Combining measurements and modelling to quantify the contribution of atmospheric fallout, local industry and road traffic to PAH stocks in contrasting catchments

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Abstract

Various sources supply PAHs that accumulate in soils. The methodology we developed provided an evaluation of the contribution of local sources (road traffic, local industries) versus remote sources (long range atmospheric transport, fallout and gaseous exchanges) to PAH stocks in two contrasting subcatchments (46-614 km²) of the Seine River basin (France). Soil samples (n=336) were analysed to investigate the spatial pattern of soil contamination across the catchments and an original combination with radionuclide measurements provided new insights into the evolution of the contamination with depth. Relationships between PAH concentrations and the distance to the potential sources were modelled. Despite both subcatchments are mainly rural, roadside areas appeared to concentrate 20% of the contamination inside the catchment while a local industry was found to be responsible for up to 30% of the stocks. Those results

have important implications for understanding and controlling PAH contamination in rural areas of early-industrialized regions.

Keywords: PAHs; soil; source contribution; spatial variation; model

Capsule: Source contributions to PAH soil contamination were investigated with distance-based models.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are widespread organic contaminants that are well known for their mutagenic or carcinogenic properties, and therefore represent a risk to the ecosystems and the human health (Grimmer et al., 1991; Nielsen et al., 1996; Tsai et al., 1995). They are mainly emitted during the incomplete combustion of fossil fuels or biomass (Wild and Jones, 1995) and they can be disseminated across large regions from their initial source through long-range atmospheric transport (LRT) (Sehili and Lammel, 2007). They are ubiquitous in the environment, but their concentrations were reported to be much higher in soils located in the vicinity of urban or industrialized areas as well as in atmospheric fallout collected in those areas (Wilcke, 2000). As in most early industrialized countries, the PAH issue is particularly problematic in the Seine River basin, in France, where excessive concentrations in Polycyclic Aromatic Hydrocarbons (PAHs) are reported in sediment (AESN, 2010), thereby compromising the achievement of the good chemical status required by the European Union (Water Framework Directive 2000/60/EC). In their study modelling PAH long-range transportation at the worldwide scale, Sehili and Lammel (2007) concluded that 64 to 97 % of some PAHs remained stored in the soils. Similarly, Wild and Jones (1995) estimated that in UK more than 90% of PAHs accumulated in soils. This highlights the role of this compartment as a buffer of PAH contamination in the environment. As atmospheric PAH emissions have decreased during the last decades in Western Europe (Fernández et al., 2000; Pacyna et al., 2003), the soils represent secondary sources, and are likely to play an important role in the current and future

environmental persistence of those contaminants. Villanneau et al. (2013) reported the presence of higher PAH concentrations driven by historical mining and industrial activities in soils of Northeastern France. In the Seine River basin, certain studies identified Paris City as the main source delivering PAHs into the atmosphere (Garban et al., 2002), whereas other investigations showed that PAH concentrations in soils were mainly associated with the presence of urban or industrial areas in their vicinity (Motelay-Massei et al., 2004). Consequently, to move the debate forward and given the importance of legacy contamination in northwestern Europe, the respective contribution of regional atmospheric fallout and local sources supplying PAHs to the soils must be further investigated.

Interactions between soils and PAHs have been extensively studied for many years and appear to be very complex (Xing and Pignatello, 1997). Because of their high lipophilicity, PAHs tend to bind strongly to the particles (Yang et al., 2013). Numerous studies have also highlighted the role played by organic matter (OM) in the sorption of those substances and showed that soils enriched in OM generally contain higher PAH concentrations (Bogan and Sullivan, 2003). Once deposited onto the soil surface, some contaminants gradually migrate to deeper soil horizons. This transfer mainly depends on the solubility of the compounds, their affinity for soil components and the magnitude of water infiltration into the soil (Enell et al., 2004; Yang et al., 2013). PAHs are both poorly soluble in water and highly lipophilic, and leaching is therefore limited to the upper soil layers. This leads to an accumulation of PAHs in the uppermost layers of the substrate as observed in undisturbed forest soils by Krauss et al. (2000). Some laboratory experiments showed that a very small fraction of PAHs is recovered when injecting a large amount of water through a soil core (Enell et al., 2004). In this context, PAH leaching is often considered to be negligible. However, high PAH concentrations have also been observed in deep horizons of heavily contaminated soils (Liao et al., 2012). In conclusion, the entire distribution of PAH contamination in soil horizons must be considered to correctly quantify their inventory in the substrate.

Overall, to the best of our knowledge, there is little information in the literature combining PAH contamination in soils, its evolution with depth and the relationship with the distance to the sources at the entire catchment scale. In this study, the PAH distribution is investigated in

soils of two agricultural catchments to verify the relevance of factors that need to be taken into account when estimating contaminant stocks. a) The concentrations of PAHs in 336 soil samples collected in 2 catchments are reported. b) The variation of PAH content with depth in soils is investigated. c) The relationships between soil contamination and the distance to potential local sources (charcoal factory or road traffic) are investigated. d) Finally, the relative contribution of local and regional sources within the two catchments are detailed and the corresponding PAH stocks are calculated. Overall, this study is representative of the contaminant concentrations and stocks that may be found in most rural and agricultural catchments of early industrialized countries. The results of this study provide original and novel information on PAH stock distribution at the catchment scale. They may be useful to design and implement large scale remediation programmes required to achieve the legislative environmental targets.

2. Materials & Methods

2.1 Study sites

In order to compare the importance and the relative contribution of several PAH sources in the environment, soils from two catchments located in upstream parts of the Seine River basin (Fig. 1) were sampled and analysed. Site 1 is the Avenelles catchment located 70 km eastward from Paris City and draining a 46-km² area. Site 2 is the Saulx catchment, located 210 km eastward from Paris City and constituted of 3 subcatchments covering a total area of 614 km². According to CORINE Land Cover (2006), both catchments are dominated by cropland and grassland (covering 82% of the total surface in Site 1 and 57 % in Site 2), the rest of the surface being occupied by woodland (Site 1: 17 %; Site 2: 42 %) and sparse human settlements (including roads; 1%). Climate is semi-oceanic in Site 1 and semi-continental in Site 2. Monthly mean temperature varies between 0.6 °C (January) and 18.0 °C (August) in the Avenelles catchment and between -2.0 °C (February) and 18.2 °C (August) in the Saulx catchment. Prevailing winds blow mainly from the southwest and the west, or from the northeast. Altitudes are higher and slopes are steeper in Site 2 (mean altitude: 362 m and mean slope: 3.7 %) than in

Site 1 (mean altitude: 148 m and mean slope: 2.5 %). A charcoal factory is located close to the northwestern boundary of Site 2.

2.2 Sampling

Transects across the catchments

Soil samples (n=106) were collected along two transects across both catchments (Fig. 2) between March 2011 and February 2012. To this end, 10 subsamples of surface material (top 8 cm) were systematically collected and well-mixed to provide a homogeneous sample. Coarse organic fragments were removed from the surface layer. Soils were sampled at a minimum distance of 50 m from the closest road to avoid direct PAH deposition and to be representative of the entire plot. Once collected, samples were placed in glass recipients in an ice box (4°C) and carried back to the laboratory to be frozen and freeze-dried.

Detailed soil profiles under 4 different land covers

To investigate the evolution of PAH concentration with depth in the upper layer of the soils, 4 soil cores were collected at 3 undisturbed sites (i.e., garden in a built-up area [O9], woodland [O2] and grassland [O15]) as well as under cropland [O8]. Those samples were cut into 1 cm-depth increments and chemical analyses were conducted on each subsample (n=30).

Detailed transects in a forest plot and a cropland field along roads

Two plots of land (CP and WP in Figure 2) were sampled in Site 1 according to a regular grid in order to investigate the local impact of roads on the nearby soils. The two sampled plots were selected in the Choqueuse forest (dense hardwood forest) and in a cropland area (bare soil at the time of sampling). Cropland site was almost flat and situated 1 m above the roadside ditch bottom level. Woodland site was flat as well but situated at the same level as the ditch bottom. The latter was separated from the rest of the plot by a 1 m-high embankment. During sampling, 5 transects separated by a distance of 2 m and oriented perpendicularly to the road were followed. The first sampling points of each transect were located in the middle of the roadside

ditch, and they were used as reference points to measure the distance to the road. The following samples (n=200) were subsequently taken at 0.5, 1, 2, 3, 5, 10, 20, 30 and 40 m along the transects.

2.3 Distance to the local sources

To document the role of road traffic on soil contamination by PAHs, we investigated the relationship between the PAH concentration in soils and the distance to the closest road in both catchments. Distances were calculated using the Route 500® database provided by the French National Geographic Institute. All the roads of the study area are characterized by a similar traffic density typical of this kind of rural zone. In Site 2, a similar approach was performed to investigate the contribution of both the road traffic and the charcoal factory to the catchment contamination. A regression analysis between PAH concentrations in soils and the distance to those sources was conducted. The modelling curves described in Equation (1) were chosen between several models (inverse first order, exponential decay, etc.) as they appeared to better fit with the contamination at both plot and catchment scales:

$$y(x) = \frac{aL + bx}{L + x} \quad (1)$$

Where y is either the standard or the OC normalized PAH concentration in soils (respectively ng.g^{-1} or ng.g^{-1} OC), and x is the distance (m) to the closest source (road network or charcoal industry). a and b (ng.g^{-1} or ng.g^{-1} OC) are respectively the PAH concentration in the vicinity of the source and the local background signal of the contamination. L (m) is the characteristic distance of the contamination i.e. the distance at which the PAH concentration reaches the mean value between the source and the background signal. Outliers displaying much higher PAH concentrations or different contamination signature were removed from analysis to avoid potential biases due to the contribution of additional unsampled sources or to the local heterogeneity. Curves were fitted using the least squares method. At the plot scale, a lower weight was attributed to the data collected at a shorter distance from the road as they appeared to be more scattered.

2.4 Chemical analyses

After extraction and purification, PAHs were analysed by gas chromatography (Agilent GC system 7890A) coupled with a mass spectrometer (Agilent 5975C inert XL MSD). MS signal acquisition was performed in Selected Ion Monitoring (SIM) mode. Thirteen US EPA PAHs could be determined: Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FTH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene + Benzo(k)fluoranthene (BbF+BkF), Benzo(a)pyrene (BaP), and Benzo(g,h,i)perylene (BghiP). More detailed descriptions of extraction and analysis methods can be found in Gateuille et al. (2014). Organic carbon was measured using a CHN Elemental Analyzer to determine the carbon weight percent in soil samples after carbonate removal.

Maps of the PAH contamination were drawn using a Geographic Information System software (ArcGis ®). Interpolations were carried out using the inverse distance weighting method.

2.5 Radionuclide analyses

Soil samples were packed into 4-ml pre-tared polyethylene specimen cups and sealed airtight. The ^{137}Cs and excess ^{210}Pb activities in this material were determined by gamma spectrometry using the very low-background HPGe detectors available at LSCE (Evrard et al., 2010). Those radionuclides have rather long half-lives, i.e. 30 years for ^{137}Cs and 22 years for ^{210}Pb . The first radionuclide is artificial and was produced by the thermonuclear bomb testing during the 1960s and in 1986 by the Chernobyl accident (Forsberg et al., 2000; Bossew and Kirchner, 2004). The second is supplied to soils by decay of both geogenic ^{238}U and atmospheric ^{222}Rn . The latter source regularly supplies an additional activity (excess ^{210}Pb) to the soil during rainfall. Both radionuclides are concentrated at the soil surface and concentrations rapidly decrease with depth in undisturbed soils (Wallbrink and Murray, 1993).

3 Results and discussion

3.1 Migration of PAHs in depth

Depth profiles of PAH concentrations in soils under different land covers are given in Figure

3. Three types of behaviour were found.

- First, in undisturbed soils (i.e. woodland), concentrations in all measured parameters decreased with depth except for PAH in the two first centimetres. This trend may be explained either by higher PAH losses (biodegradation or volatilization) in the uppermost layer of the soil or by lower atmospheric inputs during the last decades. On the one hand, volatilization and degradation are likely to reach higher rates at the air-soil interface and may lead to a decrease in PAH content in the uppermost layer. On the other hand, lower PAH input may lead to lower PAH concentrations in the surface layer because of the slow migration of PAH towards deeper horizons. This slow migration of PAHs in depth is confirmed by a similar behaviour of ^{137}Cs and of $^{210}\text{Pb}_{\text{xs}}$. Based on the $^{210}\text{Pb}_{\text{xs}}$ profile, the maximum PAH emission period may be estimated to ca. 1950. Those results remain consistent with previous findings on PAH emissions in Western Europe (Fernández et al., 2000). PAH concentrations were much higher under woodland than under land covers, but a similar enrichment factor of ca. 6 was found in fallout radionuclide measured in samples collected in close areas under other land uses (PAH: 231 ng.g^{-1} ; $^{210}\text{Pb}_{\text{xs}}$: 11 Bq.kg^{-1} ; ^{137}Cs : 4 Bq.kg^{-1}). Traditionally, the forest canopy leads to a higher interception of atmospheric contaminants, and they are found in higher concentrations in areas with elevated organic matter contents (Gaspar and Navas, 2013; Wilcke, 2000). Overall, PAH concentration dropped to less than 20% of its maximum value at a depth of 7 cm showing that PAH stocks were mainly concentrated in the surface layer.

- Second, the cropland sample appeared to be representative for homogeneously disturbed soils where parameters showed very small variations with depth. PAH concentrations decreased until 60% of the maximum value and remained stable below a depth of 4cm. This homogeneity may be explained by the regular ploughing of soils. The higher values found in surface may originate from PAH supply during farming operations. In cropland, PAH contamination likely reaches the maximum ploughing depth (Doick et al., 2005).

- Third, soils under built-up areas and grassland were characterized by an increase in PAH content in the two or three first centimetres of the soil. Then, concentration remained stable down to 3 or 4 centimetres before decreasing again. However, the PAH concentration remained high in depth of those samples (78% and 58% of the maximal values for built-up area and grassland, respectively) suggesting that PAH contamination may have reached deeper soil layers. In these samples, OC content decreased with depth as under woodland. However, ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ activities displayed different patterns. This suggested that soils may have been disturbed after 1986 (i.e., last significant ^{137}Cs input in the region, Evrard et al., 2012). Contamination depth could therefore not be estimated in these two plots as it was found to depend on local soil disturbances.

3.2 Distribution at the catchment scale

Maps of PAH contamination in the soils (normalized to OC) and values of BaA/(BaA+CHR) ratio were drawn for both catchments. Values of other PAH ratios are not presented as they displayed less clear variations within the catchments. The literature suggests that samples with BaA/(BaA+CHR) values higher than 0.35 were likely contaminated by pyrolytic sources whereas low ratio values indicate the contribution of a petrogenic source (Guo et al., 2003; Soclo et al., 2000; Yunker et al., 2002).

In Site 1 (Fig. 4) located the closest from Paris, total PAH concentrations in soils varied between 64 and 5618 ng.g^{-1} (mean of 666 ng.g^{-1}). When normalized to the OC content of soils, those concentrations ranged from 5000 to 295 400 ng.g^{-1} OC (mean of 33 600 ng.g^{-1} OC). A poor correlation was observed between the PAH concentrations and the OC contents in soils ($r^2=0.12$; $p < 0.05$). The BaA/(BaA+CHR) ratio varied from 0.38 to 0.56 (mean of 0.44). There was no clear spatial trend in the distribution of those parameters although the highest values of both contamination and ratio were measured in samples collected in the middle part of the catchment. This distinctive feature may be due to its vicinity with Doue village that may provide a very local source of PAHs because of household heating by fuel oil or wood burning. At this location, both the PAH concentration (5618 ng.g^{-1}) and the BaA/(BaA+CHR) ratio

(0.56) were significantly higher than the corresponding values measured in the other samples inside the catchment.

When excluding the samples collected in built-up areas and their surroundings (O12, O9 and OS3), the mean PAH concentration reached $205 \pm 146 \text{ ng.g}^{-1}$ with 95% of the values remaining below 500 ng.g^{-1} . In the following calculations, this value was therefore chosen as a benchmark to distinguish between soils strongly influenced by local sources and those with PAH concentrations close to the regional background signal. A similar value (600 ng.g^{-1}) was previously reported to distinguish between slightly and strongly contaminated soils (Jones et al., 1989; Malisweska-Kordybach, 1996).

In Site 2 located further away from Paris (Fig. 5), total PAH concentrations in soils varied between 95 and $13\,657 \text{ ng.g}^{-1}$ (mean of 2137 ng.g^{-1}). Concentrations normalized to the OC content of soils ranged from $5\,700$ to $195\,400 \text{ ng.g}^{-1} \text{ OC}$ (mean of $36\,300 \text{ ng.g}^{-1} \text{ OC}$). Again, a poor correlation was observed between the PAH concentrations and the OC contents in soils ($r^2=0.30$; $p<0.001$). The BaA/(BaA+CHR) ratio varied between 0.39 and 0.54 with a mean of 0.45. Pyrolytic sources were therefore likely the main contributor of PAH contamination in both sites. As in Site 1, one sample was significantly more contaminated than the others ($13\,657 \text{ ng.g}^{-1}$). This point may be considered as contaminated by another local source as both PAH concentration and BaA/(BaA+CHR) appeared to have the highest values among all the samples. In this catchment, a clear spatial trend was observed as both PAH concentrations and BaA/(BaA+CHR) ratio values appeared to decrease with increasing distance from the charcoal factory. Site 2 may therefore be representative for catchments under the strong influence of a local industry emitting PAHs.

A good relationship (Eq. (2) $r^2=0.66$; $p<0.001$) was found between the normalized concentrations of PAHs in soils and the distance to the road network in Site 1 (Fig. 6). In Site 2, the soil contamination was mainly driven by the distance to the charcoal factory (Eq. (3) $r^2=0.84$; $p<0.01$) as a weaker relationship was found with the distance to the road network (data not shown). Using the benchmark previously determined (500 ng.g^{-1}), it appeared that the pollution plume of this factory had a larger spatial extent than the road contamination and it supplied significant PAH contamination up to 8 km in cropland and 12 km in woodland. The

minimum background signals given by the models were lower ((1) 14 ng.g⁻¹ OC; (2) 25 ng.g⁻¹ OC) than the minimal values measured in the samples ((1) 5 050 ng.g⁻¹ OC; (2) 5 650 ng.g⁻¹ OC). This suggests that the ubiquity of local sources may prevent PAH concentrations to reach the expected background levels in soils. Indeed, the most remote areas that we sampled in Site 1 were located at a distance of 1110 m from the road network. In Site 2, no experimental data were available in the most remote areas.

3.3 Distribution along roads

Total PAH concentrations in the cropland and woodland fields investigated in detail are shown in Figure 7. The soil samples collected the closest to the roads were the most contaminated as total concentrations reached respectively about 43 000 ng.g⁻¹ under woodland and 45 000 ng.g⁻¹ under cropland at those locations. This highlights the important contribution of road traffic as a local but ubiquitous PAH source at the catchment scale. Then, concentrations gradually decreased when distance from the ditch increased. In both plots, total concentration reached the local background level (about 350 ng.g⁻¹) at less than 40 m from the road except for the middle transect under cropland where contamination remained significantly higher (about 800 ng.g⁻¹) at a longer distance from the road. Furthermore, spatial variations in PAH contamination were characterized by different trends in both plots. PAH concentration under cropland regularly decreased from the ditch to the most remote points with some local exceptions that will be detailed below.

High values (> 2000 ng.g⁻¹) were observed as far as 10 meters from the roads along all transects except for the middle transect where soil sampled 30 meters away from the road was still heavily contaminated. Under woodland, the pollution range was more limited. High PAH concentrations were restricted to the soils sampled nearby the road (< 5m). Samples taken at 2 and 3 meters from the road were more contaminated than the ones collected on the embankment. This may be explained by the spatial redistribution of PAHs due to leaching. Part of PAHs deposited close to the road may have been washed out, explaining the increase in PAH contamination measured at the bank foot.

To further investigate the impact of road traffic on PAH pollution, spatial variations in the BaA/(BaA+CHR) ratio values were plotted in Figure 8. Under woodland, a similar pattern was observed for all the transects within the plot. The averaged ratio was almost constant and equal to 0.51 within a distance of 3 m from the road. Then, it decreased until reaching the local background value of 0.42. Under cropland, a similar trend was observed in 3 of the 5 transects although the changes were less pronounced. The ratio measured in the ditch was about 0.48 whereas it reached 0.43 in samples collected at a longer distance from the road. Significant variations were only observed in the third transect where the BaA/(BaA+CHR) ratio reached 0.80. This suggests the contribution of an additional source responsible for the higher PAH concentrations along this transect. As no change in the ratio was observed along other transects, the locally higher values measured in PAH concentrations within a distance of 10 meters from the ditches may be explained by runoff and contaminant redistribution. Under woodland, the same pattern of variations in both PAH concentration and BaA/(CHR+BaA) ratios confirmed that the high values observed at the embankment foot (at 2 and 3 m) were due to local contaminant redistribution.

Regression curves were calculated based on measurement of PAH concentrations in soils of both plots (Figure 9). Some data were removed from further analysis as they appeared to be affected by either contaminant redistribution (i.e., samples from the embankment foot in woodland plot) or by sources other than direct emissions of road vehicles (i.e., middle transect under cropland).

A good correlation was observed between PAH concentration in soils and the distance to the road under both woodland (Eq. (4) $r^2=0.98$; $p < 0.001$) and cropland (Eq. (5) $r^2=0.93$; $p < 0.001$). The fitted curves highlighted the important role played by the vegetation cover. It appeared that the PAH concentration decreased more rapidly with the distance in the woodland plot. However, the local background signal appeared to be lower (71 ng.g^{-1}) in cropland than in woodland (94 ng.g^{-1}). This difference may be due to the plot location, as they were situated in different parts of Site 1 and along different roads so that limited variations in local background signal may exist between plots at the catchment scale. Moreover, background signals appeared to be higher at the plot scale than at the catchment scale even though they remained in the same

order of magnitude. Different processes may therefore be responsible for contaminant diffusion at both scales.

The spatial extent of road traffic influence on contamination was determined using the 500 ng.g⁻¹ value selected as a benchmark to characterize soils under the strong influence of local sources (section 3.2). This extent reached between 20 and 30 m in the two plots. When upscaling the results at the catchment scale, we therefore considered that soils located within less than 30 m from the road were under the strong influence of road traffic.

3.4 Source contributions to PAH stocks in soils

The proportions of PAH stocks supplied to the soils by regional atmospheric fallout and local road traffic emissions were calculated (Table 1). To this end, PAH contamination in soils located at less than 30 m from the road were estimated using Equations (4) or (5) depending on the land use. PAH stocks in the first 30 meters along the roads reached about 10.4 g.m⁻¹ under woodland and 30 g.m⁻¹ under cropland per unit length of road.

In Site 1, PAH stocks supplied by regional atmospheric fallout were calculated using the mean concentrations measured in woodland and cropland. In woodland, a 8-cm depth layer was considered to be contaminated as undisturbed soil profile showed that PAH mainly remained in the surface layer. In cropland fields, contamination was assumed to affect the entire ploughing layer and a soil density of 1.35 g.cm⁻³ was estimated. Consequently, stocks in soils were calculated to vary between 19 mg.m⁻² in woodland and 76 mg.m⁻² in cropland.

In Site 2, the atmospheric fallout was supposed to be mainly controlled by the distance to the charcoal factory. To quantify associated PAH supply, PAH concentrations were calculated using Equation (3) and OC contents were estimated from values measured on samples collected in plots located under similar land use. As defined previously, soils were considered to be strongly affected by the charcoal factory within a distance of 8 km under cropland and 12 under woodland. Stock in the 1-km radius circle around the charcoal factory was not taken into account as it appeared to strongly depend on the modelling parameters and no experimental data were available in this catchment part. The calculated stocks ranged between 13 mg.m⁻² in the

most remote woodland and 735 mg.m^{-2} in cropland close to the charcoal factory. PAH stocks reached 87 kg.km^{-2} in Site 1 and 74 kg.km^{-2} in Site 2. The presence of local industries may have a large impact on the contamination of rural catchments as a single charcoal factory appeared to be responsible for one third of the total contamination in Site 2. Overall, it appears that even though the close areas along the roads covered only ca. 4% of the total catchment surface, they concentrated 20% of the total PAH contamination. These results showed that the road traffic emissions should not be neglected when calculating the fluxes at the catchment scale, and that they remain of significant importance compared to regional atmospheric fallout. Specific PAH inputs from farming activities could not be distinguished from atmospheric contamination. However, as the two studied catchments were mostly agricultural, they may be responsible for a part of the contamination far from local sources. In this context, implementation of mitigation measures should be concentrated on roadside areas located along cropland.

4. Conclusions

This study conducted in two rural catchments located at varying distance from the main regional source of contamination provided original results on PAH contamination in soils. First, soil contamination level and depth was shown to strongly depend on land use. At the catchment scale, PAH concentrations in soils displayed large variations and were shown to be partly controlled by the distance to local sources (road network or a charcoal factory). In terms of stocks, our calculations demonstrated that even though roads covered only 4 % of the total catchment surface, 20% of the soil contaminants were found within a distance of 30 meters from the roads. In future, the management of roadside areas should be given the priority as road traffic appeared to be an important and ubiquitous source of PAHs.

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Figure captions

Fig. 1: Location of the Seine River basin and the 2 sampling sites.

Fig. 2: Site 1, Site 2, and location of soil samples. Samples were collected between March 2011 and February 2012. WP and CP are two plots located along roads where samples were specifically collected to investigate PAH contamination associated with the road traffic.

Fig. 3: Changes in concentrations of PAHs, OC, ^{137}Cs , and $^{210}\text{Pb}_{\text{xs}}$ in 4 soil cores collected under different land uses (n=30).

Fig. 4: PAH concentrations (min/max: 5 000/295 400 ng.g⁻¹ OC) and BaA/(BaA+CHR) ratio measured in soils of Site 1 (n=72).

Fig. 5: PAH concentrations (min/max: 5 700/195 400 ng.g⁻¹ OC) and BaA/(BaA+CHR) ratio measured in soils of Site 2 (n=34).

Fig. 6: Relationship between normalized PAH concentrations in soils and distance to the closest road in Site 1 (n=68), and to the charcoal factory in Site 2 (n=32). Number of replicates varied between 2 and 8. Note that there is no data in the Site 2 at a distance lower than 1000 m from the charcoal factory.

Fig. 7: Concentrations of PAHs in the cropland field (a; n=100) and the woodland plot (b; n=100) (black dots: location of sampling points).

Fig. 8: BaA/(BaA+CHR) ratio values in the cropland field (a; n=100) and the woodland plot (b; n=100) (black dots: location of sampling points).

Fig. 9: Relationship between the normalized PAH concentrations in soils and the distance to the road in the cropland field [excluding the third transect] (n=80) and in the woodland plot [excluding samples collected at 2 and 3m from the road] (n=80).

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1 **Table 1**
2 Relative contribution of several PAH sources to the stocks accumulated in soils of the two catchments.

		Roadside areas	Factory contaminated areas	Remote areas	Total
Site 1	Surface (km²)	1.6 (3.5 %)	-	44 (96.5 %)	45.6
	Stocks (kg)	754 (19 %)	-	3201 (81 %)	3955
Site 2	Surface (km²)	22.4 (3.7 %)	90.1 (14.8 %)	498.2 (81.5 %)	610.7
	Stocks (kg)	9000 (20 %)	14 310 (31 %)	22 190 (49 %)	45 500

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