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

1 **Trace determination of the flame retardant tetrabromobisphenol A in the**

2 **atmosphere by gas chromatography-mass spectrometry**

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14

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 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 pg m^{-3}) to 0.85

29 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.

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1. Introduction

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

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

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

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

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1   μg m^{-3} [16]. Alaee et al. reported that concentration of TBBPA in particles was 70 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}C labeled tetrabromobisphenol A (TBBPA [^{13}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 μg mL^{-1}. Standard solutions were made from appropriate dilution of

30   the stock solution. Standard solution of TBBPA [^{13}C$_{12}$] was prepared in hexane at a

31   concentration of 2.5 μg mL^{-1}. Calibration solutions for preparing GC-MS calibration curves

32   were made by diluting 1-200 μL of the standard solutions in hexane (final volume 200 μL).

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

3

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^2.

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^3) 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.

4

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 m^3 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 [$^{13}C_{12}$] 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 m s^{-1}. Laboratory air was collected using an XAD-2 cartridge (5g XAD-2 was packed in a

14   13 cm x 1cm i.d. glass cartridge) spiked with TBBPA [$^{13}C_{12}$].

15

16   *2.2.3. Extraction and clean-up*

17

18   The PUF/XAD-2 columns were spiked with 12.5 ng of TBBPA [$^{13}C_{12}$] (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 [$^{13}C_{12}$] 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 °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 Na$_2$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 µL for derivatization.

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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 µL of

8 BSTFA + 1% TMCS was added to 100 µL 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 µL 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 [$^{13}C_{12}$]. During the field sampling, several samples were collected with

26 tandem columns. 12.5 ng of TBBPA [$^{13}C_{12}$] were spiked in the first column. The amount of

27 TBBPA [$^{13}C_{12}$] determined in the first column was used to calculate the recoveries for

28 TBBPA. The proportions of TBBPA and TBBPA [$^{13}C_{12}$] found in the second column were

29 used to describe the breaththrough of the sampling. The recoveries of spiked TBBPA [$^{13}C_{12}$]

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 [$^{13}C_{12}$]. The response factor was derived from a 5-point calibration curve made with a

6

1   series concentration from 25 to 1000 ng mL^{-1} for TBBPA and 250 ng mL^{-1} for TBBPA

2   [^{13}C$_{12}$].

3

4   **3. Results and discussion**

5

6   *3.1. Evaluation of the sampling and sample preparation*

7   *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$_2$SO$_4$ 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$_2$SO$_4$ for eliminating trace water present in the samples.

27   *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 [^{13}C$_{12}$] before the sampling in order to evaluate the risk of

7

1 insufficient extraction in the presence of other contaminants. No TBBPA [$^{13}C_{12}$] 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*

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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 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 [$^{13}C_{12}$] 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 ± 1% of TBBPA [$^{13}C_{12}$] was present in the

19 spiked samples, and no TBBPA [$^{13}C_{12}$] 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.

8

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 μL of BSTFA + 1%TMCS were added to 100 μL 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]$^-$ in order to check the efficiency of derivatizaiton. No detectable

16   un-derivatized TBBPA and TBBPA [$^{13}C_{12}$] 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$_3$] (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 [$^{13}C_{12}$]-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 [$C_6H_3Br_2OSiMe_3$] from the molecular ion. The mass difference

28   between TBBPA-TMS and TBBPA [$^{13}C_{12}$]-TMS is 12 amu confirming that the two aromatic

29   rings contain $^{13}C_{12}$. The isotopic peaks are determined by the ratio of ^{79}Br, ^{81}Br, ^{28}Si, ^{29}Si and

30   ^{30}Si in the molecular or fragment. The peak at m/z of 73 is from the characteristic ion of

31   [$Si(CH_3)_3$] 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 [$^{13}C_{12}$] 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

9

1 derivative and at m/z of 685 and 687 for TBBPA [$^{13}C_{12}$] were adopted in the GC- EI-MS

2 method.

3 The full mass spectra of TBBPA-TMS and TBBPA [$^{13}C_{12}$]-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 $^{79}Br^-$ and $^{81}Br^-$ are present in both

7 spectra of TBBPA and TBBPA [$^{13}C_{12}$], 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$_3$)$_3$] group with abundant peak at m/z of 536. TBBPA [$^{13}C_{12}$]

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^3). 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.

29

30 **4. Environmental Application**

31 *4.1 Atmospheric concentrations of TBBPA*

32

33 The concentrations of TBBPA in the atmospheric samples collected at GKSS Research

34 Centre, over the Wadden Sea and off the Northeast Atlantic are summarized in Table 4. The

10

1   total concentrations of TBBPA in vapour and particle phases were from below the MDL (0.04

2   pg m^{-3}) to 0.85 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 pg m^{-3}) to 0.17 pg m^{-3}. A higher concentration of 0.17

7   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. Alaee et al. [17] have reported that concentration of TBBPA in the

12   particles was 70 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 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 waster water 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

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

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

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

4.2. Comment on the source of atmospheric TBBPA

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

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1 western countries are mostly deposed 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.

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6 **Acknowledgments**

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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 sits 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_{13} labelled TBBPA
8 derivative (TBBPA $[^{13}C_{12}]$-TMS) (B) obtained using GC-MS with EI mode.

9 **Figure 4** Mass spectra of the TBBPA derivative (TBBPA-TMS) (A) and C_{13} labelled TBBPA
10 derivative (TBBPA $[^{13}C_{12}]$-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^{-3}, 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^{-3}.

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

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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) Silica + Na$_2$SO$_4$	Experiment 2* Silica	Experiment 3 (n=3) Silica
Fraction 1	Solvent	A	A	A
	Recovery (%)	0	0	0
Fraction 2	Solvent	B	B	B + C
	Recovery (%)	15 ± 12	47	90 ± 6
Fraction 3	Solvent	E	C	D
	Recovery (%)	0	39	6 ± 4
Fraction 4	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

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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.

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

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

Sample	Temp. (°C)	TSP (μg m^{-3})	Ca (pg m^{-3})	Cp (pg m^{-3})	ΣC (pg m^{-3})	φ (%)
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

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