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ORIGINAL PAPER

Development of analytical procedures for trace-level determination of polybrominated diphenyl ethers and tetrabromobisphenol A in river water and sediment

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Abstract The aim of this work was to develop procedures for the simultaneous determination of selected brominated flame retardants (BFRs) in river water and in river bed sediment. The target analytes were polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA). To determine dissolved BFRs, a novel mixed-mode solid-phase extraction procedure was developed by combining a hydrophobic sorbent (C_{18}) with a silica-based anion exchange sorbent, so as to overcome the negative artefact induced by dissolved organic carbon. Extraction recoveries exceeded 73% for most analytes, except for BDE-183 and BDE-209 (57%). As regards suspended sediment and river bed sediment, extraction was carried out by means of ultrasonication (recoveries: 73–94%). These procedures, combined to gas chromatography coupled to negative chemical ionisation mass spectrometry (GC-NCI-MS), enabled the determination of BFRs at trace level: 3-160 pg L^{-1} in river water, 5–145 pg g^{-1} in bed sediment. These methods were applied to the determination of PBDEs and TBBPA in a suburban river (near Paris, France). PBDEs were systematically detected in the water column (ΣBDEs, 2,300–4,300 pg L^{-1}); they partitioned between the dissolved and particulate phases and BDE-209 was the dominant congener, followed by BDE-99 and BDE-47. TBBPA was detected in the dissolved phase only (<35–68 pg L^{-1}). All selected BFRs were ubiquitous in bed sediments and levels ranged from 3,100 to 15,100 pg g^{-1} and from 70 to 280 pg g^{-1} (dry weight), for ΣBDEs and TBBPA, respectively.

Keywords Polybrominated diphenyl ethers · Tetrabromobisphenol A · Solid-phase extraction · River water · Sediment

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Introduction

Brominated flame retardants (BFRs) consist of several families of compounds present in numerous consumer products [1]. Amongst these chemicals, TBBPA and PBDEs have the largest production volume, accounting for approximately 60% and 33%, respectively, of the worldwide BFR production in 2001 [1, 2].

TBBPA is a phenolic compound that presents structural similarities with estrogens and thyroid hormones. Therefore, the main concern regarding TBBPA toxicity is its potential as an endocrine disruptor, as both a thyroid hormone and oestrogen agonist [3]. Several reports of the occurrence of TBBPA in aquatic ecosystems have been published in recent years (review by Covaci et al. [2]). Owing to the moderately hydrophobic properties of TBBPA (log K_{OW}=5.9 [2]), most studies focused on its presence in sediment and its uptake by biota [4]. In sediment, TBBPA was detected at levels ranging from below detection limit up to several microgrammes per gramme dry weight (dw), with most samples exhibiting nanogrammes per gramme levels [2]. Very few studies, however, have addressed the occurrence of TBBPA in surface waters. Nevertheless,

TBBPA was detected in landfill leachate, as well as in influent and effluent of WwTPs, in both the dissolved phase (DP) and the particulate phase (PP) [4, 5]. Reported levels were in the nanogramme per litre range, which suggest that TBBPA may be present at trace level in rivers impacted by either of these potential sources of TBBPA. Sambe et al. [6] attempted to determine TBBPA concentrations in river water, but concentrations were lower than the detection limit of their method (10 ng L^{-1}). To the best of our knowledge, there is no other data about the occurrence of TBBPA in the water column of water bodies impacted by anthropogenic activities.

Historically, three major commercial PBDE formulations have been produced and used by the industry: penta-BDE, octa-BDE, and deca-BDE, the latter being the only one still allowed in the EU after the phasing out of the other formulations [7, 8]. PBDEs are listed as Priority Substances within the EU Water Framework Directive [9] and their occurrence in the environment has been a cause of growing concern. Like TBBPA, PBDEs are suspected to induce a disruption of the thyroid hormone function in humans and wildlife [1]. Numerous studies have reported the widespread occurrence of these chemicals in aquatic ecosystems ranging from urban environments to remote Arctic areas [8]. Due to the hydrophobic characteristics of PBDEs, most studies focused on sediment and reported concentrations in samples collected in the EU are in the picogramme per gramme to microgramme per gramme range (dw) [8]. Few studies have investigated the occurrence of PBDEs in the water column of lakes, rivers or estuaries. The limited available data, however, indicate that these contaminants can be found in both the DP and the PP, usually at low levels (picogramme per litre). Dissolved PBDEs were indeed detected in water samples collected at several locations in Europe: coastal waters at Izmir Bay (Turkey) [10] and in the Netherlands [11], rivers in Northern Russia [12], as well as in coastal and estuarine waters in China [13–15] and at several locations in the US and in Canada: San Francisco Bay [16], Lake Michigan [17], and Fraser River [18].

A number of analytical methods have been used for the determination of both PBDEs and TBBPA in sediment samples, such as assisted solvent extraction (ASE) or Soxhlet extraction [2, 19], while ultrasonication was used mainly for TBBPA [5, 19, 20]. As regards the DP, PBDEs and TBBPA are usually extracted by liquid/liquid extraction [13, 21], solid-phase microextraction [22, 23], passive samplers such as semipermeable membrane devices [11] or Chemcatcher [24], and solid-phase extraction using molecular imprinted polymers [6, 25] or conventional sorbents [10, 12, 14, 17, 26]. SPE is a method of choice when high throughput is sought, but several studies have demonstrated that dissolved organic carbon (DOC; including organic colloids) could induce a negative artefact when SPE is applied to the analysis of hydrophobic contaminants such as polychlorinated biphenyls (PCBs) [27], polycyclic aromatic hydrocarbons (PAHs) [28] or dioxins [29]. The association between DOC and such contaminants may indeed enhance analyte water solubility or alter analyte availability to the sorbent, resulting in poor recoveries.

The primary purpose of the present work was to develop a novel SPE-based method for the simultaneous determination of TBBPA and selected PBDEs (congeners 28, 47, 99, 100, 153, 154, 183 and 209) in the DP of river water samples; special attention was given to the negative artefact induced by the occurrence of DOC. As regards PBDEs, the objective was to achieve detection limits compatible with the annual average environmental quality standards (AA-EQSs) proposed within the EU Water Framework Directive (EU WFD) [30]. Meanwhile, an ultrasonication-based method was also implemented for the analysis of PBDEs and TBBPA in suspended and bed sediment. These procedures were then applied to the determination of PBDEs and TBBPA in water and sediment samples collected from a small suburban river flowing south of the Paris conurbation.

Experimental section

Chemicals and materials

Varian BondElut silica-based strong anion exchange cartridges (SAX, 0.85 meq g^{-1}) and C_{18} SPE cartridges, as well as bulk silica and neutral alumina sorbents were supplied by Interchim (Montluçon, France), while Oasis HLB (200 mg, 6 cc) and Oasis MAX (150 mg, 6 cc) cartridges were supplied by Waters (Guyancourt, France) and florisil cartridges (1 g, 6 cc) were supplied by Sigma-Aldrich (St Quentin Fallavier, France). Gas chromatography quality solvents (Merck Suprasolv), Extran MA detergent (Merck), sulphuric acid (>98%, nitrogen analysis grade), hydrochloric acid (37%, Normapur grade), formic acid (>98%) and glass fibre filters (Whatman GF/F, nominal cut-off size 0.7 μm) were supplied by VWR (Fontenay Sous Bois, France). Anhydrous sodium sulphate (analytical grade) was purchased from LGC Promochem (Molsheim, France). Sodium monohydrogen phosphate and sodium dihydrogen phosphate monohydrate were obtained from Aldrich. Ultrapure water was dispensed from an Elga Purelab Maxima water purification system (Elga LabWater, Le Plessis Robinson, France). Helium and nitrogen (99.999%) were supplied by Air Liquide (Paris, France).

A certified standard solution of PBDEs was obtained from CIL Laboratories (via LGC Promochem); it contained a mixture of eight PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), at 1 ng μL^{-1} in nonane, with the exception of BDE-209

(10 ng μL^{-1}). BDE-77 (50 ng μL^{-1} in nonane) was obtained from Sigma-Aldrich while $^{13}C_{12}$-BDE-209 (50 ng μL^{-1} in toluene), BDE 181 (50 ng μL^{-1} in nonane) and bromobiphenyl 209 (BB-209; 50 µg μL^{-1} in nonane) were obtained from Wellington Laboratories (via BCP Instruments, Irigny, France). BDE 77 was used as an internal standard (IS) for all BDEs except BDE 209, which was quantified against $^{13}C_{12}$-BDE-209. A working solution of BDE IS was prepared in isooctane: 1 ng μL^{-1} for BDE-77 and 5 ng μL^{-1} for $^{13}C_{12}$-BDE-209.

TBBPA solutions were prepared in hexane from TBBPA crystals (97%, Sigma-Aldrich), at a concentration of 50 ng μL^{-1} (stock solution) and 0.5 ng μL^{-1} (working solution). A certified solution of $^{13}C_{12}$-TBBPA was supplied by Wellington Laboratories (50 µg mL^{-1} in methanol). A working solution of $^{13}C_{12}$-TBBPA, used as IS for TBBPA, was prepared at 1 ng μL^{-1} in hexane (after methanol evaporation under a gentle nitrogen stream, at room temperature).

All solutions were stored at −20 °C, and were sonicated at room temperature for 5 min prior to their use, to ensure complete dissolution of the analytes.

Water and sediment sample collection

For method development, water samples were taken in the River Seine at the Austerlitz Quay (downtown Paris). DOC levels in these samples were in the range 3.7–4.6 mg L^{-1} (pers. com. J. Garnier). Two sediment samples were also used: (1) "blank river bed sediment" taken in the Grand-Morin rural watershed, near Paris (organic carbon 1.6%, clay 7%, silt 7%, sand 86%, pers. com. J. Garnier) and (2) sediment BROC-02, previously tested as a candidate Certified Reference Material (CRM) for PBDEs and other halogenated contaminants [31].

For method application, water and sediment samples were taken in June 2008 at five locations along a stretch of the Prédecelle river, a small suburban river (dry weather flow rate <0.3 $m^3 s^{-1}$) flowing in the southern part of the Paris conurbation (Fig. 1), downstream of suspected point-sources of BFRs such as urban storm water and WwTP effluent outfalls.

Water samples were collected in 4-L amber glass bottles previously detergent-washed and rinsed with acetone and hexane (analysis of glassware did not show any contamination). Samples were stored at 4 °C and were filtered within 24 h after collection on pre-baked (400 °C, 4 h) GF/F filters; 1-L aliquots of filtrate were kept for the DP analysis, while filters corresponding to a sample volume of 4 L were combined for suspended sediment analysis (sediment mass, 13–56 mg). Filters were stored at −20 °C until further analysis, while the DP was spiked with IS and analysed within 24 h after filtration (see "Water samples: dissolved phase" section).

Surficial sediment samples (0–2 cm) were also collected at all sites in acetone rinsed aluminium containers. After collection, sediment samples were kept frozen at −20 °C until analysis.

Sample preparation

Water samples: dissolved phase

Filtered samples were spiked with BDE-77 (1 ng) and $^{13}C_{12}$-BDE 209 (5 ng). Internal standards were first spiked to a small acetone volume (250 µL) in a 1-mL vial and the resulting acetone/isooctane mixture (98:2, *v*/*v*) was added to

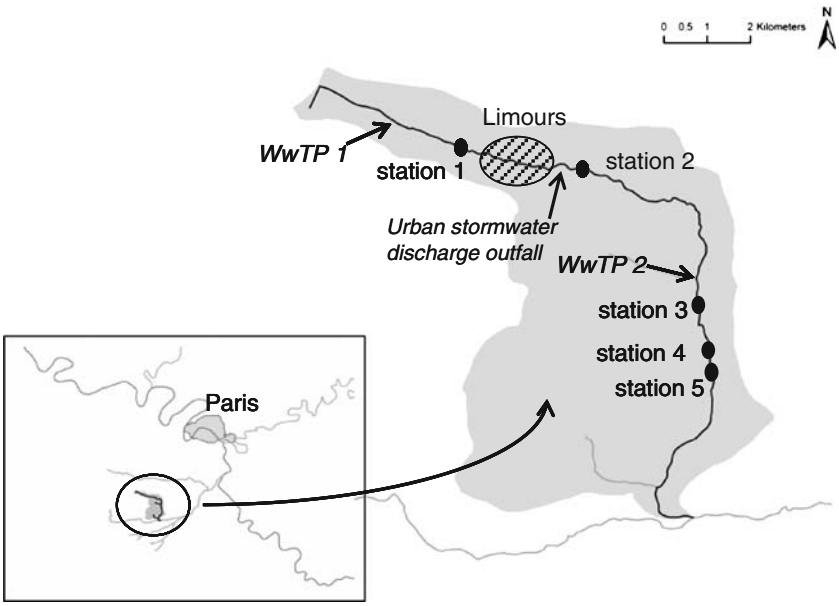

Fig. 1 Location of the sampling sites. *Station 1* upstream of Limours and downstream of WwTP 1 (Pécqueuse), *station 2* downstream of Limours, *station 3* downstream of WwTP 2 (Briis-sous-Forges), *station 4* upstream of Vaugrigneuse pond, *station 5* downstream of Vaugrigneuse pond

the water sample, just below the surface. The vial was subsequently rinsed twice with acetone aliquots (100 µL), which were transferred to the sample. Samples were then homogenised by manual shaking and were stored at 4 °C overnight for equilibration (approximately 20 h). This equilibration time was considered to be sufficient to reach near equilibrium-conditions between the DOC-associated fraction and the "freely dissolved" fraction [27, 32].

SPE cartridges were prepared by filling an Oasis MAX cartridge (150 mg, 6 cc) with a homogenous mixture of C_{18} and SAX sorbents (500 mg each). A polyethylene frit was placed on top of the sorbent bed and the so-obtained two-layer cartridge was conditioned by passing successively 10 mL of hexane/acetone (1:1, *v*/*v*), 5 mL of acetone, 10 mL of methanol and 10 mL of ultra pure water.

Water samples were passed through the cartridges without pH adjustment (typically 7.8–8.2) at a flow rate of approximately 10 mL min^{-1} and using a vacuum manifold (Supelco, St. Quentin Fallavier, France). Cartridges were vacuum-dried for 1 h and analytes were then eluted with 3 mL of acetone followed by 12 mL of hexane/acetone (1:1, *v*/*v*) and 13 mL of dichloromethane/methanol/formic acid (95:4.5: 0.5, *v*/*v*). One should note that the use of formic acid was mandatory to disrupt ionic interactions between TBBPA and the sorbent and to ensure quantitative elution. Extracts were then passed through an anhydrous sodium sulphate column (2 g) and samples were concentrated under a stream of nitrogen to a final volume of approximately 100 µL. Subsequent clean-up was performed as described in the "Clean-up" section.

Preliminarily, extraction tests were also carried out using C_{18} cartridges conditioned with 10 mL of hexane/acetone (1:1, *v*/*v*), 5 mL of acetone, 10 mL of methanol and 10 mL of ultra pure water; elution was performed with 10 mL of hexane/acetone (1:1, *v*/*v*). Oasis MAX cartridges were also tested; they were conditioned and eluted as described above for C_{18}+SAX /MAX cartridges. Recovery experiments were performed on either ultrapure water or on filtered Seine river water samples spiked with BFRs (1 ng L^{-1} except BDE-209, 10 ng L^{-1}). Spiked Seine river water samples were equilibrated for 20 h prior to extraction.

Water samples: particulate phase

GF-F filters (corresponding to a filtered volume of 4 L) were placed in a glass centrifuge tube, together with 5 g anhydrous sodium sulphate. Internal standards were added: BDE-77 (1 ng) and $^{13}C_{12}$-BDE 209 (5 ng) prior to extraction with 10 mL hexane/acetone (1:1, *v*/*v*) in a Bransonic 2510 sonication bath (130 W/42 Hz; VWR) during 20 min. Samples were centrifuged during 5 min (970×*g*) and the supernatant was collected. This procedure was repeated twice and all three extracts were combined, prior to concentration under a gentle nitrogen stream (down to 1 mL). The resulting extracts were dried over an anhydrous sodium sulphate column (2 g) and were then cleaned-up as described in the "Clean-up" section.

Sediment samples

Wet sediment samples were homogenised, sieved (1 mm) and 2-g subsamples from each sampling site were mixed with 10 g of anhydrous sodium sulphate, and spiked with BDE-77 (2 ng each) and $^{13}C_{12}$-BDE 209 (10 ng), prior to the addition of 20 mL of hexane/acetone (1:1, *v*/*v*). Extraction was carried out as described for water PP samples ("Water samples: particulate phase" section). Following concentration under a gentle nitrogen stream to a volume of approximately 1 mL, extracts were treated with HCl-activated copper strings to remove elemental sulphur, prior to clean-up ("Clean-up" section).

For each sediment sample, an aliquot was dried at 105 °C for 24 h for dry weight determination. Sediment organic matter content was estimated by the loss-on-ignition method (450 °C for 4 h).

Recovery experiments were performed on a "blank" river bed sediment sample (see the "Water and sediment sample collection" section) spiked with low levels of BFRs (1 ng g^{-1} dw, except BDE-209: 10 ng g^{-1}) and aged overnight prior to extraction (pre-spike PBDE and TBBPA levels <50 pg g^{-1} dw).

Clean-up

The first step of the clean-up procedure consisted in a fractionation on a florisil cartridge. Anhydrous sodium sulphate (0.5 g) was packed on top of the florisil cartridge, and the sorbent was preconditioned with 10 mL of dichloromethane/methanol (95:5, *v*/*v*) and 10 mL of hexane in sequence. Extracts obtained as described in the "Water samples: dissolved phase" and "Water samples: particulate phase" "Sediment samples" sections were passed through the cartridges. After sample loading, PBDEs were eluted with 8 mL of hexane (fraction 1, F1). The cartridge was rinsed with 10 mL of hexane/diethyl ether (8:2, *v*/*v*; discarded) and Fraction 2 (F2), containing TBBPA, was then eluted with 10 mL of dichloromethane/methanol (95:5, *v*/*v*).

Fraction F1 was concentrated (~500 µL) and purified on a multi-layer column consisting of 1 g of H_2SO_4 impregnated silica (40%, *w*/*w*), 1 g of silica (activated at 150 °C for 12 h) and 1 g of neutral alumina (activated at 150 °C for 12 h) (top to bottom). Columns were conditioned with 20 mL of hexane/dichloromethane (8:2, *v*/*v*) followed by 20 mL of hexane. After sample loading, columns were rinsed with 21 mL of hexane (discarded) and PBDEs were eluted with 15 mL of hexane/dichloromethane (8:2, *v*/*v*). Samples were

concentrated to less than 1 mL and transferred to a 1 mL injection vial, together with 25 μL isooctane added as solvent keeper. Finally, F1 extracts were concentrated to a final volume of approximately 15 μL and they were stored at −20 °C until analysis (see the "PBDEs" section).

Fraction F2 was taken to dryness and reconstituted in 1 mL of hexane/diethylether (6:4, *v*/*v*). This fraction was further cleaned-up on a 1-g activated silica cartridge, previously conditioned with 10 mL of hexane/diethylether (6:4, *v*/*v*). After sample loading, TBBPA was eluted with 10 mL hexane/diethylether (6:4, *v*/*v*). Finally, extracts were taken to dryness under a gentle stream of nitrogen and were derivatised using a procedure adapted from [33]: 50 μL of bis(trimethylsilyl)trifluoroacetamide / trimethylchlorosilane (99:1) was added and the sample was placed at 60 °C for 1 h. This derivatisation step, leading to the formation of a bis-trimethylsilyl (TMS_2) derivative, was carried out just prior to analysis (as described in the "TBBPA" section).

Analysis

PBDEs

PBDEs were analysed by gas chromatography coupled to mass spectrometry, in the negative chemical ionisation (GC-NCI-MS). Analyses were carried out using a 7890A GC coupled to a 5975C MS (both from Agilent Technologies, Massy France). The system was fitted with a deactivated silica guard column (0.53 μm) from Phenomenex (Le Pecq, France) connected to a J&W HP-5MS analytical column (15 m, 0.25 mm ID×0.25 μm film thickness; Agilent Technologies) using a capillary tubing connector from Supelco (St Quentin Fallavier, France). It was operated in pulsed splitless injection mode (1.7 bar, 1.5 min) with an injector temperature of 275 °C. The helium carrier gas flow rate was 1.8 mL min^{-1} and the oven temperature programme was as follows: 100 °C (0.1 min), 185 °C (25 °C min^{-1}), 275 °C (15 °C min^{-1}), 305 °C (45 °C min^{-1}, held for 6 min. Methane was selected as reagent gas (ion source pressure, 2.0×10^{-4}torr) and the interface, source and quadrupole temperature were set at 300 °C, 250 °C and 150 °C, respectively. Ions were monitored in SIM mode using two different time windows, with a dwell time set at 100 ms. $[Br]^-$ (*m*/*z* 79 and 81) was monitored for BB-209 and tri- to hepta-BDEs, while $[M\text{-}C_6Br_5]^-$ was monitored for deca-BDE (*m*/*z* 485/487 and *m*/*z* 495/497 for BDE-209 and $^{13}C_{12}$-BDE-209, respectively).

TBBPA

Quantification of TBBPA-TMS_2 was carried out by GC/MS using the GC-NCI-MS system described above (same settings). The temperature programme was as follows: 80 °C (0.1 min), 225 °C (30 °C min^{-1}), 265 °C (10 °C min^{-1}), 290 °C (40 °C min^{-1}, held for 6 min). Ions corresponding to $[M\text{-}Br]^-$ were monitored in SIM mode [33], with a dwell time set at 100 ms.

Quality assurance/quality control

Identification of analytes and IS was performed by comparing retention times with standards. Furthermore, for a given peak, the ratio of quantification ion area to confirmation ion area was compared to that obtained with an authentic standard, prior to definitive attribution of the peak (margin applied, 25%). Quantification was carried out by calculating the response factor of each analyte relative to its corresponding IS. Concentrations were determined using a least-square linear regression analysis of the peak area ratio versus the concentration ratio. This five-point calibration curve (R^2>0.98) covered the range of concentration found in our samples. Furthermore, BDE-181 and BB-209 were used as performance standards to determine the recovery rates of BDE-77 and $^{13}C_{12}$-BDE-209, respectively.

Triplicate procedural blanks were analysed for each series of samples. TBBPA was not detected in any blank sample, while BDE-209 (37–240 pg), BDE-99 (5–38 pg) and BDE-47 (5–28 pg) were the analytes most consistently detected. As regards water samples, blank levels accounted for up to 30% of the experimental value and were subtracted from the latter. In sediment extracts, however, blank levels accounted for less than 5% of BDE levels; still, PBDE sediment concentrations were blank corrected. For analytes detected in procedural blanks, method detection limits (MDLs) were calculated as three times the standard deviation of the procedural blanks [34]. For those analytes that were not detected in blanks, MDLs were determined as the concentration with a signal to noise ratio of three in unspiked samples. Instrument detection limits (IDLs) were determined as the concentration with a signal to noise ratio of three on the injection of standard solutions (2 pg on column for each analyte).

Results and discussion

Analysis of water samples (dissolved phase)

Sample extraction and fractionation

Initial recovery experiments were performed on spiked 1-L ultrapure water samples at either pH 2 (adjusted with diluted HCl) or pH 8 (adjusted with phosphate buffer). These preliminary tests were carried out using C_{18} cartridges and analytes were eluted with hexane/acetone (1:1, *v*/*v*). Recoveries higher than 62% were

obtained for PBDEs regardless of pH, which is consistent with results previously reported for other hydrophobic contaminants such as PCBs [27]. TBBPA, however, was poorly recovered at pH 8 (Table 1). At this basic pH, TBBPA is partially ionised (pK_{a1}=7.50, pK_{a2}=8.50) [35], which may explain its low retention on the C_{18} sorbent. At pH 2, however, TBBPA recovery was satisfactory. When spiked river water samples were extracted using the same procedure, poor recoveries were obtained for all analytes at pH 8 (Table 1). At pH 2, however, TBBPA was satisfactorily retained, which is consistent with results obtained on ultra pure water. On the contrary, PBDEs were poorly recovered (<40%), regardless of pH. This is consistent with findings by de la Cal et al. [24], who observed that the recovery of dissolved BDE-47 and BDE-153 were low (<30%) when either C_{18} or Oasis HLB cartridges were used as sorbents in passive samplers. This is likely due to the presence of natural DOC, which can interfere with the extraction of dissolved hydrophobic compounds from water samples. This is of particular concern for SPE procedures and several studies have reported on the negative effect of DOC on the retention of contaminants such as PAHs [28, 32, 36], PCBs [27, 37, 38] or dioxins and furans [29].

Several solutions have been previously proposed to overcome this problem: (1) selection of an appropriate equilibration time after IS addition [27, 32], (2) DOC oxidation prior to SPE [38] or (3) improvement of the contaminant/DOC complex retention [28]. The latter option has been developed by Li et al. [28], who optimised a method termed "Dynamic Ion Exchange". Their method relies on mixed-mode retention, achieved through the use of C_{18} cartridges previously conditioned with cetyltrimethylammonium bromide (CTAB), an anionic surfactant consisting of a long carbon chain with a quaternary amine group. Such sorbent may retain analytes through both hydrophobic and ionic interactions and has been successfully applied to the extraction of PAHs from water samples containing humic acids [28, 36]. However, its potential for BFR extraction has never been explored. We attempted to develop a similar method in our laboratory and tests were carried out on filtered Seine River water spiked with PBDEs and TBBPA using CTAB conditioned-C_{18} cartridges. This greatly improved the recovery yield of most BFRs, which ranged from 60% to 72%; BDE-209 was the only analyte exhibiting poor recovery (<35%; data not shown). The major drawback of this method was, however, that using a vacuum manifold, the highest sample flow rate achieved during the extraction step was extremely low (<2 mL min^{-1}). It seemed that using N_2 positive pressure, as described in the original paper by Li et al. [28], was mandatory to obtain reasonably high flow rates (~10 mL min^{-1}). Therefore, two alternative options were tested, both being based on mixed-mode retention: (1) Oasis MAX cartridges (polymeric sorbent functionalised with dimethyl butylamine groups, 0.2 meq g^{-1}) and (2) a novel, lab-prepared, sorbent resulting from the combination of C_{18} sorbent with SAX (quaternary amines). The efficiency of these sorbents was investigated at pH 8 only, since the use of anion exchangers was meant to favour the retention of anions such as deprotonated TBBPA or humic and fulvic acids (and, hence, that of DOC-associated PBDEs). Oasis MAX cartridges were suitable for TBBPA extraction, but PBDE recoveries were poor with this sorbent (Table 2). A possible explanation for the low PBDE recoveries could be size-exclusion of some DOC constituents, as observed for some PS-DVB polymers [39], therefore possibly disfavouring the retention of a fraction of the DOC-associated PBDEs. Conversely, both TBBPA and PBDEs were satisfactorily retained on the C_{18}+SAX sorbent, although high-molecular-weight BDEs (namely, BDE-183 and BDE-209) still exhibited lower recoveries (47–53%). Absorbance measurements (280 nm) revealed that DOC retention was higher on the C_{18}+SAX sorbent

Table 1 Recovery rates of PBDEs and TBBPA from 1-L spiked water samples (spike level, 1 ng L^{-1}; except BDE 209, 10 ng L^{-1}) using C_{18} cartridges

Mean recovery (%)	Milli-Q water		Seine River water	
	pH 2 (n=2)	pH 8 (n=2)	pH 2 (n=2)	pH 8 (n=2)
BDE 28	87.2	75.6	28.5	39.7
BDE 47	100.6	78.4	19.7	30.5
BDE 99	86.4	79.6	14.8	23.1
BDE 100	79.1	71.5	32.3	16.5
BDE 153	81.9	76.6	19.7	18.5
BDE 154	89.4	85.9	23.1	11.4
BDE 183	66.2	62.2	13.8	24.5
BDE 209	95.6	85.3	24.5	38.4
TBBPA	82.2	28.5	77.7	33.0

Table 2 PBDE and TBBPA recovery rates from 1-L spiked Seine river water samples (spike level, 1 ng L^{-1}; except BDE 209, 10 ng L^{-1}) using mixed-mode SPE (pH 8)

Mean Recovery (%)	Oasis MAX (n=2)	C18+SAX (n=3)	C18+SAX / MAX (n=6)
BDE 28	40.6	90.4±12.5	94.5±4.7
BDE 47	42.9	82.1±6.7	100.8±9.1
BDE 99	35.8	67.9±4.1	83.3±13.1
BDE 100	39.0	78.4±18.2	89.1±11.4
BDE 153	41.1	63.2±9.3	73.1±5.3
BDE 154	38.5	54.6±7.9	76.2±6.1
BDE 183	23.4	53.1±12.1	57.7±5.0
BDE 209	36.3	46.9±7.0	56.6±4.1
TBBPA	102.0	62.4±9.7	103.8±11.9

than on the C_{18} sorbent (46% vs. 13%), which might explain the increased retention of PBDEs on the former sorbent without the need for sample acidification.

In the light of the above findings, and so as to optimise the recovery rates of all analytes, the final extraction procedure consisted in using a two-layer cartridge, combining a C_{18}+SAX layer overlying an Oasis MAX layer (see "Water samples: dissolved phase" section for preparation details). This sorbent proved efficient since recoveries exceeded 73% for most analytes, with RSD<16% (Table 2), although BDE-183 and BDE-209 were recovered to a lesser extent (57%). The lower recovery rates achieved for BDE-183 and BDE-209 were not due to loss through sorption onto the container walls, since rinsing the bottles with acetone and hexane did not increase significantly recoveries (<2%). Therefore, these lower recoveries are more likely due to lower retention on the sorbent during the extraction step.

The separation of PBDEs and TBBPA presented in the C_{18}+SAX/MAX extracts was optimised on commercial florisil cartridges. Owing to the occurrence of hydroxyl groups in the structure of TBBPA, it was possible to separate PBDEs from TBBPA using a solvent polarity gradient. Similar to the procedure developed by Xie et al. using silica gel [33], PBDEs recovery was higher than 95% in non-polar F1 (hexane), while TBBPA was eluted in a

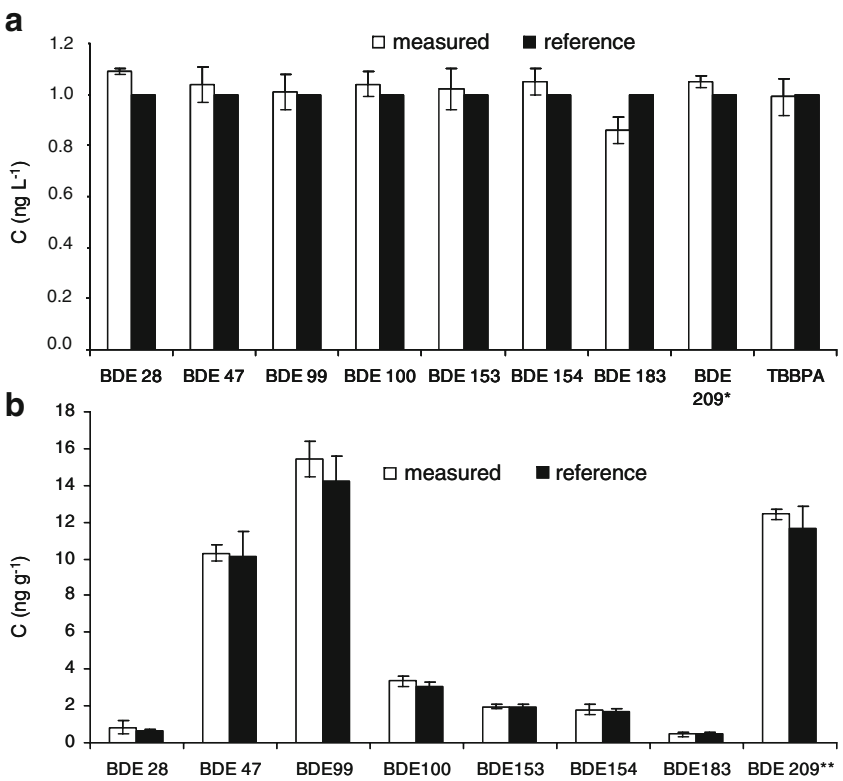

Fig. 2 Evaluation of the of the quantitation procedure performance. **a** 1-L spiked Seine river water sample (1 ng L^{-1}; except BDE 209, 10 ng L^{-1}); **b** BROC-02 reference sediment sample. Results are plotted as mean value and *error bars* represent the 95% confidence interval (n=4). For the sake of clarity, BDE 209 values were divided by a factor 10 (*) and 100 (**)

Table 3 Instrument detection limits (IDLs) and method detection limits (MDLs) for river water (dissolved phase, DP, and particulate phase, PP) and riverbed sediment (picogramme per gramme, dw)

	IDLs (pg)	MDLs		
		River water		Riverbed sediment
		DP (pgL^{-1})	PP (pgL^{-1})	(pg/g, dw)
BDE 28	0.4	15	15	25
BDE 47	0.2	12	10	10
BDE 99	0.2	13	12	10
BDE 100	0.2	4	4	5
BDE 153	0.6	4	6	9
BDE 154	0.3	3	4	6
BDE 183	0.1	3	4	5
BDE 209	0.5	150	95	145
TBBPA	1.2	35	45	50

more polar fraction with dichloromethane/methanol (95:5, *v*/*v*; recovery rate, 96±8%). Prior to the elution of TBBPA, a rinse with hexane/diethyl ether (8:2, *v*/*v*), discarded, allowed for the elution of compounds such as phthalates and some PAHs (data not shown) and provided additional clean-up of F2.

Since the clean-up step-up was nearly quantitative (recoveries >85% for most analytes), whole-procedure recovery rates were largely controlled by the SPE recovery rate. Indeed, whole-procedure recoveries (extraction+clean-up), as determined for spiked river water samples, ranged from 50±6% (BDE-209) to 81±13% (BDE 47), while TBBPA recovery rate was 101±12%.

Analysis: accuracy and detection limits

The method was further validated by performing a quantitation test on filtered river water samples spiked with BFRs and IS before the extraction step (equilibration time 20 h). The use of appropriate IS (BDE-77, $^{13}C_{12}$-BDE-209 and $^{13}C_{12}$-TBBPA) allowed for good accuracy: experimental results were within 15% of nominal concentrations, even for high-molecular-weight BDEs (Fig. 2). IS recoveries were 51±7% and 85±10% for $^{13}C_{12}$-BDE-209 and BDE-77, respectively.

Instrument detection limits achieved by GC-NCI-MS are presented in Table 3; they were determined by injecting 2 pg on column for each analyte.

MDL achieved for TBBPA was in the picogramme per litre range, while PBDE MDLs ranged between 3 pg L^{-1} (BDE-153/154) and 150 pg L^{-1} (BDE-209; Table 3) and were comparable with previously reported MDLs, determined for larger samples [10, 14].

Analysis of suspended sediment and riverbed sediment

The extraction of BFRs from both suspended and river bed sediment samples was validated using a river bed sediment sample spiked with BFRs. Ultrasonication extraction recovery rates higher than 73% were achieved for all PBDEs, while whole-procedure recoveries ranged from 76% (BDE-99) to 100% (BDE-209; Table 4). Such recoveries are in good agreement with data reported by Salgado-Petinal et al. [40] for tetra- to hexa-brominated congeners. These findings also provide evidence, for the first time, of the efficiency of ultrasonication for extracting high-molecular-weight PBDE congeners such as BDE-183 and BDE-209. TBBPA ultrasonic extraction recovery was 93.3±4.9%, which is consistent with previously reported data [5, 20].

The method was further validated by determining PBDE levels in reference sediment BROC-02 [31]. Accurate quantitation was achieved, with relative standard deviation lower than 20% (Fig. 2). These results validated the quantification procedure and further confirmed the efficiency of ultrasonication for tri- to deca-PBDE extraction from sediment samples. IS recovery rates were 86±9% and 88±13% for BDE-77 and $^{13}C_{12}$-BDE-209, respectively. MDLs achieved for sediment samples by GC-NCI-MS ranged from 5 to 145 pg g^{-1} (dw), depending on the analyte (Table 3); these MDLs are comparable with previously reported detection limits [2].

As can be seen from Table 3, PBDE MDLs in water sample PP ranged from 4 to 95 pg L^{-1}. Taking into account the MDLs achieved for the DP, these detection limits are therefore compatible with the AA-EQSs proposed for PBDEs within the EU WFD: 500 pg L^{-1} for the sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 in inland waters (total concentration, dissolved+particulate) [30].

Table 4 Recovery rates of PBDEs and TBBPA in river bed sediment spiked at 1 ng g^{-1} (10 ng g^{-1} in the case of BDE 209). Results are expressed as mean ± standard deviation (n=4)

	Ultrasonication Extraction yield (%)	Whole-procedure recovery (%)
BDE 28	73.1±3.6	86.1±3.2
BDE 47	81.3±5.5	94.0±4.0
BDE 99	97.8±13.5	76.1±2.1
BDE 100	99.4±15.9	99.5±4.0
BDE 153	77.4±11.4	99.8±5.9
BDE 154	80.7±6.0	97.9±4.8
BDE 183	88.3±7.8	89.6±8.7
BDE 209	92.4±7.1	100.3±8.4
TBBPA	93.3±5.9	98.9±4.9

Table 5 PBDE and TBBPA concentrations in river water (pg L^{-1}) and sediment (pg g^{-1}, dry weight) at selected locations along the Prédecelle River

Station	Sample type	TBBPA	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209	ΣBDEs	ΣBDEs / OM[a]	BDE 209 / ΣBDEs (%)
1	Water (DP)	< 35	29	33	4	7	4	7	870	954	–	91
	Water (PP)	< 35	52	44	9	8	5	10	1230	1358	–	90
	Water (total)	–	81	77	13	15	9	17	2100	2312	–	91
	Sediment	140±20	610±20	790±50	150±10	120±10	70±10	80±20	7300±1900	9150±1900	150±30	80
2	Water (DP)	< 35	19	20	4	8	5	3	770	829	–	93
	Water (PP)	< 35	27	26	20	6	8	9	1700	1796	–	95
	Water (total)	–	46	46	24	14	13	12	2470	2625	–	94
	Sediment	100±20	330±20	340±40	100±10	90±20	100±10	42±9	2130±270	3130±480	243±37	68
3	Water (DP)	64	43	41	6	7	4	14	1660	1775	–	94
	Water (PP)	< 35	162	140	22	15	10	18	2150	2517	–	85
	Water (total)	64	205	181	28	22	14	32	3810	4292	–	89
	Sediment	130±10	325±70	760±90	170±30	120±30	90±10	30±5	3780±510	5405±600	289±31	67
4	Water (DP)	50	15	15	5	8	4	8	950	1005	–	95
	Water (PP)	< 35	51	39	15	8	5	5	1190	1313	–	91
	Water (total)	50	66	54	20	16	9	13	2140	2318	–	93
	Sediment	65±10	190±10	460±35	92±10	70±10	50±10	20±10	2180±550	3052±580	300±57	72
5	Water (DP)	58	16	13	5	8	5	4	940	991	–	95
	Water (PP)	< 35	67	56	24	30	20	6	1540	1743	–	88
	Water (total)	58	83	69	29	38	25	10	2480	2734	–	91
	Sediment	280±20	780±60	2990±390	540±80	130±30	80±10	90±20	10600±1200	1 15,220±772	274±14	70

Sediment levels are given as mean value±standard deviation (n=3)

Station 1 upstream of Limours, *station 2* downstream of Limours, *station 3* downstream of the Briis-sous-Forges WwTP, *station 4* upstream of the Vaugrigneuse pond, *station 5* downstream of the Vaugrigneuse pond

[a] Organic matter normalised PBDE levels (nanogrammes per gramme OM)

BFR determination in the Prédecelle River

The optimised analytical procedures described above were applied to the determination of TBBPA and PBDE levels in the Prédecelle River. TBBPA and PBDEs were ubiquitous in this river and analytes were detected in both the water column and the river bed sediment (Table 5).

In the water column, TBBPA was detected in the DP only, probably as a direct consequence of the fact that its solubility in water can vary with pH and temperature. At the typical pH of the Prédecelle river water (7.8–8.2), TBBPA is under anionic form and, hence, it is several orders of magnitude more soluble than at pH below pK_{a1} [41]. These findings are also in good agreement with the fact that TBBPA was detected primarily in the DP of UK WwTP influents (2.6 to 85.0 ng L^{-1}) [4]. TBBPA concentration were <MDL upstream of $WwTP_2$ (stations 1 and 2) but ranged from 50 to 64 pg L^{-1} downstream of this WwTP, suggesting that this WwTP was a point source of TBBPA to the river. To the best of our knowledge, this is the first report of TBBPA occurrence in river water.

Contrary to TBBPA, PBDEs were detected in both the DP and the PP. BDE-209 was the dominant BDE, accounting for 94% and 90% of ΣBDEs in the DP and PP, respectively. This reflects the fact that BDE-209 is the main congener of the deca-BDE mixture, the only one still used in the EU after the ban of octa- and penta-BDE mixtures in 2004. ΣBDEs (DP+PP) ranged from 2,300 to 4,290 pg L^{-1}. Such levels are higher than those usually reported in the literature [11, 12, 16–18], most likely because of the relatively large input of wastewater into the Predecelle river. These concentrations are, however, lower than those reported by Guan et al. [14] for the Pearl River Delta, which are the highest ever reported.

The partitioning of PBDEs between the DP and the PP might be influenced by factors such as DOC, particulate organic carbon and suspended solids levels [15]. In the present case, PBDEs were dominant in the PP, although DP represented a significant fraction of the total water column concentration (32–40%, depending on congener). These observations are consistent with previous reports [10, 13, 17], the main difference being that dissolved BDEs were systematically detected in our samples. Mean log K_p (water–particle partition coefficients) ranged from 2.3 (BDE-183) to 2.7 L kg^{-1} (BDE-100), while log K_{OM} (OM-normalised K_p) ranged from 3.0 to 3.5 L kg^{-1}. These values are given as indicative values only since, in several samples, some PBDE levels in the DP were higher than MDL but lower than the method quantification limit (set at three times MDL); they are, however, consistent with previously reported data [15, 17, 42].

In sediment, total PBDE concentrations ranged from 3.0 to 15.1 ng g^{-1} dw and all targeted PBDEs were detected (Table 5), with the notable exception of BDE-28 (Fig. 3). Such levels are in the range of previously reported levels in the EU (typically nanogramme per gramme to tens of nanogrammes per gramme [8]). The congener pattern was similar to that previously reported in the literature (review by Law et al. [8]), BDE-209 being the most abundant congener (68–80% of ΣBDEs), followed by BDE-99, BDE-47, BDE-100 and BDE-153/154. This is also in good agreement with the molecular fingerprint observed in the water column. PBDE sediment levels did not reflect the occurrence of PBDE point source discharges in the Prédecelle River. Indeed, OM-normalised PBDE levels were fairly homogenous along the investigated river stretch (Table 5), which would tend to indicate that PBDEs introduced via point-sources were transported along the whole river stretch investigated in the present study.

TBBPA levels in river bed sediment ranged from 70 to 280 pg g^{-1} (dw) and were at least one order of magnitude lower than those of total PBDE, which is in good agreement with findings by Zhang et al. [43]. TBBPA levels were positively correlated with Σ8BDEs (R^2=0.96, p=0.009), which suggests that these compounds have similar sources in the Prédecelle river catchment.

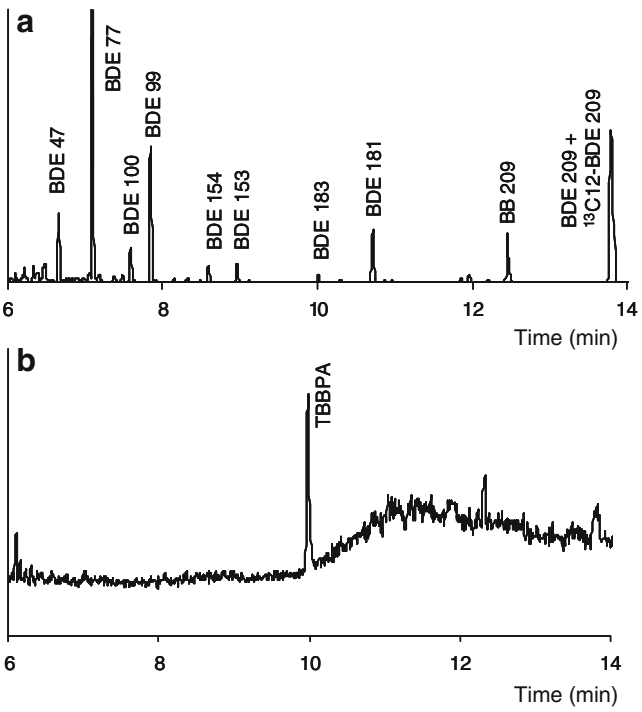

Fig. 3 GC-NCI-MS chromatogram of a sediment extract (station 3), acquired in SIM mode. **a** Total ion current (TIC) signal for PBDEs, **b** SIM trace of *m/z* 607 (*TBBPA*)

Conclusion

A novel SPE method for the simultaneous analysis of TBBPA and selected PBDEs in river water samples was developed in this study. This method relies on mixed-mode retention, using a combination of C_{18}, SAX and Oasis MAX sorbents. Although this SPE procedure is perhaps not the most cost-effective procedure for the determination of dissolved BFRs, it may be used on a routine basis for the determination of PBDEs and TBBPA in surface waters since. Indeed, it proved efficient to reduce the negative artefact caused by DOC and observed when using C_{18} sorbent. Using appropriate IS and equilibration time, accurate quantitation was achieved for all analytes, including high-molecular-weight PBDEs. Meanwhile, an ultrasonication-based method was also developed for the determination of BFRs in suspended and bed sediment. Detection limits were compatible with the AA-EQSs proposed in the EU WFD.

These procedures enabled the determination of TBBPA and PBDEs at trace levels in the Prédecelle River. Analytes were detected in all investigated samples, at levels higher than the AA-EQSs in the case of PBDEs. The sediment compartment was an obvious sink for both TBBPA and PBDEs with levels up to 5,500-fold higher than in the water column. In the water column, TBBPA was detected in the DP only, while PBDEs partitioned between the DP and the PP. Even in the case of high-molecular-weight congeners, the DP accounted for a significant proportion of total PBDEs; this might have an impact on PBDE transport and bioaccumulation in aquatic ecosystems. Research is needed to gain further insight into PBDE partitioning in surface waters and into the factors controlling this partitioning.

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