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Fayez Abuhelou, Laurence Mansuy, Catherine Lorgeoux, Delphine Cattelain, 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

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

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Abstract

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

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

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Introduction

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

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

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

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

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

Material and methods

Characteristics of sampling sites

The Orne River is a left side tributary of the Moselle River, northeast of the Lorraine region, France (Fig 1). It is a small river (Strahler order 4), with an extended watershed area of 1,268 km², covered by forest (26.5 %), agriculture

(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 averaged flow fluctuates between 1.5 and 19 m³ s⁻¹ with a mean flow of 8.1 m³ s⁻¹ and maximum flow rates reaching at 170 m³ s⁻¹. This river has been highly impacted by iron ore extraction and steel-making industries during the whole 20th century. Five different sampling sites were chosen based on criteria of representativeness and accessibility for the field continuous flow centrifuge in the lower part of the Orne river, on the last 23 km before the confluence with the Moselle River: Auboué (AUB), Homécourt (BARB), Joeuf (JOAB), Moyeuvre-Grande (BETH) and Richemont (RICH). BETH site at Moyeuvre-Grande is located at a dam that influences the river hydrology: the water depth ranges between 3 and 4 m while it is meanly 1 m at the other sites and the water speed (<0.5 m s⁻¹ at the dam) is 1.5 to 5 times lower than at other sites.

SPM collection

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

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

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

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

Analytical methods

Global parameters and elemental content

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

Sample treatment

Up to 2 g of dry matter of SPM_{CFC} and from 0.06 to 1.4 g of dry matter SPM_{FT} were extracted with an Accelerated Solvent Extractor (Dionex® ASE350). ASE cells were filled with activated copper powder (to remove molecular sulphur) and sodium sulfate (Na_2SO_4 to remove remaining water) and pre-extracted for cleaning. Samples were extracted at 130°C and 100 bars with dichloromethane (DCM) with two cycles of 5 min (Biache et al. 2008). After adjusting the volume at 5 mL, a 1 mL aliquot was taken out for clean-up step. It was spiked with external extraction standards (mixture of 6 deuterated compounds: $[\text{}^2\text{H}_8]\text{Dibenzofuran}$, $[\text{}^2\text{H}_{10}]\text{Fluorene}$, $[\text{}^2\text{H}_{10}]\text{Anthracene}$,

[²H₈]Anthraquinone, [²H₁₀]Fluoranthene, [²H₁₂]Benzo[ghi]perylene) to control the loss during the sample preparation. The 1 mL aliquot was then evaporated to dryness using a gentle N₂ flow, diluted into 200 µL of hexane and transferred onto the top of a silica gel column pre-conditioned with hexane. The aliphatic fraction was eluted 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 methanol/DCM (50/50; v/v). The latter fraction was spiked with 20 µL at 12 µg mL⁻¹ of internal quantification standards (mixture of 8 deuterated compounds: [²H₈]Naphthalene, [²H₁₀]Acenaphthene, [²H₁₀]Phenanthrene, [²H₁₀]Pyrene, [²H₁₂]Chrysene, [²H₁₂]Perylene and [²H₈]9H-fluorenone) before evaporation and the volume was adjusted to 100 µL with DCM. To improve the chromatographic resolution, the sample was derivatized by adding BSTFA in (1:1; v/v) and finally injected in 200 µL volume in the gas chromatograph–mass spectrometer (GC–MS).

Analysis

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

Validation and quality control

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

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

Results

Sampling campaign characteristics

The global parameters (Table 1) exhibited different hydrological situations in the successive sampling campaigns. May 2014 and October 2015 corresponded to the lowest flow conditions with a daily mean water discharge around $1.5 \text{ m}^3 \text{ s}^{-1}$ and rather high water temperature (13 to 17°C). The turbidity and the SPM contents were respectively lower than 3 NTU and 6 mg L^{-1} . The water discharge in May 2015 ranged between 8 and $21 \text{ m}^3 \text{ s}^{-1}$ with turbidity values around 30 NTU and SPM contents from 16 to 54 mg L^{-1} . Higher water discharges, although rather moderate 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 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 during the flood of May 2016. The highest turbidity and SPM content were observed during the first high flow of the season the 5th of November 2014 (109 NTU and 122 mg L^{-1}) and during the flood of May 2016 (94 NTU and 90 mg L^{-1}). The POC ranged between 3 and 12.5 mg g^{-1} and the highest value was recorded during the low flow event of May 2014. DOC varied between 4 and 11 mg L^{-1} with the highest DOC observed in May 2015 and the 5th November 2014. Concerning, the grain size distribution of raw waters, the decile D50 was shown to vary very slightly from 5 to $15 \mu\text{m}$ for the different reported campaigns. The lowest value of the D50 ($\approx 5 \mu\text{m}$) was measured in February 2015 during a high flow event (Table 1 and Fig 2). The measured particle size distributions covered relatively narrow 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 content) with no strong shift of particle size.

PAC concentration and distribution in SPM_{FT} and SPM_{CFC}

Table 2 displays the contents in PAHs, O-PACs and N-PACs and the main characteristics of their distribution according to the sampling methods (CFC and FT) and to the sampling dates and locations. The comparison of the 16 PAH concentrations in SPM_{FT} and SPM_{CFC} revealed a contrasted effect of the separation techniques.

When the whole set of data is considered, the sum of the 16 PAH concentrations in SPM_{CFC} ranged between 2 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 of variations was rather narrow, the 1st and 3rd quartiles being at 3.6 and 5.3 $\mu\text{g g}^{-1}$ respectively (Fig 3a). For SPM_{FT} 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 dispersion of the PAH concentrations was observed, the 1st and 3rd quartiles being at 7.2 and 3.4 $\mu\text{g g}^{-1}$ respectively (Fig. 3b). For all samples, O-PAC and N-PAC concentrations were much lower than PAHs, accounting for 10 to 30% of the total PACs except for BETH site in May 2014. The differences of O-PAC concentrations in SPM_{FT} and SPM_{CFC} 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 $\mu\text{g g}^{-1}$ respectively in SPM_{FT} and SPM_{CFC}. However, as observed for PAHs, the dispersion of the O-PAC concentrations was higher in SPM_{FT} than in SPM_{CFC} (Fig 2c and 2d).

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

The comparison of polar PAC concentrations in SPM_{FT} and SPM_{CFC} also revealed discrepancies between the two sampling methods (Fig 3b). In February 2015 and May-June 2016, polar PACS were six to thirty times more concentrated in SPM_{FT} than in SPM_{CFC}. In May 2014, polar PAC concentrations were fifteen times higher in SPM_{FT} at BETH than in SPM_{CFC}.

The distribution of individual PAHs was also strongly and diversely affected by the method of sampling. In SPM_{CFC}, the 4 to 6 ring-PAHs were easily detected and well represented in the distribution, representing 50 to 90% of the all

PAHs (except in May 2014), even though they could vary in abundance according to the sampling campaign (Table 2). In SPM_{FT} , 2 to 3 ring-PAHs were systematically more represented than in SPM_{CFC} and accounted for 40 to 70% of the total PAH concentration except during the November 2014 and May 2015 campaigns. The ratio of each individual PAH concentration in SPM_{FT} over its concentration in SPM_{CFC} was plotted against the $\log K_{ow}$ of each 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 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 differences were observed in Feb 2015 and May-June 2016 and to a lesser extent in Nov 2014, May 2014 and October 2015. Thus, it appeared that the 2 to 3-ring PAHs and to a lesser extent the 4-ring PAHs were the molecules the most affected by the sampling methods.

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

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

PACs in the filtered SPM of the inlet and outlet waters of the CFC

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

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

Discussion

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

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

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

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

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

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

Conclusions

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

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

Acknowledgements

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

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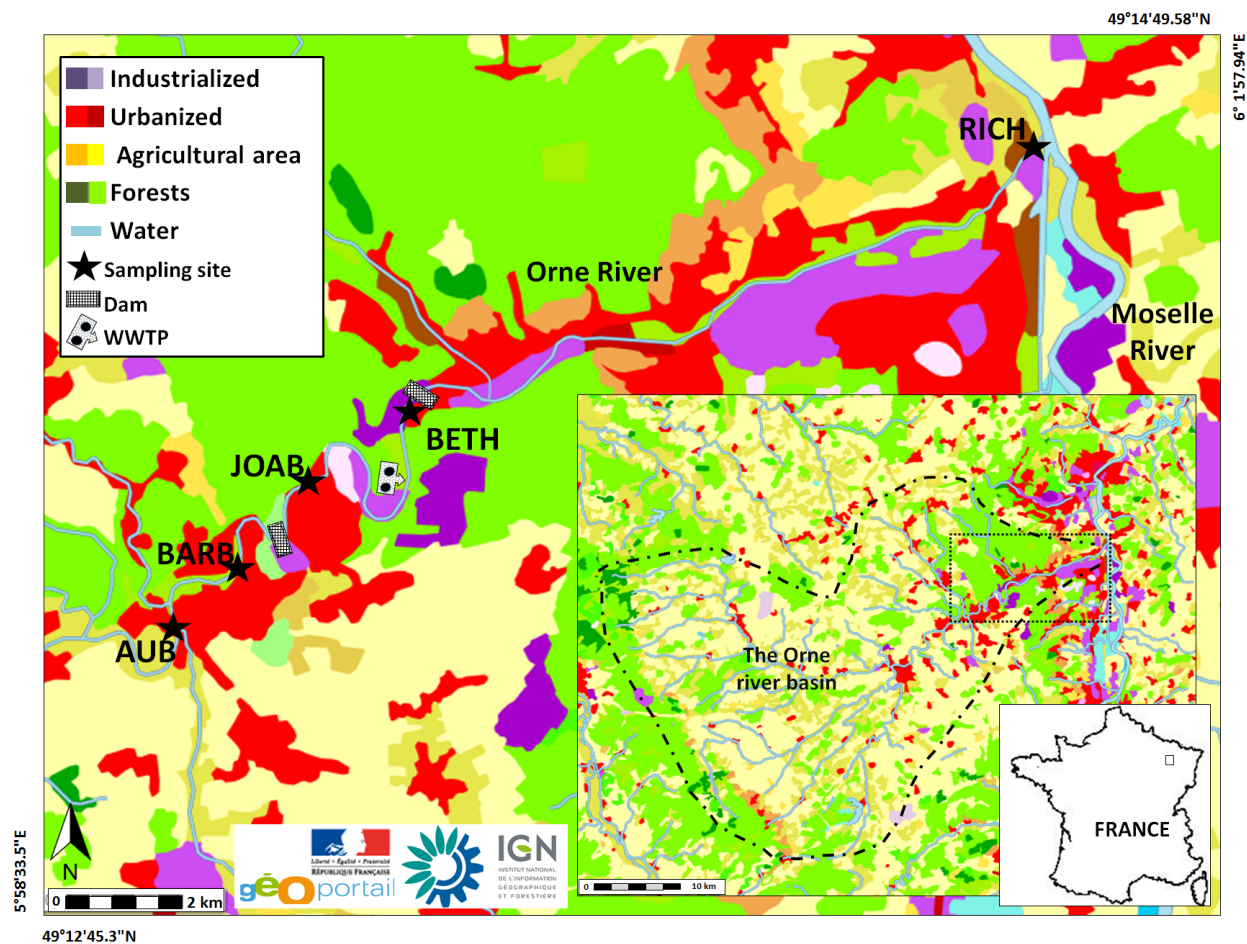


Fig. 1 Lower part of the Orne River catchment, showing the five selected sampling sites and the land cover and use (Map source: CORINE Land Cover, 2012).

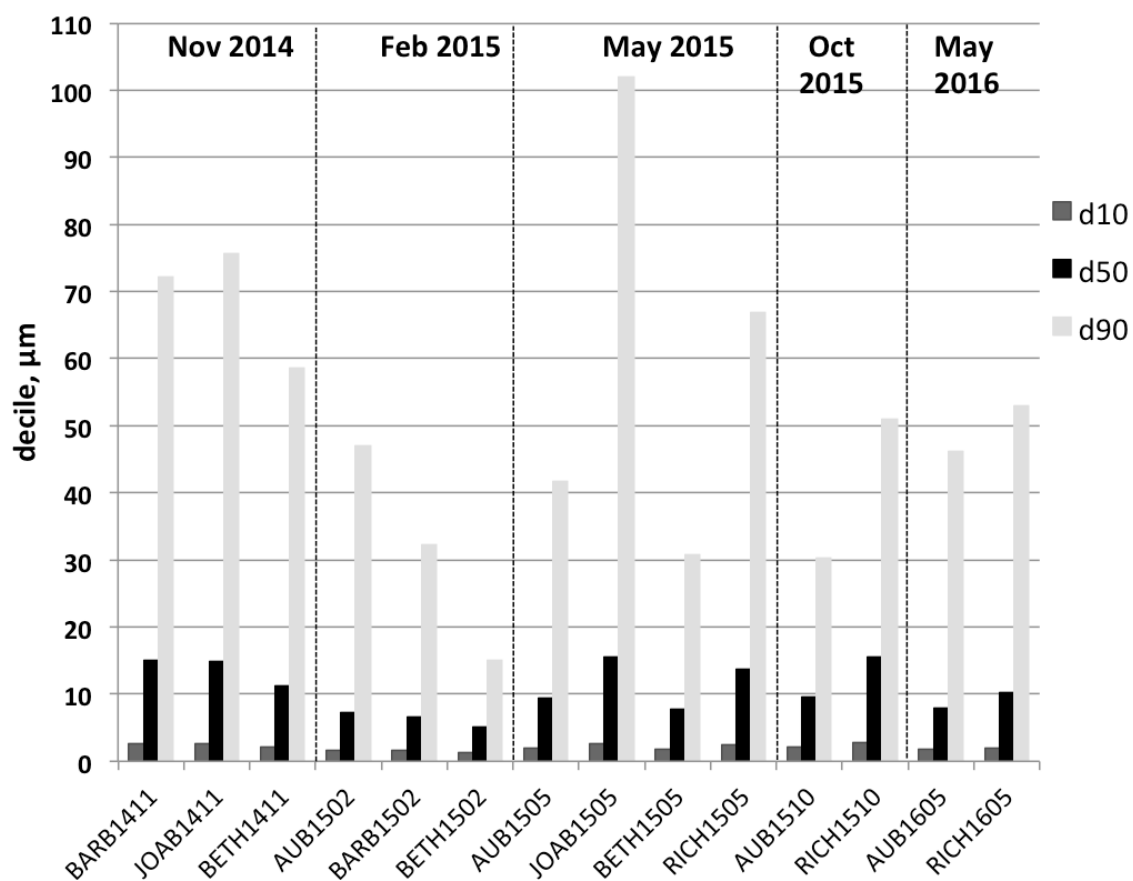


Fig. 2 Grain size distribution deciles (d10, d50 and d90) of raw waters measured for the campaigns from November 2014 to May 2016.

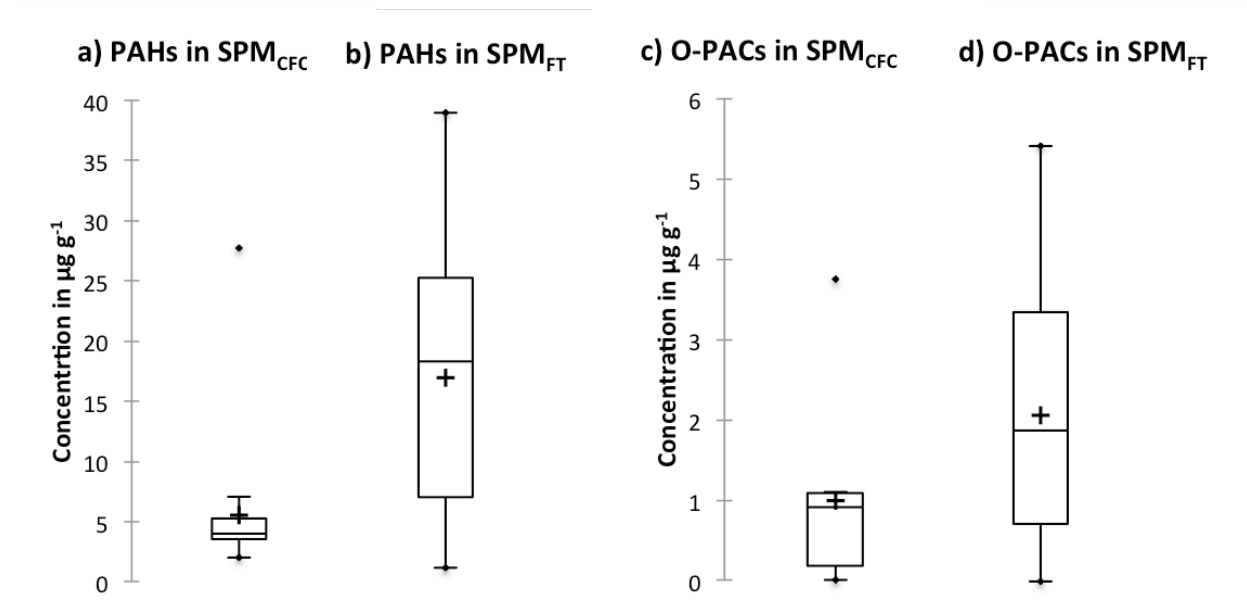


Fig. 3 Box plots of Σ PAH, and Σ O-PAC concentrations in SPM_{CFC} (a) and (c) and in SPM_{FT} (b) and (d) for all samples. The boundaries of the box indicate the 25th and 75th percentiles; the line within the box marks the median; the + is the mean value; and values on the top and bottom of the box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

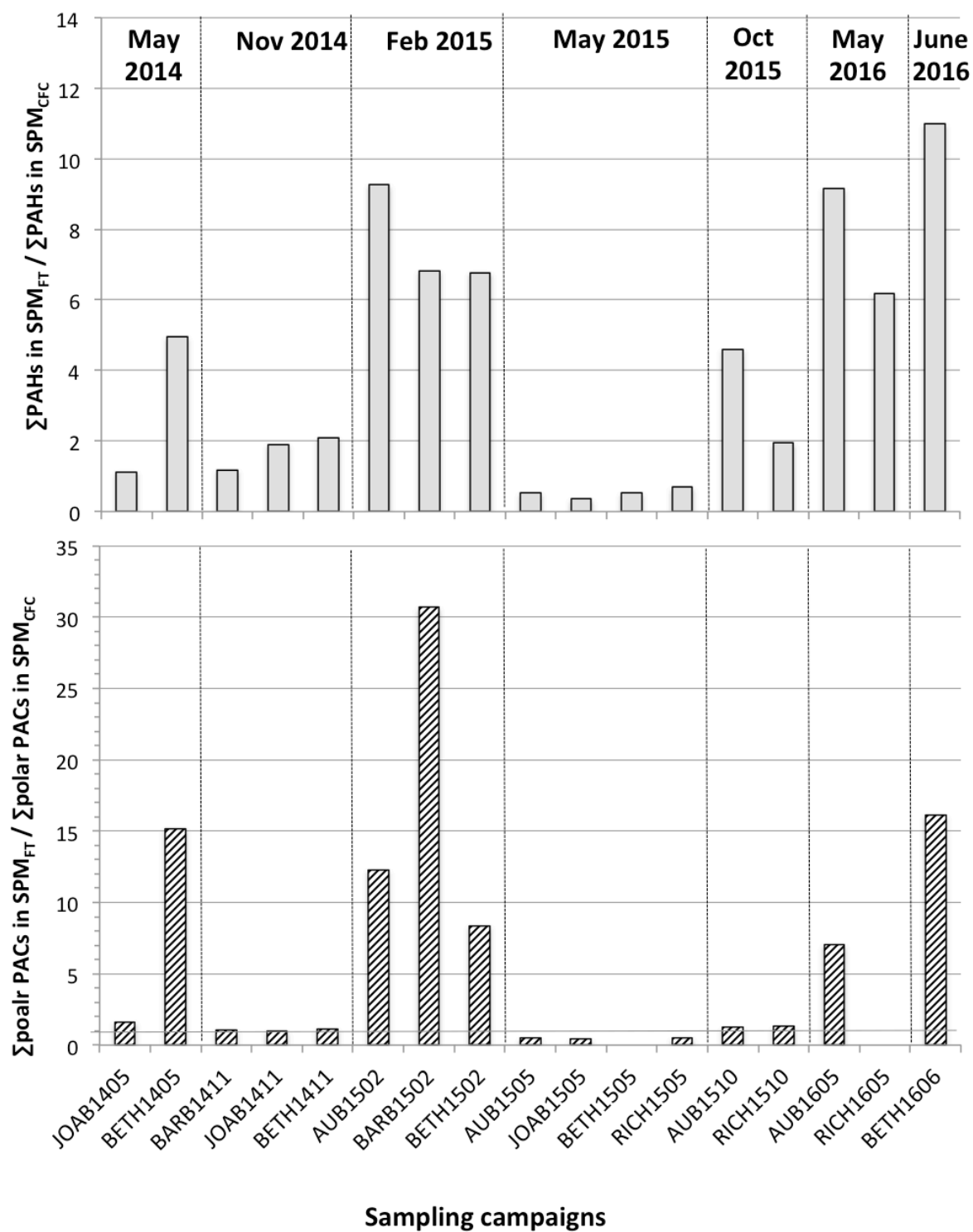


Fig. 4 Comparison of the ratios of PAH content in SPM_{FT} over PAH content in SPM_{CFC} (a) and of polar PAC content (11 O-PACs+ 5 N-PACs) in SPM_{FT} over polar PAC content in SPM_{CFC} (b) for each sample of the campaigns.

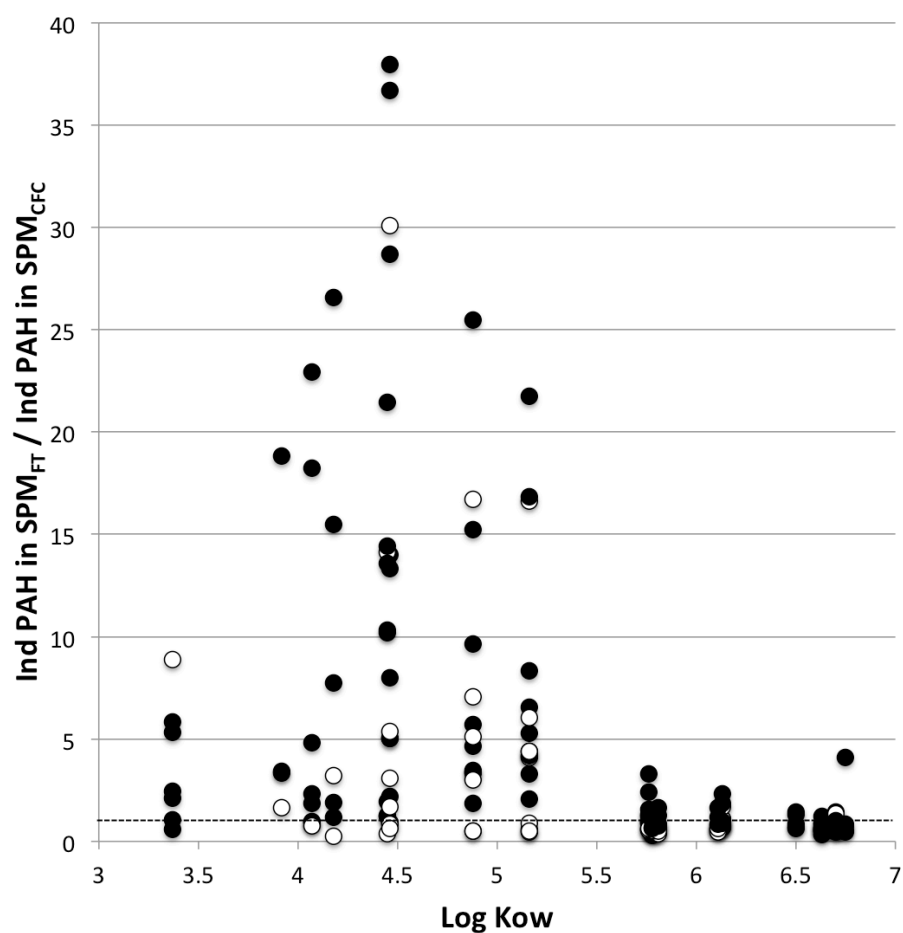


Fig. 5 Ratios of individual PAH concentration in SPM_{FT} over their concentration in SPM_{CFC} plotted against the $\log K_{ow}$ of these PAHs. Black circles represent the campaigns of November 2014, February 2015 and May-June 2016, and white circles represent the other sampling campaigns.

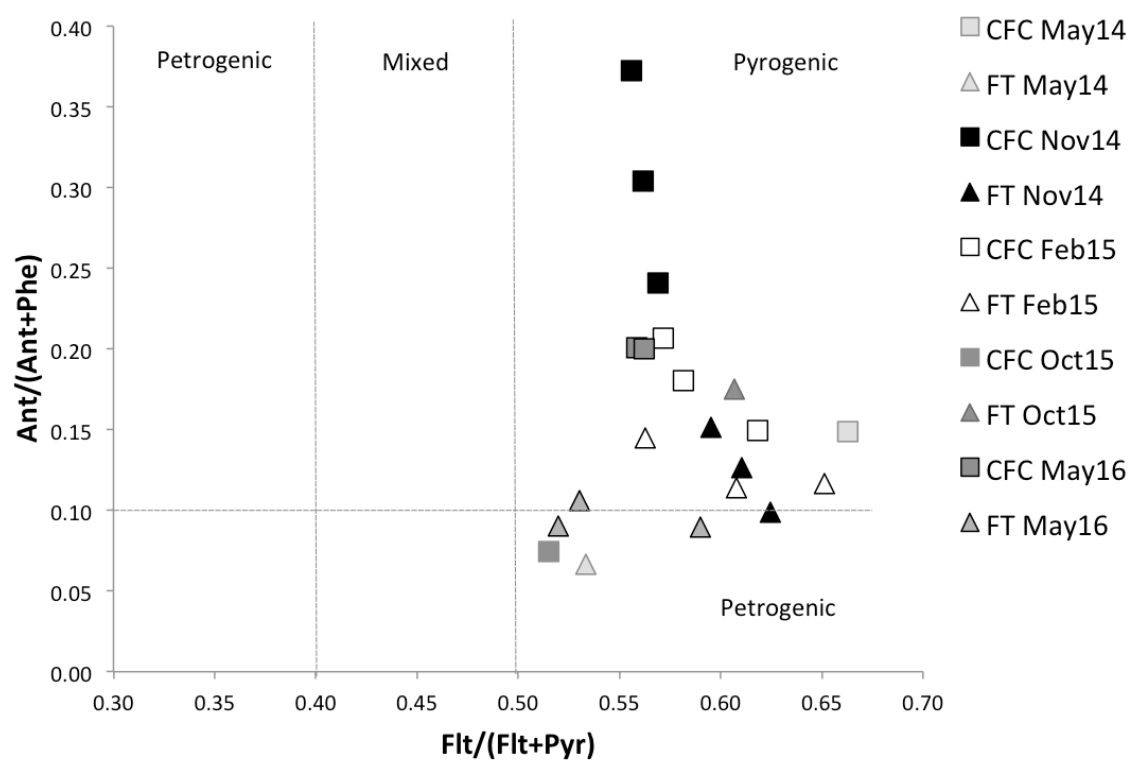


Fig. 6 $\text{Ant}/(\text{Ant}+\text{Phe})$ vs $\text{Flt}/(\text{Flt}+\text{Pyr})$ diagnostic ratios calculated in SPM_{CFC} and SPM_{FT} . Dashed lines represent the limits of petrogenic/ pyrogenic domains after Yunker et al. (2002)

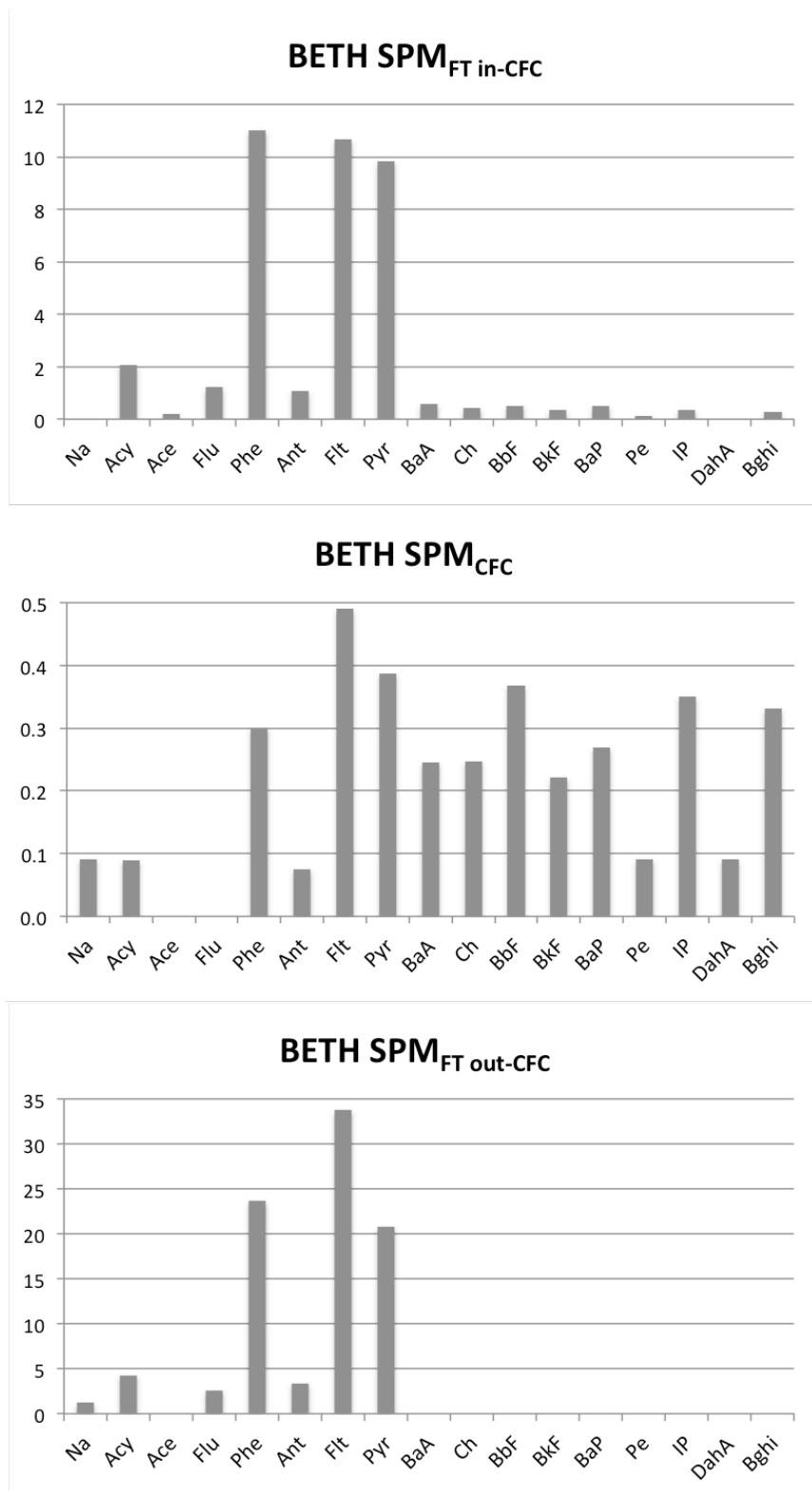


Fig. 7 Distributions of PAHs in $\mu\text{g g}^{-1}$ in (a) SPM_{FT} In-CFC (b) the SPM_{CFC}, (c) the SPM_{FT} Out-CFC

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 ($\text{m}^3 \text{s}^{-1}$)	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 ($^{\circ}\text{C}$)	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 ($\mu\text{S cm}^{-1}$)	1039	1019	904	845	548	535	574	594	563	617	616	697	710	710	358	405	521
SPM content (mg L^{-1})	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^{-1})	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 ($\text{m}^3 \text{s}^{-1}$) (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 ($^{\circ}\text{C}$), turbidity (NTU), electric conductivity EC ($\mu\text{S cm}^{-1}$) measured on site and SPM concentration (mg L^{-1}), decile 50 of the grain size distribution (d50 in μm), DOC (mg L^{-1}), 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
PACs in SPM_{CFC}																	
Σ 16PAHs (μg g ⁻¹)	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 ⁻¹)	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 ⁻¹)	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 ⁻¹)	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%
PACs in SPM_{FT}																	
Σ 16PAHs (μg g ⁻¹)	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 ⁻¹)	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 ⁻¹)	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 ⁻¹)	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_{CFC} and SPM_{FT} (μg g⁻¹ dw) and molecular ratios of PACs. <LQ: under the limit of quantification.

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

Table 3 PAC concentrations in µg g⁻¹ in the SPM_{CFC} and in the SPM collected by filtration of the waters entering the CFC (SPM_{FT In-CFC}) and of the waters collected at the outlet of the CFC (SPM_{FT Out-CFC}). 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 μm pressurized filtration	0.23-1.03	0.05-0.31
Ko and Baker 2004	Susquehanna River, USA	Glass-fiber filters 1 μm pressurized filtration	3.00-9.00	0.20
Mitra and Bianchi 2003	Mississippi	Glass-fiber filters 0.7 μm	0.065-7.00	0.002-0.006
Sun et al 2009	Yellow River	Glass-fiber filters 0.7 μm	0.500-10.50	0.1-1.3
Maioli et al 2011	Brasilian estuaries	Glass-fiber filters 1.2 μm	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 μm	1.80-89.00	0.87-4.8
Guo et al. 2007	Daliao River, China	PFFE - 0.45 μm	0.3-239	0.02-25
This study	Orne River, France	Glass-fiber filters 0.7 μm	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 ($\mu\text{g g}^{-1}$)
PAH		
[$^2\text{H}_8$]Naphthalene [136]	Naphthalene [128]	0.12
[$^2\text{H}_{10}$]Acenaphthylene [164]	Acenaphthylene [152]	0.12
	Acenaphthene [153]	0.12
	Fluorene [166]	0.06
	Phenanthrene [178]	0.06
[$^2\text{H}_{10}$]Phenanthrene [188]	Anthracene [178]	0.06
	Fluoranthene [202]	0.06
[$^2\text{H}_{10}$]Pyrene [212]	Pyrene [202]	0.06
	Benz[a]anthracene [228]	0.06
[$^2\text{H}_{12}$]Chrysene [240]	Chrysene [228]	0.06
	Benzo[b]fluoranthene [252]	0.06
	Benzo[k]fluoranthene [252]	0.06
	Benzo[a]pyrene [252]	0.06
[$^2\text{H}_{12}$]Perylene [264]	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
O-PAC		
[$^2\text{H}_{10}$]Acenaphthylene [164]	Dibenzofuran [168]	0.06
[$^2\text{H}_8$]9HFuorenone [188]	9H-fluorenone [180]	0.06
	Perinaphthenone [152]	0.12
	Anthraquinone [208]	0.06
	Cyclopenta(def)phenanthrone[204]	0.12
[$^2\text{H}_{10}$]Pyrene [212]	Methylanthracene-9.10-dione [165]	0.12
	Benzo(a)fluorenone [230]	0.12
[$^2\text{H}_{12}$]Chrysene [240]	Benzanthrone [258]	0.06
	Benzoanthracenedione [258]	0.06
	Naphtacene-5.12-dione [228]	0.06
	Benzo(cd)pyrenone [254]	0.12
N-PAC		
[$^2\text{H}_7$]Quinoline [136]	Quinoline [129]	0.12
[$^2\text{H}_8$]9HFuorenone [188]	Benzo(h)quinoline [179]	0.06
	Acridine [179]	0.06
	Carbazole [167]	0.06
[$^2\text{H}_{10}$]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 (%)
[$^2\text{H}_8$]Dibenzofuran [176]	83.6 \pm 17.0
[$^2\text{H}_{10}$]Fluorene [176]	93.5 \pm 13.1
[$^2\text{H}_{10}$]Anthracene [188]	91.8 \pm 12.0
[$^2\text{H}_8$]Anthraquinone [216]	77.9 \pm 17.6
[$^2\text{H}_{10}$]Fluoranthène [212]	92.5 \pm 12.4
[$^2\text{H}_{12}$] Benzo[ghi]perylene [288]	94.5 \pm 16.8