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# Investigation of sorption phenomena by solid phase extraction and liquid chromatography for the determination of some ether derivatives of tetrabromobisphenol A

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## Abstract

Observed sorption and chromatographic behaviour served as a starting point for examination of four ether derivatives of the flame retardant tetrabromobisphenol (TBBPA); dihydroxyethyl (DHEE), dimethyl (DMe), diallyl (DAE) and dibromopropyl (DBPE). To date, there is little or no information about these compounds in the scientific literature. The targets in the present study had calculated log  $K_{ow}$  values of 6.0–10. A broad range of different types of solvents were used in order to elucidate the mechanisms of sorption onto silica (glass) and two solid phase extraction cartridges based on polystyrene divinylbenzene polymers, hydroxylated (Isolute ENV+) and vinylpyrrolidone (Oasis HLB) containing units. Also, three chromatographic columns (C18, C8, and dual C18-based, i.e. a polar ligand together with C18 on a silica surface) were evaluated. The following were observed: desorption of the targets from silica surface by 1-propanol showed the best results and the yields were further improved by silylation of the surface. Regardless of the experimental test conditions applied, the lowest recovery was seen for the DMe derivative, followed by TBBPA itself, which had calculated log  $K_{ow}$  values in between the other targets. A washing solution containing up to 70% of methanol could be used without elution of the targets from the . The dihydroxyethyl ether derivative of TBBPA is most probably not affected by environmental relevant pH due to a likely high  $pK_a$  (*ca* 15). Also, this study shows that the polar character of the dual-phase column was not as pronounced as asserted by the manufacturer.

## Introduction

Tetrabromobisphenol A (TBBPA) is the most extensively used brominated flame retardant (BFR),<sup>1</sup> with a global market of about 170 000 tonnes in 2004, representing more than 50% of the production of all BFRs.<sup>2</sup> The success of TBBPA arises from the fact that it is cheap, it is highly effective in fire prevention, and, most importantly, it is not considered to constitute a threat to either human health or environment.<sup>3</sup> This profile is unique compared to the characteristics of other BFRs, such as polybrominated diphenyl ethers. Accordingly, TBBPA and oligomers and ether derivatives of TBBPA are incorporated into a broad range of plastic products and epoxy resins that are used in electrical and electronic equipment and installations worldwide.<sup>2,4</sup> Together, the TBBPA derivatives utilized as flame retardants and TBBPA oligomers represent 18% of the total sales of TBBPA.<sup>2</sup> To our knowledge, few data are available on only one of the individual derivatives. That is unfortunate, since there are about 75 different BFRs, and thus the derivatives represent a substantial part of the compounds in use, even though each one hypothetically constitutes only 1% of the TBBPA family (i.e. 1700 tonnes). It should also be mentioned that the derivatives are relatively new as BFRs, and the proportions in use are expected to increase.<sup>5</sup>

The two hydroxyl groups on the TBBPA molecule make it possible to reactively incorporate the compound into the backbone of the polymeric product, as is done in epoxy resins in printed circuit boards.<sup>6</sup> This process represents the most prevalent commercial application of TBBPA, although the compound is also employed to a lesser extent as a regular additive, for example in acrylonitrile butadiene styrene (ABS) plastics used in electronic housings. Moreover, the ether derivatives are used as reactive or additive flame retardants, depending on whether or not they contain reactive groups (*e.g.*

hydroxyls; cf. Table 1). However, the TBBPA oligomers are only added reactively and are part of the main constituents in the plastic resin.

Data on the various physico-chemical properties of the ether derivatives of TBBPA are scarce in the literature, although TBBPA itself has been studied extensively. Compared to all its derivatives, TBBPA has the lowest molecular weight with a log  $K_{ow}$  of 4.5.<sup>1</sup> Thus, the TBBPA family is very hydrophobic, and, considering environmental partitioning, its members would preferably adsorb to solids and concentrate in sediments.<sup>7,8,9</sup> The same might be true for the ether derivatives, although to our knowledge there are no studies that support that conclusion. Field analyses have detected the dimethoxy derivative of TBBPA (TBBPA-DMe) in tissues of marine organisms,<sup>7</sup> but reports are conflicting as to whether TBBPA-DMe is actually used as a flame retardant; for instance, Alaei *et al.*<sup>10</sup> and de Wit<sup>4</sup> have claimed that it is indeed the case, whereas the Bromine Science and Environmental Forum (BSEF) asserts that it is not (K.P. Rothenbacher, 2008, pers. comm.). Furthermore, it has been suggested that TBBPA-DMe is a product of microbe-mediated transformation of TBBPA.<sup>7</sup>

Sorption of hydrophobic constituents is usually ascribed to the organic (carbon) content of the matrix of interest, such as soil and sediment, but adsorption of hydrophobic compounds to mineral surfaces has been studied as well.<sup>11</sup> Non-ionic compounds may adsorb to silica-based constituents like the surface of laboratory glass,<sup>12</sup> which can lead to confusion when interpreting analytical results.<sup>13</sup> The latter problem is seldom discussed in the scientific literature, although Furtmann<sup>14</sup> and Sjödin<sup>15</sup> have considered these polar surface attraction phenomena in investigations of phthalates and organohalogens, respectively.

Liquid-liquid extraction using an organic solvent is the most commonly applied method for analysis of TBBPA in sediments or wastewater,<sup>16,17</sup> and solid phase extraction (SPE) has been employed to determine TBBPA in human plasma<sup>9,18</sup> and serum.<sup>19</sup> Although much analytical and environmental data on TBBPA have been accumulated and a paper concerning analysis of the derivative TBBPA bis(2,3-dibromopropylether) has been published<sup>5</sup>, little has been reported about the ether derivatives in the TBBPA family. Accordingly, we chose to investigate aspects of the analysis of some of those compounds and the problems associated with their adsorption on polar and non-polar surfaces, specifically silica (glass) and two types of polystyrene-divinyl benzene (PS-DVB) polymers used for solid phase extractions. We employed different solvents in the extractions, because our aim was to study and compare the derivatives, not to optimize analytical protocols. The higher molecular weight derivatives are not amenable to analysis by gas chromatography, and hence we used liquid chromatography instead. This work was an essential part of a comprehensive study of degradation of the ether derivatives, the results of which are to be reported separately.<sup>20</sup>

## Experimental

### Chemicals and equipment

This study targeted four ether derivatives of TBBPA: TBBPA (97%, cas 79-94-7), TBBPA-dihydroxyethylether (TBBPA-DHEE, > 95%, cas 4162-45-2), TBBPA-diallylether (TBBPA-DAE, > 95%, cas 25327-89-3), TBBPA-dibromopropylether (TBBPA-DBPE, > 90% cas 21850-44-2), and TBBPA-dimethyl ether (TBBPA-DMe, 98%, cas 37853-61-5). The chemical structures and molecular weights of those derivatives are given in Table 1.

TBBPA was purchased from Sigma-Aldrich (Sweden) and three of the TBBPA derivatives were from Tokyo Chemical Industry (Labora Chemicon, Sweden). Dimethylated TBBPA was synthesized in our laboratory (see below). Several solvents representing a wide range of polarities and dipole moments were used (see Table 2 where the solvents are listed in order of increasing polarity): pentane, hexane, toluene, dichloromethane, 1-propanol, tetrahydrofuran (THF), ethyl acetate, acetone, methanol, and acetonitrile. The methanol and 1-propanol were of HPLC grade, and all other chemicals were of *pro analysis* quality (VWR International, Sweden). The solvents were chosen not only on the basis of

1  
2 polarity, but also with regard to elementary structure and functional groups, considering them as  
3 aromatic (toluene), hydroxylated (n-propanol, methanol), ether (THF), halogenated (dichloromethane),  
4 ketone (acetone), and ester (ethyl acetate) eluents.  
5

6  
7 In the SPE analyses, we used Isolute ENV+ and OASIS HLB cartridges (200 mg; purchased from  
8 Sorbent and Waters, respectively), and both types were packed with PS-DVB-based polymers that had  
9 been produced as general sorbents suitable for compounds with properties ranging from hydrophilic to  
10 lipophilic. According to the manufacturer, this is feasible because ENV+ and OASIS HLB contain,  
11 respectively, hydroxybenzene and vinylpyrrolidone units in the PS-DVB backbone.  
12

### 13 14 **Synthesis of TBBPA-dimethyl ether**

15 The non-commercial TBBPA-DMe (*i.e.* the methyl ether derivative of TBBPA) was synthesized by  
16 the following procedure. First, sodium was added to methanol to generate methoxide, and then  
17 TBBPA was added and transformed to its deprotonized form as it dissolved in the strong alkaline  
18 solution. Next, methyl iodide was added, and the solution was stirred for 15 min and then refluxed at  
19 40 °C. The target compound, sodium, and methyl iodide were added in molar proportions of 5:12:24.  
20 The target was gradually methylated, and small aliquots of the solution were subsequently analysed by  
21 full-scan GC-MS to confirm the identity of the reaction product, and then the solution was diluted in  
22 water and extracted with three portions of dichloromethane. The collected organic phase was purified  
23 from unreacted reagents by extraction with two portions of water. Thereafter, the cleaned extract was  
24 dried using sodium sulphate and then evaporated to complete dryness to give the TBBPA-DMe (98%)  
25 as white crystals. A chromatographic system comprising a Hewlett-Packard 6890 GC and 5973 MS  
26 was used to establish the identity and purity of the product. Separation was done on a capillary column  
27 (5% phenyl VF-5MS, dimensions 15 m, 0.25 mm, and 0.25  $\mu\text{m}$  i.d.; Scantec Lab, Sweden). The  
28 extract was silylated with TMS (trimethylsilyl) reagent prior analysis. The TMS reagent was prepared  
29 from bis(trimethylsilyl)-trifluoroacetamide (BSTFA), chlorotrimethylsilane (TMCS) in pyridine  
30 (10:1:10). Detection was performed by electron ionization (70 eV) in the full-scan mode ( $m/z$  50–700),  
31 and the mass spectrum obtained is shown in Fig. 1.  
32  
33  
34  
35  
36

### 37 **Instrumentation and chromatographic conditions**

38 The targets were analysed using a Waters HPLC instrument (pump 510) equipped with a UV detector  
39 (Waters 481) at a wavelength of 280 nm, which had proven to be relevant for all the targets. Retention  
40 of the targets was evaluated using traditional silica-based columns: C8 and C18 (4.6  $\times$  150 mm, 5  $\mu\text{m}$   
41 particle size; Waters, Sweden), and a reversed-phase Synergi column (4  $\mu$  Fusion-RP 80A; dimensions  
42 4.4  $\times$  100 mm) comprising a dual phase with a polar non-nitrogen-containing ligand together with C18  
43 on a silica surface purchased from Phenomenex (Genetec AB, Sweden). Unfortunately, it was not  
44 possible to obtain any additional information on the chemical structure of the polar-embedded C18  
45 Synergi column.  
46

47  
48 The mobile phase consisted of selected concentrations of methanol (Table 3) and 3% acetic acid to  
49 ensure complete protonization of the phenolic targets. The analyses were performed under isocratic  
50 conditions at a flow rate of 1  $\text{mL min}^{-1}$ , and the extract (20  $\mu\text{L}$ ) was injected into the system (Waters  
51 717 plus autosampler). Chromeleon software (version 6, Dionex) was used to evaluate the  
52 chromatograms.  
53  
54  
55

### 56 **Extraction procedures**

57 Each test was performed in duplicate, and the areas of the chromatograms were compared with the  
58 area recorded by direct analysis of the target. Calibration curves including five different concentrations  
59 (range 0–100  $\text{mg l}^{-1}$ ) of each target showed  $R^2 = 0.99\text{--}1.00$ .  
60

### **Liquid extraction of the solid silica phase**

Prior to use, all glassware was washed and heated as previously described<sup>23</sup> in order to avoid contamination. Glass bottles (120 mL) were used as sample vessels in the silica sorption tests. The target (20 µg) was spread on the glass surface by drop-wise application of acetone (1.00 cm<sup>3</sup>). Thereafter, the acetone was allowed to evaporate at ambient temperature for 20 h, and the target was subsequently extracted using two portions of solvent (10 cm<sup>3</sup> each). The bottles were capped with Teflon-coated rubber stoppers. To increase the extraction capacity, the bottles were heated at 60 °C for 5 min in a water bath and then vigorously shaken by hand for 10 min. The extraction was continued for 20 min on a rotary table at 180 rpm, after which the extract was transferred to a conical glass tube and evaporated to dryness under a gentle stream of nitrogen gas. The residues were diluted in methanol (200 µL) before analysis. A test showed that there had been no losses during the evaporation process.

In some experiments, we also silanized the inside of the glass sample bottle with dimethyl-dichlorosilane (Sigma-Aldrich, Sweden; 3.4% in toluene) in an attempt to reduce adsorption of the targets to the silica surface. After the silanization, the bottles were dried for approximately 6 h at ambient temperature before performing the drop-wise addition of target solutions. The extraction was performed as described above.

Different extraction protocols (including varied volumes and portions of solvent) and procedures (variation in time, temperature, and performance) were tested to ensure a robust and reliable method for accurate comparisons of the solvents that were investigated.

#### ***Solid phase extraction of the water phase***

The SPE cartridges were conditioned and dried according to the protocol provided by the manufacturers: conditioning with methanol (3 cm<sup>3</sup>); equilibration with the same matrix as the sample (3 cm<sup>3</sup>); application of the sample; vacuum drying (30 min); elution with the chosen solvent.

#### ***K<sub>ow</sub> calculations***

A log K<sub>ow</sub> value was available for TBBPA (4.5; WHO, 1995) but not for the other investigated derivatives. To allow comparison of the results, log K<sub>ow</sub> values for all derivatives were calculated with ALOGPS 2.1 software,<sup>21</sup> which uses several calculation programs and reports average values and standard deviations (Table 1).

## **Results and discussion**

#### ***Desorption from a silica surface***

A more comprehensive test protocol including a wide range of solvents with different polarities and dipole moments (Table 2) was employed for the most hydrophobic derivative (TBBPA-DBPE), since we had initially experienced difficulties with desorption of that target. The use of two hydrophobic solvents, hexane (representing n-alkane solvents) and toluene (representing aromatic solvents), which presumably appealed to the hydrophobic and aromatic properties of the TBBPA-backbone structure, showed that toluene was not favoured over hexane. In fact, the best recovery was achieved using hexane (44% compared to 21% for toluene), which has both a lower polarity index and a smaller dipole moment than toluene. Acetonitrile was the most powerful water-soluble extraction medium for the DBPE derivative (yield 73%), probably because that solvent has a high polarity index in combination with a large dipole moment (Table 2). Methanol was a poor solvent (extraction yield 39%), perhaps because it lacks hydrophobic properties due to the presence of only one carbon atom in the molecular structure. Acetone, the chosen solvent for the stock solutions, was completely unable to desorb the DBPE derivative (below detection limit). Consequently, the ability of the solvents to extract the TBBPA ether derivatives from the silica surface of the experimental vessel could not have depended solely on the solubility properties of the derivatives, but must have also been determined by the degree to which sorption sites were exposed on the solid surface. In other words, a polar surface

1  
2 attracts hydrophobic compounds better than a liquid with the same polarity.<sup>24</sup> When a solution of the  
3 target is spread on a glass surface and the solvent is then allowed to evaporate, as in our study, the  
4 silica sites participating in the adsorption mechanism will be maximized. The best overall recoveries  
5 in our investigation were obtained using 1-propanol (Table 3).  
6

7  
8 Adsorption of hydrophobic compounds on silica (glass) surfaces is a well-known problem for  
9 analytical chemists trying to evaluate their protocols. Also, since considerable amounts of the target  
10 compounds can escape analysis due to adsorption on the glassware that is used, it is important to  
11 conduct experiments in a manner that will avoid that phenomenon. For example, the glass surface can  
12 be wetted with a hydrophobic solvent such as hexane before the targets (*e.g.* phthalates) are introduced  
13 into the sample vessel.<sup>14</sup> Another well accepted procedure is to treat silica surfaces with silylating  
14 agents in order to reduce polar interactions (*e.g.* with organosulphur compounds<sup>25</sup>). In our study,  
15 silanization of the glass vessels increased the extraction yield of the DBPE derivative from 53% to  
16 86% when 1-propanol was used as solvent. In general, solvent extractions of the silica surface resulted  
17 in relative standard deviations (RSDs) of up to 12% ( $n = 3$ ), and the highest value was valid for  
18 TBBPA-DMe. In fact, we found that the smaller the yield of the target, the larger the RSD value.  
19  
20

### 21 22 ***Desorption from PS-DVB based polymers***

23 All targets were completely adsorbed on both ISOLUTE ENV+ and OASIS HLB in tests using SPE  
24 columns, as confirmed by analysis of the matrix solution that passed through the cartridges. In runs  
25 using the ENV+ cartridge, only methanol was to some degree capable of extracting all targets, with the  
26 exception of the two most hydrophobic compounds TBBPA-DAE and TBBPA-DBPE (data not  
27 shown). It is very likely that the aromatic structure of the SPE cartridge in combination with the  
28 hydroxyl moiety of the hydroxylated polymer appealed to the inherent characteristics of the most  
29 hydrophobic derivatives to such an extent that neither the hydrophobic nor the polar interactions were  
30 diminished by any of the solvents. In an earlier study performed in our laboratory,<sup>25</sup> it was found that a  
31 highly hydrophobic compound (diethylhexyl phthalate) was adsorbed to PS-DVB polymers via  
32 hydrophobic as well as polar interactions. The results of that investigation showed that polar  
33 attractions were indeed involved and that it was necessary to use a polar eluent to achieve better  
34 recovery. Obviously, none of the characteristics of the solvents used in the present study possessed the  
35 desorption properties needed to extract the two most hydrophobic compounds (highest calculated  $\log$   
36  $K_{ow}$ ) from ISOLUTE ENV+.  
37  
38

39  
40 OASIS HLB exhibited the same behaviour when methanol was applied as eluent. Nonetheless, in tests  
41 using that polymer, ethyl acetate proved to be the best eluting solvent for all targets, including the  
42 troublesome TBBPA derivatives DAE and DBPE (Table 3). Regardless of the solvent employed, the  
43 lowest recovery was seen for TBBPA-DMe (18% and 45% for methanol and ethyl acetate,  
44 respectively).  
45  
46

47 To avoid difficulties associated with chromatographic separation of compounds co-eluted from an SPE  
48 column, it is advisable to carry out a washing step prior to the elution. In our study, no targets were  
49 observed in the eluted extracts when we used up to 70% methanol as washing solution. However, it  
50 should be kept in mind that complex sample matrices may lower the adsorption capacity of the SPE  
51 cartridge, and therefore each matrix should be tested to ensure a safe washing solution.<sup>26,27</sup>  
52

53 In general, elution of the OASIS HLB cartridge resulted in RSD values of up to 7.5% ( $n = 3$ ), and as  
54 for the sorption study with silica, the highest value was valid for TBBPA-DMe, *i.e.* as for the  
55 desorption from the silica surface, the smaller the yield, the larger the RSD.  
56  
57

58 The solid phase extraction sorbents were chosen to appeal to the targets with both hydrophobic and  
59 hydrophilic properties. However, the strong hydrophobic properties of the TBBPA derivatives with  
60 highest calculated  $\log K_{ow}$  values (DAE and DBPE) should probably benefit from a sorbent with less  
pronounced hydrophobic attraction, *e.g.* silica based, in order to reduce the 1) dual sorption power of  
the sorbent and 2) subsequent dual elution capacity of the eluting solvent.

### Chromatographic retardation

The TBBPA derivatives with the highest log  $K_{ow}$  values were too strongly retarded on the HPLC columns when lower concentrations of methanol were used as mobile phase, and hence retention times longer than 60 min were excluded from the test protocol. Furthermore, to eliminate the influence of various column dimensions on the retention times, we used the dimensionless capacity factor ( $k$ ) presented in Table 4, which were calculated according to the following equation:

$$k = \frac{tR - tM}{tM} \quad (\text{eq. } 1)$$

where  $tR$  and  $tM$  refer to retention times for the target and the mobile phase, respectively. It is usually recommended to have peaks with capacity factors that are greater than 1 but less than 10–15, and the latter limit is considered appropriate due to problems associated with resolution and detection.<sup>28</sup> We found that when using weaker mobile phases (*i.e.* lower methanol concentrations), retardation was less pronounced (lower capacity factors) on the dual-phase column than on the C8 and C18 columns (Table 4). The weakest overall retardation of the targets occurred on the C8 column, and even though the dual-phase column comprised polar units, the influence of its non-polar C18 units predominated, as indicated by the higher capacity factor values for the dual-phase than for the C8 column. These observations suggest that a C8 column is just as suitable as the studied Synergi dual-phase column for analysis of targets with a broad range of hydrophobicities. Increasing the fraction of the polar units among the C18 chains would probably enhance the characteristic identity of the Synergi column as compared to the traditional alkyl columns, and thereby strengthen the manufacturer's assertion that dual columns are more suitable for compounds with widely varying hydrophobicities. A literature survey shows that, the relatively new Synergi Fusion-RP column employed in the present study has been in use since 2006 but has been utilized in only a few scientific studies. Two of those investigations<sup>29,30</sup> indicated that the Synergi column offered chromatographic benefits, and one<sup>31</sup> suggested that it has drawbacks compared to other columns, and the remaining four studies merely mentioned that the Synergi column had been used, without any further comments.

### Physico-chemical characteristics of the TBBPAs

To fully understand the extent of partitioning processes, it is necessary to consider the importance of uneven distribution of electrons on the target molecules. The compounds of interest here consist of ether or hydroxyl functional groups together with bromine atoms attached to the carbon skeleton, thus they are inherently monopolar (ether and bromine) and bipolar (hydroxyl). Additionally, the aromatic ring structure also gives the molecules polarizing effects. Such physico-chemical properties have a substantial impact on adsorption to surfaces and the ability to desorb into and dissolve in the surrounding medium.<sup>24</sup>

The highest calculated log  $K_{ow}$  values (Table 1) were noted for TBBPA-DBPE and TPPBA-DAE, which have the same number of carbon and hydrogen atoms but differ in that the former has two bromine atoms on each ether group, and the latter contains a double bond (allyl). The allyl groups in the TBBPA-DAE molecule add exposed delocalized electrons that contribute more to the polar characteristics than is the case for the electronegative bromines in TBBPA-DBPE. This is indicated by the lower log  $K_{ow}$  (Table 1) and capacity factor values of the DAE derivative compared to TBBPA-DBPE (Table 4), although that conclusion was neither confirmed nor refuted by the findings of the SPE experiments (Table 3).

Comparing the two hydroxylated targets, *i.e.* TBBPA and TBPPA-DHEE, the three dimensional positions of the hydroxyl groups suggest that on TBBPA the hydroxyls are hidden to a greater extent than the bromine atoms are and hence cannot exert a polar effect that is as powerful as that of the more exposed hydroxyl groups on the DHEE derivative (*cf.* molecular structures in Table 1). In other words, the hydroxyl groups on the DHEE derivative should have a greater influence on the polarity of the

1  
2 molecule than the hydroxyl groups on TBBPA do. This is indeed indicated by the shorter retention  
3 times of TBBPA-DHEE, noted as lower capacity factors in HPLC analysis (Table 4) and a lower  
4 calculated log  $K_{ow}$  value (Table 1).  
5

6 The polarity of hydroxyl groups is effectively concealed by methylation.<sup>24</sup> In our study, this is shown  
7 by the observation that TBBPA had a lower log  $K_{ow}$  (Table 1) and lower capacity factor values  
8 compared to its methoxylated derivative TBBPA-DMe (Table 4). The fact that the lowest recoveries  
9 of TBBPA-DMe were seen upon extraction from silica and desorption from the SPE cartridge  
10 indicates that polar and non-polar sorption strengths are equal for this compound, and thus both must  
11 be complemented in the extraction/eluting solvent. Consequently it will be necessary to find a more  
12 powerful eluting medium for this compound before a satisfactory analytical protocol can be achieved.  
13 In our experiments, compared to TBBPA-DMe, extraction yields were greater for targets with lower  
14 calculated log  $K_{ow}$  as well as those with higher such values, which suggests that those compounds will  
15 be easier to extract from environmental matrices than TBBPA-DMe.  
16  
17

18 It is highly likely that the targets exposing free hydroxyl groups, *i.e.* TBBPA and TBBPA-DHEE, are  
19 influenced by the pH of the surrounding medium. A study has indicated  $pK_a$  values of 7.5 and 8.5 for  
20 TBBPA<sup>1</sup>, which shows that this compound is at least partly deprotonated under normal environmental  
21 conditions. The molecular structure of the DHEE derivative suggests that its  $pK_a$  should be at least one  
22 or probably several units higher than the corresponding value for TBBPA, since the alkoxides are not  
23 stabilized as extensively by the aromatic backbone and its bromine atoms as is the case for the  
24 phenolate on the TBBPA molecule. By comparison, 2-phenoxyethanol has a  $pK_a$  of 15.1.<sup>32</sup>  
25 Consequently, we suggest that DHEE is a very strong base and therefore exist as a neutral compound  
26 in nature.  
27  
28

## 30 Conclusions

31 The observed results from the partitioning tests show that the inherent physico-chemical properties of  
32 the studied ether derivatives of TBBPA differ to such extent, and therefore cover a wide range of  
33 sorption properties, that it is impossible to cover the targets with sufficient yields in one single  
34 analytical protocol. In common for all compounds were i) the inherent properties cover both polar and  
35 nonpolar characteristics, which are not consistent with their calculated log  $K_{ow}$  values and ii) the  
36 polarization property of the silica hydroxyl groups on glassware surfaces, which exert strong sorption  
37 qualities on the targets, suggests that glassware used in the analyses should be treated prior usage in  
38 order to reduce this sorption effect.  
39  
40

41 For the individual compounds, it was definitely shown that the methoxy derivative of TBBPA, *i.e.*  
42 TBBPA-DMe, showed strongest sorption properties in all studied extraction perspectives, since this  
43 compound presented the lowest recoveries irrespectively of studied adsorbent and eluting solvent.  
44 These findings would definitely obstruct environmental trace analyses of this compound.  
45  
46

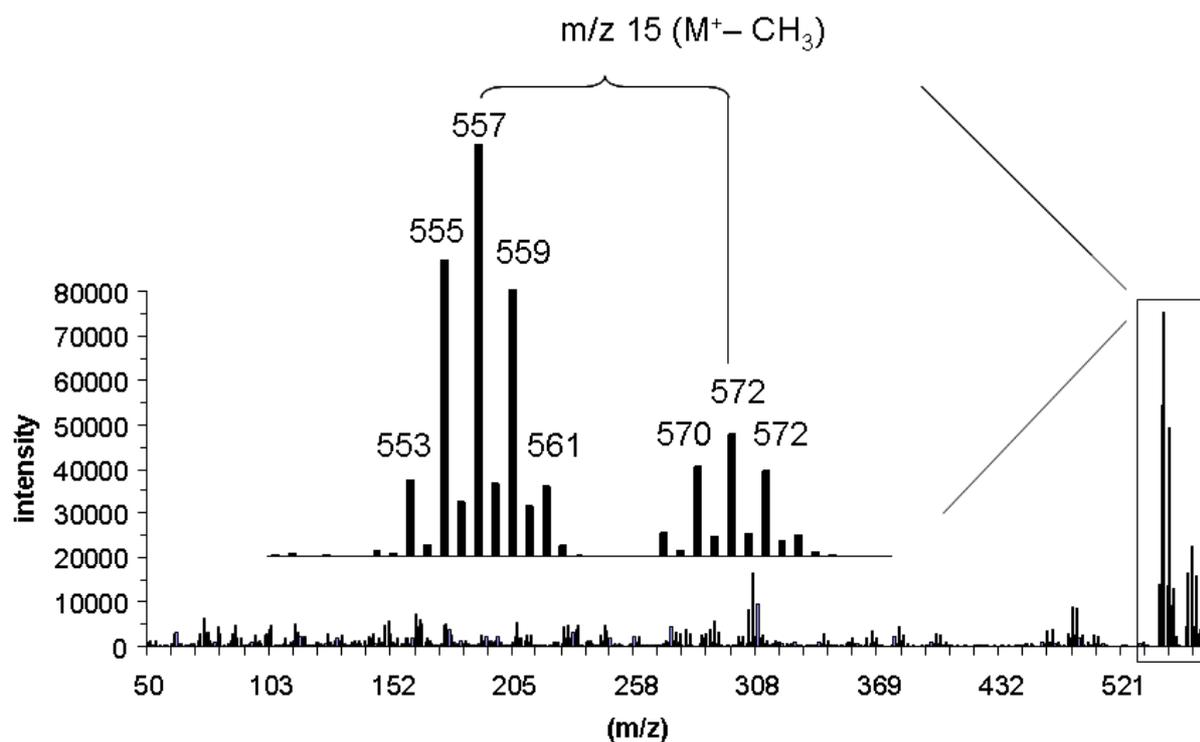
47 Regarding the two hydroxylated targets TBBPA and its DHEE derivative, pH should be taken into  
48 consideration for TBBPA during analysis. The extraction pH of TBBPA should be 5.5 or less, which  
49 is two pH units below the lowest  $pK_a$  for that compound. In contrary, the DHEE derivative most  
50 probably exists only as a neutral compound in aqueous environments and is therefore not affected by  
51 pH changes during analytical extraction procedures.  
52  
53

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59  
60

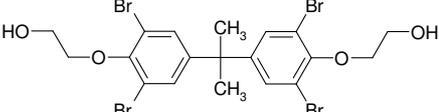
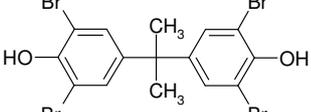
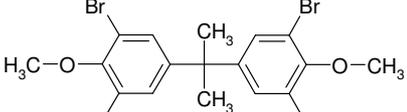
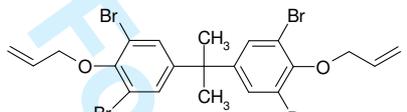
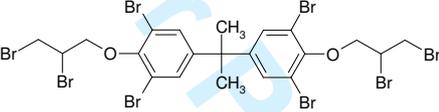
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29 **Fig. 1.** Mass spectrum of the synthesized TBBPA-DMe. The isotope ratios (derived from the four  
30 bromine atoms on the TBBPA skeleton) of the mass fragments in the two clusters were  
31 18:72:100:65:17 (litt. 17:68:100:65:16). Other investigators<sup>7</sup> have used m/z 555, 557, 559, and 572  
32 as diagnostic fragments for this compound.  
33

**Table 1.** Chemical structures, molecular weights, and octanol-water partitioning coefficients (log  $K_{ow}$ ) of the target compounds listed in order of increasing log  $K_{ow}$  values

| Ether derivative | Chemical structure  | Mw  | Log $K_{ow}$ <sup>a)</sup> |
|------------------|---|-----|----------------------------|
| TBBPA-DHEE       |  | 632 | 6.02 (± 0.68)              |
| TBBPA            |  | 544 | 6.70 (± 0.62)              |
| TBBPA-DMe        |  | 572 | 7.36 (± 0.79)              |
| TBBPA-DAE        |  | 624 | 8.63 (± 1.03)              |
| TBBPA-DBPE       |  | 944 | 9.99 (± 1.56)              |

<sup>a)</sup> Log  $K_{ow}$  was calculated using ALOGPS 2.1 software<sup>21</sup>.

**Table 2.** Polarity index and dipole moment of each of the solvents used in this study (Tables Polarity Index and Dipole Moment<sup>22</sup>), listed in order of increasing polarity index, and extraction yields of TBBPA-DBPE from silica

|                 | Polarity Index* | Dipole Moment* | Yield of DBPE from silica (%) |
|-----------------|-----------------|----------------|-------------------------------|
| Pentane         | 0.0             | 0.0            |                               |
| Hexane          | 0.1             | 0.1            | 44                            |
| Toluene         | 2.4             | 0.3            | 21                            |
| Dichloromethane | 3.1             | 1.1            |                               |
| THF             | 4.0             | 1.8            |                               |
| 1-Propanol      | 4.0             | 3.1            | 64                            |
| Ethyl acetate   | 4.4             | 1.9            |                               |
| Acetone         | 5.1             | 2.7            | b.d                           |
| Methanol        | 5.1             | 2.9            | 39                            |
| Acetonitrile    | 5.8             | 3.4            | 73                            |

\*For comparison, water has a polarity index of 10 and dipole moment of 1.9

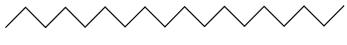
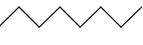
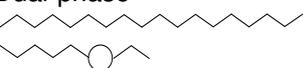
**Table 3.** Yields of TBBPA and ether derivatives of that compound obtained using different solvents in extractions from a silica surface (glass) or a solid-phase cartridge consisting of vinylpyrrolidone units on a PS-DVB polymer backbone; OASIS HLB.

| Sorbent<br>Desorbing solvent | Silica surface | OASIS HLB |               |
|------------------------------|----------------|-----------|---------------|
|                              | 1-propanol     | Methanol  | Ethyl acetate |
| TBBPA-DHEE                   | 67             | 96        | 99            |
| TBBPA                        | 65             | 52        | 61            |
| TBBPA-DMe                    | 23             | 18        | 41            |
| TBBPA-DAE                    | 69             | b.d.      | 47            |
| TBBPA-DBPE                   | 72             | b.d.      | 72            |

b.d. = below detection limit

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**Table 4.** Capacity factors of the TBBPA derivatives listed according to their calculated  $\log K_{ow}$  values (Table 1) at different methanol concentrations (70–98%) when eluted from three different HPLC columns.

| Column     | C18  |     |     |     | C8  |     |     |     | Dual-phase  |     |     |     |
|------------|---|-----|-----|-----|--|-----|-----|-----|--|-----|-----|-----|
|            | 98%   | 90% | 80% | 70% | 98%  | 90% | 80% | 70% | 98%  | 90% | 80% | 70% |
| TBBPA-DHEE | 0.3   | 0.9 | 2.5 | 8.3 | 0.4  | 0.8 | 2.1 | 7.1 | 0.1  | 1.1 | 1.9 | 5.6 |
| TBBPA      | 0.5   | 1.2 | 3.7 | 13  | 0.5  | 0.9 | 2.8 | 9.7 | 0.2  | 1.4 | 2.7 | 8.5 |
| TBBPA-DMe  | 2.2   | 5.8 | 26  | *   | 0.7  | 2.5 | 9.4 | 41  | 1.6  | 1.7 | 12  | 56  |
| TBBPA-DAE  | 2.0   | 12  | *   | *   | 1.0  | 3.2 | 23  | *   | 2.0  | 4.5 | 24  | *   |
| TBBPA-DBPE | 3.6   | 26  | *   | *   | 1.3  | 5.8 | *   | *   | 3.9  | 11  | *   | *   |

\*Capacity factors corresponding to retention times > 60 min.

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