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Development and validation of a method for determination of trace levels of alkylphenols and bisphenol A in atmospheric samples

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Abstract

A method has been developed and validated in order to assess the occurrence of the alkylphenols tert-octylphenol and the isomers of technical nonylphenol as well as bisphenol A in gasphase and aerosol samples of a remote area. Gasphase samples were adsorbed to XAD2 resin, aerosol samples were taken on glass fiber filters. After ultrasonic extraction, clean-up by column chromatography and silylation of the analytes, ten nonylphenol peaks were quantified separately using a GC-MSD-SIM method. The absolute limits of detection and determination are in the range of a few pg per compound, which is a prerequisite for the quantification of the analytes in relatively unpolluted air. The precision of the whole analytical method is in the range of 1–17% and the recoveries range from 57% to 80%. Problems were encountered during method development due to the tendency of the analytes to sorb to glass surfaces. Silanisation of glassware was crucial to achieve acceptable recoveries. The widespread use of the analytes in plastic resins resulted in sample contamination. For this reason a careful choice of sampling material was necessary. Measured concentrations in gasphase samples (lower nanogram per m^3 range) and aerosol samples (upper picogram per m^3 range) are one to three orders of magnitude below already published concentrations.

Keywords: Tert-octylphenol; Nonylphenol; Bisphenol A; GC-MSD; Gasphase and aerosol samples

1. Introduction

Alkylphenols and bisphenol A have been identified as xenoestrogenic in vitro and in vivo (Dodds and Lawson, 1936; Dodds and Lawson, 1938; Mueller and Kim, 1978; Jobling and Sumpter, 1993; White et al., 1994; Soto et al., 1995; Lye et al., 1999). 4-tert-octylphenol (OP), technical 4-nonylphenol (NP) and bisphenol A (BPA) are produced in large amounts (several 100.000 t per year worldwide) (Staples et al., 1998; European Union Risk Assessment Report, 2001) and despite their main use as intermediates they are released into the environment. BPA is mainly used as monomer in the fabrication of epoxide resins and polycarbonate plastics. Releases into the environment mainly occur during manufacturing (Staples et al., 1998; Markey et al., 2001). OP and NP have been identified in the early 1980s as persistent metabolites of the nonionic surfactants alkylphenolethoxylates (Giger et al., 1981; Stephanou and Giger, 1982) and have been detected in aerosols emitted from a sewage treatment plant aeration tank (Lepri et al., 2000). Besides NP enters the environment as emulsifying agent for pesticides (Sundaram et al., 1980), or it can be emitted from sewage sludge used as fertilizer in agriculture (Düring et al., 2000; Hesselsoe et al., 2001). The occurrence of OP, NP and BPA has widely been studied in aquatic environments (Giger et al., 1984; Ahel et al.,

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1994; Thiele et al., 1997 (and articles cited therein); Rudel et al., 1998; Fürhacker et al., 2000; Kannan et al., 2000; Heemken et al., 2001; Kuch and Ballschmitter, 2001; Spengler et al., 2001). OP and NP belong to the class of semivolatile organic compounds (SOC) which move easily between different environmental compartments. In spite of this fact only one study so far has dealt with the occurrence of OP and NP in the atmosphere. The study area was the Lower Hudson River Estuary which was identified as source of atmospheric OP and NP (Dachs et al., 1999; van Ry et al., 2000). No measured data are available concerning the occurrence of alkylphenols at less polluted rural sites. BPA is not likely to occur in the gasphase of the atmosphere as it has got a very low vapor pressure. But as atmospheric releases of some 100 t per year of BPA are reported during production (Staples et al., 1998; Markey et al., 2001) an association with aerosol particles could be possible. Peltonen and Pukkila (1988) measured BPA in aerosol samples taken during spraying of paint containing BPA and Matsumoto and Hanya (1980) detected BPA in deposition samples in the Tokyo area. Although BPA is short lived in the atmosphere (Howard, 1991) nothing is known about photolytic degradation of particle-bound BPA. To assess the atmospheric occurrence (gasphase and particle phase) of OP, NP and BPA at a mountain site in the Fichtelgebirge (NE-Bavaria, Germany) analytical methods were developed. Emphasize was put on low limits of detection and determination as the expected concentrations were low compared to the published concentrations of van Ry et al. (2000). Besides the method should at least be partially able to reveal information about the composition of the mixture of NP-isomers.

2. Materials and methods

2.1. Sampling

Sampling took place from May to November 2001 at three locations in NE-Bavaria, Germany. Two sites are situated at about 400 m distance in the Waldstein mountain range (50°6′N, 11°51′E, about 700 m above sea level), one in a spruce forest, the other on a clearing. The third site is located near the city of Bayreuth. Gasphase samples were adsorbed to XAD2 resin (Supelco, Bellefonte, CA, USA). Two glass gastraps were operated in series in order to monitor eventual breakthrough of analytes. For every sample the two traps were analyzed separately. If the second trap contained more than 25% of the total amount of analytes, the sampling was regarded as not reliable. Particles were separated from the sampled air by a glass fiber filter (GF92, 50 mm diameter, Schleicher & Schüll, Dassel, Germany) attached directly in front of the first gas trap. Only metal or teflon devices were used for sampling purposes after the use of a plastic filter holder had contaminated samples in the beginning. Silanized glass wool was put on top of the XAD resin to prevent disturbance of the XAD bed. Aerosol samples were taken on glass fiber filters (GF9, 150 mm diameter, Schleicher & Schüll, Dassel, Germany). The gasphase and aerosol phase were sampled separately because of the different concentration ranges present in aerosol and gasphase. For gasphase samples a flow rate of 2 $m^3 h^{-1}$ was sufficient for a two weeks sampling period. The aerosol samples instead were taken at a flow rate of about 60 $m^3 h^{-1}$. These high flow rates were only achieved without further resistance caused by the two gas traps. Flow rates were measured with temperature corrected flowmeters. The sampling device was carefully checked for leakages before every sampling period. Glass fiber filters were baked at 290 °C overnight, and transported on ice sealed in petri dishes.

XAD resin was cleaned by accelerated solvent extraction with hexane:acetone 1:1 v:v and transported already packed in the gas traps sealed with aluminium foil in an ice box. If samples were not extracted immediately, they were stored at −20 °C, filters in petri dishes in an desiccator and gasphase samples in erlenmeyer flasks sealed with teflon rings.

2.2. Standards

All solvents used were of highest purity available and received from Mallinckrodt Baker (Paris, KE, USA). Solvent blanks were always free of analytes. Stock solutions of OP (~90%, CAS: 104-66-9, Merck Schuchhardt, Darmstadt, Germany), NP (technical grade, ~85%, CAS: 84852-15-3 (25154-52-3), Fluka, Buchs, Switzerland), BPA (>99%, CAS: 80-05-7, Sigma-Aldrich, Steinheim, Germany), *n*-Heptylphenol (HP) (>98%, CAS: 72624-02-3 Avocado, purchased from ABCR, Karlsruhe, Germany) and BPAd6 (98%, CAS: 80-05-7 propane-deuterated, Cambridge Isotope Laboratories, Andover, MA, USA) were prepared in toluene at a concentration of 100 $\mu g\,ml^{-1}$ for OP, BPA, HP and BPAd6 and at 500 $\mu g\,ml^{-1}$ for NP (sum of all isomers). From these stock solutions mixed standards were prepared freshly every two weeks at a concentration of 1 $\mu g\,ml^{-1}$ (5 $\mu g\,ml^{-1}$ for NP(sum)) in cyclohexane:ethylacetate 1:1 v:v for quantification and in hexane for spiking purposes. Different concentrations for quantification were achieved by transferring the corresponding amount of mixed standard (1–1000 μl) with a microliter-syringe in 2 ml brown glass vials (Agilent, Waldbronn, Germany) before they were derivatized concurrently with the samples. Heptachlor (PolyScience, Warsaw, Poland) was dissolved at a concentration of 100 $\mu g\,ml^{-1}$ in toluene.

2.3. Losses of analytes

The analytes showed a high tendency to sorb to glassware during clean-up. In a test 50 ml of cyclohexane containing 100 ng of OP and BPA and 500 ng NP (sum of all isomers) where concentrated to one milliliter on a rotary evaporator. BPA was almost completely lost (Table 2). As BPA is a compound with very low volatility (3×10^{-9} to 7×10^{-12} Pa at 25 °C (Staples et al., 1998), evaporation as reason for the losses could be excluded.

To solve this problem the use of butanol as competing compound and the deactivation of the glass surfaces by silanisation were tested using the same amounts of analytes and test setup as previously described.

After silanisation high recoveries and acceptable reproducibility were obtained (Table 2). Thus all glassware used throughout sample preparation (except for columns and funnels) was silanised using a solution of 5% (v:v) dimethyldichlorsilane (Fluka, Buchs, Switzerland) in toluene. Further tests were carried out concerning losses during storage of underivatized samples in brown glass vials over night at 4 °C (Table 2). Losses were higher for less concentrated standards. Consequently all samples and standards were derivatised immediately after completion of clean-up.

To further improve reproducibility, the influence of the duration of the evaporation process was assessed. Recovery was better if the time necessary for rotary evaporation was as short as possible while avoiding boiling of the solvent.

2.4. Blanks

In blank controls OP, NP and BPA were found in the range of 10–20 ng in all samples in the beginning. The contamination could be reduced by cleaning the microliter syringes used to add derivatisation reagent and standards in an ultrasonic bath after their use. BPA was still regularly found in blank samples. We discovered that the water purified by passing it through a Milli-Q apparatus (Millipore Corporation, Bedford, MA, USA), which was used to partition the extracts of the particle samples was contaminated with BPA up to several hundreds of nanograms per liter. The contamination was probably due to the cartridges for the ion exchange resin of the millipore apparatus being made out of polycarbonate plastics which contains BPA as a monomer. HPLC-grade water (Lichrosolv, Merck, Darmstadt, Germany) was used instead of the Millipore water. But still very low BPA concentrations were measured regularly in the control samples. For this reason every preparation of samples was accompanied by at least one blank preparation. Results were always reported blank corrected and only regarded as reliable if their content was more than two times higher than the corresponding blank sample (Rudel et al., 2001).

2.5. Extraction

Extraction procedures had to be developed for XAD resin for the gasphase samples and for glass fiber filters for the aerosol samples. For the gasphase samples the only extraction procedure tested was ultrasonic treatment with hexane (three times with 80/50/50 ml) as the analytes are considered to be relatively easy to leach out of the XAD resin and an ultrasonic extraction has already proven to be suited by Rudel et al. (2001) for this matrix. Their findings were confirmed by our recoveries ranging from 72% to 78%.

For the glass fiber filters different methods were tested. Soxhlett extraction (150 ml of solvent, 20 h), accelerated solvent extraction on an ASE 100 (Dionex, Sunnyvale, USA) (120 °C, 90 MPa, two static cycles, 20–30 ml of solvent) and extraction in an ultrasonic bath were compared. Each method was tested using dichloromethane and hexane:acetone 1:1 v:v as extraction solvents. The ultrasonic extraction was also performed after acidification of the samples with 0.5 ml of H_2SO_4:H_2O 1:1 v:v. Acidification was not possible for ASE because the extraction cells would have been damaged.

Results are summarized in Fig. 1. ASE showed unexpected low recoveries. This is probably not due to the extraction procedure but to the fact that analytes are lost in the tubing through which the extract is delivered to the vial. These findings were confirmed by repeated extractions. Highest extraction efficiencies for OP and NP were achieved with ultrasonification of the acidified samples. For that reason the aerosol samples were extracted three times in an ultrasonic bath with 80/50/50 ml of hexane:acetone 1:1 v:v.

2.6. Clean-up

For the aerosol samples as well as for the gasphase samples a clean-up by column chromatography was necessary. As BPA is more polar than the alkylphenols these different compounds were collected in two separate fractions. Otherwise polar matrix compounds eluting together with bisphenol A from the column were interfering with the NP-peaks during GC-MSD measurements, especially in the case of aerosol samples. A column of 3 g silica II (100-200 mesh, Merck, Darmstadt, Germany) conditioned with hexane was used.

For the gasphase samples it was necessary to elute a fraction of 30 ml hexane first to remove unpolar compounds from the column before eluting the alkylphenol fraction with 70 ml of hexane:ethylacetate 9:1 v:v. The third fraction consisting of 40 ml hexane:ethylacetate 3:7 contained BPA.

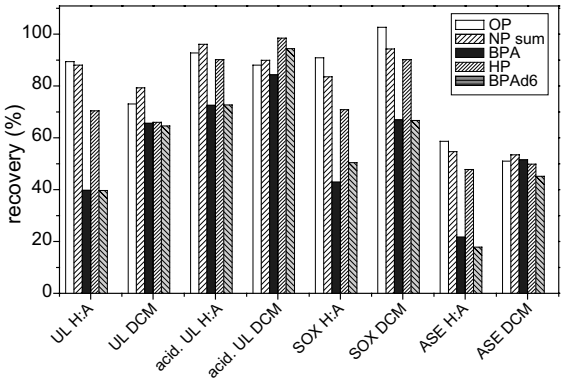

Fig. 1. Extraction efficiencies for different extraction methods (abbreviations: UL = ultrasonic bath, H:A = hexane:acetone 1:1 v:v, acid = acidified samples (20 drops of 1 M H_2SO_4), SOX = Soxhlett extraction, ASE = accelerated solvent extraction).

The same fractionation was used for the aerosol samples except for the hexane fraction which could be omitted. The extracts of the aerosol samples had to be extracted with water before column-chromatography to remove very polar compounds which otherwise caused the formation of insoluble precipitation pellets during rotary evaporation.

The fractions were concentrated to 1 ml on a rotary evaporator, transferred to 2 ml silanised brown glass vials, reduced to 0.5 ml under nitrogen and silylated. After addition of 5 μg internal quantification standard, samples were measured at the GC-MSD.

2.7. Derivatisation

The analytes OP, NP and BPA are quite polar due to their hydroxyl groups. Their chromatographic behavior can be improved by modifying this functional group. Besides better peak shape and thus better resolution, lower limits of detection and easier clean-up can be achieved.

Three derivatisation reagents were tested: acetic anhydride (AE, Fluka, Buchs, Switzerland), pentafluorobenzyl bromide (PFBBr, Fluka, Buchs, Switzerland) and a mixture of the silylating reagents trimethylchlorosilane (TMCS) and bis-N,O-(trimethylsilyl-)trifluoroacetamide (BSTFA) called Sylon BFT (Supelco, Bellefonte, CA, USA). After optimizing the conditions for the derivatisation reactions, the different reagents were compared regarding detector response, separation of the different NP-peaks and handling.

Best results were achieved using Sylon BFT which showed high detector response compared to AE and better peak separation compared to PFBBr and was easiest to handle as no addition of base, complexing agent or phase transfer was necessary as for the other reagents. The long derivatisation time of 5 h necessary to complete the reaction described by Rudel et al. (2001) could be reduced to 2 h at 60 °C shifting the mixing ratio of BSTFA:TMCS from 9:1 to 99:1 v:v. 50 μl of the mixture were sufficient for a complete derivatisation.

After cooling down for 5 min after completing the silylation, excess reagent was purged by a stream of nitrogen.

The kinetics of the silylation reaction is strongly dependent on the solvent (Li et al., 2001). For that reason the standards for derivatisation were prepared in the same solvent-mixture as the samples were obtained after clean-up.

2.8. Internal standards

In this study different internal standards were used: One substance was used as internal standard for quantification to correct for slight deviations in sample volume and to control eventual fluctuations during injection. Heptachlor was used for this purpose because it could not be detected in atmospheric samples at the Waldstein sampling site (G. Streck, unpublished results), showed no tailing and eluted at a suitable time from the column. As this compound has got no similarity concerning structure and functional groups to the analytes, different internal standards were tested to control the accuracy and the precision of the whole analytical method. Heptylphenol (HP) showed very similar behavior to OP and the NP isomers. BPA deuterated at the propane moiety (BPAd6) was used as surrogate compound for BPA.

2.9. GC-MSD analyses

All measurements were carried out using a HP 5890 gaschromatograph with a HP 8596 autosampler coupled to a HP 5970 Mass Selective Detector. Transfer line temperature was kept at 300 °C. Electron impact ionisation at 70 eV was used. A DB-5 column (30 m, 0.25 mm id, 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) was used to separate the analytes with the following temperature program: 80 °C (1.5 min), 30 $K\,min^{-1} \rightarrow 140$ °C, 4 $K\,min^{-1} \rightarrow 220$ °C, 30 $K\,min^{-1} \rightarrow 300$ °C (3.5 min). Helium was used as carrier gas at a constant pressure of 74 kPa. Injections of a volume of 1 μl were performed splitless at an injector temperature of 280 °C and the photomultiplier was operated at 1600–2000 mV.

Ions used in the single-ion-monitoring mode for quantification and confirmation of the silylated analytes and internal standards are shown in Table 1.

Table 1
Ions monitored for quantification and confirmation of the analytes and internal standards

Compound/peak	Ions monitored for	
	Quantification	Confirmation
OP	207	208, 278
NP1	193	235
NP2	207	221, 263
NP3	221	207, 193
NP4	207	221, 193
NP5	235	193, 179
NP6	221	207, 249
NP7	235	193, 179
NP8	207	221, 179
NP9	207	208, 221
NP10	221	207, 179
BPA	357	358, 372
HP	179	264, 180
BPA-d6	360	378, 361
Heptachlor	100	272, 274

2.10. Isomers of technical NP

Under the described chromatographic conditions with Sylon BFT as derivatisation reagent, the mixture of more than 20 isomers (Kleist and Günther, 2000) of the technical NP was well resolved to ten peaks. Except for peak number 8 (Fig. 2), which was to small to be reliably quantified, these different peaks were integrated and quantified separately. The concentration of each single NP-peak was calculated from the peak area in relation to the sum of all NP-peak areas from a chromatogram of a 1 μg-standard acquired in the SCAN mode. SCAN mode instead of SIM mode was used for that purpose to allow for equal weighing of all produced ions. A highly concentrated standard was analyzed to minimize errors from integration. With the now available concentrations of each single NP-peak in the NP-standard, the calibration for the samples was done, considering every different peak like a different compound. Using this method no information on single isomers can be deduced, as the separated peaks consist of different isomers. In spite of that this method allows to minimize errors due to integrating the whole NP mixture as one "peak" (Dachs et al., 1999) as coeluting matrix compounds will not contribute to the area. Besides the independent quantification of the different peaks can be used as a measure for the precision of the results and the error of the total NP concentrations calculated as sum of all quantified peaks is being reduced, as random errors will decrease by averaging over nine peaks.

3. Results and discussion

3.1. Calibration

Linear ranges of the calibration curve were determined using Mandel's test (Mandel, 1964). Within each linear range at least one standard was measured concurrently with each measurement of samples.

Linear ranges for OP and BPA ranged from 2 to 10 ng per vial for a sample volume of 150 μl. For a volume of 0.5 ml linearity was true for 5–30 ng and 20–100 ng per vial. NP (sum of all isomers) showed linear calibration curves in the range of 10–50 ng per vial for 150 μl sample volume and from 25 to 150 ng and from 100 to 500 ng per vial for a volume of 0.5 ml.

Samples containing high concentrations were diluted to quantify them reliably.

3.2. Limits of detection and quantification

The limit of detection (LOD) and quantification (LOQ) were calculated using the method from Funk et al. (1985). For gasphase samples a volume of 0.5 ml in the vial was sufficient for determination of the analytes. For the aerosol samples a preconcentration to 150 μl using inserts for the vials was necessary to exceed the limit of quantification. Thus the LOD and LOQ had to be determined for both volumes, as the extra evaporation and transfer steps for the 150 μl samples might have an influence on the variability of the calibration curve. Using the described method concentrations down to the low $pg\,m^{-3}$-range can be determined. The LODs and LOQs are presented in detail in Table 3.

Table 2
Losses of analytes; recoveries in %, coefficients of variation are given in brackets, n = number of replicates

Compound	Recoveries after rotary evaporation			Recoveries after storage		
	Without treatment ($n = 3$)	Silanisation ($n = 3$)	Addition of butanol ($n = 3$)	100 ng in 0.5 ml ($n = 3$)	100 ng in 1 ml ($n = 3$)	50 ng in 0.5 ml ($n = 2$)
OP	47 (10)	100 (7)	58 (92)	71 (9)	80 (4)	37
NP (sum)	47 (7)	105 (6)	67 (89)	73 (7)	84 (8)	37
BPA	2 (26)	75 (11)	20 (110)	70 (5)	83 (5)	35

Table 3
Limits of detection and quantification for gasphase samples (sample volume = 0.5 ml) and aerosol samples (sample volume = 150 μl); injection volume: 1 μl

Compound	pg compound injected			
	LOD_{gas}	LOQ_{gas}	LOD_{ae}	LOQ_{ae}
OP	8	22	8	23
NP1	2	6	1	2
NP2	10	28	5	15
NP3	2	6	2	5
NP4	14	44	3	10
NP5	2	8	1	4
NP6	2	8	3	9
NP7	2	6	1	4
NP9	8	22	5	18
NP10	2	6	[a]	[a]
BPA	2	8	7	19

[a] Not determined.

3.3. Chromatograms

In Figs. 2–4 TIC and extracted ion chromatograms of a 100 ng standard and a gasphase sample (sampling site u near Bayreuth) containing about 200 ng OP, 500 ng NP (sum) are shown. The BPA peak in Figs. 2 and 4 does not represent real gasphase BPA concentrations as the corresponding blank sample showed elevated BPA concentrations.

3.4. Recoveries and reproducibility

Recoveries and reproducibilities of the whole analytical procedure were checked using spiked samples. For the gasphase samples four parallels of each 30 g XAD2 resin were spiked with 100 ng OP, BPA, HP and BPAd6 and 500 ng NP (sum). The samples were shaken to mix the standard and the XAD resin. After an hour of equilibration time the samples were analyzed as described.

For the aerosol samples three glass fiber filters (Schleicher and Schüll, Dassel, Germany) were treated like the XAD resin. Recoveries and reproducibilities for these spiked matrix samples are listed in the left column for each sample type in Table 4.

3.5. Matrix effects

The determination of the recovery and precision of the analytical methods was not performed on real samples, as the original matrix could not be mimicked free of analytes. Thus matrix effects were assessed using the surrogate compounds HP for OP and NP and BPAd6 for BPA. These compounds were suited well to predict the behavior of OP, NP and BPA during the analytical procedure as can be seen from the similar recoveries and reproducibilities of OP, NP and the surrogate compound HP and BPA and the surrogate compound BPAd6 in the left columns of Table 4.

Gasphase and aerosol samples analyzed for OP, NP and BPA were each spiked with 100 ng HP and BPAd6. Comparing the surrogate recoveries of real sample matrix with those of spiked XAD resin and glass fiber filters, matrix effects become obvious. The average recovery for HP in gasphase samples is 20% higher in real matrix samples than in spiked clean XAD resin. For BPA the average recovery in real aerosol samples is 26% lower than for clean spiked glass fiber filters (Table 4). The reasons for the observed effects are not completely clear. For the aerosol samples, it is probable that the analytes are stronger bound to samples with real matrix than to clean glass fiber filters and that the lower recoveries correspond to lower extraction efficiencies. The reason for the higher recoveries in real gasphase samples are not known. To overcome this problem all results were corrected for surrogate recovery.

For the gasphase samples "spiked real samples" were available because in the beginning of the sampling campaign gasphase samples were accidentally taken through glass fiber filters in a filter holder made from polycarbonate plastics. Three gasphase samples were taken using this plastic device which emitted NP to the sampled air. The contamination source was eliminated for the following sampling periods by replacing all plastic devices with metal or Teflon. But as a consequence real spiked gasphase samples were available. The sampling took place on one of the original sampling locations under different conditions concerning temperature, humidity, and radiation. Thus the emitted NP concentrations varied during the different sampling times. However, the relative amounts of the different NP isomers can be assumed to stay constant as the sampled NP stems from the same plastic source. The coefficient of variation among the three different samples can be used to estimate the error of the measured NP concentrations. This estimate is probably lower than the real errors are, because the NP concentration emitted from the plastic device was high in comparison with the background content of NP in the air. The coefficients of variation range from 2% to 12% (mean = 5%).

3.6. Measured concentrations

In Figs. 5–7 the concentration range of OP (gasphase: 0.02–0.16 $ng\,m^{-3}$ aerosol: 0.3–4.2 $pg\,m^{-3}$), NP (gasphase: 0.15–1.0 $ng\,m^{-3}$ aerosol: 1.7–117 $pg\,m^{-3}$) and BPA (aerosol: 5–15 $pg\,m^{-3}$) are shown. For OP and NP already published concentrations (van Ry et al., 2000) have been included to allow for a better comparison between the samples of van Ry et al. which were taken at the Lower Hudson River Estuary in a densely populated and more polluted urban area and the samples taken in a

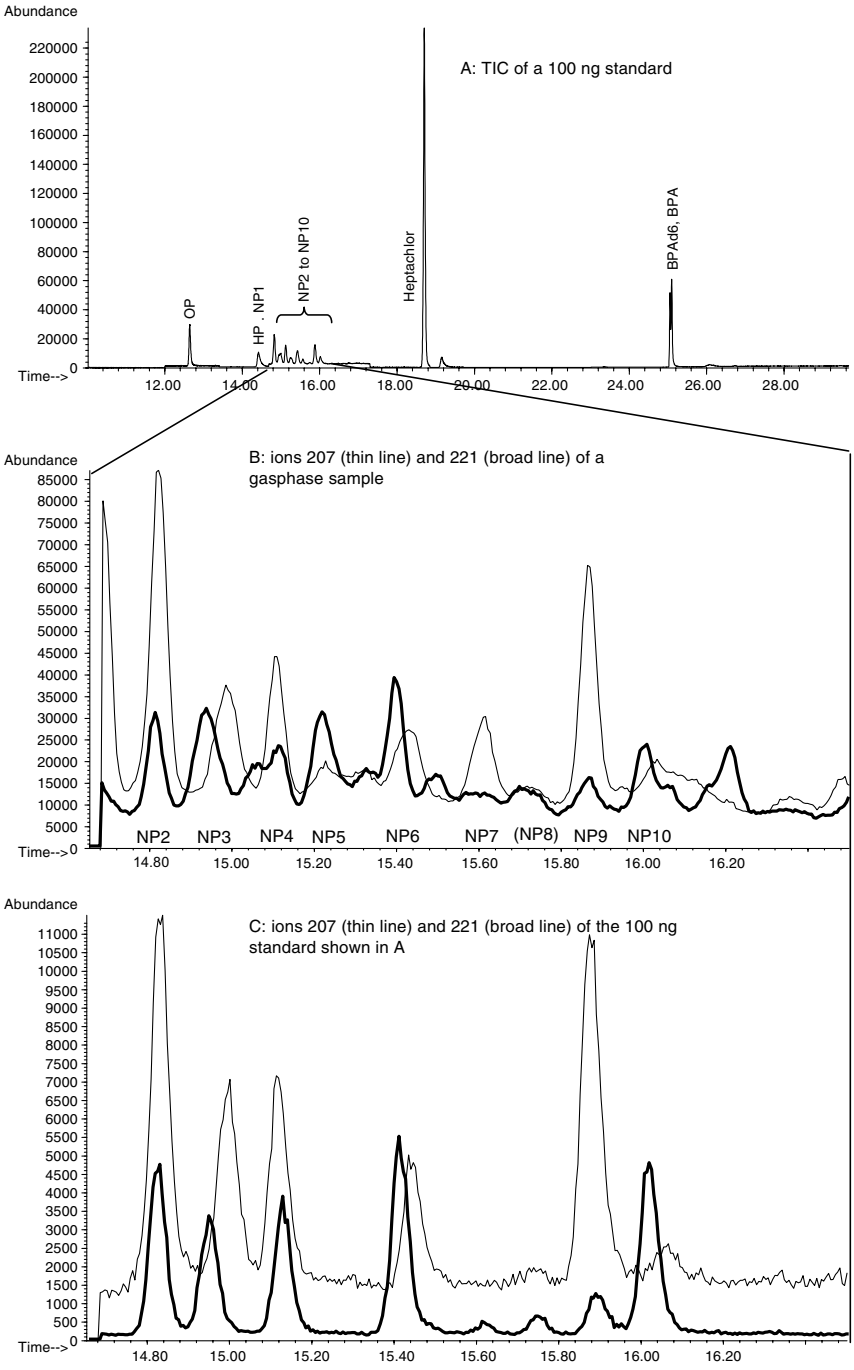

Fig. 2. (A) TIC chromatogram of a 100 ng standard; (B) The most important ions used for quantification 207 and 221 for a gasphase sample; (C) The same ions in the same time range for the 100 ng standard are shown; NP peaks are identified by numbers underneath B; other ions monitored for detection of NP isomers (Table 1) have been omitted for clarity reasons.

remote area (sampling sites p and w) and near a small town (70 000 inhabitants, sampling site u). BPA was not detected in gasphase samples. The average concentrations determined in this study are one to three orders of magnitude below the concentrations measured by van Ry et al.

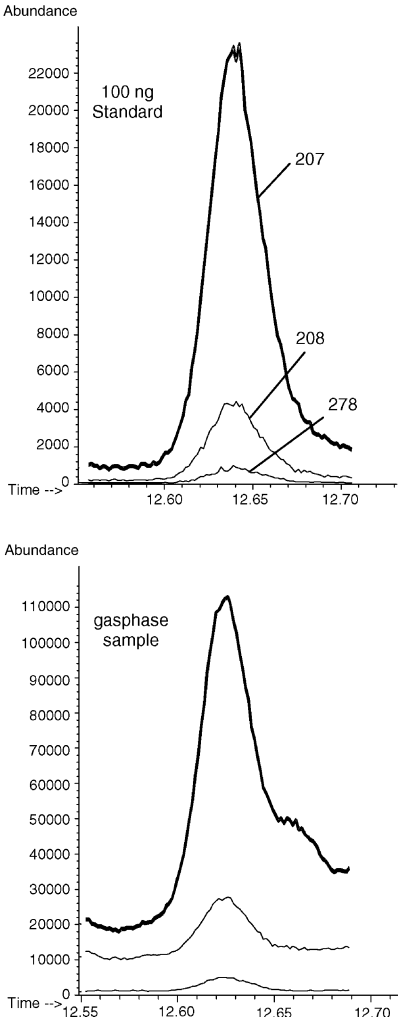

Fig. 3. OP peak in a 100 ng standard and gasphase sample, the ions are indicated in the standard.

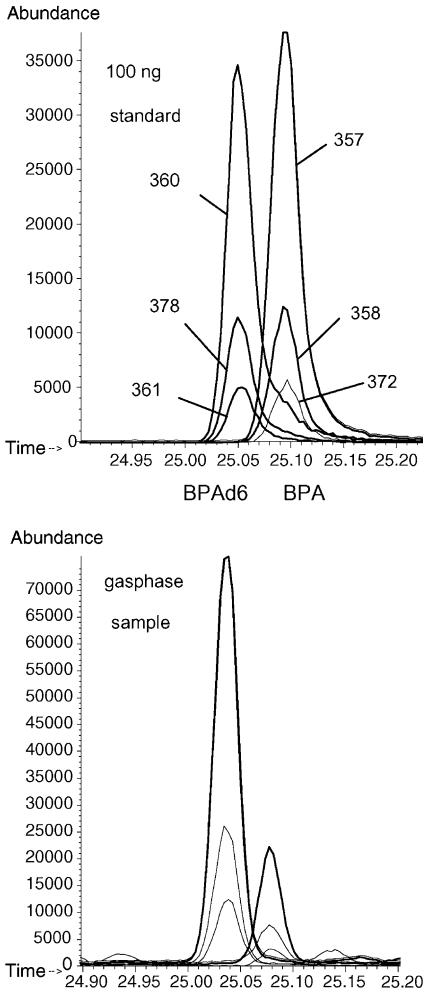

Fig. 4. BPAd6 and BPA peaks in a 100 ng standard and a gasphase sample, the ions are indicated in the standard.

Table 4
Recoveries (%) of analytes and surrogate compounds in spiked samples; standard deviations are given in brackets, n = number of replicates

Compound	Spiked XAD resin		Spiked glass fiber filters	
	Spiked matrix ($n = 4$)	Real samples ($n = 27$)	Spiked matrix ($n = 3$)	Real samples ($n = 5$)
OP	57 (9)		71 (7)	
NP (sum)	76 (8)		80 (10)	
BPA	67 (17)		38 (1)	
HP	70 (8)	90 (21)	77 (11)	70 (3)
BPAd6	69 (18)	62 (23)	35 (0,1)	9 (3)

4. Conclusion

The described analytical procedures are suited well to examine the atmospheric occurrence and the partitioning of OP, NP and BPA between gasphase and aerosol. Low limits of quantification even allow for the determination of samples from remote regions with relatively clean air.

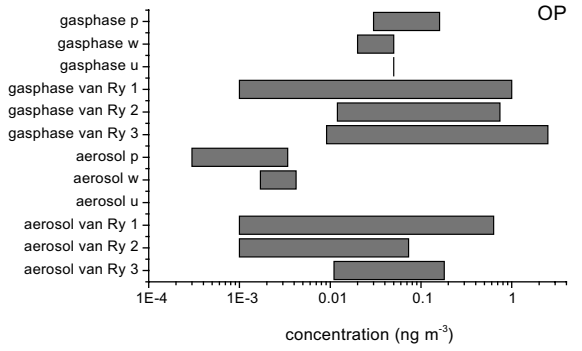

Fig. 5. Range of measured OP concentrations at three sampling sites (p = sampling site on a clearing ($n = 3$), w = sampling site in the forest ($n = 3$), u = sampling site in a more urban area ($n = 2$)); additionally the range of concentrations measured by van Ry et al. (2000) at three different sites are shown (if the lowest value was given as nd, it was set equal to the limit of detection).

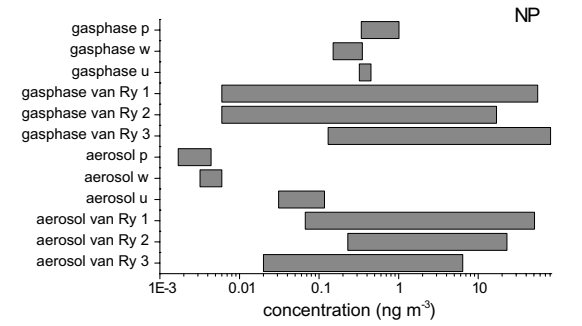

Fig. 6. Range of measured NP concentrations at three sampling sites (p = sampling site on a clearing ($n = 3$), w = sampling site in the forest ($n = 3$), u = sampling site in a more urban area ($n = 2$)); additionally the range of concentrations measured by van Ry et al. (2000) at three different sites are shown (if lowest value was given as nd, it was set equal to the limit of detection).

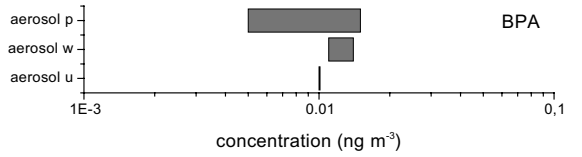

Fig. 7. Range of measured BPA concentrations at three sampling sites (p = sampling site on a clearing ($n = 3$), w = sampling site in the forest ($n = 3$), u = sampling site in a more urban area ($n = 2$)).

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