, although rather moderate  
185 compared to that of a biennial flood reaching  $130 \text{ m}^3 \text{ s}^{-1}$ , were observed in November 2014 ( $22 \text{ m}^3 \text{ s}^{-1}$  the first day  
186 and  $51 \text{ m}^3 \text{ s}^{-1}$  the second day) and February 2015 ( $50 \text{ m}^3 \text{ s}^{-1}$ ). The highest flow rates of  $120 \text{ m}^3 \text{ s}^{-1}$  were observed  
187 during the flood of May 2016. The highest turbidity and SPM content were observed during the first high flow of the  
188 season the 5<sup>th</sup> of November 2014 (109 NTU and  $122 \text{ mg L}^{-1}$ ) and during the flood of May 2016 (94 NTU and  $90 \text{ mg}$   
189  $\text{L}^{-1}$ ). The POC ranged between 3 and  $12.5 \text{ mg g}^{-1}$  and the highest value was recorded during the low flow event of  
190 May 2014. DOC varied between 4 and  $11 \text{ mg L}^{-1}$  with the highest DOC observed in May 2015 and the 5<sup>th</sup> November  
191 2014. Concerning, the grain size distribution of raw waters, the decile D50 was shown to vary very slightly from 5 to  
192  $15 \mu\text{m}$  for the different reported campaigns. The lowest value of the D50 ( $\approx 5\mu\text{m}$ ) was measured in February 2015  
193 during a high flow event (Table 1 and Fig 2). The measured particle size distributions covered relatively narrow  
194 ranges from 1.5 to  $102 \mu\text{m}$  and the increases of the flow regime resulted in a clear increase of particle loading (SPM  
195 content) with no strong shift of particle size.

196 *PAC concentration and distribution in SPM<sub>FT</sub> and SPM<sub>CFC</sub>*

197 Table 2 displays the contents in PAHs, O-PACs and N-PACs and the main characteristics of their distribution  
198 according to the sampling methods (CFC and FT) and to the sampling dates and locations. The comparison of the 16  
199 PAH concentrations in SPM<sub>FT</sub> and SPM<sub>CFC</sub> revealed a contrasted effect of the separation techniques.

200 When the whole set of data is considered, the sum of the 16 PAH concentrations in SPM<sub>CFC</sub> ranged between 2  
201 and 27.7  $\mu\text{g g}^{-1}$  with a median value at 4  $\mu\text{g g}^{-1}$ . Despite a high value measured at JOAB site on May 2014, the range  
202 of variations was rather narrow, the 1<sup>st</sup> and 3<sup>rd</sup> quartiles being at 3.6 and 5.3  $\mu\text{g g}^{-1}$  respectively (Fig 3a). For SPM<sub>FT</sub>  
203 samples, the PAH concentrations varied between 1.3 and 39  $\mu\text{g g}^{-1}$  with a median value at 18.4  $\mu\text{g g}^{-1}$  but a higher  
204 dispersion of the PAH concentrations was observed, the 1<sup>st</sup> and 3<sup>rd</sup> quartiles being at 7.2 and 3.4  $\mu\text{g g}^{-1}$  respectively  
205 (Fig. 3b). For all samples, O-PAC and N-PAC concentrations were much lower than PAHs, accounting for 10 to  
206 30% of the total PACs except for BETH site in May 2014. The differences of O-PAC concentrations in SPM<sub>FT</sub> and  
207 SPM<sub>CFC</sub> were also less contrasted. They were in a very close range, between 0 and 5.4  $\mu\text{g g}^{-1}$  and 0.1 and 3.8  $\mu\text{g g}^{-1}$   
208 respectively in SPM<sub>FT</sub> and SPM<sub>CFC</sub>. However, as observed for PAHs, the dispersion of the O-PAC concentrations  
209 was higher in SPM<sub>FT</sub> than in SPM<sub>CFC</sub> (Fig 2c and 2d).

210 The discrepancies in PAC concentrations between SPM<sub>FT</sub> and SPM<sub>CFC</sub> appeared more clearly when sampling  
211 campaigns were distinguished. The ratios of the PAH concentrations in SPM<sub>FT</sub> and SPM<sub>CFC</sub> (Fig. 4a) and of the polar  
212 PAC concentrations in SPM<sub>FT</sub> and SPM<sub>CFC</sub> (Fig. 4b) were calculated for each sample in order to highlight the  
213 differences of concentration according to the separation method and the sampling campaign. The whole campaign of  
214 May 2015, JOAB in May 2014 and BARB in November 2014 provided comparable PAH concentrations in SPM<sub>FT</sub>  
215 and SPM<sub>CFC</sub> with a ratio close to 1. However, all the samples of February 2015 and May-June 2016, BETH in May  
216 2014 and JOAB and BETH in November 2014 provided higher concentrations of PAHs with concentrations in  
217 SPM<sub>FT</sub> two to eleven times higher than in SPM<sub>CFC</sub> (Fig. 4a).

218 The comparison of polar PAC concentrations in SPM<sub>FT</sub> and SPM<sub>CFC</sub> also revealed discrepancies between the two  
219 sampling methods (Fig 3b). In February 2015 and May-June 2016, polar PACS were six to thirty times more  
220 concentrated in SPM<sub>FT</sub> than in SPM<sub>CFC</sub>. In May 2014, polar PAC concentrations were fifteen times higher in SPM<sub>FT</sub>  
221 at BETH than in SPM<sub>CFC</sub>.

222 The distribution of individual PAHs was also strongly and diversely affected by the method of sampling. In SPM<sub>CFC</sub>,  
223 the 4 to 6 ring-PAHs were easily detected and well represented in the distribution, representing 50 to 90% of the all

224 PAHs (except in May 2014), even though they could vary in abundance according to the sampling campaign (Table  
225 2). In  $SPM_{FT}$ , 2 to 3 ring-PAHs were systematically more represented than in  $SPM_{CFC}$  and accounted for 40 to 70%  
226 of the total PAH concentration except during the November 2014 and May 2015 campaigns. The ratio of each  
227 individual PAH concentration in  $SPM_{FT}$  over its concentration in  $SPM_{CFC}$  was plotted against the  $\log K_{ow}$  of each  
228 PAH for all the samples (Fig. 5). The ratio is close to 1 for the PAHs with  $\log K_{ow}$  higher than 5.5 having more than  
229 4 aromatic rings whereas it can vary from 0.5 to 38 for PAHs with 2 to 4 aromatic rings ( $\log K_{ow} < 5.2$ ). The highest  
230 differences were observed in Feb 2015 and May-June 2016 and to a lesser extent in Nov 2014, May 2014 and  
231 October 2015. Thus, it appeared that the 2 to 3-ring PAHs and to a lesser extent the 4-ring PAHs were the molecules  
232 the most affected by the sampling methods.

233 In the same way, any time we observed a significant difference of O-PAC concentration between the two sampling  
234 methods (February 2015 and May-June 2016), it could be attributed to a higher concentration in low molecular  
235 weight O-PACs, composed of three rings, mainly dibenzofuran, fluorenone and anthraquinone (Table 2).

236 Values of common PAH molecular ratios were compared (Table 2 and Fig. 6). Only, the ratios based on 3 and 4  
237 rings could be calculated in  $SPM_{FT}$  and compared to  $SPM_{CFC}$ . Whatever the sampling method, the values of  
238  $Flt/(Flt+Pyr)$  were found within a quite narrow range of 0.5-0.66 assigned to pyrogenic inputs. The values of  
239  $Ant/(Ant+Phe)$  evolved between 0.07 and 0.37 in  $SPM_{CFC}$  placing most of the samples in the pyrogenic domain and  
240 showing a variation in the contribution of these compounds according to the hydrology. Except for October 2015, the  
241 ratios  $Ant/(Ant+Phe)$  in  $SPM_{FT}$  ranging between 0.06 and 0.17, were systematically lower than in the equivalent  
242  $SPM_{CFC}$  suggesting an influence of petrogenic PAHs.

243

#### 244 **PACs in the filtered SPM of the inlet and outlet waters of the CFC**

245 The analyses of the matter collected by filtration of the inlet waters of CFC ( $SPM_{FT\ In-CFC}$ ) and the matter collected  
246 by filtration of the outlet waters of the CFC ( $SPM_{FT\ Out-CFC}$ ) allowed to better understand the partitioning of SPM in  
247 the CFC and then by the filtration process. This test was carried out at AUB, RICH and BETH in May and June  
248 2016. The quantification of the SPM collected by filtration of the inlet and outlet waters showed that CFC allowed to  
249 recover 80% of the SPM contained in the inlet waters (Table 3). In the three tests, as already described in the

250 previous paragraphs, the PAH concentrations are six to eleven times higher in  $SPM_{FT}$  than in  $SPM_{CFC}$ . The PAH  
251 concentration in the residual SPM collected by filtration of the CFC outlet waters ( $SPM_{FT\ Out-CFC}$ ) is as high or even  
252 twice higher than in the inlet water. The PAH distributions displayed at figure 7 are representative of those observed  
253 in most of the  $SPM_{FT}$  and  $SPM_{CFC}$ . PAH distributions in  $SPM_{CFC}$  are characterized by the abundance of 4 to 6-ring  
254 PAHs whereas they are in very low abundance in  $SPM_{FT}$  and not detectable in  $SPM_{FT\ Out-CFC}$ . Thus, the CFC retains  
255 SPM containing low PAC concentrations made of high molecular weight compounds and the SPM not retained by  
256 the CFC but collected by the filtration of the outlet waters is highly concentrated in PACs mainly made of  
257 phenanthrene, fluoranthene and pyrene. The PAH distribution in  $SPM_{FT\ In-CFC}$  and  $SPM_{FT\ Out-CFC}$  are very similar  
258 showing that the contribution of the fine matter collected in the outlet waters largely contributes to the SPM collected  
259 in the total SPM collected on filters (figure 7).

260

## 261 **Discussion**

262 Our results show that the two methods of SPM collection strongly influence not only the concentration but also the  
263 distribution of PACs. PACs in  $SPM_{CFC}$  were found in a narrow range of concentrations independently of the  
264 sampling location and the hydrological situation. The PAH distributions were dominated by 4 to 6 ring- PAHs. On  
265 the contrary, in  $SPM_{FT}$ , the spreading of PAH concentrations was much higher, and the PAH distribution was  
266 dominated by low molecular weight compounds when a noticeable discrepancy was observed compared to  $SPM_{CFC}$ .  
267 From reported results in literature, a non-exhaustive inventory of PAH concentrations and distributions according to  
268 the SPM collection method, regardless of the spatial and hydrological context was summarized on Table 4. This  
269 inventory shows that the concentrations remain in a relatively narrow range (the maximum concentration does not  
270 exceed five times the minimum concentration) when the SPM collection method is CFC (Wölz et al. 2010; Le Meur  
271 et al. 2017) or sediment traps (Zhang et al. 2009; Chiffre et al. 2015) or pressure-enhanced filtration system  
272 (Countway et al. 2003; Ko and Baker 2004). When the SPM are collected by filtration, the PAH concentration range  
273 can be really more highly spread from one to 40 times (Deng et al., 2006; Guo et al., 2007; Luo et al., 2009; Maioli  
274 et al., 2011; Mitra and Bianchi, 2003; Sun et al., 2009; Zheng et al., 2016). One can argue that this variation might  
275 obviously depend on the river and the hydrological situation. However, if we compare the PAH distributions, it  
276 clearly appears that whenever the sampling method is filtration, 2 to 3-ring PAHs can largely dominate the

277 distribution as indicated by the LMW/HMW ratios reported in Table 5. In SPM collected by CFC or sediment traps,  
278 the low molecular weight PAHs seldom dominate the distribution.

279 Several studies have reported that filtration retains colloidal organic matter and their associated organic or metallic  
280 contaminants leading to an overestimate of compounds associated to particulate matter. Bates et al. (1983) compared  
281 centrifugation and filtration to collect particulate matter from wastewaters and riverine waters and observed a  
282 systematic higher concentration of aliphatic hydrocarbons in SPM collected by filtration and a lower proportion of  
283 dissolved hydrocarbons in the filtered water compared to the centrifuged one. They attributed it to the adsorption of  
284 dissolved an colloidal matter on the glass-fiber filter and by the matter retained on its surface. Morrison and Benoit  
285 (2001) showed that membrane clogging during filtration of riverine waters induces the decline of dissolved cation  
286 concentrations in filtered waters. Our results show variations from a factor 2 to 9 for PAH contents and 2 to 30 for O-  
287 PAC contents when SPM are separated by filtration and could be explained by the retention of colloidal and fine  
288 matter on filters. Gomez-Gutierrez et al. (2007) tested the adsorption of various organics on glass-fiber filters  
289 according to DOC values and salinity on synthetic waters. They showed an increase of the adsorption of the more  
290 hydrophobic PAHs (4 to 6 rings) with the increase of DOC and salinity but a lower adsorption of low molecular  
291 weight PAHs. In our natural waters, if we compare the PAC concentrations and distributions, we observed an  
292 opposite trend with low molecular weight PAHs being more concentrated in  $SPM_{FT}$  than in  $SPM_{CFC}$ . The higher  
293 concentration in  $SPM_{FT}$  cannot be only related to PAH adsorption on filters but might be due to the retention of  
294 colloidal or fine particulate matter (few microns), organic and mineral, particularly enriched in low molecular weight  
295 PAHs. This hypothesis is strongly supported by the abundance of low molecular weight PACs highly concentrated in  
296 the matter not retained by the centrifuge but collected by filtration of the outlet waters. Countway et al. (2003)  
297 showed that high molecular weight PAHs were rather associated to soot and particles from sediment resuspension  
298 whereas more volatile PAHs were associated to autochthonous organic matter. Wang et al. (2016) also observed  
299 enrichment in low molecular weight hydrocarbons in the finer grain-size fractions of their sediments.

300 Surprisingly, those differences are not systematic and only occur in half of the collected samples. For the samples of  
301 February 2015 and May and June 2016, the highest differences between  $SPM_{FT}$  and  $SPM_{CFC}$  are concomitant of a  
302 high flow and the finest grain size distribution of SPM ( $D_{50} < 10 \mu m$ ). In those cases, filtration allowed to recover  
303 most of the fine particles and colloids highly concentrated in PACs ( $18$  to  $43 \mu g g^{-1}$ ) while field centrifugation

304 collected coarser matter with much lower PAC concentrations (2 to 5.5  $\mu\text{g g}^{-1}$ ). Previous studies observed similar  
305 trends in other contexts. Wang et al. (2016) showed that small-size SPM (0.7 -3  $\mu\text{m}$ ) collected from estuarine and  
306 riverine waters were particularly enriched in PAHs compared to large-size SPM ( $>3 \mu\text{m}$ ). El-Mufleh et al. (2014)  
307 separated sediments from storm water infiltration basins into several density fractions and showed that the PAH  
308 amounts were 100 times higher in the lighter fractions than in the denser ones. In their study of colloids and SPM in  
309 river, Ran et al. (2000) showed the increasing content in organic carbon and ions with decreasing particle size and  
310 highlighted the importance of colloidal matter in the concentrations of micropollutants. However, in our set of data,  
311 no significant correlation could be observed between the high amount of PACs in  $\text{SPM}_{\text{FT}}$  and global parameters such  
312 as particle grain-size, water discharge, organic carbon content of SPM, water conductivity or SPM amount.

313 This comparison of PACs in  $\text{SPM}_{\text{FT}}$  and  $\text{SPM}_{\text{CFC}}$  allowed evidencing the crucial role of colloidal and fine particulate  
314 matter in the transfer of PACs. The predominant contribution of fine and/or colloidal matter in  $\text{SPM}_{\text{FT}}$  in February  
315 2015 and May-June 2016 campaigns revealed that this matter transfers mainly low molecular weight PACs  
316 compared to the coarser particulate fraction collected by  $\text{SPM}_{\text{CFC}}$ . Also, the molecular ratios suggest a different  
317 origin for PACs in colloidal and fine matter with a higher contribution of petroleum products. This suggests that  
318 distinct transfer paths of PACs coexist in this river: the PACs associated to particulate matter with a quite  
319 homogeneous molecular signature assigned to combustion corresponding to diffuse pollution in the catchment and  
320 the PACs associated to colloidal and fine matter with a more variable molecular signature that could be assigned to  
321 petrogenic contribution and could enter the river as a point-source during specific hydrological events.

322

## 323 **Conclusions**

324 Filtration on glass fiber filters (0.7  $\mu\text{m}$ ), the most commonly used technique, is easy to handle, inexpensive, adapted  
325 to any field context and the separation between particulate and dissolved matter is based on particle size. In this  
326 study, we showed that this method might collect colloidal and fine matter that can significantly affect the amount of  
327 PACs measured in the SPM fraction inducing higher concentrations and distributions enriched in low molecular  
328 compounds. These differences were not systematic over the two-year period of our investigation in a small industrial  
329 river system. On the contrary, the second sampling technique we tested on the same samples, CFC, provided SPM a

330 large amount of SPM collected out of important volumes of water (500 L) with PAC concentrations quite stable from  
331 one site to another and from one hydrological condition to another. PAC distributions were dominated by medium to  
332 high molecular weight compounds that allowed to calculate various diagnostic molecular ratios easier to interpret  
333 than with FT where the poor abundance of HMW PAC limited the interpretation of molecular ratios. Although  
334 filtration presents numerous advantages to collect SPM, one must be very careful in the interpretations of some  
335 variations that can also be attributed to the retention of some colloidal and fine matter, enriched in low molecular  
336 PACs, especially during high flow events. On the other hand, this allows to access to supplemental information on  
337 the nature of PACs transported by fine and colloidal matter. Thus, according to the sampling method, evaluation of  
338 PAC distribution between dissolved and particulate phase can be appreciably different. These results suggest that the  
339 choice of a SPM collection method is fundamental to comply with the objectives that one can defined for the  
340 monitoring of surface waters.

341

#### 342 **Acknowledgements**

343 The authors would like to thank Long-Term Ecosystem Research (LTER) France, Agence Nationale de la Recherche  
344 (ANR) project number ANR-14-CE01-0019, RésEAU LorLux and Region Lorraine through the research network of  
345 Zone Atelier Moselle (ZAM) for partially funding the work, the Syndicat de Valorisation des Eaux de l'Orne  
346 (SVEO) and the city of Moyeuvre for granting us access to the sampling sites. We thank ERASMUS MUNDUS for  
347 funding the PhD of M. Abuhelou. The final manuscript was also improved by the valuable suggestions of four  
348 reviewers.

349

350

351 **References**

- 352 Ademollo N, Patrolecco L, Polesello S, et al (2012) The analytical problem of measuring total concentrations of  
353 organic pollutants in whole water. *TrAC Trends Anal Chem* 36:71 – 81. doi:  
354 <http://dx.doi.org/10.1016/j.trac.2012.01.008>
- 355 Bamford HA, Baker JE (2003) Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and  
356 suburban atmospheres of the Mid-Atlantic region. *Atmos Environ* 37:2077 – 2091. doi:  
357 [http://dx.doi.org/10.1016/S1352-2310\(03\)00102-X](http://dx.doi.org/10.1016/S1352-2310(03)00102-X)
- 358 Bates TS, Hamilton SE, Cline JD (1983) Collection of Suspended Particulate Matter for Hydrocarbon Analyses:  
359 Continuous Flow Centrifugation vs. Filtration. *Estuarine Coast Shelf Sci* 16:107–112.
- 360 Biache C, Mansuy-Huault L, Faure P, et al (2008) Effects of thermal desorption on the composition of two coking  
361 plant soils: Impact on solvent extractable organic compounds and metal bioavailability. *Environ Pollut* 156:671–677.  
362 doi: 10.1016/j.envpol.2008.06.020
- 363 Biache C, Ouali S, Cébron A, et al (2017) Bioremediation of PAH-contaminated soils: Consequences on formation and  
364 degradation of polar-polycyclic aromatic compounds and microbial community abundance. *J Hazard Mater* 329:1 –  
365 10. doi: <https://doi.org/10.1016/j.jhazmat.2017.01.026>
- 366 Bianchi TS, Wysocki LA, Stewart M, et al (2007) Temporal variability in terrestrially-derived sources of particulate  
367 organic carbon in the lower Mississippi River and its upper tributaries. *Geochim Cosmochim Acta* 71:4425 – 4437.  
368 doi: <http://dx.doi.org/10.1016/j.gca.2007.07.011>
- 369 Chiffre A, Degiorgi F, Morin-Crini N, et al (2015) PAH occurrence in chalk river systems from the Jura region  
370 (France). Pertinence of suspended particulate matter and sediment as matrices for river quality monitoring. *Environ*  
371 *Sci Pollut Res* 22:17486–17498. doi: 10.1007/s11356-015-4897-5
- 372 Countway RE, Dickhut RM, Canuel EA (2003) Polycyclic aromatic hydrocarbon (PAH) distributions and  
373 associations with organic matter in surface waters of the York River, {VA} Estuary. *Org Geochem* 34:209 – 224.  
374 doi: [http://dx.doi.org/10.1016/S0146-6380\(02\)00162-6](http://dx.doi.org/10.1016/S0146-6380(02)00162-6)
- 375 Cousins IT, Beck AJ, Jones KC (1999) A review of the processes involved in the exchange of semi-volatile organic  
376 compounds (SVOC) across the air–soil interface. *Sci Total Environ* 228:5 – 24. doi:  
377 [http://dx.doi.org/10.1016/S0048-9697\(99\)00015-7](http://dx.doi.org/10.1016/S0048-9697(99)00015-7)
- 378 Deng H, Peng P, Huang W, Song J (2006) Distribution and loadings of polycyclic aromatic hydrocarbons in the  
379 Xijiang River in Guangdong, South China. *Chemosphere* 64:1401 – 1411. doi:  
380 <http://dx.doi.org/10.1016/j.chemosphere.2005.12.027>
- 381 El-Mufleh A, Béchet B, Basile-Doelsch I, et al (2014) Distribution of PAHs and trace metals in urban stormwater  
382 sediments: combination of density fractionation, mineralogy and microanalysis. *Environ Sci Pollut Res* 21:9764–  
383 9776. doi: 10.1007/s11356-014-2850-7
- 384 Fernandes MB, Sicre M-A, Boireau A, Tronczynski J (1997) Polyaromatic hydrocarbon (PAH) distributions in the  
385 Seine River and its estuary. *Mar Pollut Bull* 34:857 – 867. doi: [http://dx.doi.org/10.1016/S0025-326X\(97\)00063-5](http://dx.doi.org/10.1016/S0025-326X(97)00063-5)
- 386 Foster GD, Jr ECR, Gruessner B, Velinsky DJ (2000) Hydrogeochemistry and transport of organic contaminants in  
387 an urban watershed of Chesapeake Bay (USA). *Appl Geochem* 15:901 – 915. doi: [http://dx.doi.org/10.1016/S0883-2927\(99\)00107-9](http://dx.doi.org/10.1016/S0883-2927(99)00107-9)
- 389 Gocht T, Ligouis B, Hinderer M, Grathwohl P (2007) Accumulation of polycyclic aromatic hydrocarbons in rural



390 soils based on mass balances at the catchment scale. *Environ Toxicol Chem* 26:591–600. doi: 10.1897/06-287R.1

391 Gomez-Gutierrez A, Jover E, Bayona JM, Albaigès J (2007) Influence of water filtration on the determination of a  
392 wide range of dissolved contaminants at parts-per-trillion levels. *Anal Chim Acta* 583 2007 583:202–209.

393 Heemken PO, Stachel B, Theobald N, Wenclawiak WB (2000) Temporal Variability of Organic Micropollutants in  
394 Suspended Particulate Matter of the River Elbe at Hamburg and the River Mulde at Dessau, Germany. *Arch Environ*  
395 *Contam Toxicol* 38:11–31. doi: 10.1007/s002449910003

396 Keith L, Telliard W (1979) ES&T Special Report: Priority pollutants: I-a perspective view. *Environ Sci Technol*  
397 13:416–423. doi: 10.1021/es60152a601

398 Kochany J, Maguire RJ (1994) Abiotic transformations of polynuclear aromatic hydrocarbons and polynuclear  
399 aromatic nitrogen heterocycles in aquatic environments. *Sci Total Environ* 144:17 – 31. doi:  
400 [http://dx.doi.org/10.1016/0048-9697\(94\)90424-3](http://dx.doi.org/10.1016/0048-9697(94)90424-3)

401 Ko F-C, Baker JE (2004) Seasonal and annual loads of hydrophobic organic contaminants from the Susquehanna  
402 River basin to the Chesapeake Bay. *Mar Pollut Bull* 48:840 – 851. doi:  
403 <http://dx.doi.org/10.1016/j.marpolbul.2003.10.014>

404 Le Meur M, Mansuy-Huault L, Lorgeoux C, et al (2017) Spatial and temporal variations of Particulate Organic  
405 Matter from Moselle River and tributaries: A multimolecular investigation.

406 Le Meur M, Montargès-Pelletier E, Bauer A, et al (2015) Characterization of suspended particulate matter in the  
407 Moselle River (Lorraine, France): evolution along the course of the river and in different hydrologic regimes. *J Soils*  
408 *Sediments* 1–18. doi: 10.1007/s11368-015-1335-8

409 Lundstedt S, Bandowe BAM, Wilcke W, et al (2014) First intercomparison study on the analysis of oxygenated  
410 polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs)  
411 in contaminated soil. *TrAC Trends Anal Chem* 57:83 – 92. doi: <http://dx.doi.org/10.1016/j.trac.2014.01.007>

412 Lundstedt S, White PA, Lemieux CL, et al (2007) Sources, fate, and toxic hazards of oxygenated polycyclic aromatic  
413 hydrocarbons (PAHs) at PAH-contaminated sites. *AMBIO* 36:475–485. doi: 10.1579/0044-  
414 7447(2007)36[475:SFATHO]2.0.CO;2

415 Luo J, Ma M, Liu C, et al (2009) Impacts of particulate organic carbon and dissolved organic carbon on removal of  
416 polycyclic aromatic hydrocarbons, organochlorine pesticides, and nonylphenols in a wetland. *J Soils Sediments*  
417 9:180–187. doi: 10.1007/s11368-009-0081-1

418 Maioli OLG, Rodrigues KC, Knoppers BA, Azevedo DA (2011) Distribution and sources of aliphatic and polycyclic  
419 aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems. *Cont Shelf*  
420 *Res* 31:1116 – 1127. doi: <http://dx.doi.org/10.1016/j.csr.2011.04.004>

421 Mitra S, Bianchi TS (2003) A preliminary assessment of polycyclic aromatic hydrocarbon distributions in the lower  
422 Mississippi River and Gulf of Mexico. *Mar Chem* 82:273 – 288. doi: [http://dx.doi.org/10.1016/S0304-  
423 4203\(03\)00074-4](http://dx.doi.org/10.1016/S0304-4203(03)00074-4)

424 Morrison MA, Benoit G (2001) Filtration Artifacts Caused by Overloading Membrane Filters. *Environ Sci Technol*  
425 35:3774–3779. doi: 10.1021/es010670k

426 Patrolecco L, Ademollo N, Capri S, et al (2010) Occurrence of priority hazardous PAHs in water, suspended  
427 particulate matter, sediment and common eels (*Anguilla anguilla*) in the urban stretch of the River Tiber (Italy).

428 Chemosphere 81:1386 – 1392. doi: <http://dx.doi.org/10.1016/j.chemosphere.2010.09.027>

429 Qiao M, Qi W, Liu H, Qu J (2014) Oxygenated, nitrated, methyl and parent polycyclic aromatic hydrocarbons in  
430 rivers of Haihe River System, China: Occurrence, possible formation, and source and fate in a water-shortage area.  
431 *Sci Total Environ* 481:178 – 185. doi: <http://dx.doi.org/10.1016/j.scitotenv.2014.02.050>

432 Ran Y, Fu JM, Sheng GY, et al (2000) Fractionation and composition of colloidal and suspended particulate  
433 materials in rivers. *Chemosphere* 41:33 – 43. doi: [http://dx.doi.org/10.1016/S0045-6535\(99\)00387-2](http://dx.doi.org/10.1016/S0045-6535(99)00387-2)

434 Rossé P, Vignati D, Dominik J (2006) Effects of continuous flow centrifugation on measurements of trace elements  
435 in river water: intrinsic contamination and particle fragmentation. *Hydrol Process* 20:2745–2754. doi:  
436 [10.1002/hyp.6064](https://doi.org/10.1002/hyp.6064)

437 Siemers A-K, Mänz JS, Palm W-U, Ruck WKL (2015) Development and application of a simultaneous SPE-method  
438 for polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, heterocyclic {PAHs} (NSO-HET) and phenols in  
439 aqueous samples from German Rivers and the North Sea. *Chemosphere* 122:105 – 114. doi:  
440 <http://dx.doi.org/10.1016/j.chemosphere.2014.11.022>

441 Sun J-H, Wang G-L, Chai Y, et al (2009) Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach  
442 of the Yellow River, Middle China. *Ecotoxicol Environ Saf* 72:1614 – 1624. doi:  
443 <http://dx.doi.org/10.1016/j.ecoenv.2008.05.010>

444 Tsapakis M, Stephanou EG (2007) Diurnal Cycle of PAHs, Nitro-PAHs, and oxy-PAHs in a High Oxidation  
445 Capacity Marine Background Atmosphere. *Environ Sci Technol* 41:8011–8017. doi: [10.1021/es071160e](https://doi.org/10.1021/es071160e)

446 Wang X, Yuan K, Chen B, et al (2016) Monthly variation and vertical distribution of parent and alkyl polycyclic  
447 aromatic hydrocarbons in estuarine water column: Role of suspended particulate matter. *Environ Pollut* 216:599 –  
448 607. doi: <http://dx.doi.org/10.1016/j.envpol.2016.06.018>

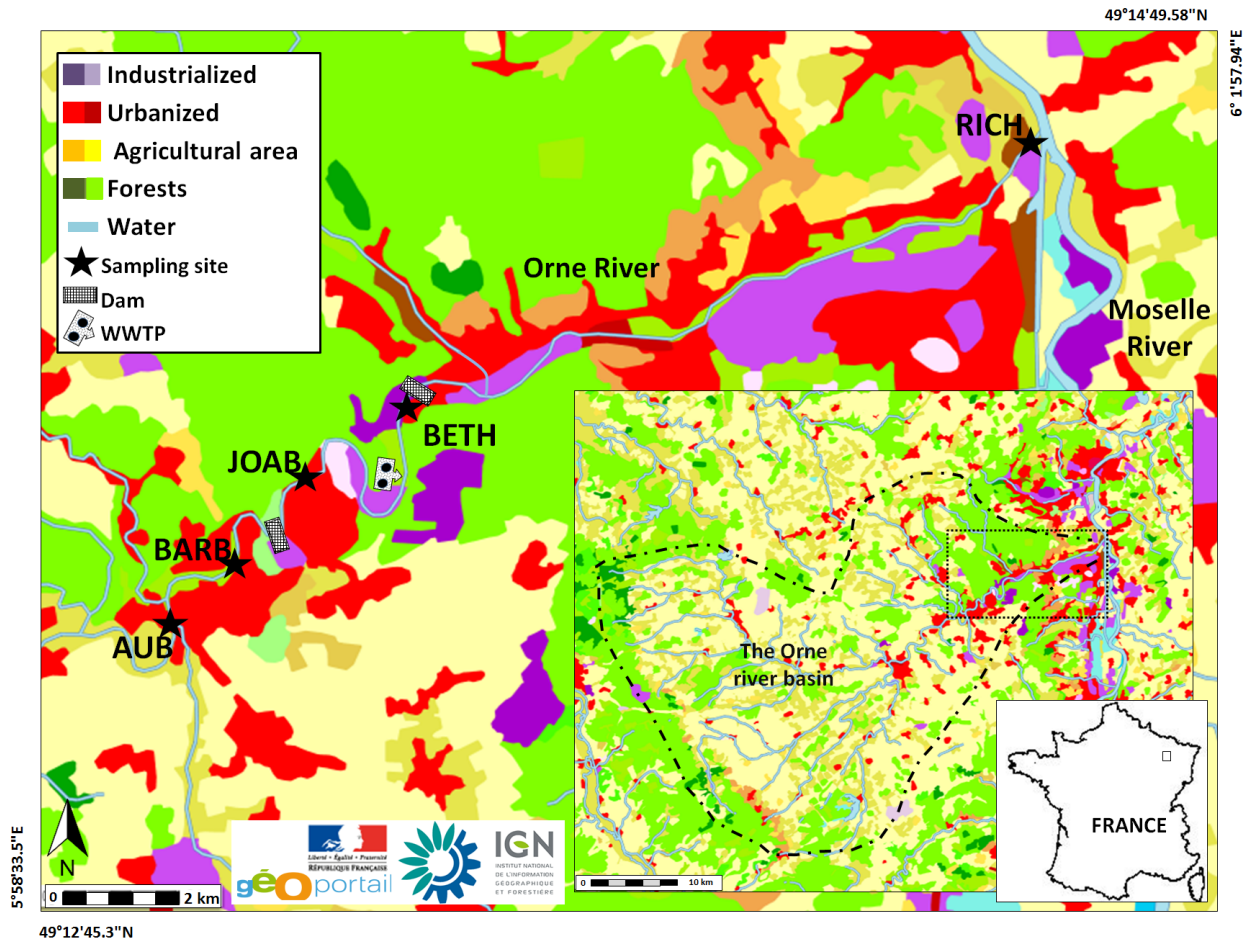
449 Wölz J, Fleig M, Schulze T, et al (2010) Impact of contaminants bound to suspended particulate matter in the context  
450 of flood events. *J Soils Sediments* 10:1174–1185. doi: [10.1007/s11368-010-0262-y](https://doi.org/10.1007/s11368-010-0262-y)

451 Zhang L, Zhang J, Gong M (2009) Size distributions of hydrocarbons in suspended particles from the Yellow River.  
452 *Appl Geochem* 24:1168 – 1174. doi: <http://dx.doi.org/10.1016/j.apgeochem.2008.12.033>

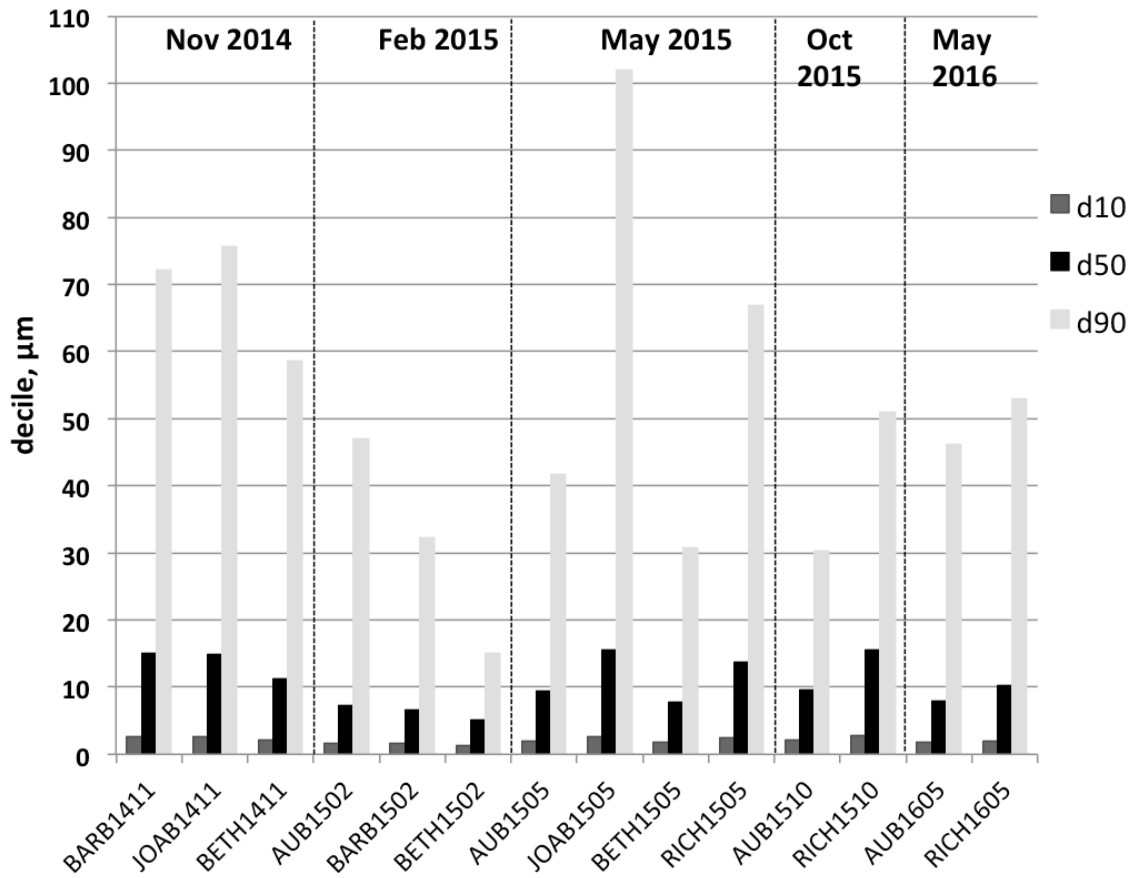
453 Zheng B, Wang L, Lei K, Nan B (2016) Distribution and ecological risk assessment of polycyclic aromatic  
454 hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area,  
455 China. *Chemosphere* 149:91 – 100. doi: <http://dx.doi.org/10.1016/j.chemosphere.2016.01.039>

456 Zhou JL, Fileman TW, Evans S, et al (1999) The partition of fluoranthene and pyrene between suspended particles  
457 and dissolved phase in the Humber Estuary: a study of the controlling factors. *Sci Total Environ* 243–244:305 – 321.  
458 doi: [http://dx.doi.org/10.1016/S0048-9697\(99\)00404-0](http://dx.doi.org/10.1016/S0048-9697(99)00404-0)

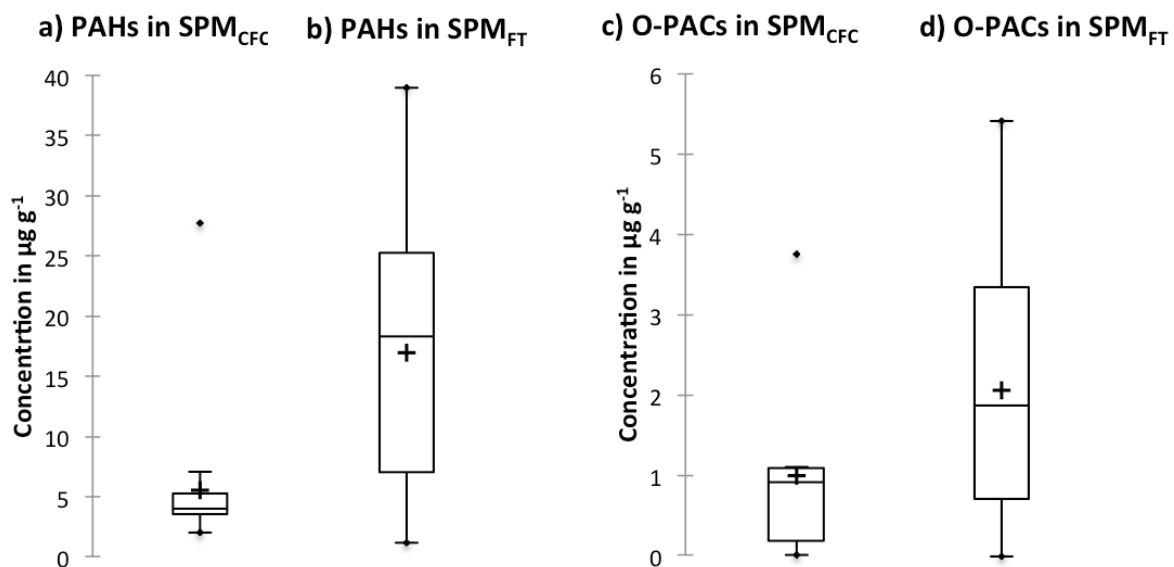
459



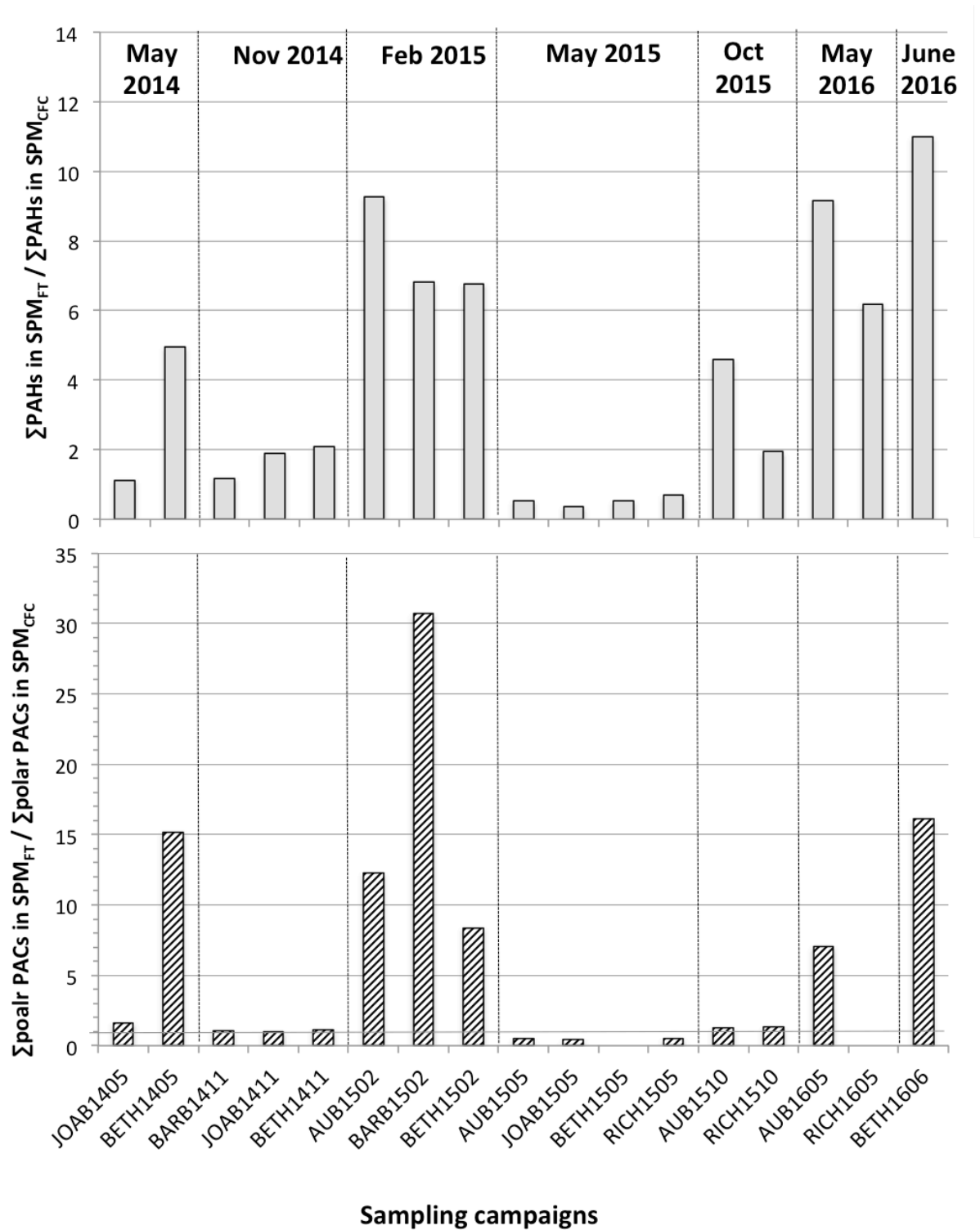
**Fig. 1** Lower part of the Orne River catchment, showing the five selected sampling sites and the land cover and use (Map source: CORINE Land Cover, 2012).



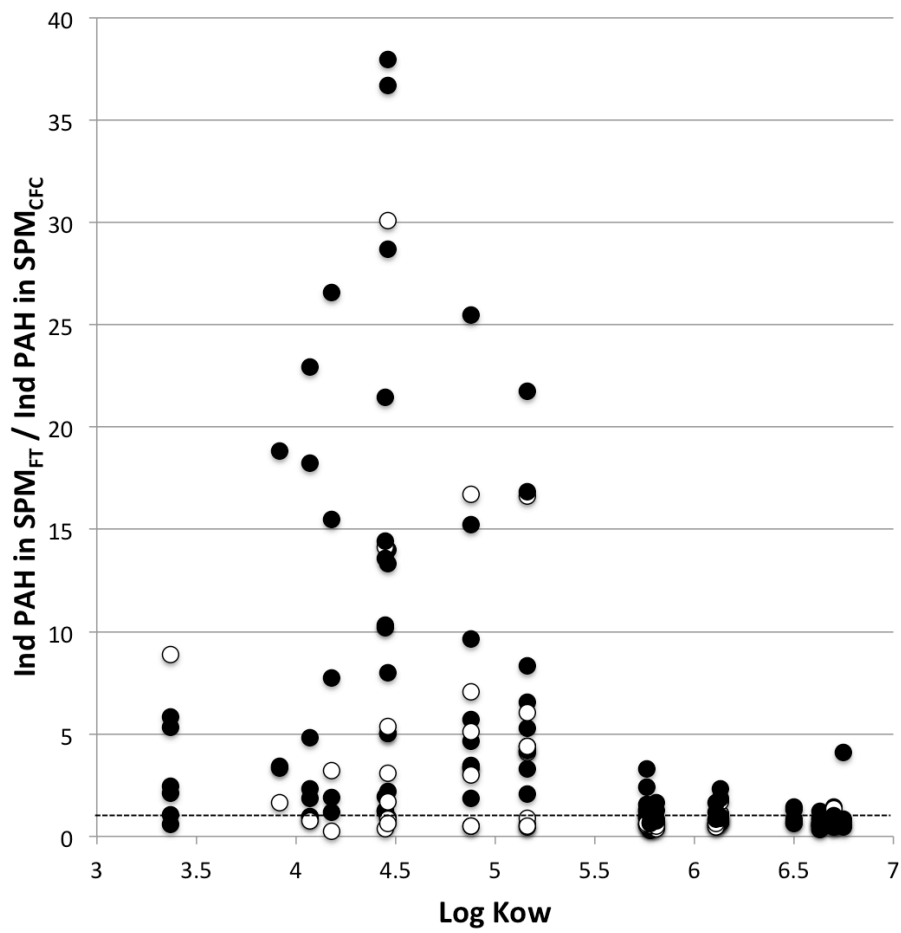
**Fig. 2** Grain size distribution deciles (d10, d50 and d90) of raw waters measured for the campaigns from November 2014 to May 2016.



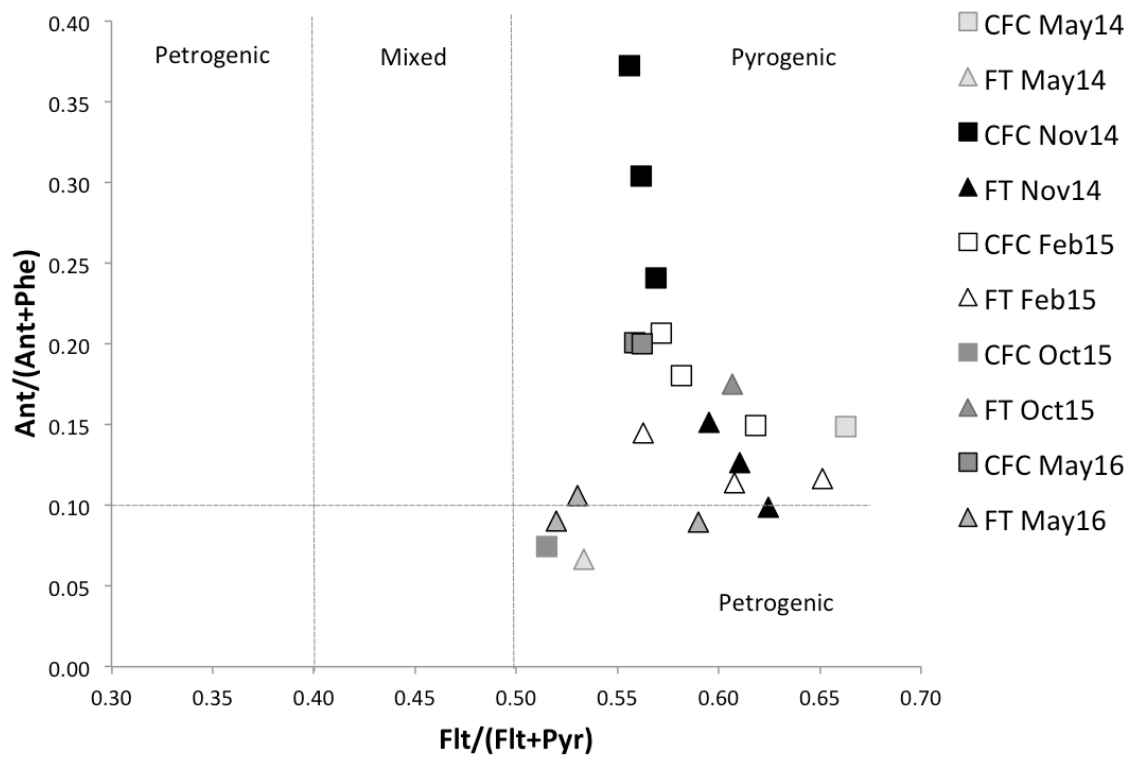
**Fig. 3** Box plots of  $\Sigma\text{PAH}$ , and  $\Sigma\text{O-PAC}$  concentrations in  $\text{SPM}_{\text{CFC}}$  (a) and (c) and in  $\text{SPM}_{\text{FT}}$  (b) and (d) for all samples. The boundaries of the box indicate the 25th and 75th percentiles; the line within the box marks the median; the + is the mean value; and values on the top and bottom of the box indicate the minimum and maximum of the distribution.



**Fig. 4** Comparison of the ratios of PAH content in SPM<sub>FT</sub> over PAH content in SPM<sub>CFC</sub> (a) and of polar PAC content (11 O-PACs+ 5 N-PACs) in SPM<sub>FT</sub> over polar PAC content in SPM<sub>CFC</sub> (b) for each sample of the campaigns.

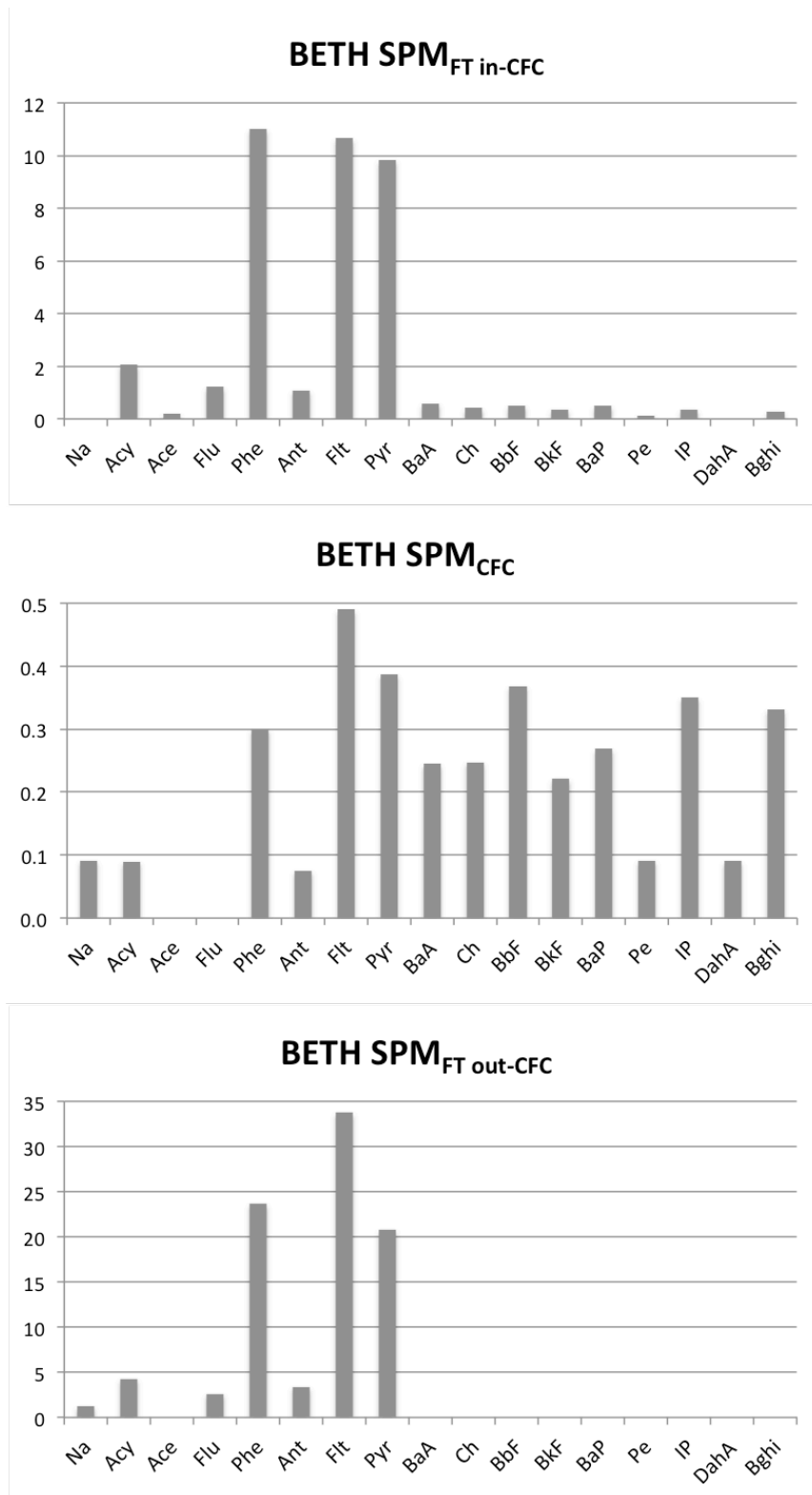


**Fig. 5** Ratios of individual PAH concentration in SPM<sub>FT</sub> over their concentration in SPM<sub>CFC</sub> plotted against the log  $K_{ow}$  of these PAHs. Black circles represent the campaigns of November 2014, February 2015 and May-June 2016, and white circles represent the other sampling campaigns.



**Fig. 6**  $\text{Ant}/(\text{Ant}+\text{Phe})$  vs  $\text{Flt}/(\text{Flt}+\text{Pyr})$  diagnostic ratios calculated in  $\text{SPM}_{\text{CFC}}$  and  $\text{SPM}_{\text{FT}}$ . Dashed lines represent the limits of petrogenic/ pyrogenic domains after Yunker et al. (2002)





**Fig. 7** Distributions of PAHs in  $\mu\text{g g}^{-1}$  in (a) SPM<sub>FT In-CFC</sub> (b) the SPM<sub>CFC</sub>, (c) the SPM<sub>FT Out-CFC</sub>

Date	May 2014		Nov 2014			Feb 2015			May 2015				Oct 2015		May 2016		June 2016
Site	JOAB	BETH	BARB	JOAB	BETH	AUB	BARB	BETH	AUB	JOAB	BETH	RICH	AUB	RICH	AUB	RICH	BETH
Water discharge (m <sup>3</sup> s <sup>-1</sup> )	1.5	1.4	22.4	22.4	50.5	49.4	49.2	49.4	23.5	11.2	11.2	23.5	1.5	1.5	120.0	120.0	29.5
Temperature (°C)	16.6	15.2	12.0	12.0	11.7	3.4	2.9	3.8	15.4	18.0	17.7	17.0	12.8	12.8	14.0	15.1	18.7
Turbidity (NTU)	1.8	2.1	19.7	24.6	108.8	35.3	31.7	34.3	37.7	35.4	33.7	29.6	2.2	2.2	93.4	94.0	56.7
EC (μS cm <sup>-1</sup> )	1039	1019	904	845	548	535	574	594	563	617	616	697	710	710	358	405	521
SPM content (mg L <sup>-1</sup> )	4.3	5.9	40.2	32.4	121.6	39.3	34.5	32.5	36.1	38.0	32.2	25.6	1.8	1.8	80.6	90.2	32.6
d50 (μm)	nd	nd	15.1	14.9	11.3	5.4	4.9	5.2	9.5	10.0	7.7	13.7	9.6	15.5	7.9	11.3	nd
POC (%)	6.9	12.5	5.4	3.9	3.3	3.3	3.1	3.2	4.2	4.8	4.9	5.8	nd	nd	3.3	4.2	3.5
DOC (mg L <sup>-1</sup> )	5.2	4.7	4.4	4.5	10.9	6.5	6.7	6.5	11.3	9.1	8.3	9.9	9.6	4.3	9.2	8.4	8.7

**Table 1 Physical-chemical parameters at each sampling campaigns: daily integrated water discharge (m<sup>3</sup> s<sup>-1</sup>) (taken from the hydrometric station in Moyeuve-Grande for May and November 2014 and calculated from the continuous recorded water level values at BETH for the campaigns of 2015 and 2016), temperature (°C), turbidity (NTU), electric conductivity EC (μS cm<sup>-1</sup>) measured on site and SPM concentration (mg L<sup>-1</sup>), decile 50 of the grain size distribution (d50 in μm), DOC (mg L<sup>-1</sup>), POC (% of SPM content) measured at the lab.**

Date Site	May 2014		Nov 2014			Feb 2015			May 2015				Oct 2015		May 2016		June 2016
	JOAB	BETH	BARB	JOAB	BETH	AUB	BARB	BETH	AUB	JOAB	BETH	RICH	AUB	RICH	AUB	RICH	BETH
<b>PACs in SPM<sub>CFC</sub></b>																	
Σ 16PAHs (µg g <sup>-1</sup> )	27.69	3.99	6.07	5.38	5.25	2.54	3.72	5.08	2.45	3.77	3.36	3.74	5.17	7.03	2.01	4.20	3.56
Σ O-PACs (µg g <sup>-1</sup> )	2.66	1.09	0.91	0.91	0.68	0.19	0.12	0.42	0.51	0.96	0.95	1.1	2.48	3.76	0.09	0.00	0.13
Σ N-PACs (µg g <sup>-1</sup> )	0.43	0.9	0.09	0.2	0.06	0.03	<LQ	0.05	<LQ	0.04	0.03	0.04	0.10	0.30	0.18	0.10	0.12
Σ All PACs (µg g <sup>-1</sup> )	30.77	5.99	7.07	6.49	5.98	2.76	3.84	5.55	2.96	4.77	4.35	4.88	7.75	11.09	2.28	4.30	3.81
Ant/(Ant+Phe)	0.15	0.18	0.24	0.3	0.37	0.21	0.18	0.15	0.32	0.32	0.34	0.36		0.07		0.20	0.20
Flt/(Flt+Pyr)	0.66	0.6	0.57	0.56	0.56	0.57	0.58	0.62	0.54	0.56	0.55	0.56	0.53	0.51	0.56	0.56	0.56
BaA/(BaA+Ch)		0.52	0.53	0.53	0.54	0.56	0.57	0.57	0.5	0.52	0.52	0.53	0.49	0.49	0.46	0.50	0.50
IP/(IP+Bghi)		0.63	0.55	0.55	0.57	0.6	0.62	0.62	0.52	0.53	0.54	0.54	0.55	0.52	0.51	0.51	0.51
2-3 ring PAHs (%)	85%	50%	20%	19%	14%	19%	36%	43%	9%	13%	11%	12%	21%	29%	13%	14%	16%
3-rings O-PACs (%)	100%	46%	34%	31%	15%	42%	100%	74%	36%	22%	20%	20%	21%	29%	100%		100%
<b>PACs in SPM<sub>FT</sub></b>																	
Σ 16PAHs (µg g <sup>-1</sup> )	31.24	19.78	7.18	10.26	10.97	23.53	25.37	34.43	1.3	1.34	1.77	2.58	23.77	13.64	18.44	25.98	39.06
Σ O-PACs (µg g <sup>-1</sup> )	3.25	0.89	0.94	0.97	0.72	2.55	3.36	3.73	0.09	0.19	<LQ	0.11	3.30	5.43	1.89	4.07	3.93
Σ N-PACs (µg g <sup>-1</sup> )	1.78	29.41	0.12	0.11	0.12	0.11	0.26	0.14	0.16	0.23	<LQ	0.45	<LQ	<LQ	<LQ	<LQ	0.15
Σ All PACs (µg g <sup>-1</sup> )	36.27	50.08	8.24	11.34	11.81	26.2	28.98	38.3	1.55	1.77	1.77	3.14	27.07	19.07	20.33	30.05	43.14
Ant/(Ant+Phe)	0.07		0.15	0.1	0.13	0.12	0.15	0.11					0.06	0.17	0.09	0.11	0.09
Flt/(Flt+Pyr)	0.53	0.59	0.6	0.62	0.61	0.65	0.56	0.61	0.58			0.57	0.58	0.61	0.59	0.53	0.52
BaA/(BaA+Ch)			0.55	0.6	0.59				0.59			0.59			0.59	0.54	0.59
IP/(IP+Bghi)			0.55	0.57	0.62		0.65	0.56	0.61			0.6			0.57	0.52	0.56
2-3 ring PAHs (%)	57%	33%	28%	31%	34%	79%	74%	84%	7%	25%	28%	24%	70%	55%	49%	49%	40%
3-ring O-PACs (%)	100%	100%	52%	63%	90%	96%	96%	100%	100%	100%		100%	100%	100%	100%	89%	100%

**Table 2 PAC concentrations in SPM<sub>CFC</sub> and SPM<sub>FT</sub> (µg g<sup>-1</sup> dw) and molecular ratios of PACs. <LQ: under the limit of quantification.**

Sample name		SPM content (mg L <sup>-1</sup> )	Σ16PAHs EPA	ΣO-PACs	ΣAllPACs
AUB May 2016	SPM <sub>FT In-CFC</sub>	83.14	18.44	1.89	20.33
	SPM <sub>CFC</sub>		2.01	0.09	2.28
	SPM <sub>FT Out-CFC</sub>	17.96	16.71	5.30	22.00
RICH May 2016	SPM <sub>FT In-CFC</sub>	94.60	25.98	4.07	30.05
	SPM <sub>CFC</sub>		4.20	0.00	4.30
	SPM <sub>FT Out-CFC</sub>	16.84	26.67	4.00	30.67
BETH June 2016	SPM <sub>FT In-CFC</sub>	23.47	39.06	3.93	43.14
	SPM <sub>CFC</sub>		3.56	0.13	3.81
	SPM <sub>FT Out-CFC</sub>	4.67	89.76	18.01	107.77

**Table 3 PAC concentrations in µg g<sup>-1</sup> in the SPM<sub>CFC</sub> and in the SPM collected by filtration of the waters entering the CFC (SPM<sub>FT In-CFC</sub>) and of the waters collected at the outlet of the CFC (SPM<sub>FT Out-CFC</sub>). This campaign was performed at AUB, RICH and BETH in May-June 2016.**

Authors	River	Sampling collection	Particulate PAHs ( $\mu\text{g g}^{-1}$ )	LMW2-3 /HMW4-6
Chiffre et al 2015	Rivière Jura	Sediment trap	0.75-2.50	0.1-0.16
Wölz et al 2010	Neckars and Rhine	CFC	1.00-5.00	0.08-0.1
Le Meur et al 2017	Moselle River	CFC	2.00-8.00	0.06-0.36
Countway et al 2003	York River	Glass-fiber filters 1 $\mu\text{m}$ pressurized filtration	0.23-1.03	0.05-0.31
Ko and Baker 2004	Susquehanna River, USA	Glass-fiber filters 1 $\mu\text{m}$ pressurized filtration	3.00-9.00	0.20
Mitra and Bianchi 2003	Mississippi	Glass-fiber filters 0.7 $\mu\text{m}$	0.065-7.00	0.002-0.006
Sun et al 2009	Yellow River	Glass-fiber filters 0.7 $\mu\text{m}$	0.500-10.50	0.1-1.3
Maioli et al 2011	Brasilian estuaries	Glass-fiber filters 1.2 $\mu\text{m}$	0.170-1.80	0.05-2.63
Deng et al 2006	Xijiang River, South China	Glass-fiber filters	0.04-0.66	0.59-2.49
Luo et al. 2004	Pearl River Estuary, China	Glass-fiber filters 0.7 $\mu\text{m}$	1.80-89.00	0.87-4.8
Guo et al. 2007	Daliao River, China	PFFE - 0.45 $\mu\text{m}$	0.3-239	0.02-25
This study	Orne River, France	Glass-fiber filters 0.7 $\mu\text{m}$	1.30-39.06	0.1-5.25
This study	Orne River, France	CFC	2.01-7.03	0.1-0.98

**Table 4 Comparison of PAH concentrations and LMW/HMW ratios in SPM according to the sampling methods, data extracted from literature.**

S1: Analyzed compounds with their corresponding Internal standard compounds and specific ions selected for quantification and their limit of quantification (LOQ) associated calculated for 1 mg sample.

Internal Standard [m/z]	Compound [m/z]	LOQ ( $\mu\text{g g}^{-1}$ )
<b>PAH</b>		
[ <sup>2</sup> H <sub>8</sub> ]Naphthalene [136]	Naphthalene [128]	0.12
[ <sup>2</sup> H <sub>10</sub> ]Acenaphthylene [164]	Acenaphthylene [152]	0.12
	Acenaphthene [153]	0.12
	Fluorene [166]	0.06
	Phenanthrene [188]	0.06
[ <sup>2</sup> H <sub>10</sub> ]Phenanthrene [188]	Phenanthrene [178]	0.06
	Anthracene [178]	0.06
[ <sup>2</sup> H <sub>10</sub> ]Pyrene [212]	Fluoranthene [202]	0.06
	Pyrene [202]	0.06
[ <sup>2</sup> H <sub>12</sub> ]Chrysene [240]	Benz[a]anthracene [228]	0.06
	Chrysene [228]	0.06
	Benzo[b]fluoranthene [252]	0.06
	Benzo[k]fluoranthene [252]	0.06
[ <sup>2</sup> H <sub>12</sub> ]Perylene [264]	Benzo[a]pyrene [252]	0.06
	Perylene [252]	0.06
	Indeno[1,2,3-c,d]pyrene [276]	0.06
	Dibenzo(ah)anthracene [278]	0.12
	Benzo[ghi]perylene [276]	0.06
<b>O-PAC</b>		
[ <sup>2</sup> H <sub>10</sub> ]Acenaphthylene [164]	Dibenzofuran [168]	0.06
[ <sup>2</sup> H <sub>8</sub> ]9HFuorenone [188]	9H-fluorenone [180]	0.06
	Perinaphthenone [152]	0.12
	Anthraquinone [208]	0.06
	Cyclopenta(def)phenanthrone[204]	0.12
[ <sup>2</sup> H <sub>10</sub> ]Pyrene [212]	Methylanthracene-9.10-dione [165]	0.12
	Benzo(a)fluorenone [230]	0.12
[ <sup>2</sup> H <sub>12</sub> ]Chrysene [240]	Benzanthrone [258]	0.06
	Benzoanthracenedione [258]	0.06
	Naphacene-5.12-dione [228]	0.06
	Benzo(cd)pyrenone [254]	0.12
<b>N-PAC</b>		
[ <sup>2</sup> H <sub>7</sub> ]Quinoline [136]	Quinoline [129]	0.12
[ <sup>2</sup> H <sub>8</sub> ]9HFuorenone [188]	Benzo(h)quinoline [179]	0.06
	Acridine [179]	0.06
	Carbazole [167]	0.06
[ <sup>2</sup> H <sub>10</sub> ]Pyrene [212]	Benzo(c)acridine [229]	0.06
	Nitropyrene []	0.12

S2: Recoveries of external standards. Average and standard deviations evaluated for 34 samples (CFC and FT).

External Standard [m/z]	Mean $\pm$ SD (%)
[ <sup>2</sup> H <sub>8</sub> ]Dibenzofuran [176]	83.6 $\pm$ 17.0
[ <sup>2</sup> H <sub>10</sub> ]Fluorene [176]	93.5 $\pm$ 13.1
[ <sup>2</sup> H <sub>10</sub> ]Anthracene [188]	91.8 $\pm$ 12.0
[ <sup>2</sup> H <sub>8</sub> ]Anthraquinone [216]	77.9 $\pm$ 17.6
[ <sup>2</sup> H <sub>10</sub> ]Fluoranthène [212]	92.5 $\pm$ 12.4
[ <sup>2</sup> H <sub>12</sub> ] Benzo[ghi]perylene [288]	94.5 $\pm$ 16.8