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Understanding polycyclic aromatic hydrocarbon transfers at the catchment scale combining chemical and fallout radionuclides analyses

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Abstract Contamination of river water and sediment constitutes a major environmental issue for industrialized countries. Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants characterized by two or more fused rings. Some PAHs present a high risk for environmental and human health because of their carcinogenic and/or mutagenic properties. However, there remains a lack of understanding regarding the various processes responsible for PAH transfers from one environmental compartment to another. This study aims to quantify PAH transfers at the catchment scale. Chemical analyses and measurement of radionuclides have been carried out on soil and sediment samples collected in one upstream subcatchment of the Seine River basin during one year. Results show a large PAH accumulation in sediment and suspended matter and this highlights the importance of local sources for PAH distributions and concentrations at the subcatchment scale.

Key words environmental contamination; polycyclic aromatic hydrocarbons (PAHs); catchment scale; pollutant transfers; fallout radionuclides

INTRODUCTION

Reducing environmental contamination constitutes a major challenge for industrialized countries. Furthermore, in the European Union, the Water Framework Directive [WFD; Directive 2000/60/EC; AESN, (2010)] requires that member states' water bodies reach good ecological and chemical status by 2015. Although emissions have decreased during the last decades, a large amount of polycyclic aromatic hydrocarbons (PAHs) have been released into the atmosphere over the last two centuries (Fernández *et al.*, 2000). In recent years, studies dealing with PAHs have grown in number, but most of them were restricted to the measurement of PAH concentrations in different environmental compartments (air, soil, sediment, water, etc.) that were investigated separately (Motelay-Massei *et al.*, 2007; Van Metre *et al.*, 2008; Zhu *et al.*, 2008). In this context, there remains a lack of knowledge about the transfers and, consequently, about the persistence of these compounds in the environment. This question is particularly acute in the Seine River basin where very high sediment-associated concentrations of PAHs have been reported, thereby compromising the good chemical status required by WFD (AESN, 2010).

POLYCYCLIC AROMATIC HYDROCARBONS

PAHs are organic compounds formed by at least two fused rings. Pyrolitic hydrocarbons are produced by the incomplete combustion of organic matter. In Western Europe, the release of these compounds is mainly associated with household heating and road traffic (Baek *et al.*, 1991; Pacyna *et al.*, 2003). Petrogenic PAHs are released into the environment through the discharge of petroleum products such as road leaching (Ngabe *et al.*, 2000).

PAHs have a relatively short half-life in the environment (Table 1), but they are considered to be persistent organic pollutants (POPs) because they are constantly being produced by common human activities. In this context, their presence in the environment cannot be completely avoided.

Table 1 Physicochemical properties and half-lives of main PAHs (Girard *et al.*, 2005).

PAH	Molecular weight ($g\ mol^{-1}$)	Solubility ($mg\ L^{-1}$)	Log K_{ow}	Half-life (day or year)
Naphtalene	128.19	33	3.37	16–48 d
Fluorene	166.23	1.685	4.18	32–60 d
Phenanthrene	178.24	1.6	4.46	16–200 d
Anthracene	178.24	0.075	4.45	50 d–1.3 year
Fluoranthene	202.26	0.265	5.33	140 d–1.2 year
Pyrene	202.26	0.175	5.18	210 d–5.2 year
Benzo(a)anthracene	228.29	0.01	5.61	102 d–1.9 year
Chrysene	228.29	0.006	5.61	1–2.7 year
Benzo(a)pyrene	252.30	0.002	5.98	57 d–1.5 year
Dibenzo(ah)anthracene	278.35	n.d.	5.97	361 d–2.6 year
Benzo(b)fluoranthene	252.32	n.d.	6.57	360 d–1.7 year
Benzo(k)fluoranthene	252.32	n.d.	6.84	2.5–5.9 year
Benzo(ghi)perylene	276.34	n.d.	7.23	0.25–1.8 year
Indéno(1,2,3-cd)pyrene	276.34	n.d.	7.66	1.6–2 year

Further, numerous studies show that PAHs constitute a potential danger to environmental and human health (Menzie *et al.*, 1992; Cachot *et al.*, 2006).

The fate of PAHs in the environment mostly depends on their molecular weight. The lightest compounds are known to be the most water soluble and the most volatile, whereas the heaviest ones are the most lipophilic (Table 1). PAHs are currently present in all the environmental compartments of the Seine River basin. Pyrolitic PAHs are mostly emitted to the atmosphere where they partly sorb onto particles. Some are photo-oxidized; others are transported by wind erosion. The heaviest PAHs mostly sorb onto particles because of their low volatility and may rapidly deposit on soil and vegetation (Smith & Jones, 2000). Once deposited onto soils, PAHs may sorb to any available organic matter.

Vegetation may constitute a buffer in the atmospheric–soil transfer of PAHs. Petrogenic compounds are directly discharged to the soils (Soclo *et al.*, 2000). During rainfall events, PAHs may be leached or eroded with soil particles, and reach water bodies. Percolation within soils is limited to the lightest compounds and can often be neglected because of their low solubility in water (Enell *et al.*, 2004). Once PAHs are in water, a new partition is established between aqueous and particulate phases, depending on the physical properties of each compound. Exported PAH fluxes mainly depend on sedimentary loads. Therefore, floods have a major impact on the transport of PAHs in rivers (Ollivon *et al.*, 2005; Mourhi *et al.*, 2008).

PAH contamination is often spatially heterogeneous because of the great variety of anthropogenic sources. Hence, PAH contamination may display markedly different temporal and spatial distributions. This high degree of spatial and temporal source variability complicates our understanding of the environmental fate of PAHs. To improve our knowledge of the transit and storage of these contaminants, this study investigated PAH transfers at the catchment scale by combining chemical analyses using GC-MS with radionuclide analyses using gamma spectrometry. This paper presents some preliminary results, as more analyses and sampling campaigns are still in progress.

MATERIALS AND METHODS

Study sites

Soil and suspended sediment samples were collected for eight months in one upstream subcatchment of the Seine River basin. In this study, a nested sampling approach was employed. A network of sediment traps (Fig. 1) were deployed on the rivers draining the 106 km^2 Orgeval

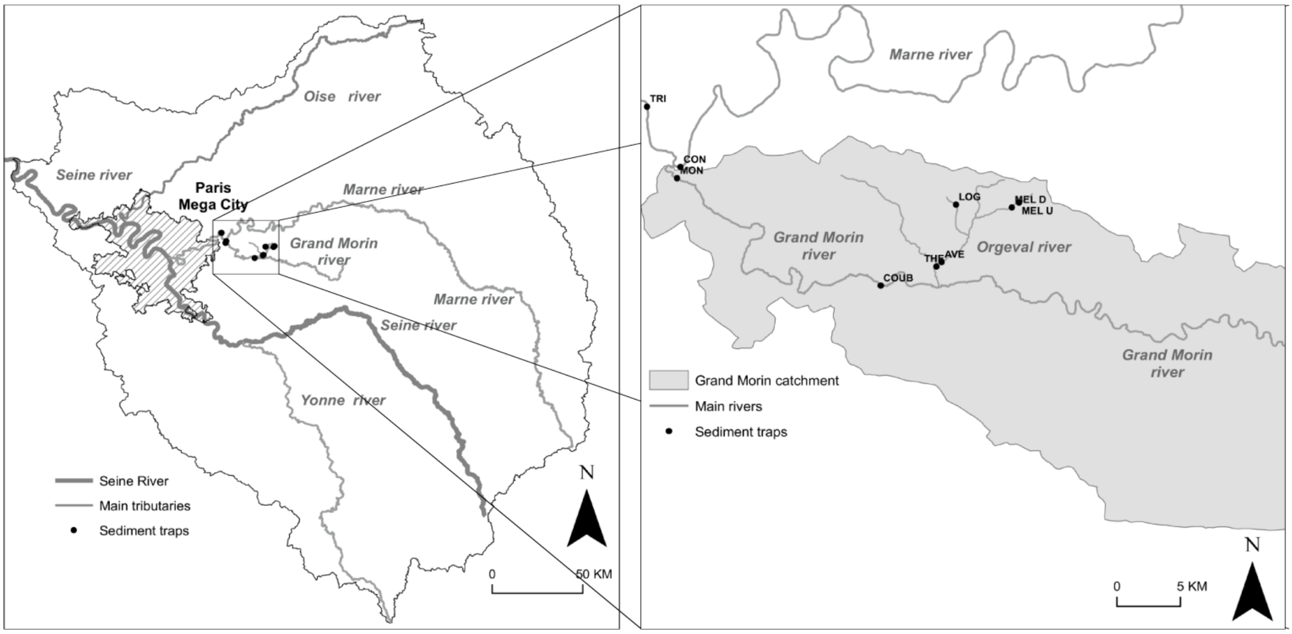

Fig. 1 Locations of sampling sites.

sub-catchment down to its junction with the Grand Morin and Marne rivers (total drainage area of 12 300 km^2).

The suburban Orgeval sub-catchment is located 70 km eastward from Paris City. The climate is semi-oceanic. Mean annual rainfall since 1963 is 646 mm. Monthly mean temperature ranges from 0.6°C (January) up to 18°C (August), and the annual mean temperature is about 11°C (Vilain *et al.*, 2012). The Orgeval sub-catchment is dominated by cropland and grassland (82% of the total surface); the rest is woodland (17%) and urban areas (including roads; 1%). About 90% of the cultivated area is subsurface drained. The catchment is relatively flat with a mean altitude of 148 m. More information on this sub-catchment can be found on the IRSTEA website (2012).

Soils were sampled at five sites susceptible to erosion and chosen to cover the entire range of land uses observed in the sub-catchment (i.e. cropland, grassland, woodland and urban soils). Ten subsamples of surface material (top 10 cm) were collected and well-mixed to provide a homogeneous sample from which three aliquots were withdrawn, after removing coarse organic material such as leaf litter.

Suspended sediment (SPM) samples were collected at nine nested stations between 30 March and 10 November 2011. Metallic cylindrical traps were submerged into the water by using a rope attached to a nearby tree trunk on the river bank. SPM samples removed from the traps were placed in glass containers and brought back to the laboratory in a cool box. They were then placed in a laboratory refrigerator and allowed to settle (at 4°C) for 24 h. After this period, the supernatant was removed and the residual suspended matter was placed in a freezer and subsequently freeze-dried.

Chemical analyses

PAH concentration spectra and fallout radionuclide (^{7}Be, ^{210}Pb, ^{137}Cs) activities were measured in 16 soil and 72 SPM samples. Based on US-EPA recommendations, 16 PAHs were selected: Naphthalene (NAP), Acenaphtylene (ACY), Acenaphtene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FTH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene + Benzo(k)fluoranthene (Bb+kF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DahA), Benzo(g,h,i)perylene (BghiP), and Indeno(1,2,3-cd)pyrene (IcdP). Naphthalene was excluded when summing PAH concentrations because of its high volatility.

Soil and SPM samples were limited to <1000-µm by sieving. Aliquots (1 g of SPM or 2 g of soil) were put in glass tubes and spiked with 20 µl of a 3.33 ng.µl^{-1} mixture of deuterated compounds (Phenanthrene D10, Pyrene D10 and Benzo(a,h)Anthracene D12). Soil and SPM were extracted by ultrasonication in 10 ml of a mixture of acetone/hexane (1:1 v/v) for 20 minutes and centrifuged for 3 minutes at 2500 r min^{-1}. The extraction was repeated once, after which the sample was rinsed with 5 ml of solvent. The three extracts were transferred to a 22 ml amber vial and concentrated to 0.5 ml under nitrogen flux. Activated copper was placed overnight in the vials. The extracts were passed through Florisil® cartridges (6 ml, 1 g) previously conditioned with a 10 ml mixture of dichloromethane (DCM)/methanol (95:5 v/v) and 10 ml of a mixture of hexane/ DCM (80:20 v/v). Ten ml of the latter were also used as an eluant. Once again, the extracts were concentrated to 0.5 ml under a nitrogen flux. The final purification step entailed using a cartridge containing 1 g of activated alumina and 1 g of activated silica, conditioned and eluted, respectively, with 10 ml and 15 ml of a mixture of hexane/DCM (1:1 v/v). The final eluants were concentrated under a nitrogen flux and placed in 400 µl amber vials. PAHs were analysed by gas chromatgraphy (Agilent GC system 7890A) coupled with a mass spectrometer (Agilent 5975C inert XL MSD) set in the Selected Ion Monitoring (SIM) mode.

Gamma spectrometry

Soil and suspended sediment samples were packed into airtight 15- or 60-ml (depending on the quantity available) pre-tared polyethylene specimen cups to contain ^{222}Rn, and to allow ingrowth of its decay products. The ^{7}Be (477.6 keV), ^{137}Cs (661.6 keV), and ^{210}Pb (46.5 keV) activities in this material were determined by gamma spectrometry using seven very low-background coaxial N- and P-type GeHP detectors (Canberra/Ortec) available at LSCE. "Excess" ^{210}Pb was calculated by subtracting the supported activity (determined using two ^{238}U daughters, i.e. ^{214}Pb, by taking the average count number at 295.2 and 351.9 keV, and ^{214}Bi at 609.3 keV) from the total activity of ^{210}Pb measured at 46.5 keV (Le Cloarec *et al.*, 2011).

When the available material was insufficient (<5 g), SPM samples were placed in sealed airtight polypropylene tubes, and counted in the well of a Ge detector. Counting time for soil and SPM samples varied between 8×10^{4} and 3×10^{5} s. Activity was corrected for background levels measured at least every two months, as well as for detector and geometry efficiencies. Results were systematically expressed in Bq kg^{-1}. Counting efficiencies and quality assurance were evaluated using internal and certified IAEA standards prepared in the same specimen cups as the samples. Efficiencies were interpolated for ^{7}Be energy.

Further, to provide an indication of the "age" of the SPM collected in the river traps, the ^{7}Be/^{210}Pb$_{xs}$ ratio was calculated following the procedures outlined in Matisoff *et al.* (2005). Monthly records of radionuclide activities in rainfall were provided by the French Radioprotection and Nuclear Safety Institute (IRSN) for the nearby Orsay continuous monitoring station. A decrease in the ^{7}Be/^{210}Pb$_{xs}$ ratio can then be explained by either: (i) an increase in the sediment residence time (given that ^{7}Be decay is faster than ^{210}Pb$_{xs}$ decay), or by (ii) the dilution of sediment enriched in ^{7}Be by sediment poorer in ^{7}Be. Consequently, calculation of this ratio could indicate aging and/or sediment dilution in the river (Evrard *et al.*, 2010).

PRELIMINARY RESULTS

The chemical signature of SPM-associated contamination

Figure 2 shows the mean value for the relative abundance of each SPM-associated PAH for the different sampling sites (Orgeval and downstream Grand Morin and Marne rivers). These values were generated by averaging the concentrations determined over the eight month sampling period (March to November 2011).

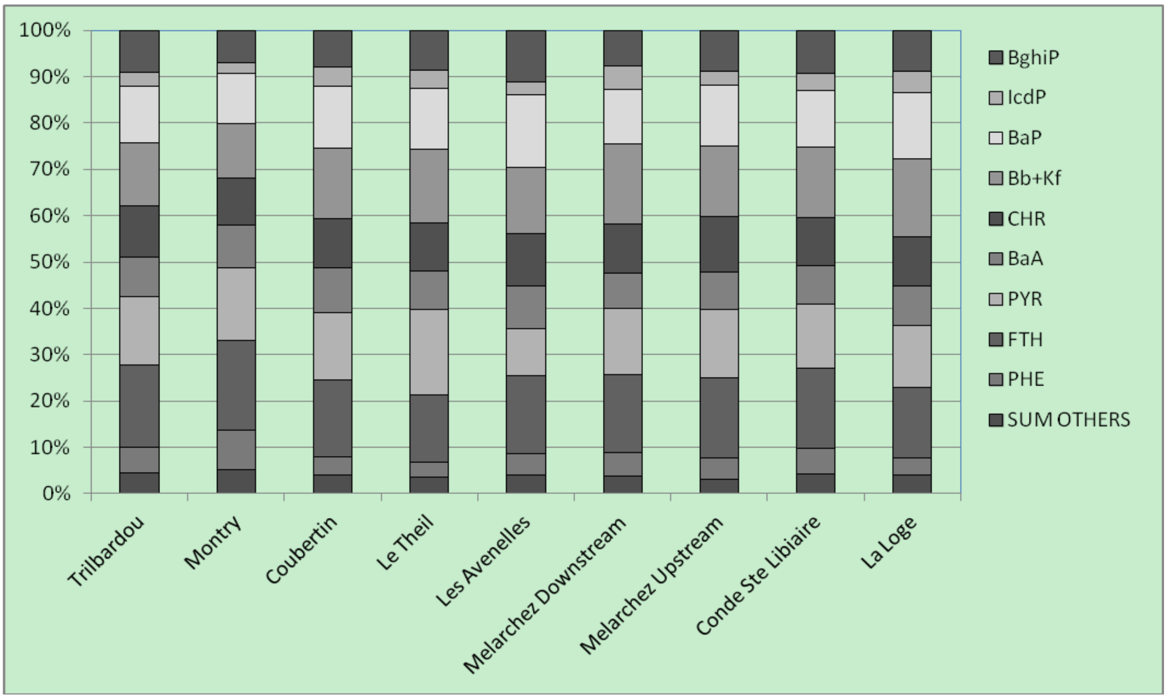

Fig. 2 Comparison of relative PAH abundances in SPM collected at the different sampling sites.

The heaviest PAHs (four or more rings) provided 75% of the mass of SPM-associated contamination. This is due to the highly hydrophobic properties of the largest compounds. The mean relative PAH abundances are similar in the SPM collected at all the stations located across the entire sub-catchment (Fig. 4). Yunker (2002) reported that contamination spectra can be used as a first indicator to infer pollutant origin(s). Homogeneity of PAH spectra in the SPM from all the sampling sites would indicate either that the contaminants came from a single and diffuse source, or that the main sources have similar chemical signatures.

Spatial variability of PAH contamination in SPM

Figure 3 shows the spatial variability of sediment-associated PAHs. These concentrations have been averaged over the eight months corresponding to a period of low river stage. PAHs that fall under the scope of the European Water Framework Directive, or do not, are symbolized by the black and white bars, respectively.

The lowest SPM-associated PAH concentrations were measured at the most upstream sampling sites (i.e. Melarchez and La Loge), draining areas of 7.1 and 9.6 km^2, respectively. Concentrations progressively increased downstream with rising population densities typically associated with increasing drainage areas (Le Theil: 22 inh km^{-2}; Les Avenelles: 33 inh km^{-2} and Coubertin: 37 inh.km^{-2}).

A large dilution phenomenon was observed at the junction between the Grand Morin and Marne rivers. Despite the high PAH concentrations measured in the SPM that originated from the Grand Morin River catchment (1200 km^2; mean annual flow: 5.4 m^3 s^{-1}), no increase was observed in SPM-associated contamination at the most downstream sampling site (12 300 km^2; mean annual flow: 96.5 m^3 s^{-1}). This result will be discussed later.

The on-going measurement of PAH concentrations for the entire duration of the project (12 months) will provide further information on the role of river discharge in pollutant transfer since floods occurred in December and January. Indeed, contaminants associated with flood periods may come from different sources; hence, the spatial distribution of PAH concentrations shown in Fig. 3 may not be representative of the mean annual distribution.

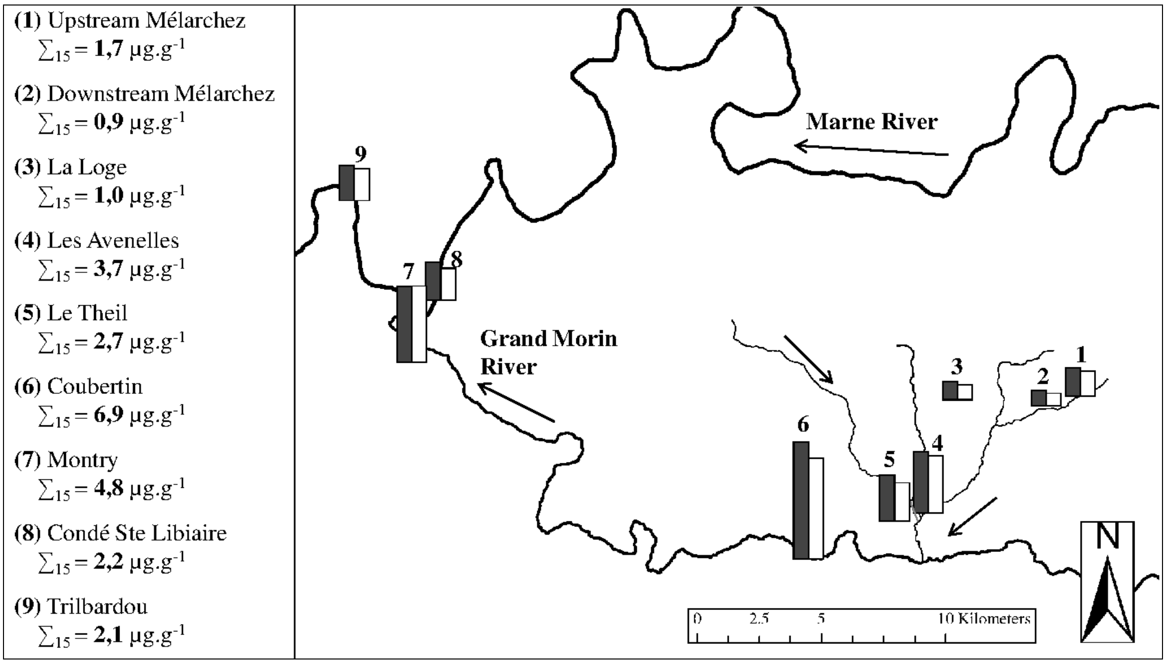

Fig. 3 PAH concentrations in SM collected in Orgeval catchment (black, WFD PAHs [ANT, FTH, Bb+kF, BaP, BghiP & IcdP]; white, non-WFD PAHs [ACE, ACY, FLU, PHE, PYR, BaA, CHR, DahA]).

Soil contamination

Soil concentration spectra are shown in Fig. 4 (woodland, croplands and grasslands are referred to as rural sites). Contamination appears to be about six-fold higher in urban soils than at the most contaminated rural sites. This difference is likely explained by their proximity to local sources. These results are consistent with those reported by Hafner *et al.* (2005) which showed a greater anthropogenic impact in a 25-km radius circle around them, and by the results obtained by Moreau-Guigon *et al.* (2010) for the same study site. Relative PAH abundances show that urban soils are proportionally richer in heavy PAHs, because of the rapid sedimentation of local atmospherically-derived particulate compounds.

Contamination in croplands appeared to be two-fold higher than in other rural soils. The difference in spectra is mainly due to the greater presence of heavy PAHs that can be partly explained by intensive farming operations carried out on those soils. In view of the greater difference in contaminant levels, this explanation can only be valid if farming operations were conducted just before the sampling campaigns. More samples have been collected to monitor the temporal evolution of contamination in this type of soil, but analyses are still underway.

The strong similarity between woodland and grassland soil-associated PAH concentrations suggest the presence of an important local source of atmospherically-derived PAHs.

The large difference in PAH concentration observed in soils and SPM can be explained either by the preferential erosion of strongly contaminated soil particles, or by an accumulation of pollutants on the particles once they enter the river. Radionuclide activities will provide a way to determine the relative importance of these two processes.

Temporal variations of PAH concentrations in SPM

Figure 5 shows the temporal evolution of SPM-associated PAH concentrations at two stations located in the Orgeval sub-catchment. At the upstream station, PAH concentrations display strong variations from one month to the next. This great variability only can be explained by the generation of PAH emissions from local and very contaminated sources. The La Loge sampling site has a 9.6 km^2 drainage area, mainly used as cropland. Contamination peaks measured in

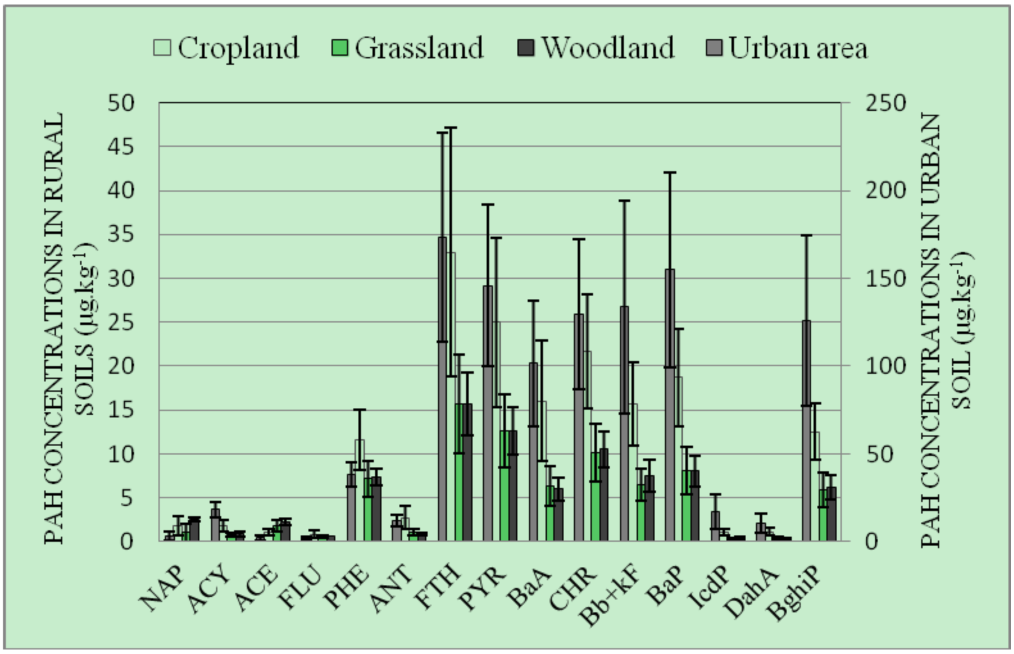

Fig. 4 Comparison of PAH contaminations in different land uses.

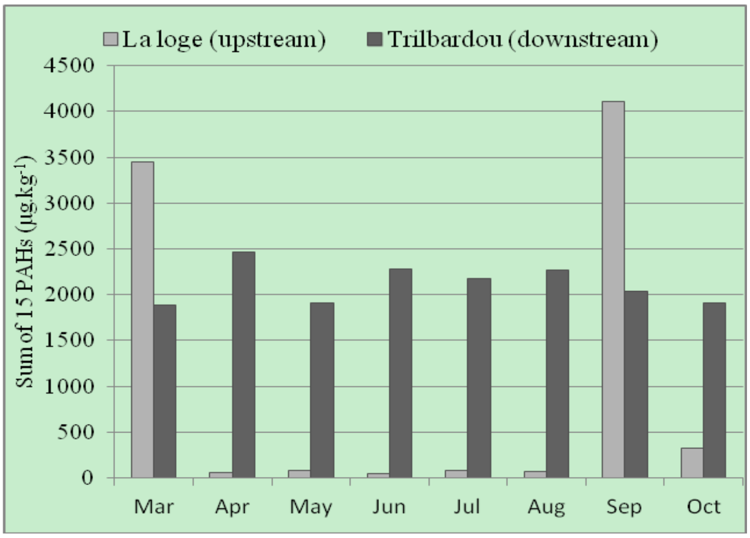

Fig. 5 Temporal evolution of PAHs concentrations in SM at two stations of the Orgeval catchment.

March and September are likely to have been produced by the intensive use of farm equipment for soil tillage. This increase in contamination was not detected at Trilbardou, where PAH concentrations remained rather constant during the entire sampling period. The larger amount of SPM conveyed by the Marne River at Trilbardou probably led to a dilution of local contamination, at this scale.

A similar dilution phenomenon was indicated by the initial ^{7}Be/^{210}PB$_{xs}$ ratios in both rainfall and SPM. Figure 6 shows the temporal evolution, in percentages, of “new” material in the SPM from three stations distributed across a downstream/upstream transect.

Rainfall events that occurred early in June only affected the Orgeval sub-catchment. At upstream sampling sites, the calculated percentages of new sediment sharply increased, up to 80%, because of local soil and/or river bank erosion. The increase in new sediment observed at the downstream sampling site was lower because of the dilution of freshly supplied material by older

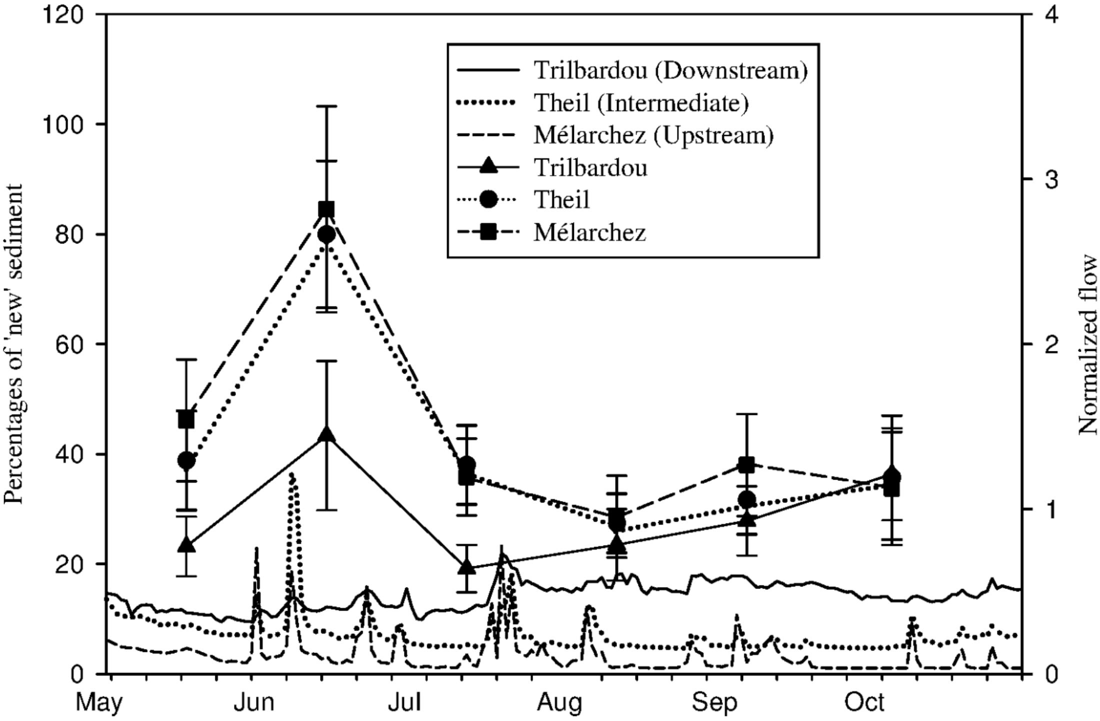

Fig. 6 Mean proportion of recent sediment at three nested stations (Mélarchez is upstream of the Orgeval sub-catchment; Le Theil, is the outlet of the Orgeval sub-catchment where it flows into the Grand Morin River; Trilbardou is further downstream at the junction of the Grand Morin and Marne rivers).

sediment that had originated from the rest of the Marne River basin. Those results regarding the evolution of the percentages of fresh sediment in the river are consistent with PAH concentrations measured in SPM. The strong variability of both sediment age and contamination observed at upstream sampling sites tends to decline as the material transits downstream.

Combined analyses of both the percentage of recent sediment and PAH contamination, during larger-scale floods should provide a powerful tool to determine the relative importance of contaminant sources at the catchment scale. Three hypotheses can be put forward. If sediment age and contamination are confirmed to be strongly and positively correlated, it would mean that the bulk of the contamination is supplied to the river during heavy rainfall when secondary sources (i.e. urban area and road leaching, wastewater discharge) release PAHs. If there is no correlation, the major source would be historical deposits of soil-associated PAHs. Finally, if both parameters are found to be negatively correlated, it would mean that PAH concentrations in sediments progressively increase during temporary storage in the river.

CONCLUSIONS

The initial results of this study indicate the need to determine the distribution and concentration of PAHs at the catchment scale. The great variability of PAH sources associated with human activities makes it difficult to fully understand their transfer pattern(s). In this context, combining chemical analyses and measurements of radionuclide activities in both rainfall and river sediment provide crucial information needed to estimate contaminant residence times in soils and sediment. Measurement of PAH concentrations in soils and SPM highlights the major role of urban areas as PAH sources. Urban soils are richer in heavy PAHs than rural soils; this appears to result from the deposition of atmospherically-derived particles from nearby sources.

Further investigations are necessary to fully understand PAH transfers in the environment. SPM samples have been collected for one entire hydrological year to evaluate flood contributions to the annual export of PAHs. PAH atmospheric inputs have also been investigated to establish a contaminant mass balance and to better determine the origin(s) of PAHs in upstream sub-catchments.

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