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## Trace determination of the flame retardant tetrabromobisphenol A in the atmosphere by gas chromatography–mass spectrometry

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1 **Trace determination of the flame retardant tetrabromobisphenol A in the**  
2 **atmosphere by gas chromatography-mass spectrometry**

3  
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15 **Abstract**

16  
17 A simple and effective method has been developed for analysis of the flame retardant  
18 tetrabromobisphenol A (TBBPA) in environmental samples by using modified soxhlet  
19 extraction in combination with silica gel clean-up, derivatization with silylation reagent, and  
20 gas chromatography–mass spectrometry (GC–MS) in selected ion monitoring mode (SIM).  
21 Satisfactory recoveries were achieved for the large volume sampling, soxhlet extraction and  
22 silica gel clean-up. The overall recovery is  $79 \pm 1\%$ . The derivatization procedure is simple  
23 and fast, and produces stable TBBPA derivative. GC-MS with electronic impact (EI)  
24 ionization mode shows better detection power than using negative chemical ionization (NCI)  
25 mode. EI gives a method detection limit of  $0.04 \text{ pg m}^{-3}$  and enables to determine trace  
26 TBBPA in ambient air in remote area. The method was successfully applied to the  
27 determination of TBBPA in atmospheric samples collected over land and coastal regions. The  
28 concentrations of TBBPA ranged from below the method detection limit ( $0.04 \text{ pg m}^{-3}$ ) to  $0.85$   
29  $\text{pg m}^{-3}$ . A declining trend with increasing latitude was present from the Wadden Sea to the  
30 Arctic. The atmospheric occurrence of TBBPA in the Arctic is significant and might imply  
31 that TBBPA has long-range transport potential.  
32

33 **Keywords:** gas chromatography-mass spectrometry; derivatization; tetrabromobisphenol A; atmosphere

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## 1 **1. Introduction**

2  
3 Brominated flame retardants (BFRs), particularly polybrominated diphenylethers (PBDEs),  
4 tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) have been used in a  
5 variety of commercial application. TBBPA is probably the most widely used flame retardant  
6 [1]. The worldwide market demand for TBBPA was estimated at 170,000 tonnes per year in  
7 2004 [2], 84.62% of which is used in Asia, with total market demand in America and Europe  
8 down to 9.38% and 6%, respectively. Although the market demand of BFRs decreases in  
9 Europe and Americas, as the market demand in Asia increase dramatically, the gross world  
10 production of TBBPA keeps an increasing trend.

11 TBBPA is used primarily as a reactive flame retardant in printed circuits boards (90%) but  
12 also used as an intermediate in the production of other brominated flame retardants, TBBPA  
13 derivatives and brominated epoxy oligomers [3]. TBBPA is chemically bound in the reactive  
14 applications and has no potential for emissions to the environment. In addition, TBBPA is  
15 also used as an additive flame retardant in plastics, which can be released into the  
16 environment by emission. In Europe, there are four BFRs manufacturing plants that are  
17 located in the UK, France and the Netherlands. Thus, the releases from the synthesis of BFRs  
18 are unlikely to be the dominant input source for their occurrence in Germany. In contrast, the  
19 subsequent use of polymers incorporating with BFRs in textiles, electronic equipments, paints  
20 and furniture might be a more important source [4].

21 Under the assumption that BFRs are a safe class of flame retardants, they are widely  
22 distributed in the environment. Recently, concerns have been increasing regarding their  
23 persistence and potential bioaccumulation [5,6]. TBBPA has been proved toxic and has  
24 shown significantly thyroid hormonal activities [7]. The structure similarity of TBBPA to  
25 bisphenol A has suggested that TBBPA might have the ability to bind to the estrogens  
26 receptor and disrupt signalling [8]. Moreover, TBBPA is neurotoxic in cerebellar granule cells  
27 and rat brain synaptosomes [9,10]. Although presently there is no regulated restriction on the  
28 use of TBBPA, the evaluation is currently underway in the EU, US and Asian-pacific  
29 countries [3]. The EU's Technical Committee discussed the human health part of the risk  
30 assessment on New and Existing Substances (TCNES) in December 2004. The Committee  
31 concluded that TBBPA did not present any risk to human health. However, the evaluation of  
32 the potential effects of TBBPA on the environment is currently ongoing.

33 TBBPA has been detected in sediments, sewage sludge and surface water and biota [11-  
34 15]. However, the concentration of TBBPA in air is very limited. It was reported that the  
35 concentration of TBBPA in air near production facilities in Southern Arkansas (USA) is 1.8

1  $\mu\text{g m}^{-3}$  [16]. Alaei et al. reported that concentration of TBBPA in particles was  $70 \text{ pg m}^{-3}$  at  
2 Dunai, Russia [17]. More data are necessary for better understanding its environmental fate.

3 Methods for determination of TBBPA in environmental samples have been developed  
4 based on GC-MS following derivatization of the phenolic group with diazomethane or with  
5 methyl chloroformate [18-20]. Moreover, several research groups have recently applied LC-  
6 MS or LC-MS-MS to determine TBBPA in complicated matrices [21-23]. Tollbäck et al.  
7 reported a method for determination of TBBPA in air samples by LC-MS [24]. An attractive  
8 advantage of this method is no clean-up required, which could reduce the losses during  
9 sample treatment and thus achieve a good recovery.

10 The objective of the present study was to develop and validate complementary, highly  
11 sensitive, and reliable analytical methods for determination of TBBPA in the atmosphere,  
12 which should be applicable even to determine airborne TBBPA in remote area. In the present  
13 study, GC-MS methods were developed based on derivatization of TBBPA with silylation  
14 reagent N,O-bis(trimethylsilyl)trifluoroacetamide and 1% Trimethylchlorosilane (BSTFA +  
15 1% TMCS). The performance of both EI and NCI modes were evaluated for detection of the  
16 TBBPA derivatives. In addition, the efficiency of high volume sampling for collection of  
17 airborne TBBPA was examined by the recovery and the breakthrough test in field sampling.  
18 This method has been applied to detect TBBPA in the atmosphere over the Wadden Sea and  
19 the Northeast Atlantic.

20

## 21 **2. Experimental section**

22

### 23 *2.1. Reagent and material preparation*

24

25 Tetrabromobisphenol A (TBBPA, technical) was provided by Dr. Ehrenstorfer GmbH  
26 (Augsburg, Germany), internal standard  $^{13}\text{C}$  labeled tetrabromobisphenol A (TBBPA [ $^{13}\text{C}_{12}$ ])  
27 and polybrominated diphenylether congeners (PBDEs) were supplied by Cambridge Isotope  
28 Laboratories (Andover, MA). Stock solution of TBBPA and PBDEs were prepared in hexane  
29 at concentration of  $100 \mu\text{g mL}^{-1}$ . Standard solutions were made from appropriate dilution of  
30 the stock solution. Standard solution of TBBPA [ $^{13}\text{C}_{12}$ ] was prepared in hexane at a  
31 concentration of  $2.5 \mu\text{g mL}^{-1}$ . Calibration solutions for preparing GC-MS calibration curves  
32 were made by diluting 1-200  $\mu\text{L}$  of the standard solutions in hexane (final volume 200  $\mu\text{L}$ ).

33 The solvents (methanol, acetone, hexane, dichloromethane, acetonitrile, diethyl ether) used  
34 in the method were pesticide or HPLC grade. They were distilled prior to use. The glassware  
35 and glass pipettes were initially rinsed with Milli-Q water and acetone and were then baked at

1 450 °C for at least 8 hours prior to use. The PUF/XAD-2 columns and glass fibre filters were  
2 prepared as described in [25]. The PUF/XAD-2 columns were stored before and after  
3 sampling in heat-sealed airtight polypropylene/aluminium/polyethylene bags (PP/AL/PE,  
4 Tesseraux, Germany) at -20 °C for air samples. Cleaned filters were wrapped between  
5 aluminium foil in PP/AL/PE bags and used filters were sealed in test tubes and stored at -20  
6 °C.

## 7 8 2.2. Sampling and sample preparation

### 9 10 2.2.1. Sampling Sites

11  
12 GKSS station (Figure 1) is a sampling station belonging to the GKSS Research Centre  
13 Geesthacht, situated in the Northern Germany in a rural forest area, about 37 km away from  
14 the major city Hamburg. There are 2000 inhabitants living around the Research Centre. The  
15 site is approximately 500 m from the river Elbe. Much of the land within 20 km of the GKSS  
16 Research Centre is rural. Concentrations found at this site may represent a background value  
17 for the agricultural area in the Northern Germany. The sampling campaigns were undertaken  
18 in January 2005 and February of 2006 at the GKSS station. 2-5 samples were taken during  
19 each campaign. The samples were taken over 2- or 4- day periods.

20 The Wadden Sea (Figure 1) is a part of the North Sea with consists of water and its  
21 associated coastal wetlands lying between a section of the coast of north-western continental  
22 Europe and the North Sea [26]. The Wadden Sea stretches from Den Helder in the  
23 Netherlands in the Southwest, past the river estuaries of Germany to its northern boundary at  
24 Esbjerg in Denmark along a total length of some 500 km and a total area of about 10,000 km<sup>2</sup>.  
25 It is a region continually contested by land and sea. Air systems will have passed over inland  
26 areas of the Netherlands, Germany and Denmark, and the open seas. Except from the input of  
27 the large rivers, as the density of the shipping line is intensive in this area, the discharges of  
28 ship and ferries are also part of the source for the inputs of organic contaminants into the  
29 Wadden Sea. In July 2005, two integrated air samples (> 500 m<sup>3</sup>) were collected off the  
30 Wadden Sea during a field survey with GKSS research ship '*Ludwig Prandtl*'.

31 In June to August 2004, a polar expedition cruise has been carried out with German Polar  
32 research ship '*FS Polarstern*' (See Figure 1). A sampling program was carried out to  
33 investigate the atmospheric levels of TBBPA together with other organic pollutants from the  
34 North Sea to the Arctic.

1

2 *2.2.2. Sampling Regime*

3

4 Air samples were collected using a high-volume air sampler that was operated at a constant  
5 flow rate of  $0.2 \text{ m}^3 \text{ min}^{-1}$ , which has been described in [25]. A PUF/XAD-2 column was used  
6 to collect the analyte in vapor phase and a glass fiber filter (GF/F 8), was used to collect  
7 atmospheric particles. The ship-borne air samples were collected on the upper deck of the  
8 research vessel. Land-based air samples were collected at GKSS Research Centre (GKSS)  
9 with a sampling position 5 m above the ground. During sampling at GKSS in February 2006,  
10 12.5 ng TBBPA [ $^{13}\text{C}_{12}$ ] was spiked in the column for method validation. There was no  
11 spiking for the ship-borne air samples. In order to avoid the emissions from the ship's funnel,  
12 air sampling was performed on headwind and was halted at station or wind speeds lower than  
13  $3 \text{ m s}^{-1}$ . Laboratory air was collected using an XAD-2 cartridge (5g XAD-2 was packed in a  
14  $13 \text{ cm} \times 1 \text{ cm}$  i.d. glass cartridge) spiked with TBBPA [ $^{13}\text{C}_{12}$ ].

15

16 *2.2.3. Extraction and clean-up*

17

18 The PUF/XAD-2 columns were spiked with 12.5 ng of TBBPA [ $^{13}\text{C}_{12}$ ] (if the column is  
19 not spiked before sampling) and extracted for 16 h using 300 mL of 20% (v/v) diethyl ether in  
20 hexane solution with the modified Soxhlet extractor. Particle samples were spiked with 12.5  
21 ng of TBBPA [ $^{13}\text{C}_{12}$ ] and then extracted for 16 h using 150 mL of dichloromethane with the  
22 Soxhlet extractor. After Soxhlet extraction, the samples were stored in the freezer before  
23 rotary evaporation. Two PUF/XAD-2 columns and filters were extracted for a second time  
24 (hexane+acetone (1:1) for PUF/XAD-2 and DCM + acetone (1:1) for filter) in order to check  
25 the extraction efficiency.

26 The extracts were reduced to 2 mL using a rotary evaporator at  $30 \text{ }^\circ\text{C}$  under reduced  
27 pressure and then cleaned up through a silica gel column, which is described in [25].  
28 Experiments were also performed with column packed with 2 g of  $\text{Na}_2\text{SO}_4$  (upper phase) +  
29 2.5 g of silica gel (lower phase). The loaded column was eluted with 15 mL of hexane  
30 (Fraction 1), 20 mL of hexane/diethyl ether (3:1; v/v) (Fraction 2), 20 mL of hexane/diethyl  
31 ether (1:1; v/v) (Fraction 3), and finally 20 mL of hexane/acetone (1:1; v/v) (Fraction 4). The  
32 fraction 1 was used to detect PAHs and PBDEs. Fraction 2 and fraction 3 were combined for  
33 determination of TBBPA. The extracts were subsequently concentrated in a nitrogen  
34 evaporator to 100  $\mu\text{L}$  for derivatization.



1

2 *2.2.4. Derivatization*

3

4 Three derivative reagents, e.g. n-methyl-n-(t-butyldimethylsilyl)trifluoroacetamide  
5 (MTBSTFA), BSTFA and BSTFA + 1% TMCS were tested in the experiments. In addition,  
6 the reaction time and the volume of BSTFA + 1% (v/v) TMCS added were optimised with  
7 regard to intensity of the derivatives. The optimised derivatization procedure is: 100  $\mu$ L of  
8 BSTFA + 1% TMCS was added to 100  $\mu$ L extract in the glass vial and the mixture react for 1  
9 h at 60 °C. After derivatization, the final sample volume was adjusted to 200  $\mu$ L using  
10 hexane. The extracts were ready for GC-MS without further treatment.

11

12 *2.3. GC-MS analysis*

13

14 Quantification of TBBPA was performed with an Agilent system consisting of a 6890 N  
15 gas chromatograph equipped with an Agilent 7683 series autosampler, a 7683 split-splitless  
16 temperature and pressure-programmed injector, and an Agilent 5973 quadrupole mass  
17 selective detector (GC-MS). Efficiencies of both electron impact ionisation (EI) and the  
18 negative chemical ionisation (NCI) modes were compared. Chemstation Software (2000  
19 version) was used for data processing. The general conditions used for GC-MS analysis are  
20 shown in Table 1.

21

22 *2.4. Recovery experiments, breakthrough test and quantification*

23

24 Recovery and breakthrough for TBBPA in vapour phase were determined from samples  
25 spiked with TBBPA [ $^{13}\text{C}_{12}$ ]. During the field sampling, several samples were collected with  
26 tandem columns. 12.5 ng of TBBPA [ $^{13}\text{C}_{12}$ ] were spiked in the first column. The amount of  
27 TBBPA [ $^{13}\text{C}_{12}$ ] determined in the first column was used to calculate the recoveries for  
28 TBBPA. The proportions of TBBPA and TBBPA [ $^{13}\text{C}_{12}$ ] found in the second column were  
29 used to describe the breakthrough of the sampling. The recoveries of spiked TBBPA [ $^{13}\text{C}_{12}$ ]  
30 can be estimated with spiked dibenzylphthalate [25], which was spiked as a surrogate  
31 standard after rotary evaporation.

32 Quantification of TBBPA was based on the relative response factor of TBBPA and  
33 TBBPA [ $^{13}\text{C}_{12}$ ]. The response factor was derived from a 5-point calibration curve made with a

1 series concentration from 25 to 1000 ng mL<sup>-1</sup> for TBBPA and 250 ng mL<sup>-1</sup> for TBBPA  
2 [<sup>13</sup>C<sub>12</sub>].

### 3. Results and discussion

#### 3.1. Evaluation of the sampling and sample preparation

##### 3.1.1. Clean-up

8  
9 The clean-up procedure was optimised based on the procedure described in [25]. The  
10 recoveries obtained in different fractions and with different eluting solvents are summarized  
11 in Table 2. The OH- groups in the structure of TBBPA make it more polar than PBDEs. In the  
12 clean-up experiments, PBDEs were present in the first fraction with a recovery of  
13 approximately 100%. However, TBBPA only eluted off the silica gel cartridge with more  
14 polar solvents. Therefore, with the clean-up, TBBPA was completely separated from PBDEs  
15 that might interfere with the determination of TBBPA by GC-MS [27]. As shown in Table 2,  
16 recovery of TBBPA in hexane/diethyl ether (3:1, v/v) fraction was about 47%, and the  
17 remaining TBBPA could be continually eluted off with increasing the proportion of diethyl  
18 ether in the mixture of solvents. Experiment 3 shows that the average recovery of TBBPA  
19 reached 90 ± 10% when the fractions of hexane/diethyl ether (3:1, v/v) and hexane/diethyl  
20 ether (1:1, v/v) were combined. 6 ± 4% of TBBPA was found in the last fraction that eluted  
21 with polar solvents. During tests with real samples, it was observed that the matrices could be  
22 coeluted with the hexane/acetone fraction (1:1, v/v). Therefore, the hexane/acetone (1:1, v/v)  
23 fraction was not collected together with other two fractions. Poor recoveries present in the  
24 experiment 1 indicated that TBBPA could strongly adsorb on to the Na<sub>2</sub>SO<sub>4</sub> powder due to its  
25 OH- groups. Therefore, the extracts were put into freezer (-20 °C) to remove water before  
26 clean-up, instead of using Na<sub>2</sub>SO<sub>4</sub> for eliminating trace water present in the samples.

##### 3.1.2. Soxhlet extraction

28  
29 The recoveries of TBBPA for soxhlet extraction procedure were tested by spiking TBBPA  
30 in the PUF/XAD-2 column and filter before extraction. The averages of recoveries were 90 ±  
31 10% (n=3) for PUF/XAD-2 column and 95 ± 4% (n=3) for glass fibre filter, respectively. A  
32 second extraction was performed with more polar solvent hexane/acetone (1:1, v/v) for two  
33 samples spiked with TBBPA [<sup>13</sup>C<sub>12</sub>] before the sampling in order to evaluate the risk of

1 insufficient extraction in the presence of other contaminants. No TBBPA [ $^{13}\text{C}_{12}$ ] was detected  
2 in these additional extracts. These results suggested that the proposed soxhlet extraction  
3 procedure is sufficient for extraction of TBBPA from both PUF/XAD-2 column and glass  
4 fibre filter.

5

### 6 *3.1.3. Laboratory blank, breakthrough and recoveries of air sampling*

7

8

9 All laboratory treatments were performed in a clean-lab. However, in previous studies we have  
10 found relatively high concentrations of nonylphenol and phthalate esters when they were analyzed  
11 in the laboratory blanks [25]. Surprisingly, concentration of TBBPA in laboratory air was  
12 relatively low ( $< 20 \text{ pg m}^{-3}$ ), indicating emissions from electric equipments in the clean-lab made  
13 no significant blank for the sample treatments and analysis. Additionally, TBBPA was not  
14 detectable in the field blank samples.

15 The sampling efficiency was examined by recovery tests with TBBPA [ $^{13}\text{C}_{12}$ ] spiked samples  
16 incorporating with breakthrough tests with tandem cartridges. As the concentration of TBBPA  
17 present in the vapour phase was relatively low, generally there was no detectable TBBPA present  
18 in the second column. An average recovery of  $79 \pm 1\%$  of TBBPA [ $^{13}\text{C}_{12}$ ] was present in the  
19 spiked samples, and no TBBPA [ $^{13}\text{C}_{12}$ ] was detected in the second columns, thus indicates no  
20 breakthrough happened during air sampling. However, in an air sample collected over the Atlantic  
21 Ocean, TBBPA was also determined in the second column with a proportion of 17%.  
22 Hypothetically, in the marine environment, sometimes the air mass contains high proportion  
23 of water due to the sea spray and wave broken. Because of the washout effect, the  
24 breakthrough may happen for the sampling. Although this result is not critical for the sampling  
25 method, it indicated that the marine condition such as high humidity and sea sprays might affect  
26 the sampling efficiency. Figure 2 shows chromatograms of TBBPA in the standard, blank and in  
27 an air sample collected in the Northeast Atlantic with tandem PUF/XAD-2 columns (upper: ARK  
28 XX A1 C1, Lower: ARKXX A1 C2).

29

### 30 *3.1.4. Derivatization*

31

32 Derivatization of TBBPA has been performed in most laboratories with diazomethane  
33 resulting in methoxy derivatives [20]. Recently, methyl chloroformate was introduced for  
34 derivatization of TBBPA, which shows many advantages over diazomethane [19]. As an  
35 alternative technique, derivatization with silylation reagents was applied in this study.

1 There is no peak present in the chromatogram for silylation with MTBSTFA because of the  
2 major ion of the TBBPA derivative is beyond the mass range of the equipped MS detector  
3 ( $\leq 700$  amu). Good results were achieved using both BSTFA and BSTFA + 1% TMCS. The  
4 TBBPA derivative (TBBPA-TMS) shows excellent GC-MS properties, e.g. sharp peak shape  
5 and good response in both EI and NCI modes. The intensity of the TMS product of TBBPA  
6 was increased by a factor of 3-5 relative to that without derivatization. The reaction was  
7 performed at elevated temperature of 60 °C, and completed in 10 min. Relative standard  
8 deviations (RSDs) of 5% and 3% were achieved respectively for the responses of TBBPA-  
9 TMS with different reaction time (10 min, 30 min, 60 min and 120 min) and with different  
10 amount of reagents (5%, 25% and 50% BSTFA+1% TMCS in hexane), indicate satisfactory  
11 reproducibility for the derivatization. In order to simultaneously detect TBBPA with other  
12 phenolic compounds, e.g. alkylphenols and estrogenic steroids, the derivatization procedure  
13 was performed as follows: 100  $\mu$ L of BSTFA + 1%TMCS were added to 100  $\mu$ L sample in  
14 hexane and kept reacting at 60 C° for 1 h. GKSS samples were also analyzed using GC-MS-NCI  
15 with ions of 79 and 81 for [Br]<sup>-</sup> in order to check the efficiency of derivatization. No detectable  
16 un-derivatized TBBPA and TBBPA [<sup>13</sup>C<sub>12</sub>] were present on the chromatograms, indicates  
17 derivatization of TBBPA was complete in the real samples.

### 18 3.2. GC-MS analysis with EI and NCI

19  
20 By reaction with BSTFA+1%TMCS, TBBPA has two [-SiMe<sub>3</sub>] (TMS) group attached on  
21 both phenolic groups. The analyte is thus turned into highly electrophilic derivative. Electron  
22 capture and dissociative electron capture can be used as dominant ionization processes. The  
23 full mass spectra of TBBPA-TMS and TBBPA [<sup>13</sup>C<sub>12</sub>]-TMS obtained in EI mode are shown  
24 in Figure 3A and B, respectively. The molecular ion is present in the spectrum with isotopic  
25 peaks from m/z of 684 to 693. The major fragment (m/z: 669 - 679) is formed by losing of a  
26 methyl group from the molecular ion. Moreover, the fragment at m/z of 365 (abundant peak)  
27 is formed by losing of [C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>OSiMe<sub>3</sub>] from the molecular ion. The mass difference  
28 between TBBPA-TMS and TBBPA [<sup>13</sup>C<sub>12</sub>]-TMS is 12 amu confirming that the two aromatic  
29 rings contain <sup>13</sup>C<sub>12</sub>. The isotopic peaks are determined by the ratio of <sup>79</sup>Br, <sup>81</sup>Br, <sup>28</sup>Si, <sup>29</sup>Si and  
30 <sup>30</sup>Si in the molecular or fragment. The peak at m/z of 73 is from the characteristic ion of  
31 [Si(CH<sub>3</sub>)<sub>3</sub>] lost from the TBBPA derivative. Although the ion at an m/z of 73 gives high  
32 intensity as compared to the other major ions, it was excluded from the method due to its  
33 presence in both spectra of TBBPA and TBBPA [<sup>13</sup>C<sub>12</sub>] and its complicated background in the  
34 chromatogram of real sample. In practice, the major peaks at m/z of 673 and 675 for TBBPA

1 derivative and at  $m/z$  of 685 and 687 for TBBPA [ $^{13}\text{C}_{12}$ ] were adopted in the GC- EI-MS  
2 method.

3 The full mass spectra of TBBPA-TMS and TBBPA [ $^{13}\text{C}_{12}$ ]-TMS obtained in NCI mode are  
4 shown in Figure 4A and 4B, respectively. Since the NCI is a relatively soft ionisation, it  
5 yielded very pure mass spectrum for TBBPA derivative. No molecular ion is present in the  
6 spectrum. The major ions at  $m/z$  of 79, 81 resulting from  $^{79}\text{Br}^-$  and  $^{81}\text{Br}^-$  are present in both  
7 spectra of TBBPA and TBBPA [ $^{13}\text{C}_{12}$ ], thus they are not suitable as quantification ions. The  
8 isotopic peak clusters ( $m/z$ : 604 - 612) are the fragments formed by losing [Br] from the  
9 molecular ion (Figure 4A). In addition, second peak clusters are for fragment formed by  
10 losing one [Br] and one [Si(CH<sub>3</sub>)<sub>3</sub>] group with abundant peak at  $m/z$  of 536. TBBPA [ $^{13}\text{C}_{12}$ ]  
11 derivative shows a spectrum that has a fragment pattern similar to the original TBBPA  
12 derivative with a difference of 12 amu. Therefore, the ions at  $m/z$  of 607 and 609 for TBBPA  
13 and the ions at  $m/z$  of 619 and 621 were applied in the GC-MS-NCI method.

14 The instrumental limits of detection (LODs) were calculated as 3-time height of noise for  
15 both NCI and EI modes. TBBPA was found neither in field blanks nor laboratory blanks, so  
16 the detection limits of the methods (MDLs) were derived from the LODs according to the  
17 average sample volume (typical air sample volume: 1000 m<sup>3</sup>). The LODs and MDLs  
18 calculated for determination of TBBPA with both NCI and EI modes are shown together with  
19 literature values in Table 3. As compared to the detection limits reported in the literatures, the  
20 LOD achieved with GC-EI-MS for TBBPA derivative was comparable to that obtained using  
21 GC coupled to high-resolution mass spectrometry (GC-EI-HRMS) [20], and was one order of  
22 magnitude lower than those obtained using LC-EI-MS and LC-EI-MS-MS [22-24]. It is  
23 indicated that the method developed in this study is alternative for determination of trace  
24 levels of TBBPA in the environment. Several samples collected at GKSS station were  
25 determined using both EI and NCI modes. The results showed that the sensitivity of GC-EI-MS  
26 was better compared to GC-NCI-MS for determination of trace TBBPA. Therefore, the  
27 concentrations in air samples from the Wadden Sea and the Arctic were determined only with  
28 GC-EI-MS.

## 30 4. Environmental Application

### 31 4.1 Atmospheric concentrations of TBBPA

32 The concentrations of TBBPA in the atmospheric samples collected at GKSS Research  
33 Centre, over the Wadden Sea and off the Northeast Atlantic are summarized in Table 4. The  
34

1 total concentrations of TBBPA in vapour and particle phases were from below the MDL (0.04  
2  $\text{pg m}^{-3}$ ) to  $0.85 \text{ pg m}^{-3}$ . Comparable concentrations of TBBPA were present in GKSS station  
3 and over the Wadden Sea. As the GKSS Research Centre is located in a rural forest area,  
4 these concentrations could represent a regional background for atmospheric occurrence of  
5 TBBPA in the Northern Germany. Concentrations TBBPA in the Arctic ranged from less than  
6 the method detection limit (MDL:  $0.04 \text{ pg m}^{-3}$ ) to  $0.17 \text{ pg m}^{-3}$ . A higher concentration of  $0.17$   
7  $\text{pg m}^{-3}$  was present in the sample collected off the West Norwegian coast, indicating an input  
8 source from land to ocean transport. As shown in Figure 5, a declining latitude trend is  
9 present from the near-coast to the open ocean.

10 To our knowledge, so far there is only one report for the occurrence of TBBPA in the  
11 coastal atmosphere. Alae et al. [17] have reported that concentration of TBBPA in the  
12 particles was  $70 \text{ pg m}^{-3}$  at Dunai, Russia, which was determined from archived, filter samples  
13 collected in the Arctic region. This concentration is 3 orders of magnitude higher than those  
14 determined in this work. The concentrations of individual PBDE congeners have been  
15 determined in three locations in Western Europe [28] and in the Baltic Sea [29]. In  
16 comparison, the concentrations of TBBPA present in the GKSS station and in the Wanden  
17 Sea were lower by 1 order of magnitude than those of major PBDE congeners, e.g. BDE-47  
18 and BDE-99, but similar to those of other PBDE congeners. Concentrations of TBBPA found  
19 in the Arctic are similar to those of PBDEs present in Mace Head, which represents a  
20 background of the Atlantic Ocean.

21 Although TBBPA in the Arctic is present at very low concentrations, TBBPA could  
22 accumulate in snow pack and ice, and thus become persistent [30]. Besides, trace levels of  
23 TBBPA have been detected in polar animals in several cases [31]. In an investigation for the  
24 occurrence of BFRs in Norwegian predatory bird eggs, TBBPA could be detected in all  
25 samples with concentrations from lower than the quantification limit to  $13 \text{ pg g}^{-1}$  wet weight  
26 [32]. The atmospheric occurrence of TBBPA in the Northeast Atlantic might be an  
27 explanation for the detection of TBBPA in polar animals. As TBBPA mostly partition to the  
28 sewage sludge and sediment in the wastewater treatment plants and in the rivers, the  
29 discharge of the TBBPA through the river run likely accumulated in the estuaries [23]. The  
30 transport through ocean current should not be significant. Although TBBPA showed relatively  
31 low concentrations in this study, its occurrence in the coastal atmospheric samples suggests  
32 that TBBPA has atmospheric long-range transport potential. Because most parts of Arctic are  
33 very remote, with very few activities that constitute local sources of POPs, the Arctic is an  
34 important indicator region for assessment of persistence and bioaccumulation of persistent

1 organic pollutants (POPs) [30]. Any organic pollutants found in this area can be evidently  
2 regarded as emerging POPs. Therefore, the occurrence of TBBPA in Arctic air might be  
3 significant for assessment of its risk as one of environmental pollution.

4 The particle-bound proportions of TBBPA ranged from 28 to 98% (Table 4). Generally,  
5 because of declining particle concentrations from the land to the ocean, the particle-bound  
6 proportions of TBBPA were decreasing. Sampling campaigns were performed in winter at  
7 GKSS station and in summer for Nutex-5 and ARK XX-1/2 cruise, so some of the declining  
8 particle-bound proportions also resulted from the sampling temperature. The samples  
9 collected at GKSS station in January of 2005 were under a dry condition, which resulted in  
10 high particle concentrations and high particle-bound proportions for TBBPA. In contrast, low  
11 particle-bound concentrations were present in the samples collected at GKSS station in  
12 February of 2006 that was carried out during several snowfalls. These results suggest the  
13 possibility for dry and wet depositions of atmospheric TBBPA. In addition, these observations  
14 are generally consistent with model predictions and field results for PCBs and PBDEs  
15 [33,34]. In the marine environment, aerosols are mostly generated by sea sprays and sea salts,  
16 therefore with calm weather, the concentrations of the particles in the air above the open  
17 Atlantic Ocean are usually at low concentrations.

18 At present, there is no data available for the degradation of TBBPA in the atmosphere. As  
19 compared to the organochlorines, organobromines are more photolabile because the C-Cl  
20 bond strength is 2.6 times higher than that of C-Br. On the other hand, bromine substitutes  
21 cause resistance against the reaction with OH radical and hence prolong the atmospheric  
22 lifetime [35]. Nevertheless, more reliable data are necessary for conforming the long-range  
23 transport potential and better understanding atmospheric fate of TBBPA.

24

#### 25 *4.2. Comment on the source of atmospheric TBBPA*

26

27 Results from studies on the BFRs in indoor air at an electronics recycling plant have shown  
28 extremely high concentrations of TBBPA in the indoor air [24,36,37]. Average concentrations  
29 of TBBPA were from 30 to 150 ng m<sup>-3</sup>, which are 3-4 orders of magnitude higher than those  
30 found in ambient air in this study. Obviously, the occurrence of TBBPA in ambient air may  
31 result from increased emissions from the growing industry for recycling of electronic goods.  
32 In the rural area, open-hearth domestic fires, using a variety of fuels, are often used to dispose  
33 of domestic waste that may contain large proportions of TBBPA and other BFRs [28]. In  
34 China and India, huge amount of electronic wastes produced inland and imported from

1 western countries are mostly deposited by combustion or open-hearth domestic fire after  
2 recycling [38]. The emissions from these kinds of diffuse sources may become a significant  
3 concern for the local environment and are potentially exported and redistributed via  
4 atmospheric transport.

5

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7

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13 ARK XX-1/2.

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1 **Figure captions**

2 **Figure 1.** Map of air sampling site at GKSS research centre, and the sampling routes during  
3 the Nutex-5 cruise in the Wadden Sea with *Ludwig Pradtl* and the expedition cruise through  
4 the Northeast Atlantic with *Polarstern*. Sampling sites are given at average position.

5 **Figure 2.** GC-MS-EI chromatograms of TBBPA in standard solution, field blank and in air  
6 sample ARK XX A1 column1 (ARK XX A1 C1) and column 2 (ARK XX A1 C2).

7 **Figure 3** Mass spectra of the TBBPA derivative (TBBPA-TMS) (A) and C<sub>13</sub> labelled TBBPA  
8 derivative (TBBPA [<sup>13</sup>C<sub>12</sub>]-TMS) (B) obtained using GC-MS with EI mode.

9 **Figure 4** Mass spectra of the TBBPA derivative (TBBPA-TMS) (A) and C<sub>13</sub> labelled TBBPA  
10 derivative (TBBPA [<sup>13</sup>C<sub>12</sub>]-TMS) (B) obtained using GC-MS with NCI mode.

11 **Figure 5.** Latitude distribution of TBBPA concentrations from German coast to the Arctic.  
12 The average concentrations of TBBPA at GKSS and over the Wadden Sea are 0.48 and 0.58  
13 pg m<sup>-3</sup>, respectively. It is noted that the concentrations of TBBPA present in the ARK XX A3-  
14 A6 are below the method detection limit of 0.04 pg m<sup>-3</sup>.

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Table 1-4

**Table 1.** GC-MS conditions for determination of TBBPA derivative with EI and NCI modes (QM: Quantification mass; IM: Identification mass)

| GC-MS                            | Method 1  | Method 2   |
|----------------------------------|---|--|
| <b>Ionization source</b>         | Electron impact ionization (70 eV) (EI)   | Negative chemical ionization (NCI)   |
| <b>Column</b>                    | HP-5ms (5%-phenyl-95% methylpolysiloxane, 30 m x 0.25 mm i.d., 0.25 $\mu$ m film thickness; J&W Scientific, Folsom, CA, USA)                            |  |
| <b>Injection</b>                 | 1 $\mu$ L   |  |
| <b>Inlet temperature program</b> | 60 $^{\circ}$ C (10 second), 600 $^{\circ}$ C min $^{-1}$ to 300 $^{\circ}$ C (10 min) (pulse splitless mode, 20 psi for 2 min)                         |  |
| <b>Carrier gas</b>               | Helium, 1.0 mL min $^{-1}$  |  |
| <b>Purge gas</b>                 | Helium, 250 mL min $^{-1}$  |  |
| <b>Reagent gas</b>               | -   | 40% Methane (Purity: 99.999%)  |
| <b>Oven temperature program</b>  | 60 $^{\circ}$ C (1 min), 30 $^{\circ}$ C min $^{-1}$ to 150 $^{\circ}$ C, 5 $^{\circ}$ C min $^{-1}$ to 300 $^{\circ}$ C, then 300 $^{\circ}$ C (5 min) |  |
| <b>Interface temperature</b>     | 280 $^{\circ}$ C  |  |
| <b>Ion source temperature</b>    | 230 $^{\circ}$ C  | 150 $^{\circ}$ C   |
| <b>Quadrupole</b>                | 150 $^{\circ}$ C  | 150 $^{\circ}$ C   |
| <b>Selected ion (at m/z)</b>     | TBBPA: 673 (QM), 675 (IM)<br>TBBPA [ $^{13}$ C $_{12}$ ]: 685 (QM), 687 (IM)  | TBBPA: 607 (QM), 609 (IM)<br>TBBPA [ $^{13}$ C $_{12}$ ]: 619 (QM), 621 (IM) |

**Table 2.** Optimization for the clean-up of TBBPA (50 ng) with silica gel column and different solvents for elution

| Experiment        |              | Experiment 1(n=3)                        | Experiment 2* | Experiment 3 (n=3) |
|-------------------|--------------|--|---------------|--------------------|
|                   |              | Silica + Na <sub>2</sub> SO <sub>4</sub> | Silica        | Silica             |
| <b>Fraction 1</b> | Solvent      | A  | A             | A                  |
|                   | Recovery (%) | 0  | 0             | 0                  |
| <b>Fraction 2</b> | Solvent      | B  | B             | B + C              |
|                   | Recovery (%) | 15 ± 12                                  | 47            | 90 ± 6             |
| <b>Fraction 3</b> | Solvent      | E  | C             | D                  |
|                   | Recovery (%) | 0  | 39            | 6 ± 4              |
| <b>Fraction 4</b> | Solvent      | -  | D             | -                  |
|                   | Recovery (%) | -  | 3             | -                  |

A: 15 mL of hexane; B: 20 mL of hexane/diethyl ether (3:1; v/v); C:20 mL of hexane/diethyl ether (1:1; v/v); D:20 mL of hexane/acetone (1:1; v/v); E: 20 mL of dichloromethane/acetonitrile (1:1; v/v)

\*Single experiment

**Table 3.** Ions (m/z) of TBBPA derivative used for GC-MS quantification with EI and NCI mode. The instrumental detection limits (LOD, S/N=3) and method detection limits achieved in this work are compared to the literature values.

| <b>Instrument</b>   | <b>Derivatization</b> | <b>QM</b>  | <b>IM</b>  | <b>LOD (pg)</b> | <b>MDL (pg m<sup>-3</sup>)</b> | <b>Ref.</b> |
|---------------------|-----------------------|------------|------------|-----------------|--------------------------------|-------------|
| <b>GC- EI- MS</b>   | BSTFA+1% TMCS         | 673        | 675        | 0.2             | 0.04                           | This work   |
| <b>GC-NCI-MS</b>    | BSTFA+1% TMCS         | 607        | 609        | 1.0             |                                | This work   |
| <b>GC-EI-LRMS</b>   | Methyl chloroformate  | 556.8      | 554.8      | 1.0             |                                | [20]        |
| <b>GC-EI-HRMS</b>   | Methyl chloroformate  | 556.7, 608 | 554.7, 629 | 0.2             |                                | [20]        |
| <b>LC-ESI-MS</b>    | -                     | 540.9      |            | 50              |                                | [22]        |
| <b>LC-ESI-MS-MS</b> | -                     | 543/81     | -          | 5               |                                | [23]        |
| <b>LC-ESI-MS</b>    | -                     | 418        | 528        | 3,1             |                                | [24]        |

**Table 4.** Collection data, total suspended particulate (TSP), vapour concentration (Ca), particle concentration (Cp), and particle-bound proportion of TBBPA ( $\phi = C_p / \Sigma C \times 100\%$ ) at GKSS Research Centre, in the Wadden Sea (Nutex-5 A1, A2) and in the Northeast Atlantic (ARK XX A1-A6)

| Sample       | Temp.<br>(°C) | TSP<br>( $\mu\text{g m}^{-3}$ ) | Ca<br>( $\text{pg m}^{-3}$ ) | Cp<br>( $\text{pg m}^{-3}$ ) | $\Sigma C$<br>( $\text{pg m}^{-3}$ ) | $\phi$<br>(%) |
|--------------|---------------|---------------------------------|------------------------------|------------------------------|--------------------------------------|---------------|
| GKSS05 A1    | 3             | 201                             | <MDL                         | 0.85                         | 0.85                                 | 98            |
| GKSS05 A2    | 4             | 111                             | 0.05                         | 0.16                         | 0.21                                 | 76            |
| GKSS06 A1    | <0            | 6.0                             | 0.23                         | 0.32                         | 0.55                                 | 58            |
| GKSS06 A2    | <0            | 6.1                             | 0.25                         | 0.36                         | 0.61                                 | 59            |
| GKSS06 A3    | <0            | 9.2                             | 0.12                         | 0.25                         | 0.37                                 | 68            |
| GKSS06 A4    | <0            | 10.1                            | 0.08                         | 0.23                         | 0.31                                 | 74            |
| GKSS06 A5    | <0            | 19.4                            | 0.11                         | 0.35                         | 0.46                                 | 76            |
| Nutex-5 A1   | 18            | 10                              | 0.50                         | 0.19                         | 0.69                                 | 28            |
| Nutex-5 A2   | 18            | 10                              | 0.21                         | 0.10                         | 0.31                                 | 32            |
| ARK XX A1 C1 | 12            | -                               | 0.17                         | <MDL                         | 0.17                                 | 0             |
| ARK XX A1 C2 | 12            | -                               | <MDL                         | -                            | -                                    | 0             |
| ARK XX A2    | 7             | -                               | 0.05                         | <MDL                         | 0.05                                 | 0             |
| ARK XX A3    | 3             | -                               | <MDL                         | <MDL                         | <MDL                                 | 0             |
| ARK XX A4    | 5             | -                               | <MDL                         | <MDL                         | <MDL                                 | 0             |
| ARK XX A5    | 5             | -                               | <MDL                         | <MDL                         | <MDL                                 | 0             |
| ARK XX A6    | <0            | -                               | <MDL                         | <MDL                         | <MDL                                 | 0             |















