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Alkylphenol and bisphenol A contamination of urban runoff: an evaluation of the emission potentials of various construction materials and automotive supplies

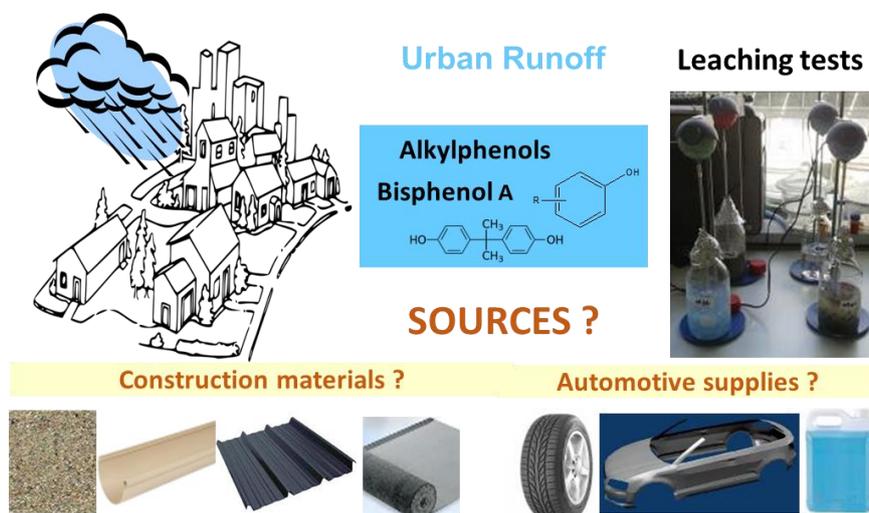
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GRAPHICAL ABSTRACT



KEYWORDS

Alkylphenols, Bisphenol A, Automotive supplies, Construction materials, Emission factor, Leaching test, Urban runoff.

ABSTRACT

Alkylphenol (AP) and bisphenol A (BPA) contamination of urban runoff has already been established. Potential sources of these contaminants in runoff are endogenous to the urban watershed and are mainly related to traffic and leaching from construction materials. This article summarizes the results of experimental work carried out on a selection of building materials, automotive materials and consumables, which can be in contact with rain, to assess their potential emission of alkylphenols, alkylphenol ethoxylates and bisphenol A into runoff. 36 samples of materials, new and used, across 7 major families of building materials (PVC, concrete, polycarbonate, SBS modified bitumen, drainage materials) and automotive materials (body, tires) were subjected to leaching tests with methanol and then, for a selection of them with water. Automotive fluids were also directly analysed. The results demonstrate the ubiquitous presence of APs and BPA in urban materials and their extractable character with water. The compounds with the strongest emission rates were bisphenol A and nonylphenol. The most important BPA emissions into water (10 to 300 ng/g) were measured for polycarbonate, tires, some car bodies and PVC. Nonylphenol was leached in large quantities (1 to 10 ng/g) from PVC, some concretes, SBS modified bitumen and body samples. The tires were the only materials having a strong emission in octylphenol (1 to 10 ng/g). The analysis of automotive fluids confirmed the presence of BPA (0.3 to 5.5 g/L) and nonylphenol (2.3 to 2.9 mg/L) in brake fluids, while APs and BPA were found at trace levels in coolants and windscreen washer.

INTRODUCTION

Alkylphenols (APs), alkylphenol ethoxylates (APEOs) and bisphenol A (BPA) are synthetic compounds used in the production of numerous industrial products such as coatings, agricultural pesticides, oils and fuels, metals, plastics and paints (Hellgren et al. 1999; ECB 2002, 2008, 2010; OSPAR 2003; INERIS 2010, 2011, 2016; ANSES 2011). Their presence in air, soil and water as a result of emissions generated by anthropic activities has been documented at significant concentrations (Vethaak et al. 2005; Peng et al. 2007; Micic and Hofmann 2009; Navarro-Ortega et al. 2010; Bressy et al. 2011; Wang et al. 2011; Wu et al. 2013; Gasperi et al. 2014). Epidemiological studies carried out on these molecules proved their toxicological potential as endocrine disruptors in humans and animals (Sohoni et al. 2001; Harreus et al. 2002; Park and Choi 2007; Soares et al. 2008; Benachour and Aris 2009; Mørck et al. 2010). Recently, the reduction of human exposure to the substances listed as endocrine disruptors has become a subject of prior interest within the European Union. Therefore, the implementation of new regulations and the achievement of voluntary agreements with industrials are leading to a gradual decrease or even the restriction in the use of some of these substances. This is the case of nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) for which the use has been prohibited by the European Directive 2003/53/CE (European Union 2003) at

concentrations above 0.1% for several uses (industrial and institutional cleaning products, domestic cleaning products, textiles and leather processing, emulsifier in agricultural teat dips, metal working, cosmetic products, co-formulants in pesticides and biocides). BPA is prohibited since 2011 (European Union 2011) by the European Union in the manufacture, import and placing on the market of baby bottles. The French law No. 2012-1442 (2012) extends this prohibition by suspending the manufacture, importation, exportation and placing on the market of any food packaging containing BPA. This prohibition became effective on 1 January 2015. Nonylphenol and octylphenol (OP) are on the list of priority substances in the Water Framework Directive 2000/60/EC (European Union 2000). BPA is listed in Annex III of the same Directive as a substance subject to review for identification as possible priority substance or priority hazardous substance. Despite these efforts, the fields of application for APs and BPA remain relatively numerous, and their emissions into the environment are far from being removed.

The occurrence of APs and BPA in urban runoff water has been reported in some studies (Corsi et al. 2003; Aabøe et al. 2004; Fries and Püttmann 2004; Rule et al. 2006; Eriksson et al. 2007; Kueh and Lam 2008; Björklund et al. 2009; Becouze-Lareure 2010; Bressy et al. 2011; Zgheib et al. 2012; Gasperi et al. 2014). Concentrations of APs and BPA vary considerably between studies. For NP and OP these values are generally higher than the Environmental Quality Standards fixed to 0.3 and 0.1 µg/L (European Union 2008). The authors agree that urban construction materials (concrete, paints, plastics) as well as the automotive sector are important pathways of AP and APEO in stormwater runoff (Björklund et al. 2009; Bressy et al. 2011; Zgheib et al. 2012; Gasperi et al. 2014). However, given the diversity of materials compositions and the very general nature of the information reported in the literature about the applications of APs, APEOs and BPA (Hellgren et al. 1999; ECB 2002, 2008, 2010; OSPAR 2003; INERIS 2010, 2011, 2016; ANSES 2011), it is quite difficult to characterize the actual risk of emission of these compounds in the urban environment. Potential sources of these contaminants in runoff waters still remain badly identified. Their evaluation is difficult as these compounds are present at trace concentrations in the industrial products. The formulation of these products generally falls within the trade secret, is likely to differ significantly from one producers to another and may have evolved rapidly over the last years.

The present study has been conducted within the framework of the French research programs: INOGEV (Innovations for a sustainable management of urban water-knowledge and control of the contamination of urban stormwater) and TVGEP (Conception of green roofs for urban stormwater management). These projects aimed at improving knowledge, assessment tools and management of stormwater pollution as part of a multidisciplinary approach. In this context, special attention was paid to APs and BPA emissions. The aim of this paper is to provide deeper insight on the identification and the prioritization of primary sources of APs, APEOs and BPA into urban runoff so as to guide strategies of source reduction and provide inputs for SFA models. It is based on an experimental approach, carried out for a wide array of urban and automotive

materials ($n=47$). Leaching tests in both methanol (MeOH) and water were performed in order to identify the presence of APs and BPA, and their potential release into water.

MATERIALS & METHODS

Selection of urban materials and automotive supplies.

Urban materials and automotive supplies have been selected taking to account: literature review about the applications and uses of BPA, APs and APEOs (Hellgren et al. 1999; ECB 2002, 2008, 2010; OSPAR 2003; INERIS 2010, 2011, 2016; ANSES 2011), market research analysis focused on typical building materials used in France (MSI Reports Ltd 2006, 2007, 2009, 2010, 2011) and safety data sheets for automotive supplies.

APs are used mainly as a raw material for APEOs production. In addition, APs are used in the preparation of phenolic resins, polymers, heat stabilizers, antioxidants and curing agents (Hellgren et al. 1999; ECB 2002; OSPAR 2003; INERIS 2011, 2016). APEOs are principally used as emulsifying, wetting, dispersing or stabilizing agents. They are or have been widely employed in polymer industry, civil engineering, paint production and textile industry (ECB 2002; OSPAR 2003). BPA is used as a raw material for the manufacture of polycarbonate (PC) and epoxy resins (EPs) and as a precursor of flame retardants (Tetrabromobisphenol A (TBBPA), tetrachlorobisphenol A (TCBPA) and bisphenol A bis(diphenyl phosphate) (BDP)) (ECB 2010). BPA is also used as an antioxidant in manufacturing of plastics such as polyvinylchloride (PVC) (ECB 2010; INERIS 2010; ANSES 2011). Table 1 summarizes the uses of bisphenol A, nonylphenol, octylphenol, nonylphenol ethoxylates and octylphenol ethoxylates (OPEOs) in the manufacture of urban materials and automotive supplies likely to come into contact with rainwater.

Based on Table 1, six major families of construction materials (PVC, concrete, polycarbonate, drainage materials used in green roofs, polymer modified bituminen sealing membranes and lacquered steel), 2 families of automotive supplies (tyres and car bodywork) and 3 types of automotive fluids (brake fluids, windshield washer fluids and coolants) were chosen for this study.

French market studies (MSI Reports Ltd 2006, 2007, 2009, 2010, 2011) show that PVC, lacquered steel, polycarbonate and SBS waterproofing membranes are construction materials that have been widely used over the last decades in the building envelope. PVC represented in 2011 62% of the window frame market, 54% of shutters and 21% of doors (frame and panels). Polycarbonate is used in 27% of porch roofs. Bituminous membranes accounted for 74% of the sealant-roofing market in 2005, of which 80% are elastomeric bituminous membranes made of SBS (styrene butadiene styrene) modified bitumen and 20% are plastomeric bituminous membranes made of APP (atactic polypropylene) modified bitumen. Lacquered aluminum and lacquered steel are widely present in the residential, commercial and industrial sector at the level of roofs, cladding and joinery.

Table 1. Uses of APs, APEOs and BPA and applications in the manufacture of urban materials and automotive supplies likely to come into contact with rainwater (Hellgren et al. 1999; ECB 2002, 2008, 2010; OSPAR 2003; MSI Reports Ltd 2006, 2007, 2009, 2010, 2011, INERIS 2010, 2011, 2016; ANSES 2011)

	Uses	Applications
BPA	Production of polycarbonate	In construction sector as sheets for roofing, conservatory glazing, green house glazing, cover for solar panels, cladding, verandas. In automotive sector as headlamp, bumpers, transparent and retractable roof modules, radiator grills, windstops in convertibles.
	Production of epoxy resins	Epoxy resins are employed as composite floor coating, coated steel reinforcement, coated metal surfaces, anticorrosion paints for vehicles (undercoat).
	Antioxidant and inhibitor in PVC production	PVC is used in manufacturing of several construction materials such as windows, doors, cladding, pipes, gutters, roller blinds.
	Production of tetrabromobisphenol A (TBBPA)	TBBPA is used as precursor of flame retardants and antioxidant in brake fluids.
	Production of phenolic resins	Use as adhesives and tackifiers in the tyre rubber industry (SBR, EPDM, BR*).
NP	Production of NPEOs	NPEOs are used as : <ul style="list-style-type: none"> - Dispersant additives used in manufacture of plastic materials polymerized by emulsion as SBR, PVC, polyvinyle acetate. - Manufacture of nonylphenol ether sulphates used as additives of certain types of concrete. - Manufacture of additives used for fuels and lubricants oils. - Air-entraining admixture in concrete. - In the bitumen emulsion. - Wetting agents, emulsifiers and dispersants in lacquers, varnishes and water paints.
	Production of phenolic resins	Use as adhesives and tackifiers in the tyre rubber industry (SBR, EPDM, BR*).
	Catalyst in the curing of some epoxy resins	Epoxy resins are employed as composite floor coating, coated steel reinforcement, coated metal surfaces, anticorrosion paints for vehicles (undercoat).
	Production of tri-(4-nonylphenyl) phosphate (TNPP)	TNPP is often used in a water emulsion to stabilize polymers as SBR, EPDM, Vinyl polymers, polystyrene, polycarbonate.
NP, OP	Production of phenolic resins	Used as adhesives and tackifiers in the tyre rubber industry (SBR, EPDM, BR*).
OP	Production of OPEOs	Emulsifier agents used in the manufacture of polymers such as acrylics and vinyl acrylics resins (resins used as paints for roofing, facade and anti-corrosion).

*SBR: Styrene-Butadiene Rubber, EPDM: Ethylene propylene diene monomere, BR: polybutadiene Rubber

Concerning automotive sources, we focused on the parts and fluids that are essential to the good functioning of the car and are of widespread use. Thus car care products, like polish or waxes, have not been studied here even if they may content APEOs. Motor oils and fuels, although potential sources of AP (Diehl et al. 2004), have not been studied in this work due to analytical impossibilities.

A total of 29 urban materials, 7 automotive supplies and 11 automotive fluids, new and used ones, were collected (see Table 2). New urban materials were purchased in a DIY store of materials and constructions products. Old urban materials, tyres and bodyworks were collected at waste collection centers. Automotive fluids were purchased in supermarkets, selecting a variety of brands, ranging from the first price to the high end. Except for PVC and concrete, 1 to 4 samples were tested per material or supply family so as to take account of the variety of products in use, and both in new and in used state to identify a possible evolution over product formulation. For PVC and concrete families, a larger number of samples (8 for PVC materials and 12 for concrete materials) were chosen in order to take account of the multiple uses in urban areas and the different formulations.

Leaching tests.

Selected materials and supplies were first subjected to leaching tests with methanol in order to identify the presence or absence of extractable APs, APEOs and BPA. Though not representative of environmental conditions, methanol extraction gives an overview of the prevalence of these contaminants in urban materials. Based on these results a selection of relevant materials was done. Their potential of emission into rainwater was further tested through leaching tests with deionised water. Automotive fluids were directly analyzed after dilution (1/10) in ultrapure water and extraction.

Prior to the leaching experiments, each sample was cleaned with tap water, ultrapure water and finally rinsed with methanol in order to remove surface contamination of the materials. PVC materials, bituminen SBS sealing membranes, drainage layers and geotextile were finely chopped to obtain pieces smaller than 4 mm. Concrete materials were ground, sieved to 2 mm and subsequently freeze-dried for 48 h using an Alpha 1-2 LD Plus (Bioblock Scientific). Tyres were cut into fine shavings. For bodywork and steel panel, pieces of 3.5 x 3.5 cm and 5.0 x 3.0 cm were used for methanol and water leaching tests respectively. All samples were stored in glass bottles in the dark until analysis.

To date, there are no standards to characterize the emission of organic compounds by the urban materials and automotive supplies. So, leaching tests were performed following the recommendation from the standard NF EN 12457-2 (AFNOR 2002). Adaptations of these standard methods were necessary for the specificity of our study. Leaching tests were carried out in static conditions with both methanol and water as leaching agent. Methanol was used as leaching reagent in order to facilitate the extraction of APs, APEOs and BPA. To avoid degradation of the studied molecules, all leaching tests were conducted in dark glass bottles, at room temperature (20°C), under stirred conditions and over 24 h for methanol leaching tests and 48 h for water leaching tests. Blank samples (methanol and ultrapure water placed in the same experimental conditions) were subjected to each test series.

Table 2. Summary of the materials subjected to leaching tests (with methanol and/or water) or direct analysis

Family	Material or supplie		Leaching tests		Direct analysis
	Type	Condition	Methanol	Water	
PVC	Gutters	New 1	X	X	
		New 2	X	X	
		New 3	X	X	
		Old 1	X	X	
		Old 2	X	X	
	Pipe	Old	X		
	Roller blinds	New	X	X	
Concrete	Sidewalks	Old 1	X		
		Old 2	X	X	
		Old 3	X		
		Old 4	X	X	
	Reinforced	New	X		
	Conventional	New	X		
		Old 1	X		
		Old 2	X		
	Structural	New	X		
	Sewer pipe	Old	X		
	Slab	New	X		
Roof tile	Old	X			
Polycarbonate	Panel	New		X	
Drainage	Layer in polypropylene	New	X	X	
	Layer in polyamide/ polyethylene (PO/PE)	New	X		
	Layer in polystyrene	New	X	X	
	Filtering geotextile	New	X	X	
	Sealing membrane 1	New	X	X	
SBS	Sealing membrane 2	New	X		
	Sealing mat	New	X	X	
Tyres	Moto	Old	X		
		Old 1	X	X	
		Old 2	X	X	
Steel	Lacquered	Old 3	X		
		New	X	X	
		Old	X	X	
Bodywork	Roof	Old	X	X	
	Hood	Old	X	X	
Automotive fluids	Brake fluid 1	New			X
	Brake fluid 2	New			X
	Brake fluid 3	New			X
	Windshield washer fluid 1	New			X
	Windshield washer fluid 2	New			X
	Windshield washer fluid 3	New			X
	Windshield washer fluid 4	New			X
	Coolant 1	New			X
	Coolant 2	New			X
	Coolant 3	New			X
Coolant 4	New			X	

With the exception of drainage materials, lacquered steel leaching and bodyworks, the leaching tests were performed using a Liquid/Solid (L/S) quotient of 10. Methanol leaching tests were carried out with 10 g of sample and 100 mL of methanol. For water leaching tests, the sample mass and the water volume used were multiplied by five (50 g of sample with 500 mL of ultrapure water) in order to have a sufficient volume to extract BPA, APs and APEOs and perform additional analysis such as pH, conductivity and dissolved organic carbon (DOC). L/S-quotient were modified for the leaching tests conducted on materials with low density to ensure total immersion of the samples (polystyrene layer, polyamide/polyethylene (PO/PE) drainage layer and filtering geotextile). The L/S-quotient for methanol leaching test was 80 for the layer of polystyrene (1 g polystyrene in 80 mL methanol) and 20 for the PO/PE drainage layer and filtering geotextile (5 g of PO/PE drainage layer in 100 mL of methanol and 1 g of geotextile drainage into 20 mL methanol). L/S-quotient used for water leaching test was 60 for the layer of polystyrene (9 g of polystyrene in 527 mL water) and 50 for the filtering geotextile (20 g of filtering geotextile in 1000 mL water). Leaching test for steel plate and the car bodywork were performed using Liquid/Surface (L/S_{urf}). L/S_{urf} employed for leaching tests in methanol and water was respectively 1.6 mL/cm² (12 cm² of sample in 20 mL of methanol) and 8 mL/cm² (60 cm² of sample in 500 mL of water).

Analysis.

The analytical method was first developed and validated by Cladière et al. (2013). Details are given in the Supplementary Information. Briefly, after filtration and evaporation for methanol eluates and after solid phase extraction (SPE) for water eluates, samples were analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS) using an ACQUITY UPLC/TQD (Waters) equipped with an electrospray interface. The quantitation were obtained by internal calibration with surrogates (deuterated bisphenol A -BPA-d16-, n-nonylphenol-n-NP-, n-monoethoxylate-n-NP1EO-, n-nonylphenol monoethoxy acetic acid -n-NP2EC-) added before injection. Extraction recoveries on SPE cartridges were calculated using 10 replicates (5 samples, 5 spiked samples). The obtained values for this method were: 108 ± 14% for BPA, 80 ± 20% for NP, 72 ± 18% for NP1EO, 90 ± 15% for NP2EO, 91 ± 18% for NP1EC, 82 ± 17% for OP, 67 ± 12% for OP1EO and 73 ± 9% for OP2EO. Also, quality parameters of the instrumental method such as linearity, sensitivity and repeatability were followed and resumed in the Table 3. The limits of quantification (LQ) have been determined for each molecule according to the French method-validation standard NF XPT 90-210 (AFNOR 1999). The LOQ values used for this analysis were: 13 ng/L for bisphenol A (BPA), 14 ng/L for 4-nonylphenol (NP), 16 ng/L for nonylphenol monoethoxylate (NP1EO), 4 ng/L for nonylphenol diethoxylate (NP2EO), 5 ng/L for nonylphenoxy acetic acid (NP1EC), 10 ng/L for 4-octylphenol (OP), 8 ng/L for octylphenol monoethoxylate (OP1EO) and 8 ng/L for octylphenol diethoxylate (OP2EO). Cladière et al. (2013) evaluated the measurement uncertainties of the method. For 4-NP, NP1EC, and NP2EO, the relative deviations were within the 0–15 % range and

the maximum values reached 20 % for 4-NP. The measurement uncertainty of BPA and NP1EO were evaluated respectively at 10 and 14 %. The developed analytical method was validated by participating in two inter-laboratory tests. The first one (2012) concerned the BPA and the 4-NP within the framework of the Proficiency Tests according to WFD requirements (PT-WFD). The Z-score was 0.71 for the BPA and -0.52 for the 4-NP. The second one (2018) was organized by Ineris and the Z-scores were between -1.95 and 1.67 for BPA, 4-NP, NP1EO, OP, OP1EO and OP2EO.

Table 3. QA/QC parameters of the analytical methods

	Linearity R ²	LOD (ng) instrument*	LOQ (ng) instrument*	LOQ (ng/L) sample*	Extraction efficiency (%)***	Repeativity (%)**	Instrumental repeatability (%)***	Method repeatability (%)***
BPA	0.987-0.996	0.003	0.010	13	108	5.2	10	25
4-NP	0.977-0.994	0.003	0.011	14	80	13.2	17	27
NP1EO	0.989-0.999	0.004	0.013	16	72	12.7	14	23
NP2EO	0.987-0.999	0.001	0.003	4	90	6.3	7	14
NP1EC	0.994-0.999	0.001	0.004	5	91	2.7	4	6
OP	0.974-0.992	0.002	0.008	10	82	8.2	17	54
OP1EO	0.998-0.999	0.002	0.006	8	67	7.0	-	-
OP2EO	0.991-0.999	0.002	0.006	8	73	7.1	-	-

* Instrumental LOD and LOQ were calculated using the statistical errors between observed and theoretical concentrations of 5 different calibration curves ($LOD = (b + 3 \times dev_{b})/a$; $LOQ = (b + 10 \times dev_{b})/a$) ; LOQ of sample was calculated taking into account injected and extracted volumes ratios

** Repeativity was calculated on the analysis of the 5 different standards solutions

*** Instrumental and method repeatability from Cladière et al. (2013)

Table 4. Values of pH, conductivity ($\mu\text{S}/\text{cm}$), dissolved organic carbon (DOC- mg/L), APs, APEOs and BPA concentrations (ng/L) from eluates of water leaching test from construction materials and automotive supplies

Materials	Type	pH	σ	DOC	BPA	4-NP	NP1EO	NP2EO	NP1EC	OP	OP1EO	OP2EO
	<i>Blanks (mean)</i>	6.3	6.0	0.4	58	30	41	40	3	5	<LQ	2
PVC	New gutter 1	8.3	41	30	570	420	78	85	11	17	<LQ	5
	New gutter 2	8.3	59	8.2	430	220	19	58	9	12	<LQ	1
	New gutter 3	7.6	29	3.0	1 000	660	500	390	180	68	12	14
	Old gutter 1	8.4	32	20	1 000	220	30	47	16	6	<LQ	2
	Old gutter 2	8.1	64	8.0	2 200	310	20	69	21	11	<LQ	2
	New roller blind	8.5	40	1.1	390	150	28	43	15	10	6	3
	Old roller blind	8.1	31	1.6	1 500	250	23	35	16	7	<LQ	2
Concrete	Sidewalk 2	12	4 800	5.5	820	680	99	180	2 300	14	<LQ	7
	Sidewalk 4	12	5 800	6.1	102	390	52	57	210	26	9	7
Polycarbonate	Panel	6.6	16	0.5	15 000	61	110	63	4	4	<LQ	2
Drainage	Layer in polypropylene	7.0	19	0.8	250	170	29	34	3	9	<LQ	2
	Layer in polystyrene	7.2	12	0.4	80	46	24	44	7	5	<LQ	2
	Filtering geotextile	7.1	15	0.3	230	88	23	37	9	8	<LQ	2
SBS	Sealing membrane 1	7.9	130	6.8	300	690	11	12	190	28	<LQ	3
	Sealing membrane 2	7.9	81	10	180	800	24	22	27	5	<LQ	1
Tyre	Car 1	7.1	78	46	4 100	790	92	38	21	170	<LQ	<LQ
	Car 2	6.7	60	36	2 000	200	<LQ	14	<LQ	900	<LQ	<LQ
Steel	Lacquered	6.7	19	1.1	95	32	30	24	3	6	<LQ	1
Bodywork	Door	6.9	13	0.7	4 000	110	33	60	17	16	40	58
	Roof	6.8	12	0.6	43 000	100	68	47	7	16	<LQ	2
	Hood	7.0	7.0	0.9	1 500	37	180	200	110	14	8	17

RESULTS

Occurrence of alkylphenols and bisphenol A in the selected materials and consistency with literature data

Methanol leaching tests were carried out in order to identify the presence or absence of extractable APs, APEOs and BPA in selected materials. Though not representative of environmental conditions, methanol extraction gives an overview of the prevalence of these contaminants in urban materials. Indeed, while information is available on the potential use of these compounds in the production process of many urban materials there is a great uncertainty on the actual extent of their occurrence, due to the many different possible formulations, the use of alternative compounds and possible evolution of formulations over time.

Extractible content profiles (mass of pollutant extracted per mass or surface of materials) of APs, APEOs and BPA were established (Figure 1) based on methanol leaching tests for the whole range of construction materials and automotive supplies collected.

They confirm the widespread occurrence of APs, APEOs and BPA in the materials. At least one compound is quantified in significant concentration in each sample. Highest MeOH extractible contents are observed for NP and BPA whereas OPEOs and NP1EC are not frequently quantified. However, the extractible contents vary in a wide range from one sample to another within a same family of materials, and from one family to another.

PVC materials. Eight PVC materials have been tested (see Table 2). All of them leached significant quantities of BPA, yet with variable loads from one sample to another (4 to 70 ng/g). Most of the PVC samples also leached lower quantities of NP (1 to 12 ng/g) and NPEOs (, NP1EO: 1 to 6 ng/g). OP and OPEOs extracts were not significant compared to blanks. No clear relation was found between the age of the PVC or the type of use (gutter, pipe or roller blind) and the quantity of pollutants extracted. PVC emission profiles are in accordance with the information reported in the literature. Uses of BPA have been reported as antioxidant in PVC processing, as belonging to the pack of additives for the treatment of PVC, as antioxidant in the production of plasticizers used in PVC transformation, and before 2003, as inhibitor for the polymerization phase of PVC (ECB 2010; INERIS 2010). Regarding the NPEOs, the literature reports their use as dispersant additives during the manufacture of PVC polymerized by emulsion. NP may be used as plastic stabilizer (ECB 2002; INERIS 2011) and APEO as emulsifiers in the manufacture of polymers (Hellgren et al. 1999; ECB 2002; OSPAR 2003).

Elastomeric bitumen and tyres. The three elastomeric bitumen membranes (SBS modified bitumen waterproofing membranes) had the highest NP extraction rates out of all tested materials (400 to 2 400 ng/g). Two out of the four tyres also showed noticeable NP extracts in the range of 60 ng/g. NP is used for the synthesis of nonylphenol ether sulfates, which in turn is used as an emulsifier during the production of styrene and styrene butadiene (ECB 2002). NP takes also part into the production of phenolic resins as a raw

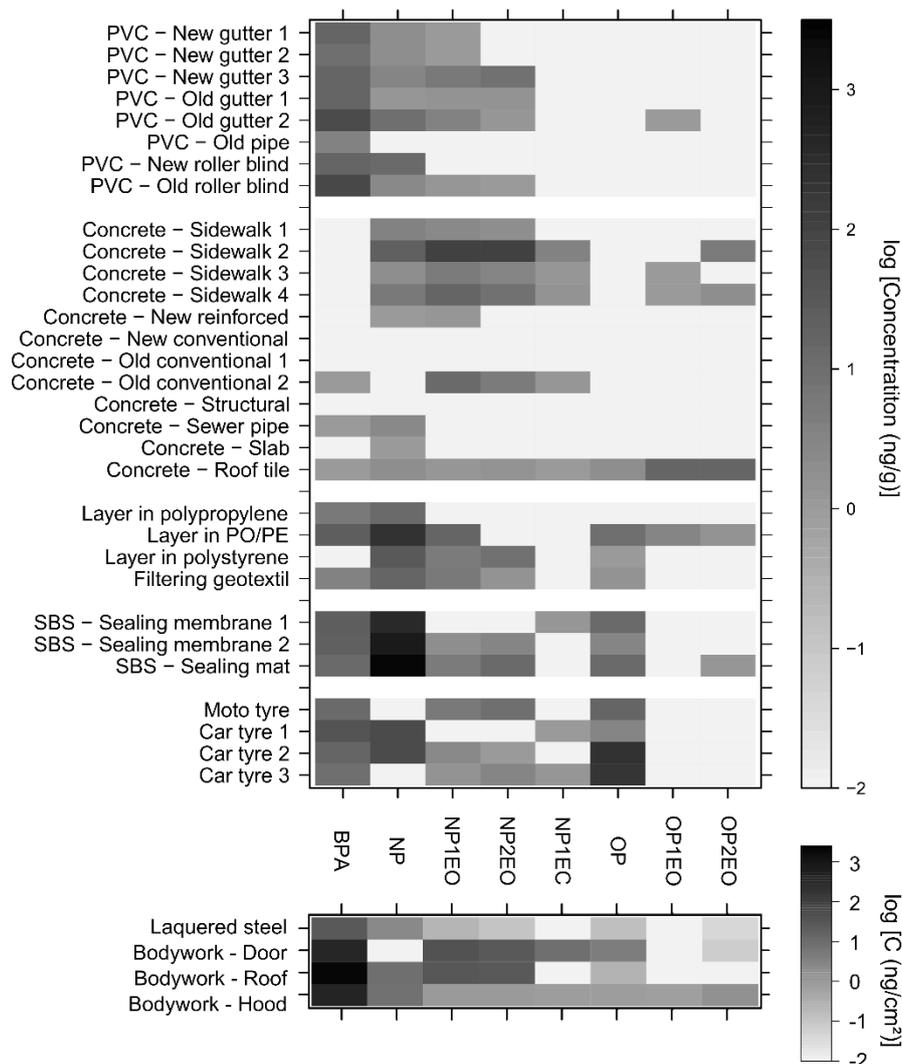


Figure 1. Emission profiles in methanol of alkylphenols, alkylphenol ethoxylates and bisphenol A per gram or per surface of material

material "monomer" and in the production of TNPP (ECB 2002), a stabilizer for synthetic rubber (SBR, EPDM) used in tyres (ECB 2008). The presence of NP in tyres is likely due to: NP unreacted during polymerization of the resin, NP present as an impurity in the TNPP (in up to 3%) and NP formed by hydrolysis of TNPP (ECB 2002, 2008).

Tyres followed by elastomeric bitumen (SBS), showed the highest OP loads, but again results vary in a wide range from one sample to another reflecting differences in formulations: 195 and 270 ng/g for two out of the four tyres, 3 to 15 ng/g for the three SBS membranes and the two other tyres. OP is employed as intermediate in the manufacturing of phenolic resins, used as adhesion promoters in the synthetic rubbers of tyres. They are added to the rubber up to 1.5%, which correspond to a maximum OP concentration in tyres of 0.3% (OSPAR 2003).

Tyres and elastomeric bitumen membranes also showed relatively stable BPA loads, comparable to PVC (tyres: 11 to 43 ng/g, SBS membranes: 14 to 23 ng/g). In tyres, BPA is used as antioxidant in the matrix of the tyres polymer (ECB 2010). We found no information on the use of OP or BPA in the manufacture of SBS membranes.

Drainage Materials. The four tested drainage and filter material are of very different composition which leads to large differences in the profiles. NP was the compound leached at the highest level for all 4 materials (12 to 240 ng/g) followed by the BPA for 3 of the 4 drainage materials (4 to 25 ng/g). The main source of NP in these materials is likely its direct use as a stabilizer in the manufacturing of some plastic materials (INERIS, 2011). The OP extractions were between 2 to 5% of NP extracts which is consistent with literature reports on the involuntary production of OP during the synthesis of commercial NP at a rate of 3 to 5% (OSPAR 2003). BPA was released by 3 of the 4 drainage materials tested (polypropylene drainage layer, PO/PE drainage layer, filtering geotextile). These materials consist mainly in synthetic polymeric products. As BPA is used as a monomer in the synthesis of different polymers (polyester carbonate, polyarylates, polysulfones, polyols, etc.) (INERIS 2010; ANSES 2011) we can suppose that the polymers constituting the drainage materials are the source of the BPA.

Concrete Materials. Among the twelve samples of concrete, the four sidewalk samples showed similar MeOH emission profiles. They mainly leached NPEOs (2 to 93 ng/g) and NP (2 to 21 ng/g). Occurrence of NPEO in 7 out of the 12 concrete samples can possibly be assigned to their use as air-entraining admixture (Ramachandran 1995; ECB 2002; Edeskär 2006; Togero 2006; Månsson et al. 2008) while NP and NP1EC contents may be attributed to the degradation of NPEO under aerobic conditions. For BPA, OP and OPEOs, no information was found on their use in the field of concrete production. Their sporadic occurrence may be due to contributions from the external environment (air and/or rain).

Metallic Materials. With regard to lacquered steel material and bodyworks, the MeOH emission was calculated per area unit. These materials mainly emit BPA and NPEOs. Extractible contents show however a large discrepancy between the 4 samples with levels ranging from 26 to 2 000 ng/cm² for BPA, from 0.2 to 39 ng/cm² for NP1EO and from 0.1 to 27 ng/cm² for NP2EO. These variations reflect the variety of formulations of paints and lacquers. The presence of BPA can be attributed mainly to the direct use of BPA in paint hardener and in the synthesis of polyols used in the manufacture of polyurethane resins which are often used in the pigment bases and varnishes applied in the topcoat bodywork (Laout 2009; ANSES 2011). NPEOs are used in paints and varnishes as wetting agents, emulsifiers and dispersants (ECB 2002). No direct use of OP and OPEO is reported in the literature for industrial varnishes and lacquers.

Water leaching results.

Based on methanol extraction results, 20 samples out of 35 with a proven content of at least one of the pollutants of interest, and representative of the diversity of methanol extraction profiles, were selected for further leaching test with deionised water (see Table 1). A 21st sample consisting in a sandwich panel in polycarbonate was added. This material was not subjected to preliminary methanol leaching as polycarbonate is known

to be produced by polycondensation of bisphenol A and there is already scientific evidence of the release of BPA by materials made from polycarbonate (Yamamoto and Yasuhara 1999; Le et al. 2008; Kubwabo et al. 2009; Cooper et al. 2011).

Concentration and physico-chemical data for all water leaching tests is given in Table 4. pH values for the blank samples vary from 5.4 to 6.8 with a mean of 6.2. Similar values were measured in eluates from drainage materials, lacquered steel, bodyworks, polycarbonate panel and tyres (pH 6.7-7.2). PVC materials, concrete sidewalks and SBS sealing membranes imposed in the water a basic pH (7.9-12). The highest pH values were measured in the eluates from the leaching of concrete slabs (pH 12). Conductivity values for the blank samples (2.0 and 16 $\mu\text{S}/\text{cm}$) were modified by most of the materials. The highest conductivity values were measured in the eluates from concrete sidewalks (4 800 - 5 800 $\mu\text{S}/\text{cm}$), followed by SBS membranes (81 to 130 $\mu\text{S}/\text{cm}$) and tyres (60 to 78 $\mu\text{S}/\text{cm}$). Dissolved organic carbon (DOC) for two-thirds of the eluates were higher than DOC of the blank samples (<LQ and 0.9 mgC/L). The lower concentrations of DOC were measured for lacquered steels and drainage materials. For PVC materials, DOC concentrations in eluates were highly variable and were up to 30 times higher than those of blanks. DOC concentrations in eluates for SBS membranes and tyres were respectively 14 to 21 and 39 to 50 times higher than the blank sample concentrations.

All samples leached BPA, NP and OP concentrations superior to the blanks, while this was the case of 17/21 samples for NP1EC, 13/21 samples for NP2EO and only 8/21 samples for NP1EO and OP2EO, and 5/21 for OP1EO. This confirms that the considered compounds are extractable by water and therefore present a risk of transfer to runoff. BPA was mainly leached from polycarbonate panel (15 000 ng/L), bodywork (1 500 to 43 000 ng/L), tyres (2 000 to 4 100 ng/L) and PVC materials (390 to 2 200 ng/L).

NP was leached at high concentration from PVC materials (150 to 660 ng/L), tyres (200 to 790 ng/L), SBS sealing membranes (690 to 800 ng/L) and concrete sidewalk (390 to 680 ng/L). Significant NP1EC concentration was observed for sidewalk concretes (210 to 2 300 ng/L), SBS sealing membranes (190 ng/L), new PVC gutter 3 (180 ng/L) and hood car (110 ng/L). NP1EC is likely produced by the aerobic degradation of long chain NPEOs. OP was the compound leached at the highest level for tyres (170 and 900 ng/L) and new PVC gutter 3 (68 ng/L). NPEOs were leached mainly by new PVC gutter 3 (NP1EO: 500 ng/L and NP2EO: 390 ng/L), car hood bodywork (NP1EO: 180 ng/L and NP2EO: 200 ng/L), concrete sidewalk 2 (NP1EO: 99 ng/L and NP2EO: 180 ng/L) and polycarbonate panel (NP1EO: 110 ng/L). OPEOs were leached by door bodywork (OP1EO: 40 ng/L, OP2EO: 58 ng/L) and new PVC gutter 3 (OP1EO: 12 ng/L and OP2EO: 14 ng/L).

Low concentrations of all pollutants were measured for the lacquered steel construction panel while bodywork panels, also made of lacquered steel, showed higher concentrations for all compounds and especially for BPA (1 500 to 43 000 ng/L). This might be linked to specificities in the formulation of car paints and lacquers, but possibly also to the exposition during the life of the car to care products containing BPA or APs.

Concentrations obtained for drainage materials were in the lower range compared to other construction materials. For two drainage materials leaching tests were conducted with L/S ratios 5 times (geotextile) and 6 times (polystyrene) higher than other materials, which might have induced a dilution effect if the emission is limited by the mass available at the surface or by the diffusion rate. However, based on methanol emission data, the available mass of NP and OP is at least 10 times the mass emitted to water, thus the differences in L/S should not induce a noticeable difference in concentrations. This is not the case for BPA which was leached at similar rates in water and in methanol.

By comparison, median NP concentrations are reported in the range of 100 to 750 ng/l for runoff from residential areas and 780 to 1700 ng/l for road runoff (Bjorklund et al. 2009, Bressy et al. 2011, Gasperi et al. 2014, Flanagan et al. 2017, Zgheib et al. 2012), while NP1EO and NP2EO concentrations are usually lower. Median OP runoff concentration are reported in the range 36-110 ng/L for residential catchments and 150-430 ng/L for road runoff while OPEOs concentrations are at least 10 times lower. Moreover literature data for OP and NP road runoff evidences increased concentrations for high traffic roads (Gasperi et al 2014, Deshayes et al. 2017), which is consistent with traffic related sources. These values are given for reference only since experimental leaching conditions are quite different from real exposition to rainfall in terms of time of contact and L/S ratio. Shorter contact time and lower surface of contact will probably lead to lower concentrations during runoff. We notice however that both the order of magnitude of concentrations and the relative importance of the different pollutants leached during batch experiments are consistent with field data.

Emission profiles in water.

Figure 2 shows the emission profiles in mass of APs, APEOs and BPA emitted in water per mass or per surface of construction materials and automotive supplies. The highest emissions were observed for BPA from polycarbonate panel (140 ng/g). PVC materials mainly leached BPA (3 to 21 ng/g) and NP (1 to 6 ng/g). Tyres showed significant BPA, NP and OP leaching (BPA: 20 to 39 ng/g; NP: 1.5 to 7 ng/g; OP: 2 to 9 ng/g). SBS sealing membranes showed the highest emissions of NP (6 to 7.5 ng/g) and the lowest quantities of BPA (1 to 2 ng/g). Concretes sidewalk mainly leached NP1EC (2 to 22 ng/g) followed by BPA (8 ng/g) and NP (6 ng/g). For drainage and filter layers the main compounds leached were BPA (1 to 9 ng/g) and NP (1 to 2 ng/g). This NP emissions might even be overestimated for the polystyrene layer and the filter layer, due to the higher L/S ratio. Alkylphenol ethoxylates (NP1EO, NP2EO, OP1EO, OP2EO) were quantified at lower quantities (<1 ng/g) for all materials.

With regard to lacquered steel material, important differences are observed between the construction panel, which showed very low emissions, and the car bodywork samples. The highest emission was observed for BPA from bodyworks (10 to 360 ng/cm²).

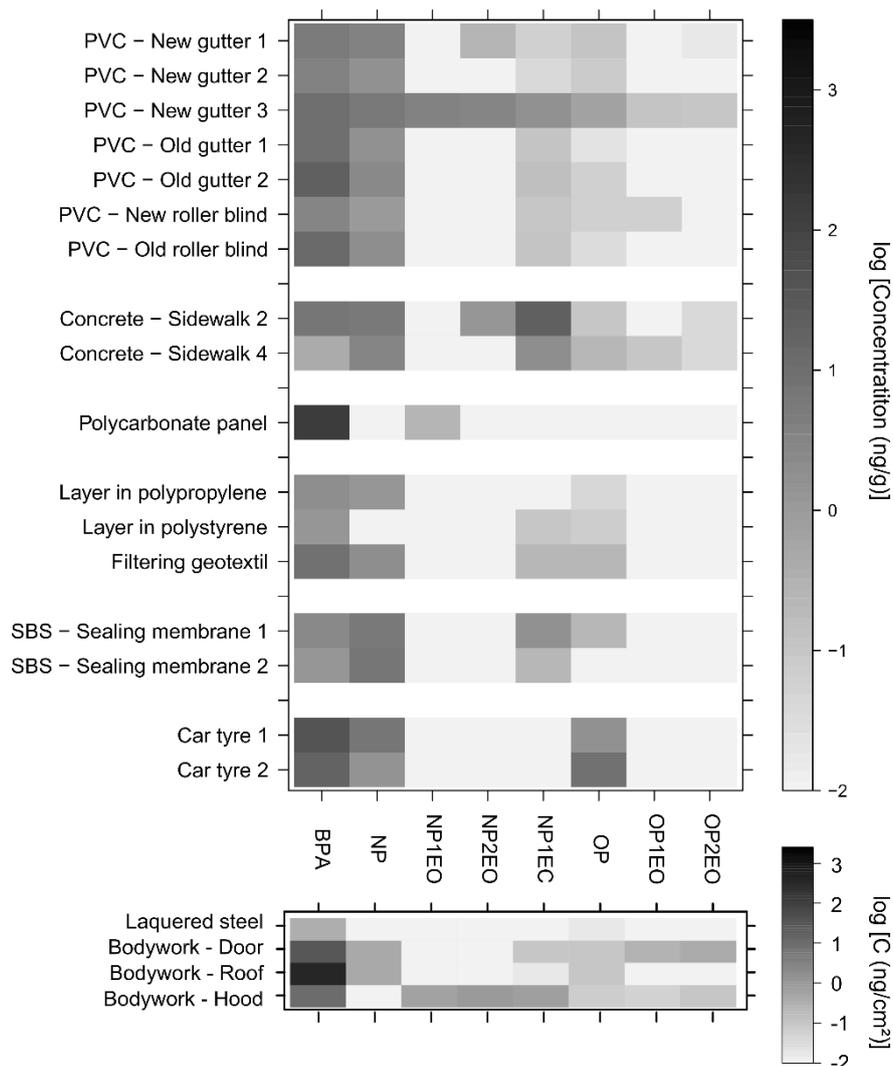


Figure 2. Emission profiles in water of alkylphenols, alkylphenol ethoxylates and bisphenol A per gram or per surface of dry material

Automotive fluids.

Analysis of automotive fluids showed the presence of NP in all the analyzed fluids, with concentrations ranging from 1.1 to 7.5 $\mu\text{g/L}$ for coolants, 2.2 to 5.2 $\mu\text{g/L}$ for windshield washer and 2 400 to 3 900 $\mu\text{g/L}$ for brake fluids. The presence of BPA was observed in a few samples. BPA concentration was high in one of the cooling fluids (1 700 $\mu\text{g/L}$) and extremely high in the three brake fluids (0.3 to 5.5 g/L). BPA is added at concentrations <1% to brake fluids as an antioxidant (ANSES 2011) and the analysis of safety data sheets often confirms its presence.

DISCUSSION

In this study, methanol leaching tests allowed to identify the presence or absence of APs, APEOs and BPA in urban materials and automotive supplies. Water leaching tests helped to identify the urban materials and automotive supplies that can release compounds in the

runoff during rainfall. In most of the samples tested, the leaching tests allowed the detection of at least one of the searched compounds at concentration significantly higher than in the blank samples. Significant differences in emissions were observed between samples of the same kind of material. This variability probably reflects the diversity of formulations and manufacturing processes, as well as inputs from the external environment (in the case of old and porous materials such as concretes that have accumulated APs and or BPA presents in air and/or rain).

The results show ubiquitous presence of these compounds in urban materials and automotive supplies. The compounds released most frequently and at highest concentrations in water leaching tests are bisphenol A and nonylphenol. As expected, high water emissions of bisphenol A were measured for polycarbonate (140 ng/g), the second most important source of BPA among construction materials being PVC (3 to 21 ng/g). BPA is also emitted to water by automobile from tyres (20 to 39 ng/g), and some car bodies (10 to 300 ng/cm²). Nonylphenol was leached in large quantities from PVC materials (gutters and window shutters), some concretes and SBS sealing membranes (1 to 10 ng/g), as well as from tyres. Between the three kinds of automotive fluids studied (brake fluid, washer fluid and coolant fluid), only brake fluid could be a significant source of bisphenol A and to a lesser extent of nonylphenol. Tyres are the only material with high octylphenol emissions (1 to 10 ng/g). However, tyre formulation used by the industry is still changing (INERIS 2016). It is therefore necessary to carry out further studies such as this one on new tyres in order to verify the octylphenol emission by new formulations. Water leaching data indicates that tyres not only contribute to the pollution of the particulate phase of urban runoff through abrasion but also to the dissolved phase. Tyre particles accumulated in stormwater sediments may thus induce long term release in the receiving waters.

A comparison between water emissions and methanol extraction under the same L/S ratio reveals that the level of water extractability varies depending on the considered pollutant but also on the considered product. NP water extraction rates are very low for rubber based materials like SBS modified bitumen membranes and tyres, while it is often comparable to methanol extraction for PVC. BPA shows on the whole more affinity for water than alkylphenols, which is consistent with its lower K_{ow} value (3.2 for BPA and between 3.9 and 4.5 for APs and APEOs).

Though leaching tests were performed on both old and new materials for PVC and for concrete, no clear trend linked to the age of the material could be established. For older materials we could have expected an exhaustion of the concentration in the surface layer, leading to lower water emissions. This phenomenon is probably not visible in our tests due to the shredding of the materials that allows water to enter into contact with the inner part. For PVC, the highest emissions were measured for some old samples. It is very likely that there has been an evolution of PVC formulation over time with a reduction or a substitution of BPA or NP uses.

This work provides an identification of the main primary sources of stormwater runoff contamination by alkylphenols and bisphenol A and a classification of their relative importance. Priorisation of primary sources of alkylphenols and BPA in urban runoff is necessary in order to guide strategies of source reduction. It is also a first step in improving substance flow analysis (SFA models) at catchment scale as it points out major sources to be considered. A methodology for substance flow analysis of nonylphenols in stormwater is presented by Björklund et al. (2007) and Björklund et al. (2010). The authors underline however “the extensive lack of available information on the chemical content in products and emission behaviour in outdoor environments”. They proposed for instance an evaluation of the annual runoff rate of the sum of nonylphenolic compounds (NP/EO) per m² of a polymeric surface (plastic or paint) based on the diffusion theory, taking into account the diffusivity given by Berens (1997) for PVC and a rough estimation of the average NP/EO content of materials. This type of data would need to be defined more precisely taking into account the specificities of runoff emission.

Estimating runoff rates per year and per m² of material based on batch leaching tests is quite hazardous as leaching conditions are limited and very different from runoff conditions (contact surface and contact time are lower during rain than in leaching tests, the composition of the water is also different). In real life urban materials will undergo a succession of dry periods, during which diffusion inside the material can stand place but also photo or thermo degradation at its surface, and relatively quick washoff periods, during which the pollutant present at the surface will leach into water at a concentration depending on the surface concentration and the chemical equilibrium constant. Based on water leaching data, a rough estimation of annual emission rates was attempted for the major sources identified among construction materials and for car bodywork. Two different hypothesis were tested for the extrapolation:

- Hypothesis 1: emission is driven by diffusion only, in this case the total mass emitted is proportional to the square root of the duration of exposure. The masses leached during the 2 days water leaching test are extrapolated to one year by multiplying by $(365/2)^{0.5}$. The mass per unit area of the material is used to convert the annual emission in $\mu\text{g}/\text{m}^2/\text{year}$.
- Hypothesis 2: the mass available at the surface of the material is not limiting the process which is driven by surface desorption, and the equilibrium is supposed to be reached instantaneously. In this case the concentration measured in the water leaching tests is applied to the annual precipitation volume (650 mm in Paris), with a runoff coefficient of 0.8 (to account for initial runoff losses).

Result are presented in Table 5. It is noticeable that both hypotheses lead to relatively similar estimations, with slightly higher emission rates for hypothesis 2. The variations from one sample to another are superior to the difference due to the calculation hypothesis. NP emission rates from PVC gutters (30 to 300 $\mu\text{g}/\text{m}^2/\text{year}$) are superior to

those given by and Björklund et al. (2010) for hard plastic ($2.8 \mu\text{g}/\text{m}^2/\text{year}$). NP emission rates from SBS bitumen sealing membranes (300 to $400 \mu\text{g}/\text{m}^2/\text{year}$) are far superior to the emission considered by Björklund et al. (2010) for roofing and cladding ($3.2 \cdot 10^{-3} \mu\text{g}/\text{m}^2/\text{year}$), but have not been established for the same material. It is very likely however that our emission rates for PVC gutters and SBS membranes are overestimated because of the shredding of the material.

Table 5. Evaluation of annual emission rates for some major sources of BPA, NP and OP

Materials	BPA ($\mu\text{g}/\text{m}^2/\text{year}$)		NP ($\mu\text{g}/\text{m}^2/\text{year}$)		OP ($\mu\text{g}/\text{m}^2/\text{year}$)	
	(1)	(2)	(1)	(2)	(1)	(2)
PVC gutters	60 - 400	200 - 1100	30 - 110	100 - 300	1 - 11	1 - 30
SBS bitumen membranes	60 - 110	60 - 120	300 - 350	300 - 400	11	12
Polycarbonate	5200	7400				
Drainage	12 - 65	10 - 100				
Bodywork	1400 - 4900	750 - 22000	60	30	9 - 14	5 - 6

(1) =hypothesis 1, diffusion only ; (2) = hypothesis 2, desorption equilibrium

This study is a first step in the search of emission sources of APs and BPA in urban areas, particularly in the automotive and urban infrastructure sectors. For a more accurate evaluation of BPA and AP runoff rates we suggest further test under simulated rainfall, after controlled durations of dry exposition. On the other hand, leaching tests were carried out on a limited number of samples and in some cases only on new or old materials. It would seem wise to expand the number of samples and to test new and used samples for each type of material in order to better evaluate the emission of APs and BPAs depending on the evolution of the formulations. In the future, it would seem necessary to move towards a systematic environmental assessment of materials and products prior to commercialization. This assessment may include production, end-of-life and emissions into the environment during the total time of the use of materials. Currently, environmental assessments of materials focus only on manufacturing and end-of-life.

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SUPPLEMENTARY INFORMATION

Detailed analytical procedure

All reagents were at analytical grade. Methanol, dichloromethane (DCM) and ethyl acetate (EtAc) were SupraSolv® reagents (purity of 99.8% from Merck-Millipore), methanol for chromatography analyses was LC-MS grade (99.99%, Fisher Scientific), ultrapure water (18.2 MΩ) was produced from an Elga Ultra system. High quality standards of organic micropollutants were purchased: bisphenol A (BPA, LGC Promochem, 99%), nonylphenol technical pestanal (NP, SIGMA ALDRICH, 94%), 4-nonylphenol-mono-ethoxylate (NP1EO, CIL CLUZEAU, 99%), 4-nonylphenol-di-ethoxylate (NP2EO, CIL CLUZEAU, 99%), 4-nonylphenoxy-acetic-acid (NP1EC, CIL CLUZEAU, 99.9%), 4-tert-octylphenol (OP, CIL CLUZEAU, 99%), 4-octylphenol-mono-ethoxylate (OP1EO, CIL CLUZEAU, 98.5%), 4-octylphenol-di-ethoxylate (OP2EO, CIL CLUZEAU, 99%), 4-n-nonylphenol (n-NP, CIL CLUZEAU, 99.5%), bisphenol A d16 (BPA-d16, LGC Promochem, 98%), 4-n-nonylphenol-monoethoxylate (n-NP1EO, LGC Promochem, 99%), p-nonylphenoxyethoxyacetic acid (n-NP2EC, LGC Promochem, 98%), bisphenol A d6 (BPA-d6, LGC Promochem, 98%), 4-n-octylphenol d17 (n-OP-d17, CIL CLUZEAU, 98%), nonylphenol-monoethoxylate d2 (NP1EO-d2, SIGMA ALDRICH, 99.9%).

All methanol eluates were spiked with 50 µL of surrogate standard mixture (BPA-d6, NP1EO-d2 and n-OP-d17), filtered and evaporated using a rotary evaporator (Rotavap Waterbath B-480, Buchi) to get a final volume of 2 mL. Extracts were concentrated under nitrogen flow and taken up in 500 µL of a mixture MeOH/H₂O (50/50, v/v). Samples were purified by SPE using OASIS® HLB (200 mg, 6 mL, Waters). Following conditioning (3 mL of MeOH and 3 mL of MeOH/H₂O (20/80, v/v)), the samples dissolved in 500 µL of a MeOH/H₂O mixture (50/50, v/v) were deposited on top of the cartridges before they were washed with 3 mL of H₂O and then eluted with 9 mL of a MeOH/DCM/EtAc mixture (40/40/20, v/v/v).

The water eluates were filtrated through a 0.7 µm glass fiber filters (GF/F, Whatman). pH, conductivity, dissolved organic carbon (DOC), alkylphenols and bisphenol A were measured in all samples. pH, conductivity and DOC were determined according to the French standards for water analysis NF XPT 90-210 (AFNOR 1999). Alkylphenols and bisphenol A were extracted by solid phase extraction using OASIS® HLB cartridges (200 mg, 6 mL). Before extraction, samples were spiked with a surrogate standard mixture (BPA-d6, NP1EO-d2, and OP-d17). After conditioning (10 mL of MeOH and 10 mL of H₂O), samples were extracted at 5 mL/min. After drying, elutions were performed using 12 mL of a mixture MeOH/DCM/EtAc (40/40/20, v/v).

The samples were analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS) using an ACQUITY UPLC/TQD (Waters) equipped with an electrospray interface. Chromatographic separation was achieved with an ACQUITY UPLC/BEH C18 column at 40°C and the injection volume was 10 µL. The quantitations were obtained by internal calibration with surrogates (BPA-d16, n-NP1EO, n-NP2EC) added before injection. The mobile phase was composed of ultrapure water (A) and methanol (B), each containing 4.5 mM NH₄OH. Electrospray interface was used in positive ionization mode (ESI+) for NP1EO and NP2EO, along with a negative ionization (ESI-) mode for all other compounds. The limits of quantification (LQ) have been determined for each molecule according to the French method-validation standard NF XPT 90-210 (AFNOR 1999). The LQ values used for this analysis were: 13 ng/L for BPA, 14 ng/L for NP, 16 ng/L for NP1EO, 4 ng/L for NP2EO, 5 ng/L for NP1EC, 10 ng/L for OP, 8 ng/L for OP1EO and 8 ng/L for OP2EO.