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CONTAMINATION OF SOILS BY METALS AND ORGANIC MICROPOLLUTANTS: CASE STUDY OF THE PARISIAN CONURBATION

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Abstract

Soils are playing a central role in the transfer and accumulation of anthropogenic pollutants in urbanized regions. Hence, this study aimed at examining the contamination levels of selected soils collected within and around the Paris conurbation (France). This also evaluated factors controlling contamination. Twenty-three trace and major elements as well as 82 organic micropollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates (PAEs), polybrominated diphenyl ethers (PBDEs), alkylphenols (APs) and perfluoroalkylated substances (PFASs) were analyzed. Results reinforced the concern raised by the occurrence and levels of metals such as Zn, Pb, Cu and Hg, identified as metallic markers of anthropogenic activities but also pointed out the ubiquitous contamination of soils by organic micropollutants in the 0.2–55,000 µg/kg.dw range. For well documented compounds like PAHs, PCBs and to a lesser extent PBDEs, contents were in the range of background levels worldwide. The pollutant stock in tested soil was compared to the annual atmospheric input. For PAHs, Pb and to a lesser extent Zn, Cu, Cd, Hg, Sb, PAEs and APs a

significant stock was observed, far more important than the recent annual atmospheric fluxes. This resulted from both i) the persistence of a fraction of pollutants in surface soils and ii) the cumulative atmospheric inputs over several decades. Regarding PBDEs and PFASs, stronger atmospheric input contributions were observed thereby highlighting their recent dispersal into the environment.

Keywords

Metals, organic micropollutants, soils, black carbon, PAHs, PCBs, perfluoroalkylated substances

1. Introduction

Soils play an important role in metal and persistent organic pollutants (POPs) transfer and budget in a river basin because they behave as pollutant reservoirs and different processes occurring in soils influence the pollutant adsorption, retention, accumulation, dissipation and finally transfer to rivers (Meijer et al. 2003b). Soil contamination depends on the anthropogenic drivers, which are mainly associated to human land use and activities (agriculture, industrialization, river basin network activities and others) as well as the natural drivers (erosion, geochemical background, etc.).

Different databases on soil monitoring coupling or not metals with organic pollutants are available worldwide. Among these databases, the Swiss Soil Monitoring Network (NABO: Nationale Bodenboebachtung) investigated 8 historical metals (Cd, Zn, Pb, Cu, Hg, Ni, Cr, and Co) and some organic micropollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and -furans (PCDD/F) (Bucheli et al. 2004, Desaules et al. 2010). The national baseline survey of soil quality in the Netherlands investigates a larger broad of metals, as well as volatile organics, chlorinated volatile organics, PAHs and some pesticides (Brus et al. 2009). For this database, the vast majority of the observations were below the limit of quantification (LOQ). As an

indication, for a little more than half of the 252 compounds, more than 95% of the observations were below the LOQ, implying that the estimated 95-percentile was smaller than the LOQ. In France, the French National Soil Monitoring Network (RMQS: Réseau de Mesures de la Qualité des Soils) measured PAHs, PCBs, PCDD/Fs and 26 herbicides (Villanneau et al. 2011). Most of these available databases, as also mainly observed in the literature, focused on a limited set of metals and well-known organic pollutants such as PAHs, PCBs and PCDD/Fs but other pollutants persistent and/or of emerging concern have been less considered. Besides, Sb is considered as a global emerging metal (Krachler et al. 2005, Le Cloarec et al. 2011) and is identified as an urbanization marker (Le Pape et al. 2012). Despite those evidences and the large reviews of trace and major elements in urban soils (Le Cloarec et al. 2011,), there are very scarce data on Sb and Ag occurrence in urban soils. For organic pollutants, data about perfluoroalkylated substances (PFASs), phthalates (PAEs), and to a lesser extent on polybrominated diphenyl ethers (PBDEs) and alkylphenols (APs) are extremely limited. Considering that i) a number of these pollutants have been both emitted in the atmospheric compartment and measured in atmospheric deposition for decades and ii) soil contamination may be mainly related to the cumulative atmospheric inputs, the first purpose of this study, carried out under the frame of the PIREN-Seine program devoted to the Seine River basin (France) was to contribute to available data in the scientific literature for these groups of pollutants. Hence, 105 micropollutants including metals, major elements and priority and emerging organic pollutants were monitored on 32 soils of the Parisian conurbation, including rural and densely urbanized sites. Furthermore, the soil parameters that may affect the contaminant sequestration in soil were investigated. Indeed, relationships between the soil organic matter (SOM) and the pollutants were investigated since SOM plays an important role in the pollutant partitioning and fate (Cornelissen et al. 1997). As black carbon (BC) is a component of SOM and is recognized as a “super sorbent” (Brandli et al.

2008, Cornelissen & Gustafsson 2005), relationships between PAHs, PCBs, PCDD/Fs and BC were also investigated (Nam et al. 2008, Villanneau et al. 2011, Wang et al. 2014). To date, correlations for other groups of pollutants such as PAEs, PFASs and APs have never been investigated. The last objectives of this paper were to assess the soil contamination in relation with land use (urban *vs*. rural soils) and finally, to evaluate the pollutant stocks in soil surface compared to recent atmospheric inputs. To date, atmospheric inputs are generally considered to assess the global pollutant budget at the scale of basin catchment (e.g., (Thevenot et al. 2007)) but their contribution to stocks in soils has never been investigated, to our knowledge, for such a large range of legacy and emerging contaminants.

2. Materials and methods

2.1 Site description and sampling strategy

In this research, 32 soil samples were tested for their mineral and organic pollutant contents (Figure 1). The tested soils were taken from a larger soil sample bank consisting of 120 soils sampled in 2009-2010 across the Greater Paris (France). The Greater Paris, hereafter referred as the Ile de France Region, is the shelter of about 12 million inhabitants while it represents less than 2% of the French territory (about 12,000 km^2) (Meybeck et al. 2007). In this area, the Seine River with its tributaries drains a basin exposed to the chronic emissions of countless human activities including: the heavy road traffic, fuel facilities, industrial and domestic heating, factories, waste incineration plants, etc. At the scale of the Seine Basin, soil erosion was estimated to between 5 and 10 t/km^2/year (Meybeck et al. 2007). The sampling locations for tested soils are given as a supplementary material (Table S1). In order to cover different land uses, both rural (n=12) and densely urbanized (n=20) soils were collected. They were sampled in 2009-2010, using an auger to collect the first 10-cm layer. The auger mouth was pre-soaked for 12 hours in a 3% TFD4 detergent solution, thoroughly rinsed with deionized water and then with HPLC-grade dichloromethane. Acetone on a clean tissue was

used to carry out a rapid on-site cleaning. In order to minimize local heterogeneity and improve data representativeness, each surface soil samples were prepared by pooling three different cores collected 5 m from one another. Furthermore, to reduce cross contamination, every first core of each series was systematically discarded. The remaining samples were then homogenized, double-bagged in polyethylene bags (organic pollutants were preliminary wrapped in aluminum foil) and immediately placed in dark conditions in a cooler with frozen gel packs. Upon return to laboratory, the samples were then freeze-dried, ground, and kept in cold storage (4°C) in plastic (for metals) and glass (for organic pollutants) bottles until analysis.

2.2 Pollutant contents and soil parameters determination

For each sample, total organic carbon (TOC) and black carbon (BC) were analyzed. TOC was analyzed after mineralization (HCl 3%) using an elemental analyzer (Shimadzu TOC-Vws). The BC content was determined with the chemothermal oxidation method (CTO-375) based on previous published method (Gustafsson et al. 2001).

The full list of compounds analyzed is given in Table 1. A total of 105 individual substances were monitored. These consisted of 23 mineral substances (trace and major elements) and 82 organic pollutants. This category comprised 15 PAHs, 19 PCBs, 8 PBDEs, 7 PAEs, 7 nonylphenol and octylphenol polyethoxylates (NPnEOs and OPnEOs,), 22 PFASs as well as 4 individual compounds: bisphenol A (BPA), tetrabromobisphenol A (TBBPA), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB). The usual abbreviation of each compound is also provided in Table 1.

For each group of compounds, some indicators were selected such as nonylphenols (NP) for APs, diethylhexyl phthalate (DEHP) for PAEs, fluoranthene for PAHs and BDE 209 for PBDEs. For PAHs, results were also expressed as ∑15PAHs or ∑6PAHs (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(cd)pyrene,

benzo(ghi)perylene) according to French standard on air quality (NF X 43-025). For PCBs, ∑19PCBs or ∑7PCBs (PCB 28, 52, 101, 118, 138, 153 and 180) which are commonly observed in environment, are given. The ∑8PCBs « dioxin-like » PCB contents (PCB 28, 33, 70, 77, 105, 118, 105 and 170) are also provided. For APs, the sum of 7 congeners (∑7Aps, nonylphenols (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), nonylphenoxy acetic acid (NP1EC)) is given.

All pollutants were analyzed according to validated methods and analytical details for each group of compounds can be found in the mentioned reference. Most of the metals were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, (Le Pape et al. 2014)). Total mercury (Hg) in soils was analyzed using an automatic mercury analyzer (AMA 254 from Courtage Analyses, (Harris-Hellal et al. 2011)). PAHs and PAEs (Alliot et al. 2014) as well as PBDEs (Muresan et al. 2010) were analyzed by using gas chromatography coupled to mass spectrometry (GC-MS) and PCBs by GC coupled to tandem mass spectrometry (GC-MS/MS; (Goutte et al. 2013)). Bisphenol A and APs (Cladiere et al. 2013) and PFASs (Munoz et al. 2015a) were analyzed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). The limits of quantification (LOQ) for each individual substance are provided in supplementary material – Table S2.

3. Results and discussion

3.1 Contamination of soils

Total organic carbon and black carbon

The TOC contents in the tested Parisian soils varied between 0.54 and 9.14%, with a mean value of 3.08 ± 2.15% (mean ± standard deviation (SD)). These values were lying typically in the middle or the upper range of commonly reported values worldwide for urban and rural soils. Besides, for British and Norwegian soils, Nam *et al*. (2008) found TOC

contents in 5.4-46% ranges. A mean TOC content of 1.34 ± 0.54% was shown by Wang et al. (2014b) for urban and sub-urban soils close to Shanghai (China). In the present study, the BC contents in soil samples varied between 0.05 and 3.07% (mean value of 0.70 ± 0.93%). These values were in the same order of magnitude than values reported for soils in the UK and in Norway, i.e., from 0.24 to 1.80% with a mean value at 0.88% (Nam et al. 2008). Similarly, in the US, BC contents around 0.25% for urban soils and around 0.14% for agricultural soils (Hamilton & Hartnett 2013) were reported. However, our results were higher than those reported by Wang *et al*. (2014) for soils, independently to the method used (0.19 ± 0.08% using CTO-375 method and 0.47 ± 0.25% using Cr_2O_7 oxidation).

As previously demonstrated in literature, the BC/TOC ratio can be used to get insight into the carbon origin, i.e. distinguishing between the burning of biomass and that of fossil fuels. BC/TOC ratio method was based specific BC/TOC ratio measured in aerosol during combustion of fuel or biomass (Gatari & Boman 2003). In soil samples considered here, the BC/TOC ratio ranged from 0.005 to 0.98 with a mean value at 0.23 ± 0.24. This was close to the one reported by Wang *et al.* (2014), i.e., 0.15 ± 0.05 according to the same BC analytical method. These authors highlighted that the BC/TOC ratios in Shanghai soils were very similar to those in the atmospheric fine particles and suggested that BC in those soils was closely related to deposited atmospheric particles. Considering that burning biomass and fossil fuel combustion are respectively featured by BC/TOC to 0.11 and 0.5, the BC origin seems to be a mixture of biomass and fossil fuel combustions.

Trace and major elements

The first and last percentiles (d10 and d90) as well as median values (d50) as mg/kg dry weight (mg/kg.dw) for metals and major elements are illustrated on Figure 2. The mean contents ± SD as mg/kg.dw for metals are compared to literature in Table 2. According to their contamination levels, three groups of metals were identified. The first group including 5

elements (Ag, Cd, Sb, Tl and Hg), was featured by low contents in the soil typically varying between 0.1 and 1 mg/kg.dw. The second group (V, Cr, Mn, Ba, Co, Ni, Zn, Pb, Cu, As and Sr) exhibited contents ranging from 1 to 200 mg/kg.dw. The last group (Fe, Na, Mg, Al, K, Ca and Ti) presented the highest contents (1,000-100,000 mg/kg.dw). That metal pattern was consistent with the typical classes observed in terrestrial environments.

As demonstrated by the first and last percentile ratios (d90 / d10 ratios), the metal contamination slightly varies. For 19 out of 23 elements monitored, the d90 / d10 ratios were lower than 5. A higher variability was observed for Ca (d90 / d10=32), Hg (d90 / d10=10), Ag (d90 / d10=7) and Pb (d90 / d10=6). It is highly probable that due to the sedimentary nature of the Parisian soils, the variability of Ca levels could reflect the local changes in the geochemical background. Other elements like Pb and Ag, which also presented pronounced variabilities, might be due to changes in sulfide soil content. This would also be partly the case for Cd and Sb. Besides, the distribution of most Hg-contaminated soils closely followed that of built areas (Betard 2015).

Table 2 provides a short review of metal contamination around the world, differentiating urban, sub-urban and rural soils. For some elements, huge variations of metal contamination can be observed. Some metals considered as markers of anthropogenic activities such as Cu, Zn, Pb and Hg are well documented, in opposite to metals of emerging concern, such as Ag or Sb. On the whole, metal contents in Parisian soils were in the middle or in the upper part of ranges reported in the literature. As an example, the Pb content (21-118 mg/kg.dw, d10-d90) were in accordance with the moderate to high values reported by Marcheselli *et al*. (2010) or by Ajmone-Marsan and Biasioli (2010) in Italy for urban or sub-urban soils, but lower than those quoted by Vazquez de la Cueva *et al*. (2014), Bermudez *et al.* (2012) and Rasmussen *et al.* (2001). Compared to literature, the contents found for Cu (12.0-45.4 mg/kg.dw, d10-d90), Cd (0.2-0.6 mg/kg.dw), Mn (277.2-591.9 mg/kg.dw) and Ni

(11.3-28.0 mg/kg.dw) were in the average to highest ranges. This comparison overall reinforced the concern for metals such as Zn, Pb and Cu. Worldwide and in the Seine River basin (Le Pape et al. 2012, Priadi et al. 2011), these elements have already been identified as long-term markers of anthropogenic emissions and, ultimately, of urbanization. Interestingly, Cd that appeared here as an anthropogenic marker in the soils, is until now not recognized as anthropogenic marker for the Seine River sediments. Hg instead, was characterized by relatively lower levels in the Parisian soils (0.05-0.51 mg/kg.dw, d10-d90) than in other European conurbations (0.015-6.3 mg/kg.dw, min-max (Rodrigues et al. 2006)). These low levels of Hg in soils could be explained by different reasons, i.e., its potential leaching during rainfall events (Barringer et al. 2010), continuous volatilization from surface soil (Gabriel et al. 2005) and low gas-phase uptake (Rutter et al. 2011). Actually, Hg would primarily either account for most recent acute pollutions (e.g., industrial releases or pesticide applications) or lower, yet chronic, contamination (i.e., transport induced emissions).

In addition to these metals, Sb is considered as a global emerging metal (Grahn et al. 2006; Krachler et al. 2005) and identified as an urbanization marker in the Seine River sediments (Ayrault *et al.*, 2013; Le Pape *et al.* 2012). As a matter of fact, no ample comparison to the existing literature could be established due to the extremely scarce amount of data. The measured Sb contents in the urban soils (mean: 2.38, 0.53-4.56 mg/kg.dw, d10-d90) were notably higher than values reported for urban soils (0.22 mg/kg.dw by Rasmussen *et al.* 2001 or 0.88 mg/kg.dw by Atapour 2015). This could reinforce the status of contaminant of emerging concern given to Sb by the US-EPA. The measured Ag contents (mean: 0.28, 0.09-0.58 mg/kg.dw, d10-d90) were similar to the contents measured in the soils of Jakobstad, a small town in Finland (mean: 0.25, 0.07-1.13 mg/kg.dw, (Phuong et al. 2016)) or in the soils of Kerman city, SE Iran (mean: 0.10, max: 0.17 mg/kg.dw, (Sussarellu et al. 2016)) and significantly lower than the content measured in the soils of Pforzheim, SW

Germany (mean: 2.1, <0.5-11.3 mg/kg.dw, (Mazurais et al. 2015)). Overall, the Parisian soil Ag content is significantly higher than the global geochemical background (0.05 mg/kg, (Ayrault et al. 2013)). Sb and Ag were recognized as anthropogenic markers in the Seine River basin, showing a 10-fold increase from upstream to downstream concentrations (Ayrault et al., 2013). Sb was identified as the most enriched element in the present day atmospheric particulate matter of the area (Ayrault et al. 2010). At present, no atmospheric particulate matter enrichment is observed for Ag; and the major source of Ag at the scale of a basin catchment appears to be wastewater effluents (Ayrault et al., 2013). To corroborate this observation, in the Berlin city (Germany), an urban context, compost was identified as a significant source of Ag to urban soils (Birke and Rauch, 2000).). To conclude, the soil inventory highlighted the anthropogenic sources for Ag, Cd, Cu, Pb, Sb and Zn to the Parisian soils (Supplementary - Figure S1), adding Ag and Cd to the list of persistent toxic elements established through river sediment study. Indeed, the concentrations of these 6 elements in the river sediment have decreased since the pollution peak in the 1960's (Le Cloarec et al. 2011; Sussarellu et al. 2016). In spite of physical and chemical processes such as physical erosion and weathering in soils leading to pollutant attenuation, the present soil data evidenced the persistence of these elements (Ag, Cd, Cu, Pb, Sb and Zn) in the soils of the Seine River basin. In particular, these findings emphasized the long-term persistence of Ag and Cd in soil under long-term urban pressure.

Organic pollutants

1. Organic contamination overview

Organic pollutant levels in soils (d10, d50 and d90, as µg/kg.dw) are illustrated on Figure 3. On 82 organic micropollutants investigated, 14 substances including 9 PFASs and 5 PCBs exhibited an occurrence below 25%, reflecting their low levels in soils. On the contrary, some substances such as NP, PAHs (acenaphthylene, phenanthrene, anthracene, fluoranthene,

pyrene, benzo(a)anthracene, chrysene, benzo(b+k)fluoranthenes and benzo(a)pyrene), BDE 47 and BDE 209 were systematically detected in soils. On the whole, the organic micropollutant pattern was featured by the predominance of PAHs (∑15PAHs, 150-55,000 µg/kg.dw, min-max), followed by phthalates (∑7PAEs, 10-1,700 µg/kg.dw) and alkylphenols (∑7APs, 30-330 µg/kg.dw). Levels for PCBs (∑19PCBs, 1-71 µg/kg.dw) and PBDE (∑8PBDEs, 0.3-13 µg/kg.dw) and to a greater extent PFAS (∑22PFASs, 0.2-3.2 µg/kg.dw) were far lower. Organic contamination levels slightly varied for alkylphenols, phthalates and PFAS (d90 / d10 ratio < 10), but the variability was higher for PCBs and PBDEs (d90 / d10 >15). The highest variability of contents was observed for PAHs (d90 / 10 = 90). PAHs are well-known combustion products and at the scale of the Parisian conurbation, PAHs are mainly emitted by road traffic. The sampling distance to the nearest trafficked road could explain the high variability observed (Clement et al. 2015, Gateuille et al. 2014b). These authors indeed observed a good relationship between normalized contents of PAHs in soils and the distance to the road edge. These authors further demonstrated that a fraction of the newly-deposited vehicular PAH was retained in the first few meters from the road whereas another part was transferred on longer ranges.

As for metals, a short review of soil contamination by organic pollutants is provided Table 3. Though the orders of magnitude reported in literature highly varied from one study to another, due to the nature of the soils studied and the year and the country considered, our levels were globally close to those previously reported. For PAHs and PCBs, results were in good agreement with local studies for urban and sub-urban soils (Meijer et al. 2003b, Motelay-Massei et al. 2004, Villanneau et al. 2011).

For PBDEs, levels observed around Paris area were also comparable to those reported in the literature (Harrad & Hunter 2006, Hassanin et al. 2004, Zou et al. 2007, Thorenz et al., 2010). For PAEs, levels in Parisian soils are mostly in the lower range of values reported

worldwide (Bergé et al. 2013). For APs, contents were far lower than those reported in the literature for urban land (50-9,000 µg/kg.dw, (Sternbeck et al. 2003)) or agricultural soils for which contents varied from several hundred to several thousand µg/kg.dw (Bergé et al. 2012). Even if APs were studied in the past, no recent values are available for soils. The occurrence of PFASs in soils is poorly documented and, to date, mainly PFOA and PFOS have been targeted although very few data are also available for a limited set of fluoroalkyl carboxylates (Strynar et al. 2012, Washington et al. 2008). Strynar *et al.* (2012) estimated global median concentrations of 0.12 and 0.47 µg/kg.dw for PFOA and PFOS, respectively, which is in excellent agreement with those determined in the present study: 0.15 µg/kg.dw for PFOA and 0.65 µg/kg.dw for PFOS.

2. Pollutant patterns

The distribution of compounds for each group is illustrated on Figure 4. For APs, NP, nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) were predominant (occurrence varied between 80 and 100%) while octylphenol (OP), octylphenol monoethoxylate (OP1EO) and octylphenol diethoxylates (OP2EO) as well as nonylphenoxy acetic acid (NP1EC) exhibited low occurrence (< LOQ-30%). The patterns were featured by NP predominance (23-123 µg/kg.dw, d10-d90) accounting for 50% of APs. These patterns were clearly different from those observed in surface water or in total atmospheric fallout (Cladière et al. 2013), likely as a result of AP degradation in soil. Actually, NP is the biodegradation end product of NPnEOs. About 80% of NP can be degraded in soils, the remaining part being refractory (Marcomini et al. 1989).

For PAEs, the following sequence was observed: DEHP (35-411 µg/kg.dw) > DiBP (19-329 µg/kg.dw, d10-d90) > DnBP (5-142 µg/kg.dw) ≅ DEP (6-112 µg/kg.dw) > BBP (2-20 µg/kg.dw) ≅ DMP (1-15 µg/kg.dw) and DnOP (2-8 µg/kg.dw). DiBP and DEHP account for 29 and 20%, respectively. The predominance of DEHP and DiBP in soils was already

observed in some studies (Bergé et al. 2013, Zeng et al. 2009). This is consistent with the application of similar commercial PAEs around the world. The PAE patterns were also in good agreement with those reported for total atmospheric fallout and surface water (Tran et al. 2015).

The PAH patterns were fairly similar among sites, featured by the predominance of high molecular weight PAHs (HMW PAHS, i.e., 4-6 benzenic rings) comparatively to the low molecular weight PAHs (LMW PAHs, i.e., 2-3 benzenic rings). According to the literature, samples contaminated by petrogenic sources are characterized by a higher proportion of LMW PAHs, while a pyrolytic contamination exhibits higher contribution of HMW PAHs (Soclo et al. 2000). In soils, the LMW/HMW PAH ratio was equal to 0.11, suggesting a pyrolytic origin of PAHs. The presence of Fluo and Pyr supported this hypothesis since both compounds are considered as pyrolytic markers. In spite of several limitations (Clement et al. 2015, Yunker et al. 2002b), different PAH ratios, such P/(P+A) or Fluo/(Fluo+Pyr), can be also used to probe PAH origins (Yunker et al. 2002a). The latter suggested a mixture of pyrolytic and petrogenic contamination but are close to the pattern observed for ambient air (Supplementary - Figure S1).

PCB patterns in soils were featured by the predominance of 7 PCBs listed as indicators in environmental contamination studies.. ∑7PCBs accounted for 70 to 100% of total PCBs. ∑8 dioxin like PCBs contributed to less than 15% of total PCBs, while PCB 153 (0.37-6.40 µg/kg.dw) and PCB 138 (0.31-5.60 µg/kg.dw) were the dominant congeners, followed by PCB 118 (0.40-2.65 µg/kg.dw) and 180 (0.25-4.89 µg/kg.dw). Patterns in soils were also clearly different from those observed for ambient air dominating by most volatile compounds (PCB 52 > 101 > 28 > 153 > 138 > 118 > 180, (Teil et al. 2016)).

For PBDEs, BDE 209 was predominant, accounting for 70% of total PBDEs. BDE 28, 154 and 153 had an occurrence below 30%. The PBDE pattern in soils was similar to that

commonly found in environmental matrices and anthropogenic areas (Hassanin et al. 2004, Muresan et al. 2010, Zou et al. 2007). It is worth noting a spatial correlation between several normalized PBDE contents, i.e., including all the congeners from BDE 28 to BDE 183 ($p < 0.1$). The identified correlations were especially significant for PBDEs ranging from BDE 47 to BDE 153 ($p < 0.05$), which pointed out the existence of a common source. Their relative contributions to the sum of all the tested congeners linearly increases with the decrease in BDE 209 contribution thereby indicating the degradation of newly-deposited BDE 209 into lower molecular weight PBDEs. This relationship was less meaningful between BDE 209 and BDE 28, 183 or 205 contributions ($p > 0.1$).

Out of the 22 PFAS monitored, 6 compounds (PFPeA, PFHxA, PFHpA, PFTrDA, PFTeDA, EtFOSA) were never detected and 2 (6:2 FTS and MeFOSAA) occasionally detected. The occurrence of remaining compounds ranged from 25% to 50% for PFHpS, EtFOSAA, PFDoA while PFOA, PFHxS, PFNA, PFDA, PFUnA and PFOS were almost always quantified. PFOS (0.28-2.05 µg/kg.dw, d10-d90) followed by PFOA (0.07-0.46 µg/kg.dw) were predominant while other compounds lied in lower ranges. These patterns were in good agreement with those reported in soils by Strynar *et al*. (2012), i.e. PFOS > PFOA > PFDoA > PFHpA > PFHxA but were quite different from those observed in surface water with predominance of PFOS and PFHxS (Loos et al. 2013, Munoz et al. 2015b) or in total atmospheric fallout with the predominance of PFOA and PFNA (Kwok et al. 2010). The differences of PFAS patterns might be linked to i) the degradation of PFOS precursors and ii) the higher lixiviation of shorter-chain carboxylic acids such as PFOA comparatively to PFOS, due to their lower solid-liquid partitioning coefficients (Munoz et al. 2015b).

3.2 Correlation between soil TOC, BC and pollutants

Considering the 32 soil samples (urban and rural soils), no significant correlation was found neither between TOC and BC nor between TOC, BC, metals and organic pollutants

(Pearson test, α=0.05). To date, no other study reported significant correlation between TOC, BC and metals. For organic pollutants, several studies examined such correlation but not for all groups of pollutants monitored in the present study. A correlation between TOC and BC in soil samples from background locations in the UK and Norway was reported (Nam et al. (2008). These authors also observed a correlation between TOC and PBDEs and to a lesser extent between TOC, PAHs and PCBs. The difference of TOC levels between Parisian soils (0.54-9.14 %) and those studied in the UK and Norway (5.4-46%), could explain this different trend. In China, Wang et *al.* (2014) reported no correlation for urban soils between TOC, BC and PAHs, contrary to the sub-urban and industrial soils. For these sites, authors quoted that BC and LMW PAHs were strongly correlated, but so less for HMW PAHs. Similarly, Villanneau *et al*. (2011) highlighted for French soils a correlation between TOC and PCBs but none between TOC and PAHs. In China, a study reported that the concentrations of PAEs were poorly correlated with soil organic carbon content, suggesting mixing process between local and on-going sources (Zeng et al. 2009).

Although BC is generally considered as a "super sorbent" playing an important role in organic pollutant partitioning in soils, the lack of correlation between BC and pollutants investigated can be due to i) differences of pollutant and BC emissions and/or ii) differences of behavior during atmospheric transport and deposition and iii) differences of behavior and partitioning in soils. Actually, some pollutants may be accidently formed or released from various incomplete combustion processes and therefore a more or less proportion can be emitted in the form of BC-pollutant complexes. For some pollutants such as PCBs, PBDEs and PAEs, a hypothesis explaining the lack of straight correlations could be that these pollutants, which are preferentially emitted from volatilization processes, are either readily exported from contaminated surface soils or (bio)degraded soon after deposition. Finally, as suggested by Nan *et al*. (2008), the lack of associations between BC and organic pollutant

could simply reflect the strong signature of the historical BC, mainly from (cumulative) combustion inputs over many centuries.

3.3 Contamination and land use

For a number of metals and organic contaminants, no significant difference of contamination between urban (n=20) and rural (n=12) soils was observed (Man-Whitney test, α=0.05). However, significantly higher levels were observed in urban soils for BC (mean at 0.34% in urban soils *vs*. 0.14% in rural soils), Cu (25.5 *vs.* 15.3 mg/kg.dw), Zn (102 *vs*. 61 mg/kg.dw), Hg (0.15 *vs*. 0.07 mg/kg.dw) and PFOS (0.95 *vs*. 0.33 µg/kg.dw). Based on the 32 soil samples, trends also appeared for PBDEs (∑8PBDEs, 0.95 *vs.* 0.53 µg/kg.dw), PCBs (∑19PCBs, 10.29 *vs*. 4.65 µg/kg.dw), PFAS (∑22PFASs, 1.00 vs. 0.37 µg/kg.dw), Sr (120.8 *vs*.66.5 mg/kg.dw) and Sb (2.38 vs. 0.88 µg/kg.dw) but these differences are not statistically significant (Man-Whitney test, α=0.05). For ∑15PAHs, similar levels are found between rural and urban soils (1,833 *vs*. 1,010 µg/kg.dw), as well as for ∑7PAEs (395 *vs*. 371 µg/kg.dw). For PBDEs, Muresan *et al*. (2010) analyzed all soils from the Paris soil bank (n=120 including the 32 soils considered), they observed that PBDE levels increased in relation to urbanization. In the latter study, no significant difference in ∑8PBDEs concentrations was observed between forested and rural soils (0.59 and 0.66 µg/kg.dw). On the whole, these results highlight both the higher contamination of urban soils, probably due to their location close to the urban sources, and also the significant dissipation of several classes of POPs in the environment at a regional scale. As previously suggested, land use alone is often a rather unreliable indicator to discriminate soil pollution (Desaules et al. 2010).

Although the effect of land use could not be evidenced for all contaminants, some soil samples were clearly more contaminated than others, and reflected a multi-contamination. Principal component analysis (PCA) was performed on metal and organic pollutant dataset (Supplementary - Figure 2) and pointed out different soil samples (#109, #100 and #70) which

exhibited significantly higher levels of pollutants in comparison to other ones. The extremely high contamination of the #100 soil sample, corresponding to a heavily urbanized parcel surrounded by industrial and commercial areas, could be related to transport sector emissions. Indeed, the sampling site is closely related to: i) a highly-trafficked road (Motorway A86), a railway station providing access to the largest wholesale food market in the world (Rungis) and the 2nd largest airport in the Ile de France Region (Orly). The marked Sr levels (217.1 mg/kg.dw), also considered as traffic related metal, support this assumption (Thorpe and Harrison, 2008). This was further testified by the high PAH (∑15PAHs, 55,800 µg/kg.dw), PCB (∑19PCBs, 25.8 µg/kg.dw), Cu (27.4 mg/kg) and Zn (117 mg/kg.dw) levels that usually depict industrial soils as well as emissions from vehicular exhaust and/or the wear of moving parts. As for #109 soil sample, the increased PAH (∑15PAHs, 7,740 µg/kg.dw) contents presumably accounted from the proximity to the largest French river port (Gennevilliers) that concentrate commercial activities, fuel storage tanks and large goods vehicle / barge traffic. The relating site was also located in close proximity to the northern section of Motorway A86. The high contamination of the #70 soil sample, corresponding to an agricultural parcel remote from heavily densely area, could be related to sludge amendment. Indeed, significant amount of PAHs were reported for sludge with individual concentrations ranging from 11 to 990 µg/kg.dw (Mailler et al. 2014). However, the contamination of this soil by other pollutants brought by sewage sludge, such as PBDEs, PAEs, PFASs and metals was not observed, suggesting probable other contamination source.

3.4 Stocks in soils vs. atmospheric fluxes

Since many studies reported the importance of soils in the global cycle and budget of POPs (Meijer et al. 2003a; Rutter et al. 2011; Strynar et al. 2012), the aims of this last section was to assess the stock of pollutants in surface soils form Greater Paris area and to evaluate the relative importance of these stocks compared to estimated annual atmospheric fallout. The

pollutant stocks as mg or µg/m² was arbitrarily estimated for the 0-10cm upper layer of soils, considering the median values obtained on the 32 soils studied and a wet soil density of 2,000 kg/m^3 (Table 4). Each pollutant stock per surface unit (mg/m² or µg/m²) was calculated according to equation 1.

$$Stock_{Polluant\ i}(mg/m^2 or \mu g/m^2) = \delta \times S \times \rho_{Wet} \times [Pollutant i] \qquad \text{(Equation 1)}$$

With

δ: depth of soil considered (δ = 0.10 m)

S: surface of soil considered (S = 1 m²)

ρ_{Wet}: Wet soil density (ρ_{Wet} = 2,000 kg/m^3)

[Pollutant i]: median content of pollutant «i » in wet soil, in mg/kg or µg/kg

For each group of compounds, annual atmospheric fluxes as mg or µg/m²/year were also provided by previous works within the framework of the PIREN-Seine program (Moreau-Guigon et al. 2016). The ratios between the stocks and the minimal and maximal atmospheric fluxes were also estimated for some relevant metals (Pb, Hg, Zn, Cd and Sb) and for each family of organic pollutants.

For PAHs and Pb, a significant stock of pollutants was present in soils, far higher than annual atmospheric fluxes. Based on the highest values of atmospheric fluxes their stock / deposition flux ratios exceeded 1,000. This evidenced the importance of the soil reservoir compared to recent atmospheric inputs. For Zn, Cu, Cd, Hg, Sb, ∑7PAEs and ∑7APs, the annual atmospheric inputs contribute up to 1.5% of soil pollutant stocks. It is highly probable that these stocks resulted from i) the persistence of a fraction of pollutants in surface soils and/or ii) the cumulative atmospheric inputs over several decades. For instance, different studies demonstrated that the emission of PAHs and Pb in the past were more important, due to the biomass, coal and lead derived fossil fuel combustion (Azimi et al. 2005, Han et al.

2015). A similar decline of PCB contamination was observed in flood plain in the Seine River (Lorgeoux et al. 2016). Similarly, the metal contamination of the Seine River suspended sediment archives decreased significantly from 1960 to day, including for Zn, Cu, Cd, Sb (Le Cloarec et al. 2011).

Furthermore, some pollutants such as Hg, PAEs and APs were industrially used since 1940's and 1960's in large range of domestic and industrial applications, leading to a wild dissemination of these xenobiotics. With regard to PBDEs and PFASs, a higher contribution of atmospheric inputs to the pollutant stocks is observed, i.e. from 3.9 to 7.8% for PFASs and from 2.8 to 3.5% for PBDEs depending on the hypothesis. The relatively large contributions of PBDE deposition fluxes likely resulted in the observed variations between data by Muresan *et al*. (2010) and Tlili *et al*. (2012) at the Parisian area scale. The first use and mass production of PBDEs started in 1980's (Hites 2004). Due to the different legislation restrictions (Water Framework Directive, Stockholm convention, etc.), however, their use would significantly decrease in the future. As concerns PFASs, their intensive implementation started earlier in 1950's (Armitage et al. 2009, Buck et al. 2011). Furthermore, short-chained PFASs might be very persistent and much more mobile than the long-chained ones or other hydrophobic contaminants (Ahrens 2011), which could lead to the underestimation of the actual contribution of atmospheric fallout to the PFAS stock in the top surface layer of soils.

4. Conclusions

This study delivered the following findings:

i) By examining the soil contamination, results reinforced the concern of metals such as Zn, Pb and Cu, identified as long-term metallic markers of (not mining, not smelting) anthropogenic activity. These additionally pointed the ubiquitous contamination of soils by several organic micropollutants: from 0.2 to 55,000 µg/kg.dw. The following pattern was

highlighted: PAHs (∑15PAHs, 150-55,000 µg/kg.dw) > PAEs (∑7PAEs, 10-1,700 µg/kg.dw) > APs (∑7APs, 30-330 µg/kg.dw) >> PCBs (∑19PCBs, 1-71 µg/kg.dw) > PBDEs (∑8PBDEs, 0.3-13 µg/kg.dw) > PFASs (∑22PFASs, 0.2-3.2 µg/kg.dw).

ii) No specific correlation was observed between organic matter parameters (TOC and BC) neither between organic matter and pollutants. This lack of correlation could be due to i) different pollutant and BC emission histories and/or ii) different behaviors during atmospheric transport and deposition and iii) different behaviors and partitioning in soils. This could also reflect the strong signature of the historical BC, mainly from (cumulative) combustion inputs over many centuries. For most of pollutants, no significant differences were observed between urban (n=20) and rural (n=12) top 10 cm soils except, however, for BC, Cu, Zn and PFOA. Slight differences, yet not significant at α=0.05 level of confidence, were also reported for ∑15PAHs, ∑8PBDEs, ∑19PCBs, ∑22PFASs and Sr. Such results highlight the higher contamination of urban soils for these pollutants, probably due to their location close to the urban sources, but they also provide further evidence for the widespread dissemination of many contaminants in the environment.

iii) The present results clearly identified the contaminants, both organic and inorganic, that could be qualified of "urban contaminants". Nevertheless, it is still not possible to define concentration threshold determining the contamination of an urban soil. Indeed, the contaminant concentration in a soil under urban influence depends on a complex mixture of factors including the emerging *vs.* legacy status of the contaminant, its source type(s), its chemical properties, the "history" of the soil sample, etc. These numerous factors are somewhat poorly understood for the whole large list of "urban" contaminants.

iv) By comparing the pollutant stocks in the first 10-cm layer of soils to the atmospheric inputs, this study highlighted that significant stocks of PAHs and Pb were present in soils

(ratio above 1,000). For Zn, Cu, Cd, Hg, Sb, ∑7PAEs and ∑7APs, annual atmospheric inputs contribute to up 1.5% of soil pollutant stocks. Higher contributions (up to 7.8%) are observed for ∑8PBDEs and ∑22PFASs. Actually, the stocks of these pollutants result from i) their persistence in soils and ii) the cumulative atmospheric inputs over several decades. The link between this pollutant reservoir and the export pollutant rate from soil to river through erosive processes needs to be better assessed, so as to better estimate the depuration times and the time needed to reach "the good chemical status" of surface water within the European Union Water Framework Directive.

One perspective of this work would be a study devoted to the processes leading to the attenuation or to the persistence of the contaminants in soils. Such an inter-disciplinary study would integrate the pedological and structural characteristics of the soil as drivers of these processes.

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Figure caption

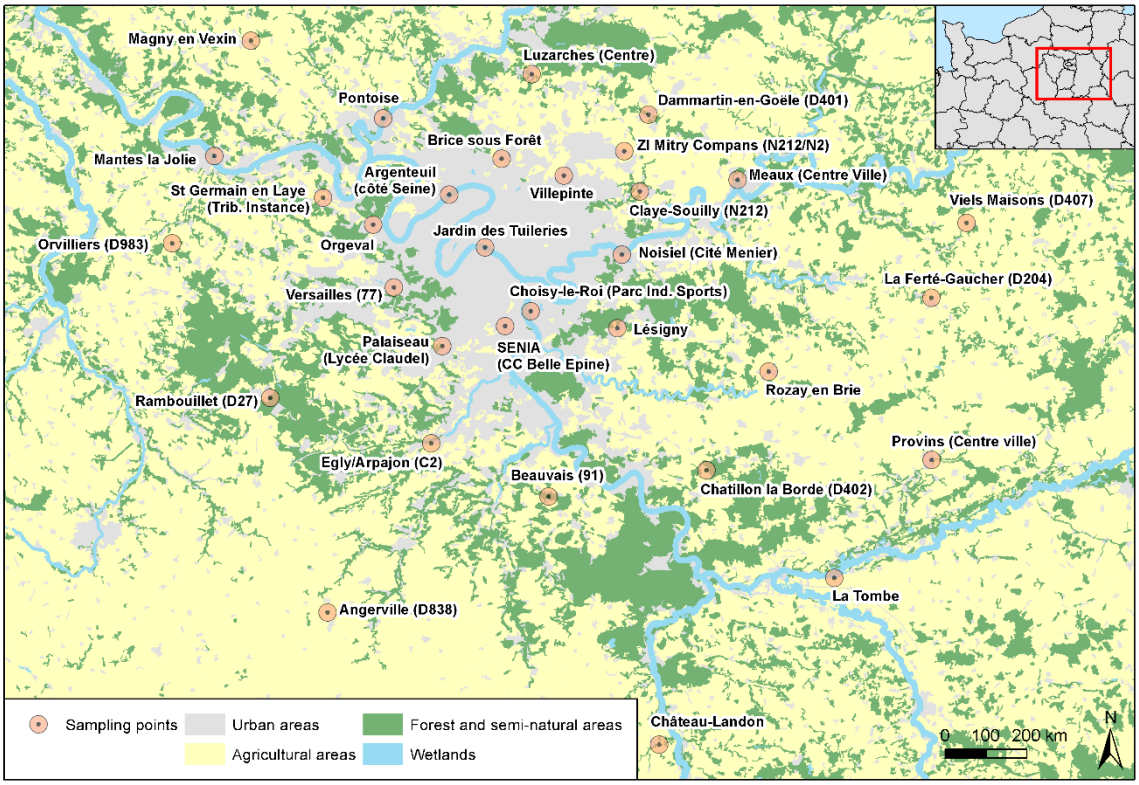


Figure 1: Location of the soils studied

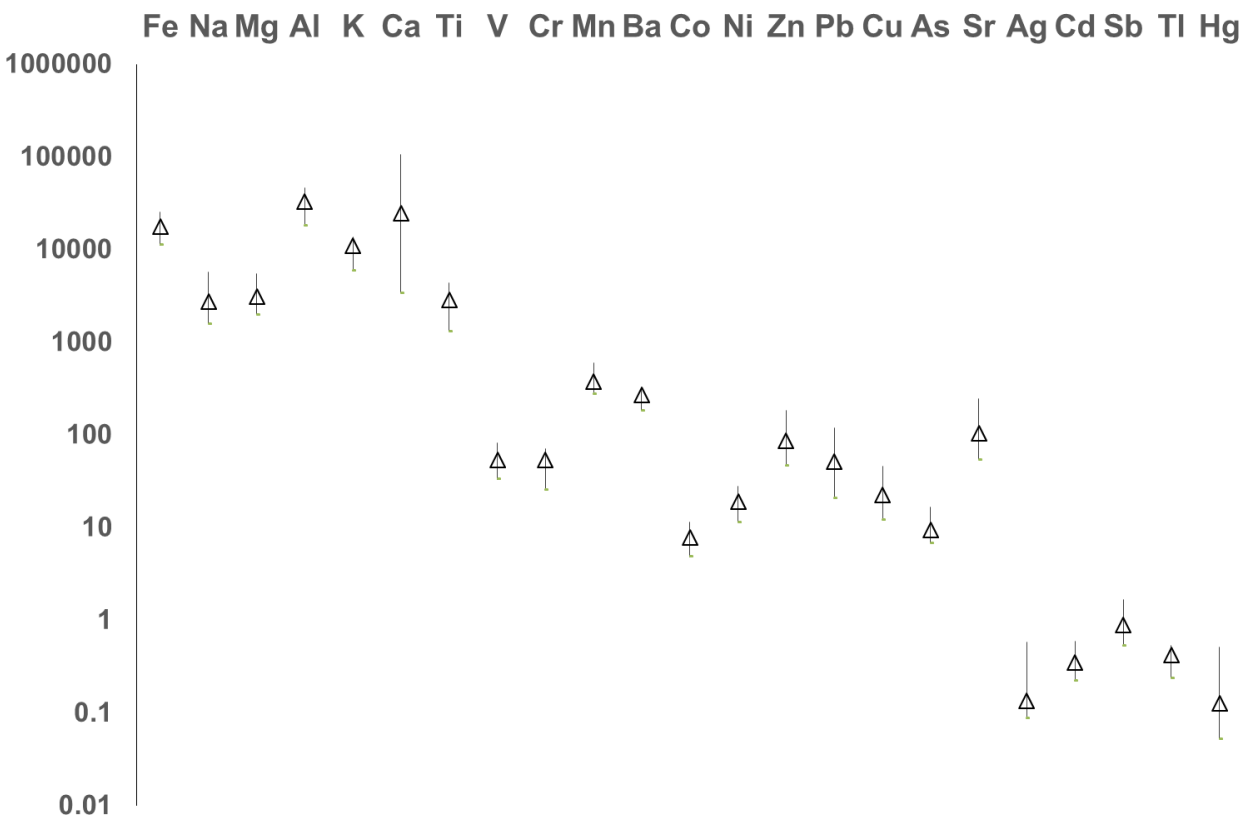


Figure 2: Metal contents in soils (d10, d50 and d90, as mg/kg.dw, n=32)

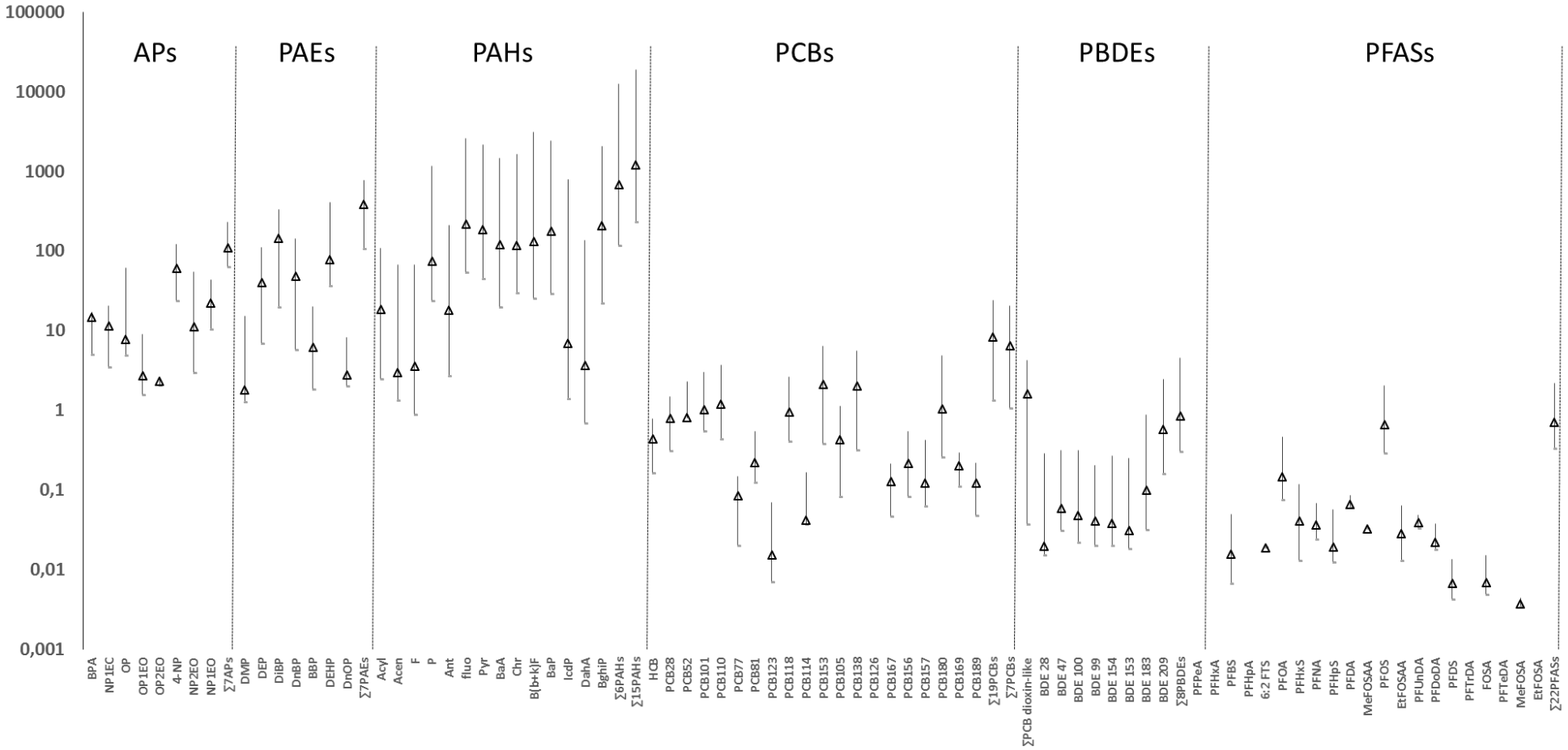


Figure 3: Organic micropollutant contents in soils (d10, d50 and d90, as µg/kg.dw, n=31-32)

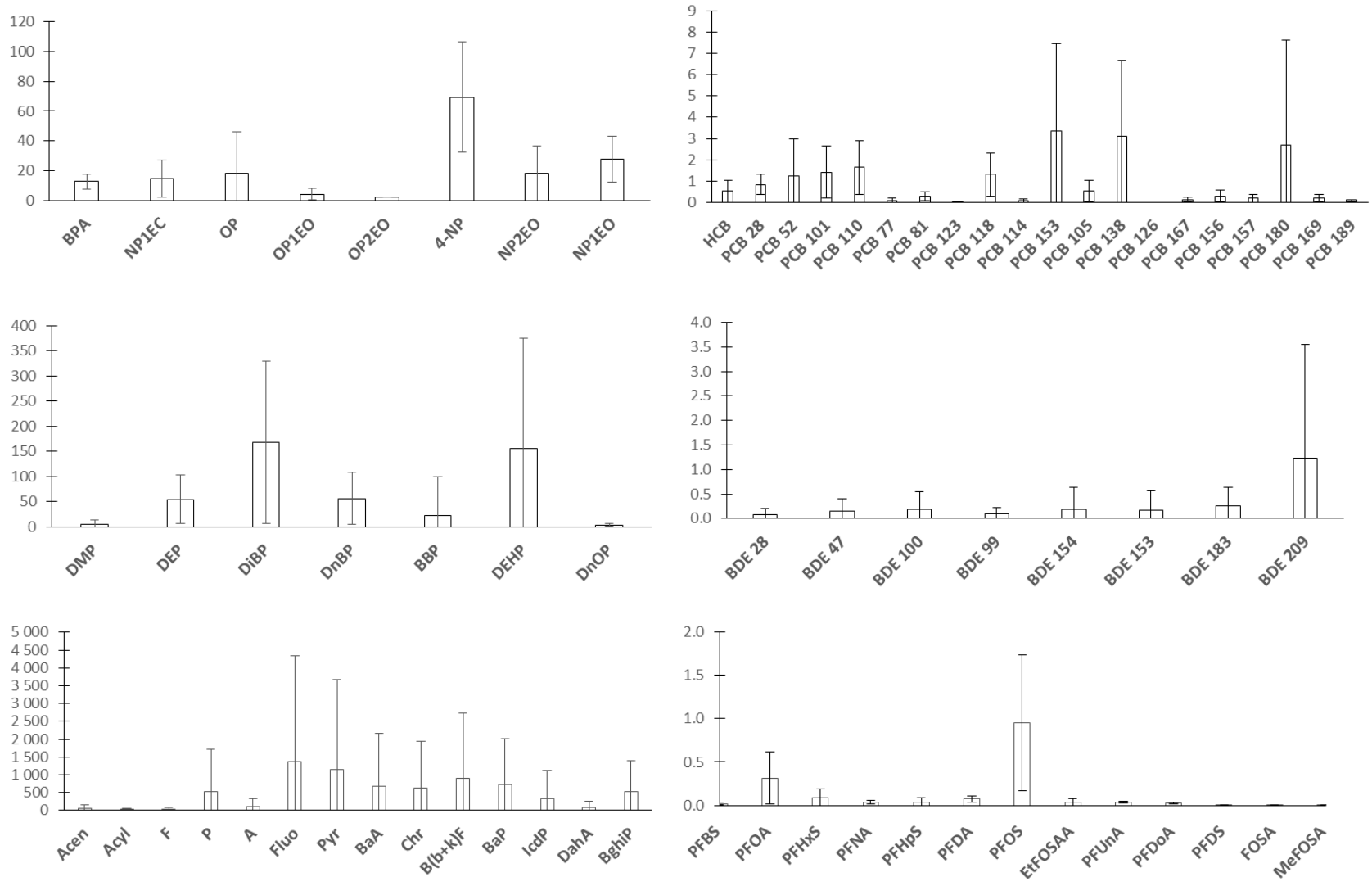


Figure 4: Organic micropollutant patterns in soils (mean ± SD, as µg/kg.dw, n=31-32)

Table caption

Table 1: Pollutants analyzed in soils

Groups	Individual compounds and abbreviation
Metals and major elements 23 compounds	sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), titan (Ti), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), zinc (Zn), copper (Cu), arsenic (As), strontium (Sr), silver (Ag), cadmium (Cd), antimony (Sb), barium (Ba), thallium (Tl), lead (Pb), mercury (Hg)
PAHs 15 compounds	acenaphthylene (Acy), acenaphthene (Acen), Fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(cd)pyrene (IcdP), dibenzo(ah)anthracene (DahA), benzo(ghi)perylene (BghiP)
PCBs 19 congeners	PCB 28, PCB 52, PCB 77, PCB 81, PCB 101, PCB 110, PCB 105, PCB 118, PCB 153, PCB 114, PCB 138, PCB 123, PCB 126, PCB 180, PCB 156, PCB 157, PCB 167, PCB 169, PCB 189
PAEs 7 compounds	di-methyl phthalate (DMP), di-ethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), di-n-butyl phthalate (DnBP), butyl-benzyl phthalate (BBP), di-ethyl-hexyl phthalate (DEHP), di-n-octyl phthalate (DnOP)
PBDEs 8 compounds	BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209
APs 7 compounds	nonylphenols (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), nonylphenoxy acetic acid (NP1EC)
PFASs 22 compounds	perfluorobutanoïc acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane sulfonic acid (PFB)S, perfluoroheptanoic acid (PFHpA), perfluoroheptanoic acid, 6:2 fluorotelomere sulfonate (6:2 FTS), perfluorooctanoc acid (PFOA), perfluorohexane sulfonic acid (PFHxS), perfluoronoanoic acid (PFNA), perfluoroheptane sulfonic acid (PFHpS), perfluorodecanoique acid (PFDA), N-Methyl perfluorooctane sulfonamidoacetic acid (MeFOSAA), perfluorooctane sulfonic acid (PFOS), N-Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorodecane sulfonic acid (PFDS), perfluorotridecanoïc acid (PFTrDA), perfluorooctanesulfonamide (FOSA), perfluorotetradecanoic acid (PFTeDA), N-Methyl perfluorooctane sulfonamide (MeFOSA), N-Ethyl perfluorooctane sulfonamide (EtFOSA)
Others 4 compounds	bisphenol A (BPA) tetrabromobisphenol A (TBBPA), hexachlorobenzene (HCB), pentachlorobenzene (PeCB)

Table 2: Metal contents (mean ± SD) in soil in this study and in literature (contents as mg/kg.dw)

	This study	(Marcheselli et al. 2010)	(Marcheselli et al. 2010)	(Ajmone-Marsan & Biasioli 2010)	(Vazquez de la Cueva et al. 2014)	(Bermudez et al. 2012)	(Rasmussen et al. 2001)	(Hernandez-Quiroz et al. 2012)	(Imperato et al. 2003)	(Rodrigues et al. 2006)
Year	*2010*	2010	2010	2006	2014	2012	2001	2012	1999	2006
Type	*Mixed*	Urban	Suburban	Urban	Suburban	Mixed	Urban	Urban	Urban	Urban
As	10.8 ± 6.6						2.8			
Cd	0.4 ± 0.2	0.43 ± 0.02	0.45 ± 0.10		0.11 ± 0.08		0.27			
Co	9.6 ± 11.3						8.05			
Cr	50.9 ± 20.5	19.5 ± 1.8	12.2 ± 1.4	157 ± 132			43.4	48.23 ± 11.44	11 ± 9	
Cu	28.0 ± 22.6	23.8 ± 1.3	22.3 ± 1.8	76 ± 48	9.50 ± 21.33	6.93 ± 0.53	12.1	30.31 ± 17.64	74 ± 56	
Fe	19,927 ± 12,149						20,750			
Mn	473.5 ± 445.2	442 ± 20	519 ± 22			365 ± 15	531.6			
Ni	19.2 ± 7.6	9.77 ± 0.67	7.88 ± 0.63	175 ± 118		7.09 ± 0.32	15.8	31.92 ± 18.15		
Pb	210.4 ± 799.3	61.7 ± 3.6	62.1 ± 3.5	117 ± 121	17.00 ± 98.73	9.40 ± 0.35	33.78	29.81 ± 11.08	262 ± 337	
Sb	1.8 ± 3.5						0.22			
V	54.3 ± 21.2						45.7	161.65 ± 126.81		
Zn	102.8 ± 60.0	205 ± 14	207 ± 15	149 ± 97	40.00 ± 22.04		100.2	125.31 ± 59.97	251 ± 253	
Hg	0.40 ± 0.67									0.015-6.3

Table 3: Organic micropollutant contents in soil in this study and in literature (contents as µg/kg.dw)

Family	Type of soils	Levels	References
BPA	*Mixed (France)*	*BPA (4.8-17.2)*	*This study*[1]
	Agricultural soils	BPA (90–110)	(Sanchez-Brunete et al. 2009)
APs	*Soils (France)*	*NP (23–123)*	*This study*
	Urban soils (Sweden)	NP (50– 9,000)	(Sternbeck et al. 2003)
	Agricultural soils (Spain)	NP (140–500)	(Andreu et al. 2007)
	Mixed	NP (10-1,620)	(Bergé et al. 2012)
PAEs	*Mixed (France)*	*DEHP (35-411)*	*This study*
	Amended soils (Denmark)	DEHP (30-40)	(Vikelsoe et al. 2002)
	Mixed	DEHP (20–264,000)	(Berge et al. 2013)
	Urban soils (China)	DEHP (1,410 –264,000)	(Zeng et al. 2009)
	Sub-urban soils (China)	DEHP (1,400–97,200)	(Zeng et al. 2009)
	Park soils (China)	DEHP (890–1,540,000)	(Zeng et al. 2009)
	Urban soils (China)	DiBP (1,630)	(Zeng et al. 2009)
	Urban soils (China)	DnBP (1,800)	(Zeng et al. 2009)
PAHs	*Mixed (France)*	*Σ15 (228-18,940)*	*This study*
	Mixed (France)	*Fluo (52-2,561)*	*This study*
	Soils (France)	Σ16 (80–400)	(Villanneau et al. 2011)
	Soils (France)	Fluo (<10–5,300)	(Villanneau et al. 2011)
	Soils (France)	Σ14 (450–5,650)	(Motelay-Massei et al. 2004)
	Mixed (France)	Σ13 (60-5,305)	(Gateuille et al. 2014a)
	Soils (UK)	Σ14 (42–11,200)	(Nam et al. 2008)
	Soils (Norway)	Σ14 (9–1,100)	(Nam et al. 2008)
PCBs	*Mixed (France)*	*Σ19 (1.3–24.3)*	*This study*
	Soils (France)	Σ20 (0.5–17)	(Villanneau et al. 2011)
	Soils (France)	Σ19 (0.1–150)	(Motelay-Massei et al. 2004)
	Mixed	Σ29 (0.03–96)	(Meijer et al. 2003)
PBDEs	*Mixed (France)*	*BDE 209 (0.2-2.4)*	*This study*
	Mixed	BDE 209 (0.6-4)	(Hassanin et al. 2004)
	Mixed (China)	BDE 209 (9-102)	(Zou et al. 2007)
PFAS	*Mixed (France)*	*PFOA (0.07-0.46)*	*This study*
	Mixed (France)	*PFOS (0.28-2.05)*	*This study*
	Mixed (6 countries)	PFOA (0.12)	(Strynar et al. 2012)
	Mixed (6 countries)	PFOS (0.472)	(Strynar et al. 2012)
	Mixed (6 countries)	Individual PFASs (0.5–79)	(Strynar et al. 2012)
	Soils (US)	∑5carboxylates (0.5–1.5)	(Washington et al. 2008)
	Mixed	PFOA (0.3–47.5)	(Zareitalabad et al. 2013)
	Mixed	PFOS (0.5–483)	(Zareitalabad et al. 2013)
	Soils (China)	PFOA (3.28–47.5)	(Li et al. 2010)
	Soils (China)	PFOS (8.58–10.4)	(Li et al. 2010)

1. *d10-d90 levels are provided in this study.*

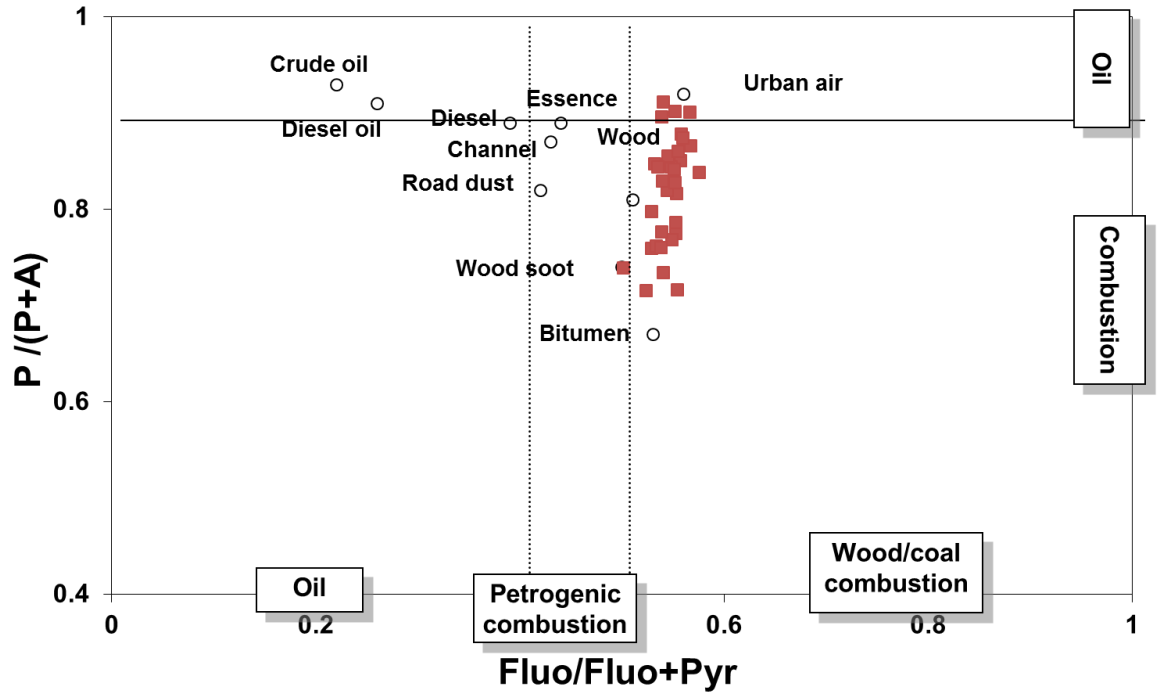
Table 4: Stocks in 10-cm soil layer *vs*. atmospheric fluxes

	Stocks* (µg/m² or mg/m²)	Atm fluxes** (µg/m² or mg/m²/year) Min	Atm fluxes ** (µg/m² or mg/m²/year) Max	References	Ratio Stocks/Flux Min	Ratio Stocks/Flux Max
BPA	2,950	11.00	56.00	(Cladière 2012)	268	53
∑7APs	22,077	50.00	117.00	(Cladière 2012)	442	189
DEHP	15,641	185.00	393.00	(Dargnat 2008)	85	40
∑7PAEs	76,781	326.00	691.00	(Dargnat 2008)	236	11
∑6PAHs	135,150	31.00	104.00	(Motelay-Massei et al. 2007)	4,359	1,299
∑15PAHs	239,500	66.00	227.00	(Motelay-Massei et al. 2007)	3,628	1,055
∑7PCBs	1,676	3.60	35.00	(Blanchard et al. 2006)	99	13
∑19PCBs	1,301	16.90	125.00	(Blanchard et al. 2006)	361	37
∑8PBDEs	170	2.50	43.00	(Tlili et al. 2012)	68	4
∑8PBDEs	337	18.00	47.45	Muresan et al., 2010)	19	7
∑22PFASs	141	4.00	5.00	(Labadie, personal communication)	35	28
∑22PFASs	282	11.00	22.00	(Kwok et al. 2010)	25	12
Zn	17,100	20.00	50.00	(Azimi et al. 2005)	854	341
Cu	4,480	8.00	15.00	(Azimi et al. 2005)	560	299
Cd	71	0.30	1.10	(Azimi et al. 2005)	235	64
Pb	10,350	5.00	10.00	(Azimi et al. 2005)	2,070	1,035
Hg	10	0.005	0.04	(Allan et al. 2013)	2,000	250
Sb	180	0.055	0.055	(Ayrault et al. 2013)	890	890

** Stocks in µg/m² for organic micropollutants and mg/m² for metals*

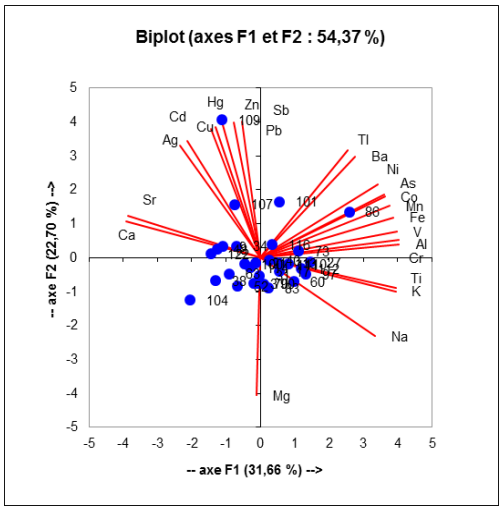
*** Atm Flux=atmospheric flux in µg/m²/year for organic micropollutants and mg/m²/year for metals*

Supplementary material caption

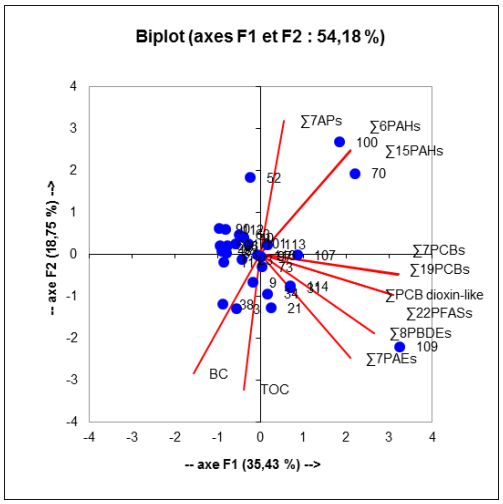


Supplementary - Figure S1: PAH ratios in soils – Red square refers to soil samples

Metals



Organic micropollutants



Supplementary - Figure S2: PCA on soil contamination for metals and organic micropollutants

1 **Supplementary - Table S1: Location of soils sampled**

Site	Description	Nr	Cat	Location	
Beauvais	Forest	91	F	48°30'9.19"N	2°28'9.27"E
Rambouillet	Forest	86	F	48°38'28.82"N	1°51'39.73"E
Rozay-en-Brie	Agricultural area	17	PA	48°41'4.60"N	2°56'53.20"E
Chatillon-la-Borde	Agricultural area	3	PA	48°32'30.54"N	2°48'44.83"E
Magny-en-Vexin	Agricultural area	31	PA	49° 9'25.33"N	1°48'25.14"E
Viels-Maisons	Agricultural area	70	PA	48°53'56.90"N	3°22'51.80"E
La Ferté-Gaucher	Agricultural area	73	PA	48°47'26.75"N	3°18'11.79"E
Egly/Arpajon	Agricultural area	83	PA	48°34'40.56"N	2°12'46.55"E
La Tombe	Agricultural area	48	PA	48°23'10.26"N	3° 5'25.77"E
Chateau-Landon	Agricultural area	52	PA	48° 8'40.46"N	2°42'42.85"E
Angerville	Agricultural area	60	PA	48°19'55.46"N	1°59'30.35"E
Orvilliers	Agricultural area	90	PA	48°51'44.07"N	1°38'29.85"E
Provins	Urban area	9	Urb	48°33'23.62"N	3°18'9.51"E
Lésigny	Urban area	21	Urb	48°44'47.69"N	2°37'3.23"E
Luzarches	Urban area	23	Urb	49° 6'47.47"N	2°25'34.42"E
Pontoise	Urban area	27	Urb	49° 2'49.87"N	2° 6'0.26"E
St Germain-en-Laye	Urban area	40	Urb	48°53'36.40"N	2° 4'52.11"E
Orgeval	Urban area	38	Urb	48°55'53.14"N	1°58'14.74"E
Dammartin-en-Goële	Urban area	63	Urb	49° 3'21.13"N	2°41'0.28"E
Mantes-la-Jolie	Urban area	34	Urb	48°59'21.80"N	1°43'50.41"E
Palaiseau	Urban area	97	Urb	48°43'8.24"N	2°14'5.88"E
SENIA	Urban area	100	Urb	48°44'22.51"N	2°22'06.72"E
Choisy-le-Roi	Urban area	101	Urb	48°46'13.85"N	2°25'40.03"E
Versailles	Urban area	107	Urb	48°48'10.56"N	2° 7'41.73"E
Argenteuil	Urban area	109	Urb	48°56'11.79"N	2°14'57.30"E
Villepinte	Urban area	111	Urb	48°57'59.78"N	2°29'54.59"E
Claye-Souilly	Urban area	113	Urb	48°56'40.50"N	2°39'54.71"E
Meaux	Urban area	114	Urb	48°57'42.41"N	2°52'45.32"E
Noisiel	Urban area	116	Urb	48°51'10.90"N	2°37'35.64"E
Jardin des Tuileries	Urban area	122	Urb	48°51'44.67"N	48°51'44.67"N
ZI Mitry-Compans	Industrial area	112	ZI	49° 0'10.20"N	2°37'49.29"E
ZI Brice-sous-Forêt	Industrial area	110	ZI	48°59'27.19"N	2°21'41.02"E

2

Supplementary - Table S2: Limits of quantification of pollutants monitored

		LOQ (µg/kg)			LOQ (µg/kg)
AP	BPA	13.5	PBDE	BDE 28	0.01
AP	NP1EC	2.0	PBDE	BDE 47	0.01
AP	OP	4.0	PBDE	BDE 100	0.01
AP	OP1EO	15.0	PBDE	BDE 99	0.01
AP	OP2EO	3.5	PBDE	BDE 154	0.01
AP	NP	7.5	PBDE	BDE 153	0.01
AP	NP2EO	7.0	PBDE	BDE 183	0.01
AP	NP1EO	5.0	PBDE	BDE 209	0.06
PAE	DMP	0.1	PFAS	PFPeA	0.01
PAE	DEP	0.3	PFAS	PFHxA	0.08
PAE	DiBP	0.07	PFAS	PFBS	0.01
PAE	DnBP	0.06	PFAS	PFHpA	0.02
PAE	BBP	0.1	PFAS	6:2 FTS	0.04
PAE	DEHP	0.6	PFAS	PFOA	0.02
PAE	DnOP	0.5	PFAS	PFHxS	0.03
PAH	acenaphthylene	0.31	PFAS	PFNA	0.05
PAH	acenaphthene	0.4	PFAS	PFHpS	0.03
PAH	fluorene	0.82	PFAS	PFDA	0.03
PAH	phenanthrene	2.49	PFAS	MeFOSAA	0.04
PAH	anthracene	1.7	PFAS	PFOS	0.02
PAH	fluoranthene	0.32	PFAS	EtFOSAA	0.03
PAH	pyrene	0.16	PFAS	PFUnDA	0.09
PAH	benzo(a)anthracene	0.17	PFAS	PFDoDA	0.04
PAH	chrysene	0.1	PFAS	PFDS	0.01
PAH	benzo(b+k)fluoranthenes	0.2	PFAS	PFTrDA	0.02
PAH	benzo(a)pyrene	0.63	PFAS	FOSA	0.00
PAH	indeno(1,2,3-cd)pyrene	0.5	PFAS	PFTeDA	0.04
PAH	dibenzo(ah)pyrene	0.5	PFAS	MeFOSA	0.01
PAH	benzo(ghi)perylene	1.81	PFAS	EtFOSA	0.01
PCB	HCB	0.08	PCB	PCB153	0.06
PCB	PCB28	0.17	PCB	PCB105	0.02
PCB	PCB52	0.3	PCB	PCB138	0.04
PCB	PCB101	0.07	PCB	PCB126	0.49
PCB	PCB110	0.05	PCB	PCB167	0.02
PCB	PCB77	0.16	PCB	PCB156	0.06
PCB	PCB81	0.08	PCB	PCB157	0.05
PCB	PCB123	0.14	PCB	PCB180	0.04
PCB	PCB118	0.10	PCB	PCB169	0.08
PCB	PCB114	0.02	PCB	PCB189	0.04