Case study of PAHs, Me-PAHs, PCBs,Phthalates and Pesticides Contamination in the Somme River water, France

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ABSTRACT: Surface waters, especially natural rivers always act as receiving waters for various kinds of organic contaminants from municipal and industrial wastewaters, agricultural activities, organic chemicals in use, non-point source pollutions. Due to their toxicity, persistency and wide diffusion, polychlorinated biphenyls (PCBs), pesticides, phthalates, polycyclic aromatic hydrocarbons (PAH) and their alkylated homologues (Me-PAHs) are among the organic contaminants the most often monitored in the environment. Determination of the contamination level is the crucial first step of environmental research. Field investigations have clearly demonstrated their importance on various studies on the contamination levels, the origin, and impact of contaminants in the aquatic ecosystems. The present paper is an effort on the field studies focusing on persistent organic pollutants: PCBs, PAHs and Me-PAHs, phthalates and pesticides in Somme River water located on Northern France. The sampling zone is characterized by fields of agriculture surrounding urbanized and industrialized areas and constitutes a place embedded with strong fishing activities. However, the river section of interest is also known for the high levels of PCB in sediments. The water were analyzed for 28 PCBs, 16 PAHs and 18 Me-PAHs, 6 phthalates and 28 pesticides with the aim to determine the dispersion trend and the water quality of the sampled water.

Key words: PAHs, Me-PAHs, Phthalates, PCBs, Pesticides, LLE, GC-MS, Somme River

INTRODUCTION

Actually, organic contaminants are major environmental concern due to their ubiquitous, their persistence, long-range transportability and potentially adverse effects on living organisms. River water acts as receiving water for various kinds of organic contaminants from municipal and industrial wastewaters (Malve *et al.,* 2003; Singh *et al.,* 2004; Zhang *et al.,* 2004). For the ecosystem protection and to keep water resources clean, it is important to identify the nature of contaminants, their contamination levels as well as their sources. Polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (Me-PAHs), polychlorobiphenyls (PCBs), phthalates and pesticides are the principal classes of organic contaminants in aquatic ecosystem. In this context, twenty-three priority substances and other priority pollutants (PPs) were established by European Commission in the Water Framework Directive 2008/105/EC (European Commission, 2008).

(*i*) Aromatic hydrocarbons including PAHs and Me-PAHs are widely disseminated in the environment with sources that can be both natural and anthropogenic (Yunker, 2002; Wang, 2007; Mostert, 2010). They are highly lipophilic compounds, ubiquitous in coastal, estuarine and river water column, as well as sediments in which they tend to accumulate (Cailleaud, 2007; Chiou, 1998; Manodori, 2006, Gaspare, 2009; Ko, 1995; Yunker, 2012; Net *et al.,* 2014). High level of aromatic hydrocarbons represents a serious threat to the ecosystem functioning and human health via food chain and water resources. Recent studies have indeed reported that marine organisms are prone to bioaccumulate these substances, particularly in lipid-rich tissues (Neff, 2002; Francioni, 2005; Dugan, 2005). Due to their toxic, carcinogenic and mutagenic effects (Straif, 2005; IARC, 2010; U.S. Department of Health and Human Services, 2011), sixteen PAHs have been recommended as priority pollutants by the United States Environmental Protection Agency (US EPA,

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2002). (*ii*) Another class of contaminant is represented by the pesticides. It is known that pesticides used for agriculture activities may lead to contamination of surface and ground waters (Kaushik *et al.,* 2010, Navarro *et al.,* 2010; Hancok *et al.,* 2008). Pesticide contamination of the aquatic environment as well as their ecotoxicological effects for aquatic flora, and human health has also been well documented (Wania and Mackay 1999; Sanborn *et al.,* 2007; Jurewicz and Hanke, 2008; Huen *et al.,* 2012). Runoff from urban areas, return flow waters from agricultural fields, and leaching are considered important inputs to pesticide contamination of surface and groundwater. (*iii*) One other group is characterized by polychlorobiphenyles (PCBs). These compounds have been commonly used as dielectric fluids or transformers and capacitors, in paints, inks and pesticides until the hazard posed to both the environment and human health by their use became evident. They are extremely stable compounds under environmental conditions (WHO, 1993). Due to their toxicity, chronic persistence and bioaccumulation, they have been banned or restricted, and some of them have been included in the list of priority pollutants in many countries. However, PCBs are still present in water and sediment and continue to affect aquatic organisms from the top of food chain (plankton, algae) to predator organisms (fish, birds, marine mammals) and consequently human health through the diet (Sun *et al.,* 2002). (*iv*) Nowadays, phthalates or phthalic acid esters have become also a group of contaminants of environmental concern. Large scales of phthalates have been produced due to the wide variety of uses. They are used in common household products, cosmetics, detergents, flame retardants, plastics, inks, adhesives and medical devices. Several million tons of phthalates have been produced each year. Some phthalates are suspected to act as endocrine disruptors (Gomez-Hens and Aguilar-Caballos, 2003; Ghisari and Bonefeld-Jorgensen, 2009; Lau *et al.,* 2005). Phthalates are currently listed as priority pollutants in many countries due to their link to several human cancer diseases (Kaneco *et al.,* 2006). According to US EPA, diethyl phthalate (DEP), dimethyl phthalate (DMP), di (2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), di-n-butyl phthalate (DBP) and di-n-octyl phthalate (DOP) should be considered Priority Toxic Pollutants (US EPA, 1999). Their entry into the surface water occurs directly from the production of plastic materials and indirectly *via* volatile emissions and leaching from their parent polymeric material (Stanley *et al.,* 2003, Petrovic *et al.,* 2001; Gomez-Hens and Aguilar-Caballos, 2003 and Kavlock *et al.,* 2002).

The aim of the present study was to investigate the concentration levels of these four classes of organic contaminants in order to assess quality of river water from fourteen sampling sites of the Somme River in Northern France. Samples were analyzed for 16 PAHs and 18 Me-PAHs, 6 phthalates, 28 pesticides and 28 PCBs, using gas chromatography/mass spectrometry (GC/MS). Results obtained from this multiresidue study aim to fill the lack of data concerning water contamination in this region.

MATERIALS & METHODS

Mixed standard solutions of PAHs and Me-PAHs were purchased from Restek Corp (Bellefonte, PA, USA). PCBs standard solution was obtained from Accustandard, Inc. (New Haven, CT, USA). Phthalates and pesticides standards were purchased from Sigma-Aldrich (Saint-Louis, USA) and Restek (Bellefonte, USA). Tetrachloronaphtalene (TCN), 2,3,3',5,6-tetrachlorobiphenyl (PCB112) and octachloronaphtalene (OCN), used for PCB quantification, were purchased from Dr Ehrenstorfer (Augsburg, Germany) Deuterated internal standards for PAHs and Me-PAHs (acenaphthene-d10 (A-d10), naphtalene-d8 (N-d10), perylene-d12 (Per-d12), phenanthrene-d10 (Phe-d10) and pyrene-d10 (Pyr-d10)) were provided by LGC-Promochem (Middlesex, UK). Benzyl benzoate and pentachloronitrobenzene with a purity of 99% and 94% respectively were used as internal standard for phthalates and pesticides, and they were purchased from Sigma-Aldrich (Saint-Louis, USA). HPLC-grade solvents (hexane, dichloromethane, methanol and acetone) were purchased from Dislab (France). No significant amount of targeted analytes was showed in procedural blanks. Ultrapure water (Milli-Q) was produced by a Millipore apparatus with 18.2 MΩ/cm resistivity. Merck silica gel 60 (70-230 mesh ASTM) activated at 450°C was heated at 120°C for 12h prior to use. Glassware was systematically washed with detergent (Decon, East Sussex, UK), rinsed with ultrapure water and acetone and finally dried at 120°C prior to use.

The sampling campaign was conducted on October 2012 in Somme River (Picardie region in northern France). The sampling was done from downstream at Béthencourt-sur-Somme to Saint-Quentin (Fig. 1). Water samples were collected from 11 sites of the Somme River from the first station at Béthencourt-sur-Somme (Station 001103) to Gauchy (station 116500). Two additional samplings were performed in two ponds around Béthencourt-sur-Somme with the aim to evaluate a potential accumulation of contaminants. The sampling zone is characterized by fields of agriculture surrounding urbanized and industrialized areas (e.g. Saint-Quentin, Ham) and constitutes a place embedded with strong fishing activities. However, the river section of interest

is also known for the high levels of PCBs in sediments (Dumoulin *et al.,* 2013). In this work, samples were analyzed for 16 PAHs, 18 Me-PAHs, 6 phthalates, 28 pesticides and 28 PCBs including 12 dioxin-like PCBs (dl-PCBs) and 7 PCBs indicators (PCBi) as following:

PAHs (16 PAHs) : naphthalene (Na), acenaphtylene (Ayl), acenaphtene (Aen), fluorene (F), anthracene (An), fluoranthene (Fl), benz*[a]*anthracene (BaA), chrysene (Ch), benz*[a]*pyrene (BaP), phenanthrene (Phe), benzo*[b]*fluoranthene (BbF), benzo*[k]*fluoranthene (BkF), benzo*[ghi]*perylene (Bghi), dibenzo*[a,h]*anthracene (DhA), indeno*[1,2,3-cd]*pyrene (IP), pyrene (Py).

Me-PAHs (18 Me-PAHs) : 1-methylnaphthalene (1M-Na), 2-methylnaphthalene (2M-Na), 1,2-dimethylnaphthalene (1,2DM-Na), 1,6-dimethylnaphthalene (1,6DM-Na), 2,6-dimethylnaphtalene (2,6DM-Na), 1-methylphenanthrene (1M-Phe), 2-methylphenanthrene (2M-Phe), 3-methylphenanthrene (3M-Phe), 9-methylphenanthrene (9M-Phe), 2-methylanthracene (2M-An), 1,7-dimethylphenanthrene (1,7DM-Phe), retene, 1-methylfluoranthene (1M-Fl), 3-methylfluoranthene (3M-Fl), 1-methylpyrene (1M-Py), 4-methylpyrene (4M-Py), 3-methylchrysene (3M-Ch), 6-methylchrysene (6M-Ch).

Phthalates (6 PAE): dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di-2-ethylhexyl phthalate ester (DEHP) and di-*n*-octyl phthalate (DNOP).

Pesticides: alpha-lindane, gamma-lindane, beta-lindane, delta-lindane, heptachlor, aldrin, trans-chlordane, cis-chlordane, 4,4'-DDE, endosulfan I, dieldrin, endrin, 4,4'-DDD, endosulfan II, 4,4'-DDT, endrin aldehyde, methoxychlor, endosulfan sulfate, endrin ketone, chloroneb, chlorothalonil, DCPA methyl ester, heptachlor epoxide (isomer A and B), trans-nonachlor, chlorobenzilate, trans-permethrin and cis-permetrin.

PCBs No.(28 PCBs) : 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209.

Water sampling was performed using pre-cleaned amber glass 2.5 L bottles that were immediately capped with Teflon-lined lid. Samples were maintained at 4°C before analysis. Back to the laboratory, samples were rapidly filtered using 0.7 μm Whatman glass microfiber filters and extracted using liquid–liquid extraction (LLE) technique. The applications of LLE in water and other liquid matrixes have been widely accepted in standard methods for various classes of organic contaminants such as PAHs, pesticides, and PCBs analysis (USEPA, 1996; JISC, 2005; Boussahel *et al.,* 2000; Barcéló, 1993;
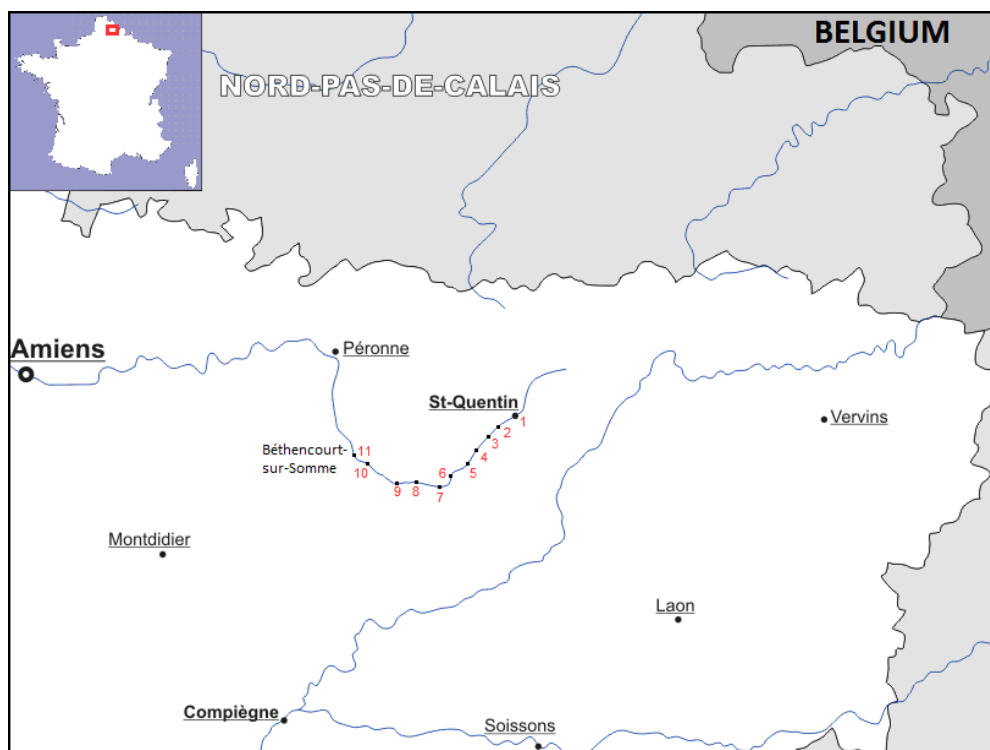

Fig. 1. Location of sampling sites in the Somme River in Picardie region, Northern France

T90-120, AFNOR 1990; USEPA, 2008). Various solvent can be used depending on the nature of interest compounds. Dichloromethane (DCM) has been widely adopted for the extraction of POPs whereas *n*-hexane has often been used for PCB and PAHs extraction (Turrio-Baldassarri *et al.,* 2005; DIN EN ISO 17993). In this study, in order to increase the extraction efficiency, each water sample (1L) was spiked with internal standards and then extracted four times with 60 mL of *n*-hexane followed by four times with 60 mL of DCM. The extracts were then pooled and dried using Na_2SO_4. Finally, the extract was concentrated using a rotary evaporator followed by a slight stream of nitrogen before analysis. The recoveries of PAHs, Me-PAHs, phthalates and PCBs using this protocol were estimated at 71.3-106.2%, 68.2-115%, 72.1-107.6%, 72.5-112.0% respectively.

The extracts were analyzed using a Varian 3900 gas chromatograph (GC) equipped with a deactivated fused-silica guard column (5 m, 0.53 mm i.d.) and a fused-silica capillary Phenomenex XLB (60 m length, 0.25 mm i.d., 0.25 μm film thickness) and coupled with a Varian Ion Trap Saturn 2000 Mass Spectrometer (MS). The carrier gas was helium, held at a constant flow rate of 1 mL/min. Samples were injected in the splitless mode at 280°C and the injector was purged with helium after 1 min. Each group of organic compounds was analyzed separately. The transfer line and the ion trap were respectively held at 280°C and 220°C. Each contaminant was identified based on the retention time and the mass spectrum from chromatogram of standard solutions acquired in full scan mode. Quantification was then performed in the single ion storage (SIS) mode for better selectivity. Response factors were determined relative to the deuterated internal standards response and to standard mixtures. Deuterated standards were chosen in order to better fit to the properties of each group of contaminants.

RESULTS & DISCUSSIONS

As depicted on fig. 2, the total concentration of the 16 PAHs (Σ16PAH) varies significantly along the river section with a mean value of 284 ng/L. Two subsurface maxima of concentration were recorded at Fontaine-les-Clercs (station 3 - Σ16PAHs = 513 ng/L) and Artemps (station 5 - Σ16PAHs = 831 ng/L). On the other hand, the total concentration of 18 Me-PAHs (Σ18Me-PAH) was also found to vary significantly from 75 ng/L at Dury (station 7) to 440 ng/L at Artemps (station 5) with an average concentration of 185 ng/L. A strong relationship can be found between the total concentration evolution of Σ_{16}PAHs and Σ_{18}Me-PAHs (R-squared = 0.78, P < 0.01). In terms of the compositional profiles (Fig. 3), the concentrations of

low molecular weight PAHs (2-3 rings) were significantly higher than high molecular weight PAHs. Three-rings PAHs accounted for the most abundant species with an average of 60 % of the total concentration of PAHs (Σ_{16}PAHs). No significant traces of five and six ring-membered PAHs were detected in the water samples. Concerning Me-PAHs, two-ring species were predominant with an average proportion of 79 % of Σ_{18}Me-PAHs.

At this stage, some PAHs diagnostic ratios were used as a tool for attempting to identify pollution emission sources (Yunker *et al.,* 2002). For example, the anthracene/(anthracene+phenanthrene) ratio (Ant/(Ant+Phe)) is commonly used to distinguish petrogenic (< 0.1) from pyrogenic (> 0.1) origins, whereas the fluoranthene/(fluoranthene+pyrene) ratio (Fl/(Fl+Py)) allows distinction between petrogenic (< 0.1), fossil fuel combustion (0.4-0.5) and grass/wood/coal combustion (> 0.5). Both these ratio have been widely used to assess contamination sources in water samples (Wang *et al.,* 2009; Opuene *et al.,* 2009; Tobiszewski *et al.,* 2010). In the case of the Somme river water, Ant/(Ant+Phe) ratios support a pyrogenic origin with a mean value of 0.46. The Fl/(Fl+Py) ratios corroborate this hypothesis with a mean value of 0.55 attributable to grass/wood/coal combustion. However, sites 1, 2 as well as the two ponds were not taken into account for the determination of the Fl/(Fl+Py) ratios since no significant trace of fluoranthene could be detected in the corresponding water samples. This might be explained by the fact that PAHs in water samples easily undergo photolysis, which may alter values of diagnostic ratios (Jacobs *et al.,* 2008; Tobiszewski and Namiesnik, 2012). Nevertheless, high proportions of parent PAHs (Σ_{16}PAHs/Σ_{16}PAHs+Σ_{18}Me-PAHs average value = 0.6) support combustion as the primary PAHs source. Moreover, discrimination between petrogenic and combustion sources was ensured using specific ratios involving alkyl PAHs in the phenanthrene/anthracene (Phe/Ant) series. With petroleum/combustion transitions set at 0.4, the C_0/C_0+C_1 (Phe/Ant) ratios determined in our samples corroborate the combustion source with a mean value of 0.77.

Large variations of phthalates concentrations ($\Sigma_6$phthalates**)** were observed, ranging from 6.93 μg/L at Artemps (station 5) to 23.34 μg/L at Pond 2 (station 13). DEHP was found to be the most abundant specie with concentration ranging from 5.16 to 20.76 μg/L for a mean value of 10.23 μg/L (accounting for 68 % of mean $\Sigma_6$phthalates). No trace of benzyl butyl phthalate and di-octyl phthalate could be detected in the samples, whereas low levels of hydrophilic phthalate
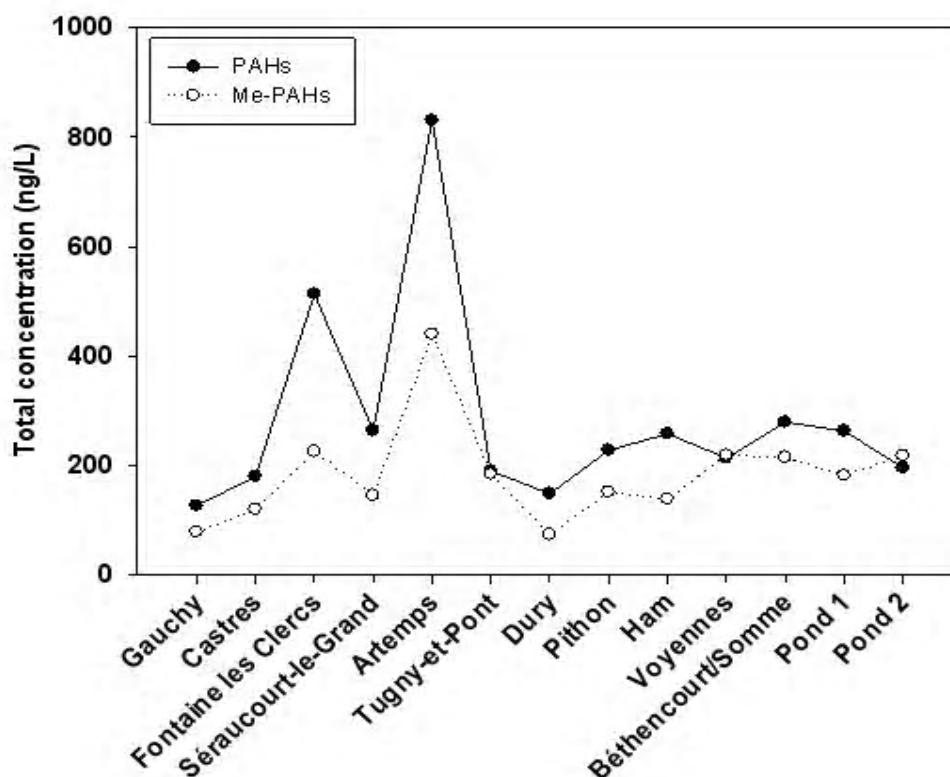
Fig. 2. PAHs and Me-PAHs repartition in surface water samples of the Somme River
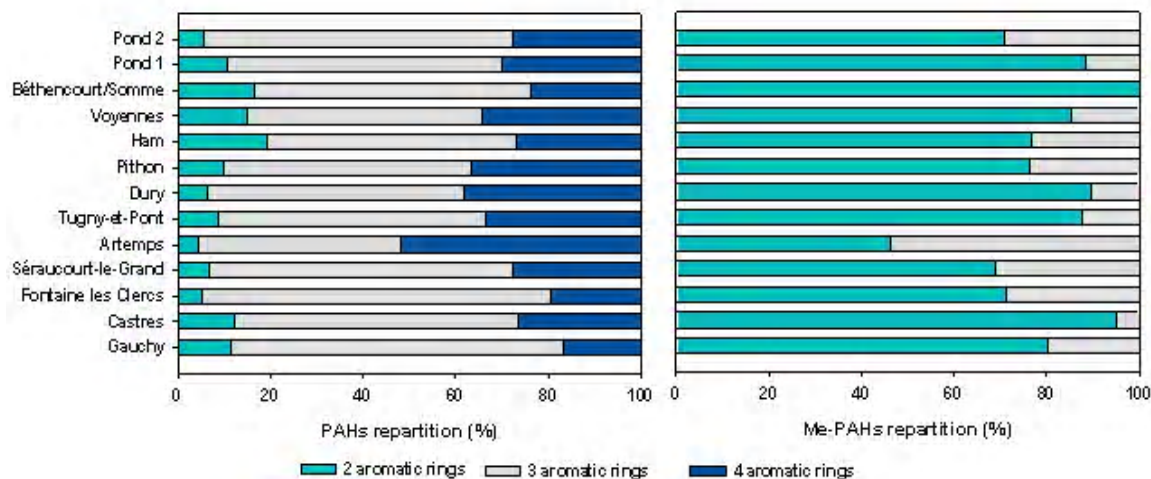

Fig. 3. PAHs and Me-PAHs composition profiles in the Somme River water samples

(DMP) were recorded. No significant correlation could be found between phthalate species distribution. Detailed concentrations are presented in Table 1. The relative high concentrations recorded for phthalates can be explained by the fact that these compounds have now become ubiquitous in water. DEHP and DBP are the most frequently detected and in surface water, wastewater and tap water with concentrations that can easily reach a few dozen µg/L (Fromme *et al.,* 2002; Aparicio *et al.,* 2007; Meng *et al.,* 2011). In our case,

the low recorded levels of DMP can be linked to the higher degradation rates of short chain phthalates (Staples *et al.,* 1997).

Among the 28 studied pesticides, only three were detected and quantified at least one time in four samples. Other compounds of interest were below the limit of detection. Gamma-lindane and chloroneb were detected in the four above-mentioned samples corresponding to sites 2, 3, 5 and 11, with concentrations respectively ranging from 177 to 281

ng/L and from 90 to 131 ng/L. The alpha isomer of lindane was only detected in sites 2 (89 ng/L) and 3 (355 ng/L) (Table 2). The sources can be attributed to the nearby agricultural activities of sampling stations. Somme River sediments are known to be highly contaminated by PCBs. The Agence de l'Eau Artois-Picardie (AEAP), which is a public institution of the Ministry for Sustainable Development, has carried out several studies on contamination of sediment of the Somme River by PCBs since 1997. These investigations have led to highlight three sites in the Somme River particularly affected by PCBs contamination of sediment: Fontaine-les-Clercs (station 3), Séraucourt-le-Grand (station 4), and Artemps (station 5), with concentrations of PCBi higher than 200 µg/kg dw of sediment. No accumulation of PCBs could be noticed downstream watershed (AEAP, 2009; Dumoulin *et al.,* 2013). Besides, no data concerning contamination levels of PCBs in the water column were indicated for these study sites. The present study also aims to provide additional information for these sampling sites with a focus on the water column. Fig. 4 showed the total concentrations (Σ_{28}PCBs), dl-PCB and PCBi in surface water of Somme River. Large variations of PCBs concentrations were observed for selected sampling sites. High concentrations of Σ_{28}PCB were detected at Artemps (201 ng/L), Pithon (246 ng/L) and Voyennes (179 ng/L) (Fig. 4), whereas PCBs were present at non-detectable levels for 6 stations (Castres, Séraucourt-le-Grand, Tugny-et-Pont, Dury, Pond 1 and Pond 2). No specific correlation could be found between Σ_{28}PCB and both indicator and dioxin-like PCBs for the seven concerned stations. PCBi were detected in only four stations and accounted for a mean value of 61 % (ranging from 26 to 100 %). On the other hand, dl-PCB, which are usually measured in biota, were detected at non-negligible levels in six water samples with concentrations ranging from 23 ng/L at Ham (station 9) to 116 ng/L at Voyennes (station 10) with a mean value of 60 ng/L. PCB77 was the dominant dioxin-like congener with an average proportion of 78 %. These concentrations in the water column were not correlated with value previously recorded in sediment for the same sampling sites (Dumoulin *et al.,* 2013). This can be explained by low solubility of PCBs in water by the non-significant remobilization of PCBs from sediment to water column in the studied river section. Moreover, dissolved PCBs in water represent a small fraction of total PCB in the water column due to their rapid association to organic entities such as sediment, algae and protozoa

(Brannon, 1993, Hargrave *et al.,* 1992, Eganhouse and Gossett, 1991 and Booij and van den Berg, 1994). However, it is interesting to note that PCBs are bioaccumulable compounds, which even at low concentration in water can affect strongly the aquatic organisms. Moreover, PCBs are extremely stable compounds under environmental conditions (WHO, 1993). Even, their concentrations in surface water were relatively low, it can contaminate underground water which could be source of drinking water and can impact consequently human health.

Numerous Water Quality Guidelines (i.e. European, Canadian, USA, Australian…) for Marine and Fresh Water Quality have been developed. The specific guidances are corresponding to the type of effluent (surface water, groundwater, freshwater) and to the intended use of the water. Nevertheless, for certain compounds, regulation of hazardous substances (organic micro pollutants) was incomplete or even not available in the literature in the past operation of worldwide water policy (Kallis *et al.,* 2001). Progressively, revisions have been developed to provide a tool for simplifying the reporting quality data. The assessment of the water quality and the contamination level evaluation of each studied site were performed by referring to the environmental quality standards (EQS) indicated through threshold values (European Commission, 2008). For River water quality, the threshold values are currently given for PAHs, phthalates and pesticides. No threshold values available for Me-PAHs. Concerning the PCB contamination, actually, insufficient data allow to set the threshold value. However, according to the circular EU-WFD 2005/12 of 28 July 2005, the interim EQS of PCBs for water inland surface, transitional and territorial marine interior is set to 0.001 µg/L (INERIS, 2011). Threshold values of EQS of individual PAH, phthalate and pesticides, and contamination levels detected in Somme River are presented in Table 3.

The results in Table 3 show the contamination level of phthalates and pesticides under the maximum allowance concentration (MAC) of EU-WFD. However, the concentration of alpha-lindane and beta-lindane exceed CWQG value (> 0.01 µg/L) for some sampling points (at Fontaine-les-Clercs and Castres for alpha-lindane, and at Fontaine-les-Clercs, Artemps, Castres and Berthencourt-sur-Somme for beta-lindane). For PAH, the concentration detected at Somme River water do not exceed the MAC of EU-WFD. Nevertheless, some measured points showed the value higher than interim guideline set by CWQG for An, Fl, BaA and Py.

Table 1. Individual phthalate concentrations in the 13 sampling sites of the Somme River

	Phthalate concentrations (µg/L)							
N° Station	Corresponding City	DMP	DEP	DBP	BBP	DEHP	DOP	$\Sigma_6$phthalates
1	Gauchy	0.08	5.35	2.92	-	13.30	-	21.65
2	Castres	-	0.46	0.24	-	20.76	-	21.46
3	Fontaine les Clercs	0.25	2.12	3.28	-	8.88	-	14.53
4	Séraucourt-le-Grand	0.20	-	3.77	-	7.46	-	11.43
5	Artemps	0.02	0.26	0.43	-	6.22	-	6.93
6	Tugny-et-Pont	0.14	1.28	2.01	-	6.57	-	10.00
7	Dury	0.03	0.48	0.45	-	17.93	-	18.89
8	Pithon	0.13	4.92	2.97	-	5.16	-	13.18
9	Ham	0.10	3.01	3.86	-	5.86	-	12.83
10	Voyennes	0.15	3.62	1.98	-	6.84	-	12.59
11	Béthencourt/Somme	0.03	0.52	0.22	-	9.39	-	10.16
12	Pond 1	0.06	6.83	0.77	-	11.23	-	18.89
13	Pond 2	0.22	6.98	2.78	-	13.36	-	23.34

* « - » : not detected « + » : value below the limit of quantification (< 0.01 µg/L)

Table 2. Pesticides repartition in the surface water in Somme River

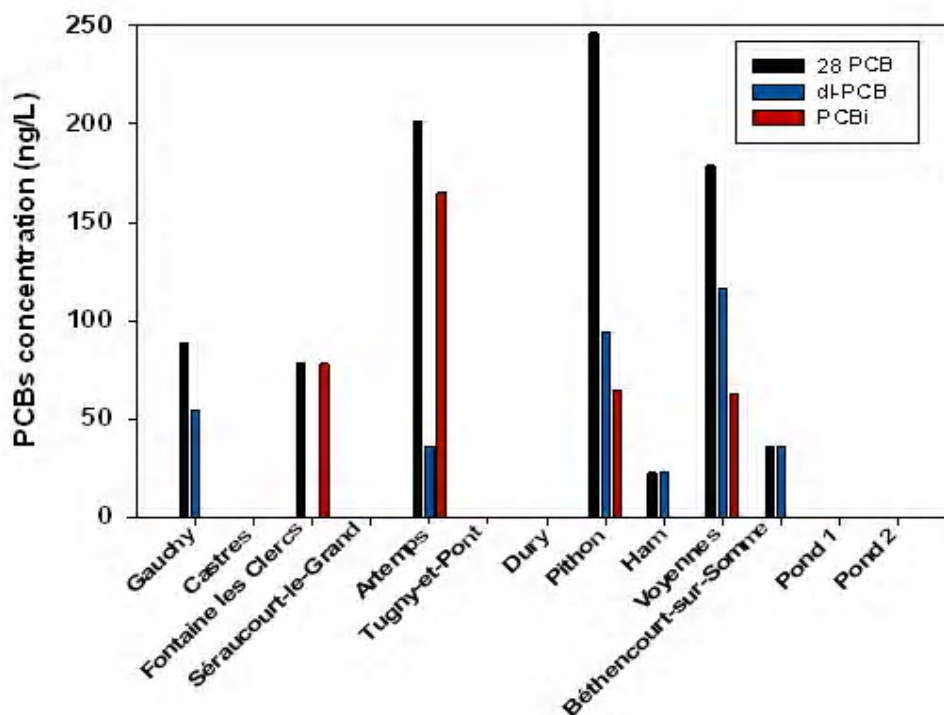| Pesticide concentrations (ng/L)													
N° Station	1	2	3	4	5	6	7	8	9	10	11	12	13
Alpha-lindane	-	89	355	-	-	-	-	-	-	-	-	-	-
Gamma-lindane	-	271	177	-	281	-	-	-	-	-	231	-	-
Chloroneb	-	90	131	-	117	-	-	-	-	-	103	-	-
Σ_{28}pesticides	-	450	663	-	398	-	-	-	-	-	334	-	-

* « - » : not detected

Fig. 4. Concentration of Σ_{28}PCB, dl-PCB and PCBi in Somme River

Table 3. Threshold values of EQS of individual PAH, phthalate and pesticide (Canadian Environmental Quality Guidelines, 2007; Directive n° 2013/39/UE of 12/08/13 modifying the directives 2000/60/CE and 2008/105/ CE), and contamination levels detected in Somme River

Compounds	EU-WFD	CWQG	Somme River (Average)
PAHs (µg/L)			
Na	130**	1.1*	0.011-0.048 (0.026)
Ayl			0.040-0.081 (0.057)
Aen		5.8*	n.d. – 0.066 (0.017)
F	0.12**	3*	n.d. – 0.060 (0.011)
An	0.1**	0.012*	n.d. – 0.044 (0.027)
Fl	0.12**	0.04*	n.d. – 0.101 (0.032)
Ch		Insufficient data	n.d. – 0.138 (0.011)
BaP	0.27**	0.015*	n.d.
Pn		0.4*	0.008-0.194 (0.047)
BbF	0.017**		n.d.
BkF	0.017**		n.d.
Bghi	0.0082**		n.d.
DhA			
IP	Insufficient data		n.d.
BaA		0.018*	n.d. – 0.068 (0.006)
Py		0.025*	0.021-0.123 (0.041)
Pesticides (µg/L)			
Alpha-lindane	0.04	0.01	n.d.-0.355 (0.029)
Gamma-lindane	0.04	0.01	n.d. – 0.281 (0.064)
Beta-lindane	0.04	0.01	n.d.
Delta-lindane	0.04	0.01	n.d.
Heptachlor	0.0003	Insufficient data	n.d.
Aldrin	Insufficient data	Insufficient data	n.d.
Trans-chlordane		Insufficient data	n.d.
Cis-chlordane		Insufficient data	n.d.
Endosulfan I	0.01**	0.02	n.d.
Dieldrin	Insufficient data	Insufficient data	n.d.
Endrin	Insufficient data	Insufficient data	n.d.
Endosulfan II	0.01**	0.02	n.d.
4,4'-DDT	Insufficient data	Insufficient data	n.d.
Endrin aldehyde		Insufficient data	n.d.
Endosulfan sulfate		0.02	n.d.
Endrin ketone		Insufficient data	n.d.
Heptachlor epoxide (isomer A and B)	0.0004**	No objet	n.d.
Chloroneb			n.d. – 0.094 (0.046)
Isodrine	Insufficient data		n.d.
P,p-DDT	Insufficient data		n.d.
Phthalates (µg/L)			
DMP			n.d. – 0.25 (0.110)
DEP		16	n.d. – 6.98 (3.001)
DBP		19	0.22 – 7.58 (2.404)
BBP			n.d.
DNOP		Insufficient data	n.d.
DEHP	Insufficient data		0.34– 20.76 (9.591)

Eu-WFD: European Union Water Framework Directive
CWGQ: Canadian Water Quality Guidelines for the protection of Aquatic life
*Interim Guideline   **Maximum Allowance Concentration

CONCLUSION

The extract water samples was analyzed for 16 PAHs and 18 Me-PAHs, 6 phthalates, 28 pesticides, 28 PCBs, using gas chromatography/mass spectrometry (GC/MS) for the total of 96 targeted compounds. Each contaminant was quantified to assess their contamination levels in 13 sites of Somme River in northern France. Recorded concentrations showed significant contaminations of Somme River. Large variation of concentration was observed from one sampling site to others for the concentration level of hydrocarbons. Hydrocarbons contaminations were dominated by two rings and three rings respectively for Me-PAHs with average of 72% and PAHs with average of 75%. This work reported for the first time the contamination level of phthalates in Somme River. The same order of magnitude of phthalate concentration was observed with fifteen sampling stations in Somme River; the $\Sigma_6$phthalates varies from 7 to 23 μg/L. DEHP and DEP are phthalates the most abundance in this River; their average represents respectively around 63% for DEHP and 20% for DEP. Among 28 targeted pesticides, only chloroneb, alpha-lindane and beta-lindane were detected and quantified. Moreover, their concentrations were relatively low close to limited guidelines for drinking water which limited the sum of pesticides at 500 ng/L. According to the guideline values set by EU-WFD, Somme River present the good quality respect to these five families selected (PAHs, Me-PAHs, PCBs, phthalates and pesticides). However, these contamination levels could affect the aquatic life because they are frequently detected at the values exceeded the guideline values set by CWQG. It is interesting to note that Somme River is a place where there is a breeding fish and local fishing activities. The generally gap information could be a major source uncertainty in evaluation of water quality and so on the decision that the authorities could take. Nevertheless, there is growing evidence that these kinds of study are potentially important sources of information which contribute to the quality evaluation of the aquatic ecosystems and some decision of local authority (i.e. fishing activities, breeding fish).

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