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Interaction of 15 priority substances for water monitoring at ng L^{-1} levels with glass, aluminium and fluorinated polyethylene bottles for the containment of water reference materials

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Abstract Certified water reference materials are currently not available for most of the hydrophobic organic pollutants listed in the EU Water Framework Directive. To find the most suitable container type for subsequent reference material productions, feasibility studies for the preparation of waters with polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and tributyltin (TBT) close to environmental quality standards in water have been performed. Due to the hydrophobic nature of these compounds and their tendency to adsorb onto container walls, an adequate selection of the most appropriate material for containment, storage and transport of water reference materials is crucial. Three different materials (aluminium, amber glass and fluorinated polyethylene, FPE) and three volumes (500/600 mL, 1000/1200 mL and 2000/3000 mL, depending on commercial availability) were tested at ng L^{-1} level of the target compounds. FPE shows by far the highest loss of analytes due to adsorption onto the container walls for all compounds studied. Aluminium and glass are equally suited for PAHs and PBDEs, but aluminium is unsuitable as container material for TBT due to acid cleaning requirements. The volume of the containers had no dramatic effect on the adsorption behaviour of target compounds for the different volumes tested.

Keywords Water Framework Directive ·
Reference materials · Hydrophobic organic pollutants ·
Bottles · Adsorption · Glass · Aluminium ·
Fluorinated polyethylene

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Introduction

The EU Water Framework Directive (WFD) 2000/60/EC [1] establishes the legal framework for protection of water bodies in Europe. It aims to reach a good ecological and chemical status by the end of 2015 ensuring the protection of water needs for society and ecosystems. In order to assess the chemical status of the waters, the amending Directive 2013/39/EC on environmental quality standards (EQS) [2] lays down concentration limits for 45 priority substances that have to be regularly monitored by the EU Member States. Polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and tributyltin (TBT) are among the priority substances due to their toxicity and widespread environmental occurrence.

To ensure the quality of the measurement data, Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status [3] requests that laboratories should use (certified) reference materials, if available, to assess that the results are traceable, accurate, reliable and comparable. Unfortunately, such reference

materials are not available for PAHs, PBDEs and TBT in natural waters [4].

A very demanding requirement of the WFD for analytical laboratories is the measurements of the whole, non-filtered water [5]. Even though analytical methods for many of the priority pollutants exist, most of them are not validated for the presence of high amounts of suspended particulate matter (SPM) [6]. This can lead to an important underestimation of concentrations in the whole water because the analytes are tenaciously bound to the particles [7].

The need for matrix certified reference materials (CRMs) certified for hydrophobic organic pollutants in whole water has frequently been highlighted as a serious drawback to fulfil the stipulated monitoring needs since the lack of these hinders the validation of analytical methods and the comparability of results [8, 9]. There have already been several attempts to prepare different water materials for interlaboratory comparisons [9–12]. The most common approaches imply a "reconstitution step" in the laboratory prior to analysis, i.e. the addition of a solution or a solid containing the compounds of interest to a specified water volume [4, 9]. Ready-to-use matrix materials are closer to real samples but display homogeneity and stability problems compared to the reconstitution approaches. Such challenges have to be resolved in order to be able to produce water matrix CRMs for hydrophobic organic compounds in the future.

The collaborative project "Traceable Measurements for Monitoring Critical Pollutants under the European Water Framework Directive" (ENV08), as part of the European Metrology Research Programme, EMRP, encompassed a feasibility study for the preparation of reference materials for the above-mentioned organic priority substances in natural waters. The aim was to prepare different fit-for-purpose and ready-to-use materials for investigating the dissolved phase and the suspended particulate matter (SPM) separately and thereafter to combine both phases trying to mimic "whole water" as close as possible. The novel concepts developed for the preparation of water reference materials in this project were recently presented in detail by Elordui-Zapatarietxe et al. [13].

It has been shown that the selection of the most appropriate containers for the storage and transportation is crucial when preparing water test materials for non-polar organic compounds [14]. Consequently, if this part of the analytical chain is seriously affected by, for example, adsorption of the target analytes to the container wall, the subsequent analysis of the sample is meaningless. Due to their hydrophobic nature, PAHs, PBDEs and TBT tend to adsorb onto solids present in natural waters such as SPM or on the colloids [15, 16]. Inside a bottle, a part of these compounds will also adsorb onto the container walls and

would be inaccessible for analysis [17–19]. This process could pose a serious problem for the homogeneity and long-term storage of reference materials [20]. Moreover, this phenomenon is more pronounced the smaller the container is, as the surface-to-volume ratio is increasing [21]. Although several studies have been performed regarding the stability of PAHs and TBT inside different types of containers, the concentrations tested in those experiments were relatively high and none of them was close to EQS levels [18, 21–23]. The information available for PBDEs is even scarcer, and the interactions of these target analytes have not been studied in aluminium bottles.

Some automated SPE extraction systems for water samples employ back-flush steps of organic extraction solvents to rinse off analytes adsorbed onto the inner walls of the sample containers. It might therefore be argued that with such systems it is irrelevant if the analytes are adsorbed on the walls or not. However, when preparing (certified) reference materials (CRMs), it is mandatory to prove and quantify low between-bottle heterogeneity. If adsorption effects are significant for certain bottle/analyte combinations, it becomes more demanding to achieve low between-bottle heterogeneity. All sample bottles in a produced batch (e.g. 2000 bottles) would have to exhibit similar adsorption behaviour. In addition, all back-flush events would have to result in a similar or quantitative release of analyte from the container walls. Finally, it might be severely limiting if a CRM is contained in one type of bottle material and routine samples in another. It is therefore much better if it can be proven that the analyte/bottle–wall interaction is as weak as possible.

In this paper, the selection process of the most suitable container to prepare test materials similar to natural waters with priority pollutants at concentrations close to EQS is described. The pre-selection of candidate containers and their testing are explained. Finally, the reasoning for the selection of the most suitable containers based on the gathered data is presented. To our knowledge, this is the first systematic study of PAH, PBDE and TBT interactions with different containers at ng L^{-1} levels which also includes aluminium bottles.

Experimental

Selection of the bottles

From a reference material production point of view, it is important that the container satisfies several criteria, such as being leakproof, lightproof, chemically inert, of low weight, durable and therefore easy to transport. Commercially available containers fulfilling these parameters were screened to find suitable bottles to be tested in the

experiment. Economic aspects were also taken into account keeping a tentative CRM production of up to 2000 bottles in mind, whereby bottles made of PFA (perflouroalkyloxy polymer) or FEP (fluorinated ethylene propylene polymer) were excluded.

Aluminium, amber glass (VWR, Leuven, BE) and fluorinated polyethylene bottles (FPE) (Nalgene, Waltham, MA, US) were selected for testing. Since large water volumes were needed to reach the limits of quantification established in the EQS Directive, 500 mL, 1000 mL and 2000 mL glass and FPE bottles and 600 mL, 1200 mL (Burkle, Bad Bellingen, DE) and 3000 mL (Alpak, Aarschot, BE) aluminium bottles were tested. The larger aluminium bottles were the only commercially available alternatives to the intended 500 mL, 1000 mL and 2000 mL containers. In all cases, the fill volumes were limited to 500 mL, 1000 mL and 2000 mL even though only slightly larger bottles could be obtained in aluminium.

Bottle cleaning

First, bottles were rinsed with isopropanol to eliminate the main organic traces that might be present and were left to dry in a clean cell equipped with a HEPA filter (Terra Universal, Fullerton, CA, US). Afterwards, they were vigorously shaken with a 2 % solution of Triton-X100 (Sigma-Aldrich, Diegem, BE) and subsequently rinsed up to 4 times with type 1 water (18.2 MΩ cm, 0.053 μS cm^{-1}, maximum of 50 μg L^{-1} of total organic carbon, Merck Millipore, Billerica, MA, US) until no foam was visible. The drying was carried out again in the clean cell to avoid any contamination. Caps were cleaned together with the bottles following the same process.

For the analysis of TBT, an extra cleaning of the bottles was performed by filling them with a solution of HNO$_3$ (10 % by volume) and leaving them standing overnight. The bottles were rinsed three times with type 1 water on the following day.

Selection of the water matrix

The water matrix for the present experiment was selected anticipating that natural waters would be used to prepare future reference materials. Several studies dedicated to the adsorption of hydrophobic organic compounds to glassware have been carried out using water of very low ionic strength such as type 1 or deionized water [21, 24]. The lack of natural ligands in these waters promotes the adsorption of the compounds onto the container walls. However, this situation does not represent the situation in natural waters where significant parts of hydrophobic organic compounds are adsorbed onto colloids such as humic/fulvic acids, and onto SPM [16, 25]. Therefore, tap water was used for these experiments. Besides its higher ionic strength, tap water also contains a varying amount of dissolved organic matter, depending on the source, which can act as natural ligands for the compounds under study [18]. The assessment of the suitability of the different container materials for future reference material preparations also becomes more realistic.

The waters used in this study varied in composition depending on the location where the different experiments were performed. Therefore, the amounts of dissolved humic substances, measured as DOC, were checked in the tap water of each collaborating laboratory, namely in Berlin in Germany for BAM (TBT analysis), Paris in France for LNE (PBDE analysis) and Geel in Belgium for IRMM (PAH analysis), in order to ensure all tap waters contained dissolved ligands. The obtained DOC values are shown in Table 1 and are in the range previously reported in the literature [16].

Spiking solution containing the target analytes

PAHs

The 8 PAHs listed in the WFD were obtained from the following suppliers: naphthalene and benzo(ghi)perylene, Fluka (St. Louis, MO, US); anthracene and indeno(1,2,3,-cd)pyrene, Dr. Ehrensdorfer (Augsburg, DE); and fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene, Sigma (St. Louis, MO, US). These non-deuterated PAHs were dissolved in acetonitrile in mass fractions from 25.44 ng g^{-1} to 763.3 ng g^{-1} and then spiked into the water samples. Deuterated PAHs were used as internal standards for quantification. Naphthalene-d$_8$, anthracene-d$_{10}$, fluoranthene-d$_{10}$, benzo(b)fluoranthene-d$_{12}$,

Table 1 Final concentrations of target compounds and dissolved organic carbon (DOC) in the prepared samples, regardless of container type and volume

Sample type	Compounds	Concentration (ng L^{-1})	DOC (mg L^{-1}) tap water
PAH	Naphthalene	1200	2.9
	Anthracene	100	
	Fluoranthene	100	
	Benzo(a)pyrene	50	
	Benzo(b)fluoranthene	40	
	Benzo(k)fluoranthene	40	
	Benzo(g,h,i)perylene	40	
	Indeno(1,2,3-cd)pyrene	40	
PBDEs	Sum of BDE28, BDE47, BDE99, BDE100, BDE153, BDE154	10	0.7
TBT	TBT	2.4	4

benzo(k)fluoranthene-d_{12}, benz(a)pyrene-d_{12}, indeno(1,2,3-cd)pyrene-d_{12} and benzo(g,h,i)perylene-d_{12} were purchased from Dr. Ehrensdorfer (Augsburg, DE) in neat crystal form. A solution in acetonitrile (Suprasolv, Merck, Darmstadt, DE) containing all deuterated compounds was prepared gravimetrically and stored in the dark at 4 °C until use.

PBDEs

For calibration, pure PBDE compounds (Chiron, Trondheim, NO), BDE 28, 47, 99, 100, 153 and 154 were weighed into brown glass bottles and dissolved with iso-octane (SupraSolv, Merck, Darmstadt, DE) to result in an approximate mass fraction of 80 µg g^{-1} each. The purity of the compounds in solution had previously been determined using both gas chromatography with mass spectrometry (GC–MS) and flame ionization (GC–FID), respectively. ^{13}C-labelled PBDE solutions in nonane (Wellington Laboratories, Ontario, CA, US) were used as internal standards. The stock solutions were prepared gravimetrically and then mixed and diluted using iso-octane to obtain the different calibration dissolutions. They were stored in the dark at 4 °C until use. The stock solutions were diluted with methanol as appropriate, and the water samples were spiked with two standard solutions (prepared in methanol) containing the native and the labelled compounds in a concentration of 0.75 ng L^{-1} and 2.23 ng L^{-1}, respectively.

TBT

The samples were spiked with a tributyltin chloride (Sigma-Aldrich, St Louis, MO, US) solution prepared in methanol (Promochem, LGC Standards GmbH, Wessel, DE) at a concentration of 2.44 ng L^{-1} (as TBT-cation). A [119]Sn-enriched butyltin mix (MBT, DBT, TBT; ISC Science, Oviedo, ES) solution in methanol was used as internal standard. The solutions were prepared gravimetrically and stored in the dark at −18 °C until use.

Sample preparation

Independent experiments were carried out for PAHs, PBDEs and TBT. Each tested bottle constituted a unique sample and the content was analysed as a whole, without taking subsamples. The same analytical method was used for all the water samples containing the same target compounds, regardless of their volume. Each bottle (500/600 mL, 1000/1200 mL and 2000/3000 mL) was filled with 500 mL, 1000 mL or 2000 mL tap water. A spike of the target analytes in the water-miscible solvents (acetonitrile or methanol) was added to each bottle to obtain the final concentrations shown in Table 1.

For each analyte group, all the samples corresponding to the same container material (40 bottles per material) were spiked simultaneously and this time point was considered as t_0. Two procedural blanks were also prepared for each material, volume and analyte type by filling bottles with tap water without adding the spikes. The samples were stored in the dark at room temperature (20–22 °C) taking special care in not shaking them. Two bottles of each volume were taken after 3, 24, 72 and 192 h, respectively. The content was poured into pre-cleaned amber glass bottles, and the internal standard was added and left to equilibrate for 24 h [26]. Thus, the difference between the added and the determined concentration of the target compound would be mainly due to losses by adsorption onto the container walls of the first bottle. The calculated concentrations of the target analytes in the water immediately after spiking were considered as the initial concentration at t_0 without adsorption.

Analysis of the water samples

PAHs

The water samples were analysed by using an in-house method for PAHs in water in the presence of humic acids. The samples were poured into 500-mL and 1000-mL separation funnels, and 30 mL of hexane Suprasolv (Merck, Darmstadt, DE) was added. They were shaken vigorously for 1–2 min, and the phases were left to separate for 15 min whereafter the organic phase was recovered. The process was repeated, and the organic phases were pooled. The 2000-mL samples were divided in two portions for analysis, and the extracts were pooled before the drying step.

Na_2SO_4 (anhydrous, purity ≥99 %, Sigma-Aldrich, Diegem, BE) was added to the samples and left for 5 min to eliminate traces of water. The organic extract was filtered through paper filters and was then pre-concentrated to about 0.5 mL, first using a rotary evaporator and then with a gentle flow of N_2.

The extracts were injected in an Agilent 6890 gas chromatograph (GC) coupled to a mass spectrometer (MS) (Agilent Technologies, Santa Clara, CA, US). The MS was operated in electron impact ionization mode with an energy of ionization of 70 eV. The column used was a DB-17 HT (30 m × 0.25 mm i.d., 0.15 µm film) (Agilent Technologies, Amstelveen, NL). A volume of 1 µL was injected in the pulsed splitless mode with a pulse maintained for 1.2 min. The purge flow was 50 mL min^{-1}, and the gas saver was set at 20 mL min^{-1} after 5 min. The carrier gas was helium with a constant flow of 1 mL min^{-1}. The GC oven programme started at 60 °C which was held for 2 min and then increased to 140 °C at a rate of 25 °C min^{-1}, up to 320 °C at 10 °C min^{-1}, and finally held for 10 min.

The MS detector was operated in selected ion monitoring using the identification ions (m/z) listed elsewhere [26]. Quantification of PAHs was performed using the internal standard method.

PBDEs

The water samples were extracted by liquid–liquid extraction using different volumes of dichloromethane (DCM). Different amounts of solvents were added depending on the sample size: 2×30 mL of DCM for 0.5 L samples and 3×30 mL DCM for 1 L samples. Samples of 2 L were treated as two independent 1 L samples, and after the extraction, the extracts were pooled. The remaining water was eliminated using Na_2SO_4. The organic extract was concentrated to about 150 µL using a gentle flow of N_2.

PBDEs were quantified in triplicate in each concentrated extract by isotope dilution using a Clarus 600 gas chromatograph coupled to a mass spectrometer (Perkin-Elmer, Waltham, MA, US). The MS was operated in the electron impact ionization mode with an ionization energy of 70 eV. The column used was a DB-5MS (30 m × 0.25 mm i.d., 0.25 µm film) (Agilent Technologies, Amstelveen, NL). A volume of 5 µL was injected in solvent vent mode. The purge flow was 50 mL min^{-1}, and the gas saver was set at 20 mL min^{-1} after 5 min. The carrier gas was helium with a constant flow of 1 mL min^{-1}. The GC oven programme started at 50 °C which was held for 3 min and then increased to 260 °C at a rate of 30 °C min^{-1}, up to 320 °C at 10 °C min^{-1}, and finally held for 6 min.

The PBDE concentrations were calculated using the internal standard method using ^{13}C-labelled PBDEs.

TBT

The whole water sample was used for analysis by applying sodium tetraethylborate (NaBEt$_4$) derivatization prior to subsequent extraction into hexane. Samples of 2 L were treated as two independent 1 L samples, and the extracts were pooled after extraction. More specifically, 10 mL of 1 mol L^{-1} sodium acetate buffer and 500 µL 1 % (by volume) NaBEt$_4$ in tetrahydrofuran/water (1:10 by volume) were added for each 1 L sample. After 10 s of shaking, the solution was left standing for 20 min, then 1 mL of hexane was added, and the bottle was shaken for 30 min. The organic phase was separated using a micro-separator. The extract was dried over sodium sulfate before being analysed using GC–ICP–MS. Triplicate analyses were performed for each extract.

In some of the samples, a gel-like foam was formed. In these cases, the extracted foam was centrifuged to obtain the liquid hexane phase.

GC–ICP–MS analysis was performed using an Agilent 7890A gas chromatograph, equipped with an Agilent DB5-MS UI capillary column. Every four to six injections of the sample extracts, solutions of neat n-hexane and solutions of tributylethylstannane were injected.

The ^{119}Sn-enriched butyltin mix (MBT, DBT, TBT) was used as an internal standard for quantification by isotopic dilution.

Results and discussion

Container material

PAHs

Recoveries, in %, of the spiked amount of compounds were calculated (electronic supplementary material 1). The interaction of the PAHs with the container walls depends to a large extent on their hydrophobicity [16]. Naphthalene, the smallest compound (2 rings), is the most water-soluble PAH tested, thus having a lower affinity towards the suspended solids [18]. This property can explain why the recoveries in glass, aluminium and FPE bottles are very similar. For anthracene (3 rings), the recoveries in the three type of materials tested are also not very different, but there is a progressive decrease in the amounts recovered as a function of time. The recovered amount of the two compounds, naphthalene and anthracene, turned out to be substantially lower at the last sampling point (192 h) what cannot be explained by any of their physico-chemical characteristics. Even though the free chlorine amount present in the tap water used for the experiment was assumed to be too low for causing any significant degradation of the compounds, the exposure to this chemical for a long period of time seems to be the most probable reason for the observed decrease. It is well known that free chlorine in water is degrading PAHs lighter than pyrene [27].

Fluoranthene (4 rings) showed an intermediate behaviour in comparison with the light PAHs (2–3 rings) and the heaviest ones (5–6 rings). Recoveries were higher and very similar in most of the cases for glass and aluminium bottles in contrast to the FPE containers. FPE bottles result in significantly lower recoveries, but the difference to the other two container materials was not as large as for PAHs with 5 rings or more.

The results for the remaining high molecular PAHs (with the exception of benzo(a)pyrene) displayed even a more marked contrast between FPE and the other materials (example in Fig. 1a). The adsorption onto aluminium and glass was very similar, and the recoveries remained relatively constant after 3 h, decreasing slightly with time
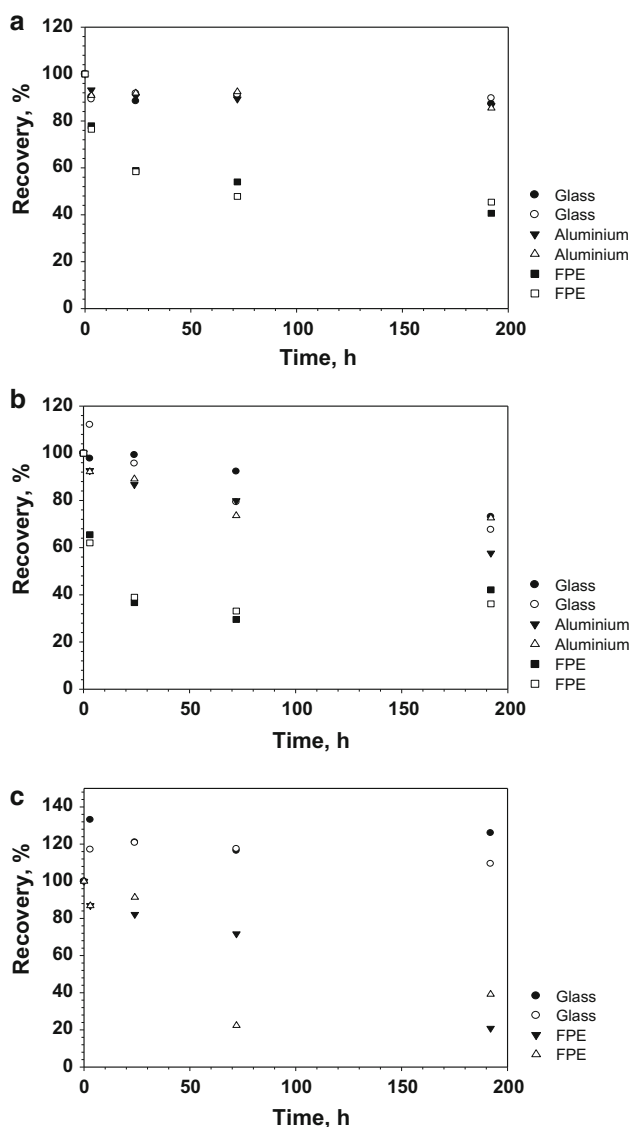
Fig. 1 Effect of the container material (glass/aluminium/FPE) on the recovery of target compounds in 1000-mL containers. **a** Benzo(b)fluoranthene (PAH), 40 ng L^{-1}, **b** BDE153, (PBDE) 2 ng L^{-1} and **c** TBT, 2.4 ng L^{-1} are shown as examples. Replicates for each series (*n* = 2) are represented individually

(final recoveries between 75 % and 95 % in glass bottles and between 70 % and 87 % for aluminium). On the other hand, their adsorption onto the FPE wall was higher (final recoveries ranging from 30 % to 48 %).

Benzo(a)pyrene (5 rings) behaved as the other high molecular PAHs with respect to the FPE container. For glass and aluminium, on the contrary, its behaviour in these materials did not resemble the other PAHs as the recovered amount was noticeably lower. In all cases, the recoveries decreased gradually to around 50 % for glass, 16 % for FPE and 40 % for aluminium after 192 h. Benzo(a)pyrene has a very similar octanol–water partition coefficient as the other investigated high molecular PAHs in the group [28].

Therefore, adsorption effects alone could not explain this phenomenon. Further literature research revealed that this compound is sensitive to chlorine and dissolved oxygen present in the water and to the storage conditions [29]. Consequently, these parameters have to be taken into account in future experiments.

There is a common trend for six out of the eight compounds regarding the evolution of the amount recovered after the different sampling periods (except for anthracene and benzo(a)pyrene). For the first 72 h, the recoveries were relatively constant and did not drop-off until the last sampling point at 192 h. Adsorption to the walls started immediately after the compounds had been added into the water [18], and it is unlikely to be the reason for the observed lower recoveries at the last sampling point. The most plausible explanation for these results is a degradation of those PAHs under the storage conditions investigated here [29].

PBDEs

The adsorption trend of PBDEs onto glass and aluminium container walls is very similar (Electronic supplementary material 2). During the first days, the recoveries are quite high and then decrease slowly until the last sampling point. However, the recoveries at $t = 192$ h are significantly higher in aluminium bottles for 500 mL and 2000 mL samples than in glass bottles. For 1000/1200-mL bottles, the difference in recoveries between aluminium and glass containers is less pronounced, although they are still higher in aluminium.

The adsorption behaviour on FPE is different. At the beginning, the loss of analytes is high, suggesting that the adsorption is very fast and then slows down. In any case, the recoveries at the end of the experiment are clearly lower than the ones observed for aluminium and glass, showing the unsuitability of FPE for the storage and sampling of water containing PBDEs (example in Fig. 1b).

TBT

The initial plan of testing aluminium bottles also for TBT was abandoned as the cleaning protocol with acid damaged these bottles. Therefore, only glass and FPE were tested for TBT. The adsorption of TBT to the container walls is dependent of the material of the bottles, as can be observed in Fig. 1c. There is a decrease in the TBT recoveries with time similar to PAHs for both of the materials, but the degree of this effect is very different. The recoveries were much lower in FPE bottles, where less than half of the added TBT was recovered after 192 h. Amber glass is clearly the best material for the bottles for the 1000 mL and 2000 mL samples.

The results obtained in this experiment are contrasting previous studies, where both types of container materials, amber glass bottles and high-density polyethylene or similar polymer materials, were deemed to be equally suitable to be used as containers for regular monitoring and sampling of TBT [23, 24, 30]. The most probable reason could be the TBT concentration in the tested water. For this experiment, the final TBT concentration was 1 ng L^{-1} (expressed as Sn), while adsorption studies in the literature were conducted at much higher concentrations, even up to $\sim 10^5$ times higher [24]. Adsorption effects are more relevant at lower concentrations [22], and this is probably the main reason why polymer bottles are less suitable for the experimental conditions of this study. It is also worth mentioning that tap water has been used in this adsorption study which poses a more complex, realistic and challenging matrix than traditionally used deionized water [24, 31]. TBT does not only adsorb to the container walls but also interacts with ions and DOC present in the tap water in contrast to almost ligand-free deionized water.

Volume of the containers

PAHs

Large differences were not found for the PAH recoveries for the different volumes tested in the present experiment (Fig. 2a). Although the surface/volume (S/V) ratio can have a large impact on the adsorption behaviour of hydrophobic organic pollutants to the container walls, most of the previous studies compared containers with extremely different S/V ratio, such as a 2-mL vial and a 1-L bottle [21]. Such large differences were not studied here. The S/V ratios of the containers are in the range 0.3–0.5 cm^2 mL^{-1} (glass and aluminium) and 0.3–0.6 cm^2 mL^{-1} (FPE) which are rather small differences compared to the ranges tested by Qian et al. [21].

The recoveries of all PAHs analysed after 192 h were independent of the volume of the bottle tested for glass and FPE containers (Electronic supplementary material 1). For aluminium, a few compounds show higher recoveries in larger containers, even if it is not a general trend. The effect of the S/V ratio is expected to be more pronounced for PAHs with higher molecular weights and lower water solubility which does not correspond with the results. The observed variability is most likely a consequence of sample preparation and the analytical process.

PBDEs

The influence of the container volume on the adsorption of PBDEs is less clear than for PAHs and TBT (Electronic supplementary material 2). In aluminium and FPE bottles,
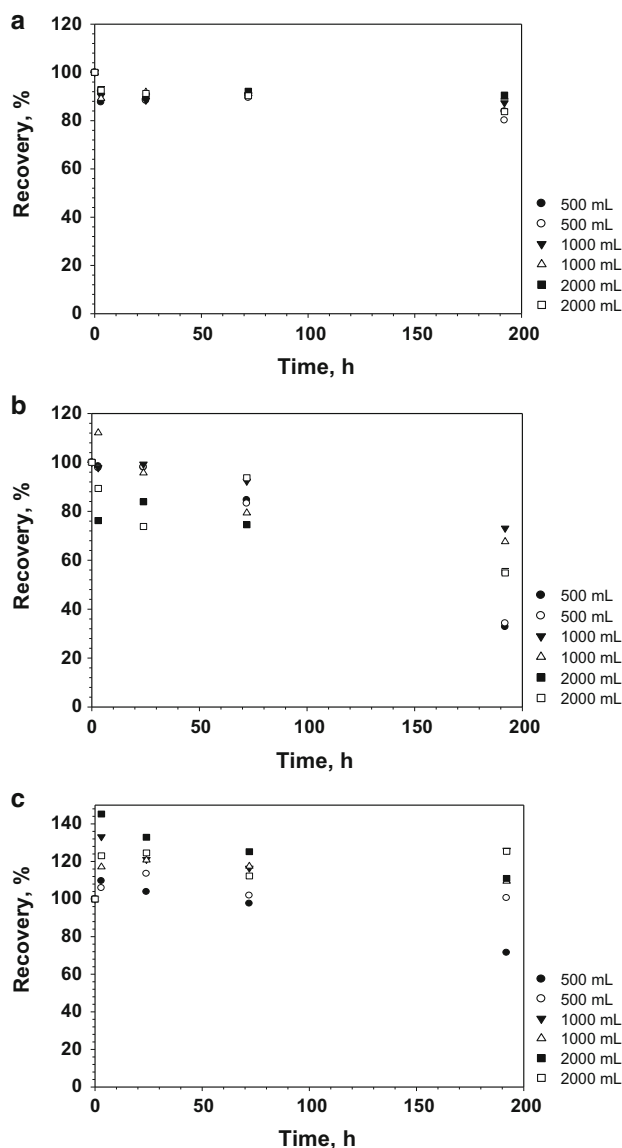

Fig. 2 Effect of the container volumes on the recovery of target compounds in glass containers. a Benzo(b)fluoranthene (PAH), 40 ng L^{-1}, b BDE153, (PBDE) 2 ng L^{-1} and c TBT, 2.4 ng L^{-1} are shown as examples. Replicates for each series ($n = 2$) are represented individually

most PBDE recoveries are unaffected by the container volume. For glass, larger containers result in higher recoveries for BDE99, BDE153 and BDE154, while no effect is observed for the other congeners. Since not all the congeners are behaving in the same way, it is not possible to conclude which container volume is the most suitable (example in Fig. 2b).

TBT

Results obtained for TBT in containers of different volumes are displayed in Fig. 2c. None of the differences

observed between the containers of different volumes were conclusive. At first glance, recoveries from 1000 mL and 2000 mL samples seem higher, but it was not possible to confirm this by a statistical test due to the data spread.

For the largest bottles, the adsorption remained constant for the last days (see from $t = 72$ h to $t = 192$ h). However, a longer sampling period should be considered to determine whether equilibrium was reached or not.

Conclusions

The suitability of different container materials for the containment, transportation and storage of water samples with PAHs, PBDEs and TBT has been evaluated. Three types of materials (glass, FPE and aluminium) and three capacities (500/600, 1000/1200 and 2000/3000 mL) were tested. Even though both aluminium and amber glass are equally suited for PAHs and PBDEs, it is not possible to include TBT, due to acid cleaning requirements for this analyte. Aluminium is therefore ruled out as a material for the selection of a common container for the three groups of compounds tested. Containment of water samples for PAH and PBDEs in aluminium bottles at ng L^{-1} levels is possible because of the high recoveries found in this study. Consequently, it is worth to take this container material into account for future work as aluminium bottles are almost non-breakable, opaque, low weight and durable in contrast to glass.

FPE containers are clearly unsuitable for all the compounds tested since the adsorption to the walls is too high especially at the very low analyte concentrations tested here.

The volume of the bottles is not affecting the adsorption behaviour of PAHs, PBDEs and TBT significantly. It could be argued that 1-L bottles are easier to transport and that they fulfil the minimum sample volumes needed for most of the existing analytical methods for the target compounds.

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