

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- $\mu\text{g}/\text{kg}$ 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

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Introduction

Soils play an important role in metal and persistent organic pollutant (POP) 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. 2003a, b). 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 (Nationale Bodenboebachtung (NABO)) investigated eight 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; Desaulles 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 95th percentile was smaller than the LOQ. In France, the French National Soil Monitoring Network (Réseau de Mesures de la Qualité des Soils (RMQS)) 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 and 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.

Materials and methods

Site description and sampling strategy

In this research, 32 soil samples were tested for their mineral and organic pollutant contents (Fig. 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 km²) (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, and waste incineration plants. At the scale of the Seine Basin, soil erosion was estimated to be between 5 and 10 t/km²/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 h 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 sample was 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.

Pollutant content and soil parameter 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).

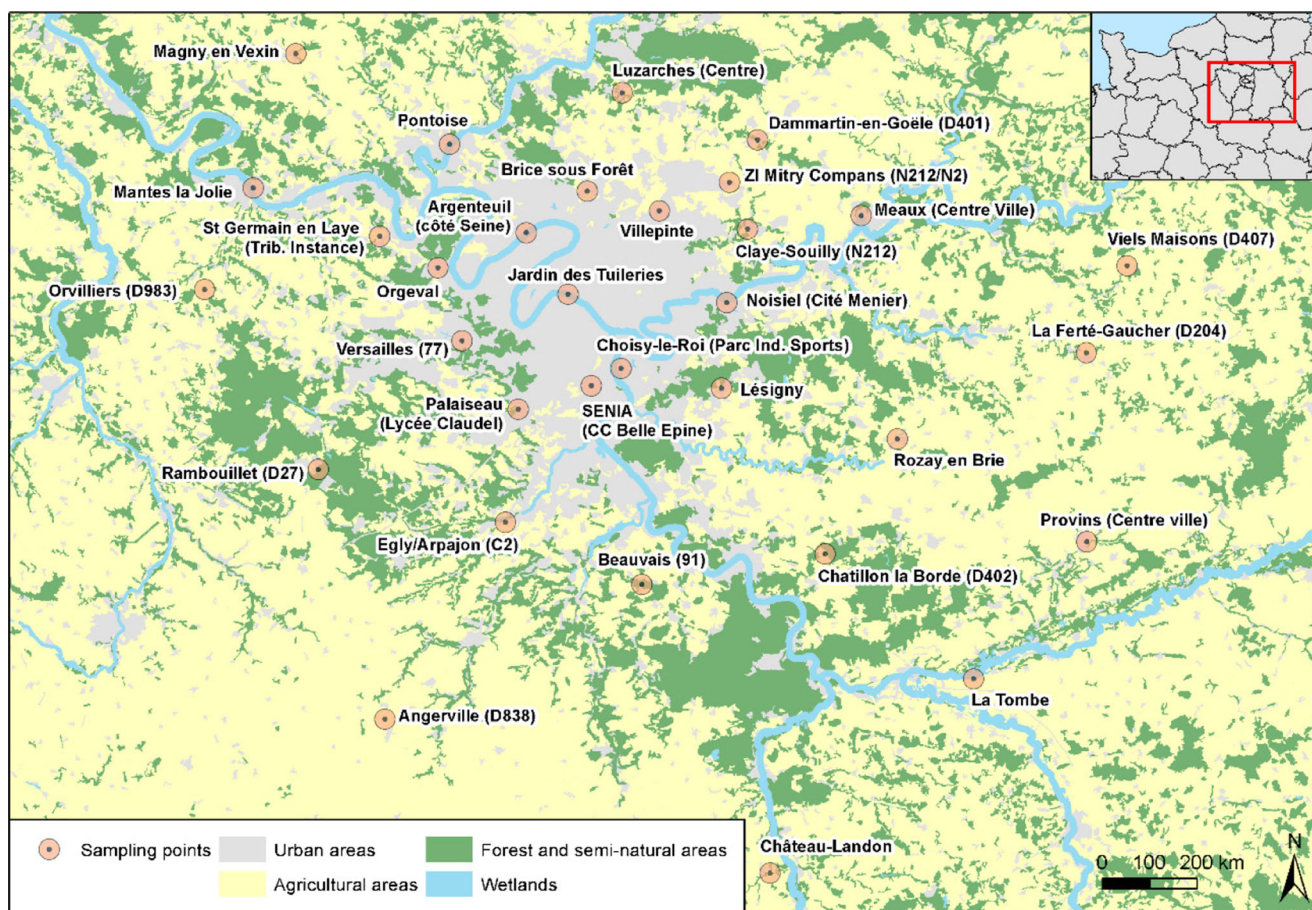


Fig. 1 Location of the soils studied

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; and the following 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 (NPs) for APs, diethylhexyl phthalate (DEHP) for PAEs, fluoranthene for PAHs, and BDE 209 for PBDEs. For PAHs, results were also expressed as $\sum 15$ PAHs or $\sum 6$ PAHs (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, $\sum 19$ PCBs, or $\sum 7$ PCBs (PCB 28, 52, 101, 118, 138, 153, and 180), which are commonly observed in environment, are given. The $\sum 8$ PCB “dioxin-like”

PCB contents (PCB 28, 33, 70, 77, 105, 118, 105, and 170) are also provided. For APs, the sum of seven congeners ($\sum 7$ APs, NPs, NP1EO, 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).

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(1,2,3-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 (NPs), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), nonylphenoxy acetic acid (NP1EC)
PFASs 22 compounds	Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane sulfonic acid (PFBS), perfluoroheptanoic acid (PFHpA), perfluoroheptanoic acid, 6:2 fluorotelomere sulfonate (6:2 FTS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFNA), perfluoroheptane sulfonic acid (PFHpS), perfluorodecanoic 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), perfluorotridecanoic 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)

Results and discussion

Contamination of soils

Total organic carbon and black carbon

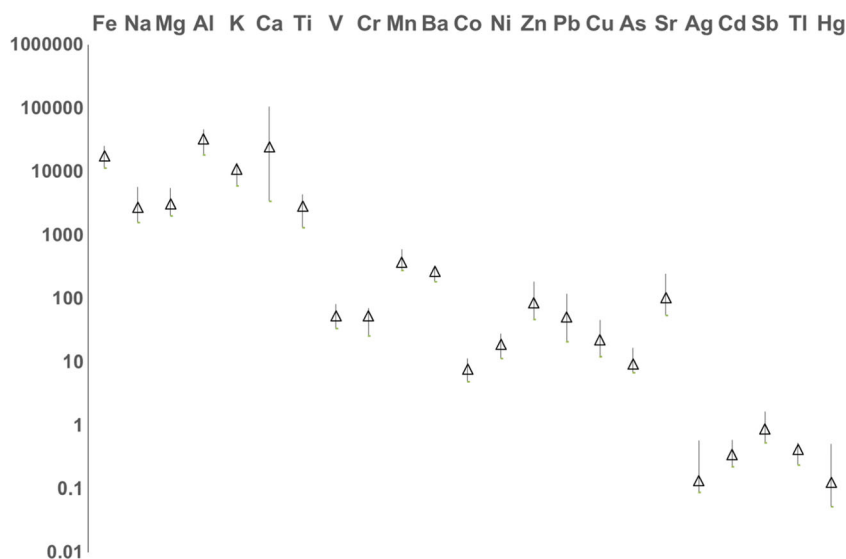
The TOC contents in the tested Parisian soils varied between 0.54 and 9.14%, with a mean value of $3.08 \pm 2.15\%$ (mean \pm standard deviation (SD)). These values were lying typically in the middle or the upper range of commonly reported values worldwide for urban and rural soils. Besides, for British and Norwegian soils, Nam et al. (2008) found TOC contents in 5.4–46% ranges. A mean TOC content of $1.34 \pm 0.54\%$ was shown by Wang et al. (2014) 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 $0.70 \pm 0.93\%$). 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 USA, BC contents around 0.25% for urban soils and around 0.14% for agricultural soils (Hamilton and Hartnett 2013) were reported. However, our results were higher than those reported by Wang et al. (2014) for soils, independently to the method used ($0.19 \pm 0.08\%$ using CTO-375 method and $0.47 \pm 0.25\%$ 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 on specific BC/TOC ratio measured in aerosol during combustion of fuel or biomass (Gatari and 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 in Fig. 2. The mean contents \pm 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

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



five 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 (1000–100,000 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 contents (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,

Table 2 Metal contents (mean \pm SD) in soil in this study and in literature (contents as mg/kg dw)

	<i>This study</i>	Marcheselli et al. (2010)	Marcheselli et al. (2010)	Ajmone-Marsan and 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 \pm 6.6						2.8			
Cd	0.4 \pm 0.2	0.43 \pm 0.02	0.45 \pm 0.10	9	0.11 \pm 0.08		0.27			
Co	9.6 \pm 11.3						8.05			
Cr	50.9 \pm 20.5	19.5 \pm 1.8	12.2 \pm 1.4	157 \pm 132			43.4	48.23 \pm 11.44	11 \pm 9	
Cu	28.0 \pm 22.6	23.8 \pm 1.3	22.3 \pm 1.8	76 \pm 48	9.50 \pm 21.33	6.93 \pm 0.53	12.1	30.31 \pm 17.64	74 \pm 56	
Fe	19,927 \pm 12,149						20,750			
Mn	473.5 \pm 445.2	442 \pm 20	519 \pm 22			365 \pm 15	531.6			
Ni	19.2 \pm 7.6	9.77 \pm 0.67	7.88 \pm 0.63	175 \pm 118		7.09 \pm 0.32	15.8	31.92 \pm 18.15		
Pb	210.4 \pm 799.3	61.7 \pm 3.6	62.1 \pm 3.5	117 \pm 121	17.00 \pm 98.73	9.40 \pm 0.35	33.78	29.81 \pm 11.08	262 \pm 337	
Sb	1.8 \pm 3.5						0.22			
V	54.3 \pm 21.2						45.7	161.65 \pm 126.81		
Zn	102.8 \pm 60.0	205 \pm 14	207 \pm 15	149 \pm 97	40.00 \pm 22.04		100.2	125.31 \pm 59.97	251 \pm 253	
Hg	0.40 \pm 0.67									0.015–6.3

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 tenfold 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 Fig. S1), adding Ag and Cd to the list of persistent toxic elements established through river sediment study. Indeed, the concentrations of these six elements in the river sediment have decreased since the pollution peak in the 1960s (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 $\mu\text{g}/\text{kg}$ dw) are illustrated in Fig. 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 ($\Sigma 15\text{PAHs}$; 150–55,000 $\mu\text{g}/\text{kg}$ dw, min-max), followed by phthalates ($\Sigma 7\text{PAEs}$; 10–1700 $\mu\text{g}/\text{kg}$ dw) and alkylphenols ($\Sigma 7\text{APs}$; 30–330 $\mu\text{g}/\text{kg}$ dw). Levels for PCBs ($\Sigma 19\text{PCBs}$; 1–71 $\mu\text{g}/\text{kg}$ dw) and PBDE ($\Sigma 8\text{PBDEs}$; 0.3–13 $\mu\text{g}/\text{kg}$ dw) and to a greater extent PFAS ($\Sigma 22\text{PFASs}$; 0.2–3.2 $\mu\text{g}/\text{kg}$ 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, and 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

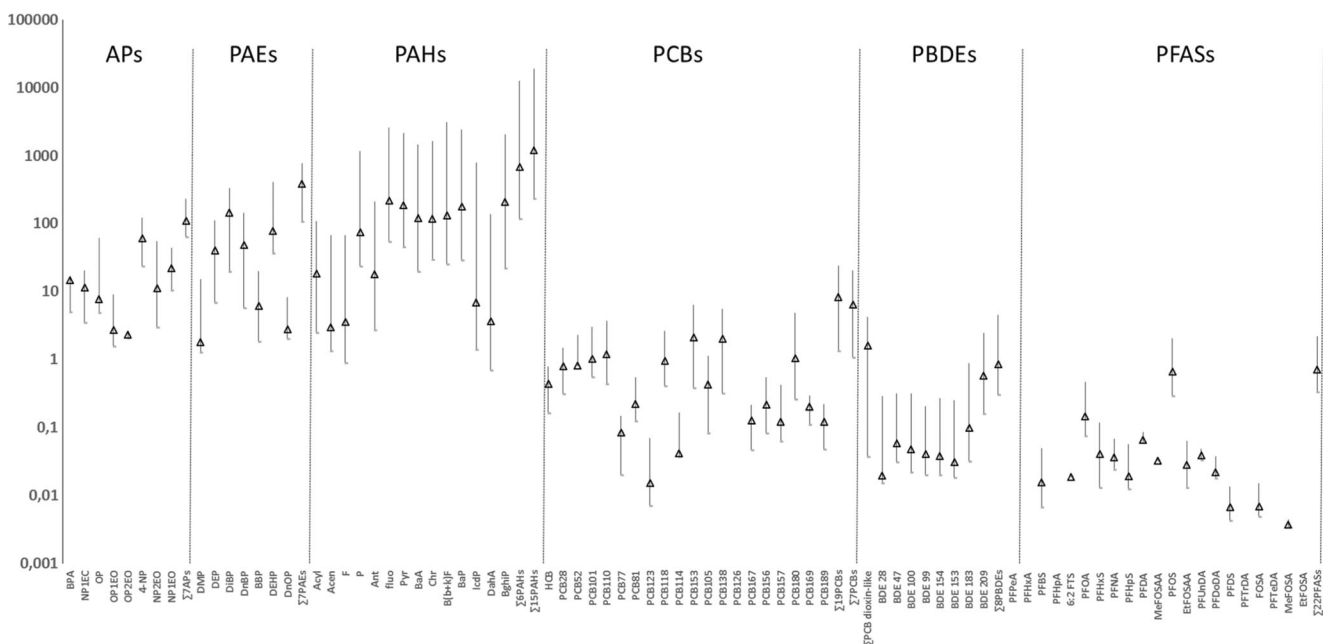


Fig. 3 Organic micropollutant contents in soils (d10, d50, and d90, as µg/kg dw, *n* = 31–32)

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 in Table 3. Although 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 and 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 (50–9000 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.

Pollutant patterns

The distribution of compounds for each group is illustrated in Fig. 4. For APs, NP, NP1EO, and NP2EO were predominant (occurrence varied between 80 and 100%), while OP, OP1EO, and OP2EO as well as 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., four to six benzenic rings) comparatively to the low-molecular-weight PAHs (LMW PAHs; i.e., two to three benzenic rings). According to the literature, samples contaminated by petrogenic sources are characterized by a higher proportion of LMW PAHs, while a

Table 3 Organic micropollutant contents in soil in this study and in literature (contents as $\mu\text{g}/\text{kg dw}$)

Family	Type of soils	Levels	References
BPA	Mixed (France)	BPA (4.8–17.2)	<i>This study</i> ^a
	Agricultural soils	BPA (90–110)	Sanchez-Brunete et al. (2009)
APs	Soils (France)	NP (23–123)	<i>This study</i>
	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)	<i>This study</i>
	Amended soils (Denmark)	DEHP (30–40)	Vikelsee et al. (2002)
	Mixed	DEHP (20–264,000)	Bergé 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)
PAH	Urban soils (China)	DnBP (1,800)	Zeng et al. (2009)
	Mixed (France)	$\Sigma 15$ (228–18,940)	<i>This study</i>
	Mixed (France)	Fluo (52–2,561)	<i>This study</i>
	Soils (France)	$\Sigma 16$ (80–400)	Villanneau et al. (2011)
	Soils (France)	Fluo (<10–5,300)	Villanneau et al. (2011)
	Soils (France)	$\Sigma 14$ (450–5,650)	Motelay-Massei et al. (2004)
	Mixed (France)	$\Sigma 13$ (60–5,305)	Gateuille et al. (2014a)
PCBs	Soils (UK)	$\Sigma 14$ (42–11,200)	Nam et al. (2008)
	Soils (Norway)	$\Sigma 14$ (9–1,100)	Nam et al. (2008)
	Mixed (France)	$\Sigma 19$ (1.3–24.3)	<i>This study</i>
	Soils (France)	$\Sigma 20$ (0.5–17)	Villanneau et al. (2011)
	Soils (France)	$\Sigma 19$ (0.1–150)	Motelay-Massei et al. (2004)
PBDEs	Mixed	$\Sigma 29$ (0.03–96)	Meijer et al. (2003a)
	Mixed (France)	BDE 209 (0.2–2.4)	<i>This study</i>
	Mixed	BDE 209 (0.6–4)	Hassanin et al. (2004)
PFAS	Mixed (China)	BDE 209 (9–102)	Zou et al. (2007)
	Mixed (France)	PFOA (0.07–0.46)	<i>This study</i>
	Mixed (France)	PFOS (0.28–2.05)	<i>This study</i>
	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 (USA)	$\Sigma 5$ carboxylates (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)

^a d10–d90 levels are provided in this study

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 as 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

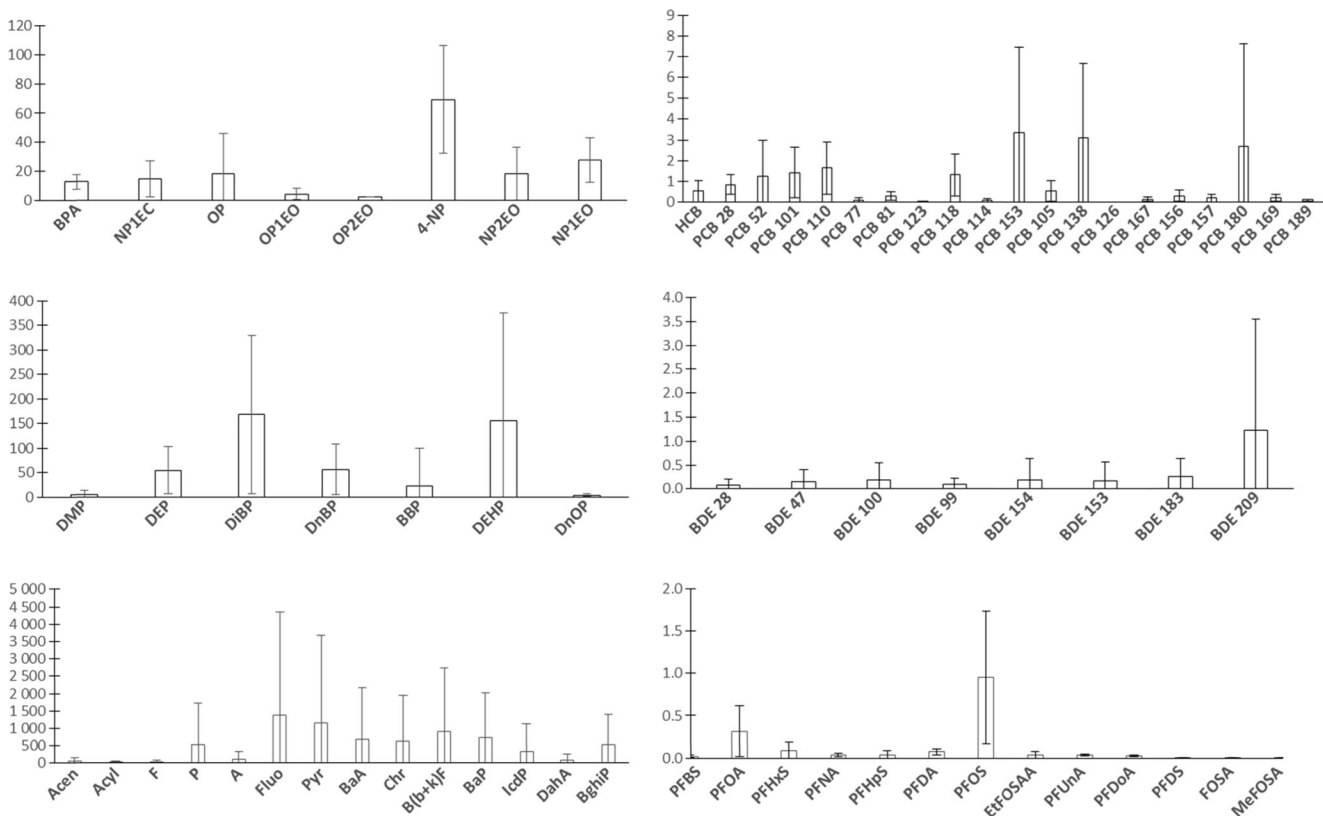


Fig. 4 Organic micropollutant patterns in soils (mean ± SD, as μg/kg dw, n = 31–32)

contamination but are close to the pattern observed for ambient air (Supplementary Fig. S1).

PCB patterns in soils were featured by the predominance of seven PCBs listed as indicators in environmental contamination studies. $\sum 7\text{PCBs}$ accounted for 70 to 100% of total PCBs. $\sum 8$ 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 increase 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, and 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).

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's test, $\alpha = 0.05$). 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 ongoing 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 accidentally 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 Nam 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.

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 (Mann-Whitney test, $\alpha = 0.05$). 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 $\mu\text{g/kg dw}$). Based on the 32 soil samples, trends also appeared for PBDEs ($\sum 8\text{PBDEs}$; 0.95 vs. 0.53 $\mu\text{g/kg dw}$), PCBs ($\sum 19\text{PCBs}$; 10.29 vs. 4.65 $\mu\text{g/kg dw}$), PFAS ($\sum 22\text{PFASs}$; 1.00 vs. 0.37 $\mu\text{g/kg dw}$), Sr (120.8 vs. 66.5 mg/kg dw), and Sb (2.38 vs. 0.88 $\mu\text{g/kg dw}$), but these differences are not statistically significant (Mann-Whitney test, $\alpha = 0.05$). For $\sum 15\text{PAHs}$, similar levels are found between rural and urban soils (1833 vs. 1010 $\mu\text{g/kg dw}$), as well as for $\sum 7\text{PAEs}$ (395 vs. 371 $\mu\text{g/kg dw}$). 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 $\sum 8\text{PBDE}$ concentrations was observed between forested and rural soils (0.59 and 0.66 $\mu\text{g/kg dw}$). 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 Fig. S2) 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 second 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 ($\sum 15\text{PAHs}$; 55,800 $\mu\text{g/kg dw}$), PCB ($\sum 19\text{PCBs}$; 25.8 $\mu\text{g/kg dw}$), 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 ($\sum 15\text{PAHs}$; 7740 $\mu\text{g/kg dw}$) 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 amounts 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.

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 were to assess the stock of pollutants in surface soils from 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 were arbitrarily estimated for the 0–10-cm upper layer of soils, considering the median values obtained on the 32 soils studied and a wet soil density of 2000 kg/m³ (Table 4). Each pollutant stock per surface unit (mg/m² or µg/m²) was calculated according to Eq. 1.

$$\text{Stock}_{\text{pollutant } i} \left(\text{mg/m}^2 \text{ or } \mu\text{g/m}^2 \right) = \delta \times S \times \rho_{\text{wet}} \times [\text{pollutant } i] \quad (1)$$

With

δ	depth of soil considered ($\delta = 0.10 \text{ m}$)
S	surface of soil considered ($S = 1 \text{ m}^2$)
ρ_{wet}	wet soil density ($\rho_{\text{wet}} = 2000 \text{ kg/m}^3$)
$[\text{pollutant } i]$	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 1000. This evidenced the importance of the soil reservoir compared to recent atmospheric inputs. For Zn, Cu, Cd, Hg, Sb, $\Sigma 7\text{PAEs}$, and $\Sigma 7\text{APs}$, 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 emissions 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, and Sb (Le Cloarec et al. 2011).

Furthermore, some pollutants such as Hg, PAEs, and APs were industrially used since 1940s and 1960s 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 1980s (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 1950s (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.

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 ($\Sigma 15\text{PAHs}$; 150–55,000 µg/kg dw) > PAEs ($\Sigma 7\text{PAEs}$; 10–1700 µg/kg dw) > APs ($\Sigma 7\text{APs}$; 30–330 µg/kg dw) \gg PCBs ($\Sigma 19\text{PCBs}$; 1–71 µg/kg dw) > PBDEs ($\Sigma 8\text{PBDEs}$; 0.3–13 µg/kg dw) > PFASs ($\Sigma 22\text{PFASs}$; 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 historical trends 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

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

	Stocks ^a ($\mu\text{g}/\text{m}^2$ or mg/m^2)	Atm fluxes ^b ($\mu\text{g}/\text{m}^2$ or $\text{mg}/\text{m}^2/\text{year}$) min	Atm fluxes ^b ($\mu\text{g}/\text{m}^2$ or $\text{mg}/\text{m}^2/\text{year}$) max	References	Ratio stocks/ flux min	Ratio stocks/ flux max
BPA	2,950	11.00	56.00	Cladière (2012)	268	53
$\Sigma 7\text{APs}$	22,077	50.00	117.00	Cladière (2012)	442	189
DEHP	15,641	185.00	393.00	Dargnat (2008)	85	40
$\Sigma 7\text{PAEs}$	76,781	326.00	691.00	Dargnat (2008)	236	11
$\Sigma 6\text{PAHs}$	135,150	31.00	104.00	Motelay-Massei et al. (2007)	4,359	1,299
$\Sigma 15\text{PAHs}$	239,500	66.00	227.00	Motelay-Massei et al. (2007)	3,628	1,055
$\Sigma 7\text{PCBs}$	1,676	3.60	35.00	Blanchard et al. (2006)	99	13
$\Sigma 19\text{PCBs}$	1,01	16.90	125.00	Blanchard et al. (2006)	361	37
$\Sigma 8\text{PBDEs}$	170	2.50	43.00	Tlili et al. (2012)	68	4
$\Sigma 8\text{PBDEs}$	337	18.00	47.45	Muresan et al. (2010)	19	7
$\Sigma 22\text{PFASs}$	141	4.00	5.00	Labadie (personal communication)	35	28
$\Sigma 22\text{PFASs}$	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

^a Stocks in $\mu\text{g}/\text{m}^2$ for organic micropollutants and mg/m^2 for metals

^b Atm flux = atmospheric flux in $\mu\text{g}/\text{m}^2/\text{year}$ for organic micropollutants and $\text{mg}/\text{m}^2/\text{year}$ for metals

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 $\alpha = 0.05$ level of confidence, were also reported for $\Sigma 15\text{PAHs}$, $\Sigma 8\text{PBDEs}$, $\Sigma 19\text{PCBs}$, $\Sigma 22\text{PFASs}$, 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 1000). For Zn, Cu, Cd, Hg, Sb, $\Sigma 7\text{PAEs}$, and $\Sigma 7\text{APs}$, annual atmospheric inputs contribute to up 1.5% of soil pollutant stocks. Higher contributions (up to 7.8%) are observed for $\Sigma 8\text{PBDEs}$ and $\Sigma 22\text{PFASs}$. 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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