

Atmospheric concentrations and air-sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in the North Sea

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“Capsule”: Air-sea vapour exchanges of estrogenic alkylphenols are studied in the North Sea and it is shown that a net deposition is occurring.

Abstract

Concentrations of nonylphenol isomers (NP), tertiary octylphenol (*t*-OP) and nonylphenol monoethoxylate isomers (NP1EO) have been simultaneously determined in the sea water and atmosphere of the North Sea. A decreasing concentration profile appeared following the distance increasing from the coast to the central part of the North Sea. Air-sea exchanges of *t*-OP and NP were estimated using the two-film resistance model based upon relative air-water concentrations and experimentally derived Henry's law constant. The average of air-sea exchange fluxes was $-12 \pm 6 \text{ ng m}^{-2} \text{ day}^{-1}$ for *t*-OP and $-39 \pm 19 \text{ ng m}^{-2} \text{ day}^{-1}$ for NP, which indicates a net deposition is occurring. These results suggest that the air-sea vapour exchange is an important process that intervenes in the mass balance of alkylphenols in the North Sea.

Keywords: nonylphenol, tertiary octylphenol, nonylphenol monoethoxylate, atmosphere, air-sea exchange, North Sea

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1. Introduction

Alkylphenol ethoxylates (APEOs), in particular, nonylphenol ethoxylates (NPEOs) are widely used as non-ionic surfactants that are discharged in high quantities to sewage or industrial wastewater treatment plants. They can also directly enter the environment in areas without wastewater treatment (James, 1999). In 1995, Germany had an alkylphenols (APs) consumption of 20.000 t, of which proximately 14.000 t was nonylphenol. The rest of 6000 t was made up of octyl-, butyl- and other alkylphenols. As proposed in the literature (Ahel et al., 1994; Ying et al., 2002), the biodegradation of NPEOs under aerobic or anaerobic conditions leads to a shortening of the polyethoxylate chain (hydrolytic cleavage of the ethoxy units). The metabolites, e.g. nonylphenol monoethoxylate (NP₁EO, C₁₇H₂₈O₂), nonylphenol diethoxylate (NP₂EO, C₁₉H₃₂O₃) and nonylphenol (NP, C₁₅H₂₄O) are more resistant to microbial degradation than higher ethoxylated compounds (Giger et al., 1981; 1984). NP, the main metabolite of NPEOs, is considered to be toxic to both marine and freshwater species (Comber et al., 1993; Servos, 1999; Ahel et al., 2000; Atienzar et al., 2002; Hill et al., 2002). In addition, NP has shown an endocrine disrupting effect in bio-tests (Soto et al., 1991; White et al., 1994; Jobing et al., 1996; Routledge and Sumpter, 1996). Concern over their environmental impacts has led to the recommendation for phasing out NPEOs from cleaning products in members of European Union since 1992 (PARCOM, 1992/8), and a restriction to be active on the sale and the use of products containing more than 0.1% NPEO or NP in Europe from January of 2005 (Directive 2003/53/EC).

APEOs and their metabolites have been detected in a variety of large rivers, lakes and in a few coastal waters and sediments worldwide (Blackburn et al., 1994; 1998; Bennie et al., 1997; Kvestak and Ahel, 1994; Kawahata et al., 2004; Ahel et al., 2000; Ferguson et al., 2001). In the North Sea, APs and APEOs in the surface water have been previously investigated (Bester et al., 2001; Heemken et al., 2001; Jonkers et al., 2003), with concentrations ranging from 1 to 84 ng L⁻¹ for NP and 0.1 to 111 ng L⁻¹ for the APEOs. Moreover, many large rivers have been previously investigated as proposed sources of input for industrial chemicals with endocrine potential or environmental relevance into the North Sea (Jonkers et al., 2003; Stachel et al., 2003).

NP and *t*-OP has also been measured in atmospheric samples. Dachs et al. first reported the concentrations of NP ranging between 2.2 and 70 ng m⁻³ in the coastal atmosphere of the New York - New Jersey Bight in 1999 (Dachs et al., 1999). Van Ry et al. (2000) from the same laboratory additionally studied the seasonal trends of NP and *t*-OP in the

atmosphere of the Lower Hudson River Estuary from June to December 1998, and reported a similar range of concentrations of NP and *t*-OP. The air-sea exchange of NP over the Lower Hudson River Estuary was evaluated based on the estimated H value of NP. The results suggest that the volatilisation should be considered as an important mechanism for the environmental fate of NP. However, a reassessment of air-sea exchange based on an experimentally derived H of NP suggested that a net atmospheric deposition of NP might dominate the gaseous exchange in lower bay (Xie et al., 2004). Although the results are different due to the significant difference of the H values used, they both demonstrated the atmospheric transport and air-sea exchange of NP is significant for the distribution of NP. Moreover, more work is clearly needed for understanding the source of atmospheric NP and their degradation mechanisms in the atmosphere (Porter et al., 2004).

Although proven that APs are ubiquitous in the environment, reliable information on the atmospheric concentrations of NP and *t*-OP in the North Sea does not exist. Therefore, an investigation is necessary to develop a better for better understanding of their distribution and transport mechanism in the North Sea. The purpose of this study is to simultaneously determine the *t*-OP, NP and NP1EO concentrations in different compartments of the North Sea and estimate the air-sea exchange fluxes of NP, *t*-OP in the coastal area. Furthermore, this study provides a consistent data set for the future evaluation of the regional mass balance of NP and *t*-OP in the North Sea.

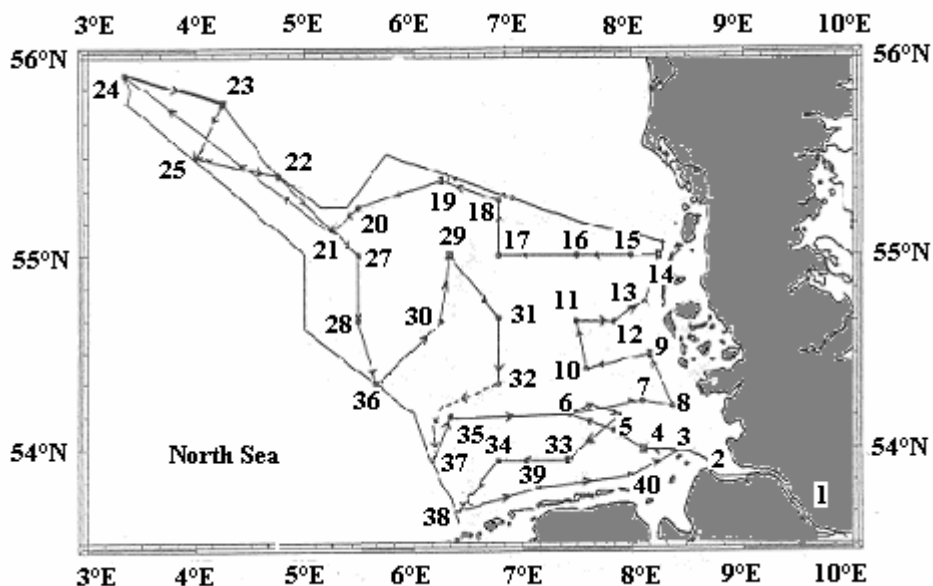


Figure 1. Sampling stations in the North Sea during the cruise 414 with research vessel “*Gauss*”, February 29-March 10, 2004.

2. Experimental Section

2.1. Air and water sampling

The air and water samples in the North Sea (German Bight) were collected during the cruise no. 414 with the research vessel 'Gauss' from February 29th to March 10th in 2004. Integrated water samples were collected at 4.5 m depth during the ship voyage. The air samples were collected on the upper deck of 'Gauss' about 9 m above the sea level. Water samples W1-W4, W10 and W11 with salinity ranging from 27.8 to 32.2‰ were simply defined as coastal water sample, and W5-W9 with salinity ranging from 34.1 to 34.9‰ were defined as open sea sample. Detailed information on the sampling station, sample volume, temperature, wind speed and dominating direction, salinity and humidity are given in Fig. 1 and Tab. 1.

Table 1. Water and air sampling.

| Sample | Date (in 2004) | Station | Volume (L) | Temp. (°C) | Salinity (‰) | Wind speed (m s ⁻¹) | Wind direction | Humidity (%) |
|--------------|-------------------|--------------|-------------------|---------------|-----------------|------------------------------------|-------------------|-----------------|
| Water | | | | | | | | |
| W1 | 29/2 | 3 - 4 | 38 | 4 | 28.5 | 9.0 | | |
| W2 | 1/3 | 4 - 6 | 174 | 5 | 30.4 | 8.7 | | |
| W3 | 1/3 | 6 - 8 | 82 | 4 | 27.8 | 10.0 | | |
| W4 | 2/3 | 10 - 13 | 175 | 5 | 30.1 | 10.0 | | |
| W5 | 3/3 | 16 - 19 | 254 | 6 | 34.1 | 6.8 | | |
| W6 | 4/3 | 23 - 25 | 410 | 7 | 34.9 | 14.0 | | |
| W7 | 5/3 | 22 - 36 | 381 | 6 | 34.6 | 11.6 | | |
| W8 | 6/3 | 29, 30, 36 | 335 | 6 | 34.5 | 4.3 | | |
| W9 | 7/3 | 35 - 37 | 201 | 6 | 34.5 | 4.2 | | |
| W10 | 8/3 | 33 - 34 | 162 | 5 | 32.2 | 7.2 | | |
| W11 | 9/3 | 34 - 39 | 81 | 5 | 31.6 | 11.4 | | |
| Air | | | (m ³) | | | | | |
| A1 | 29/2 – 2/3 | 1 - 11 | 494 | 4 | | 4 - 11 | SW and SE | 90 |
| A2 | | | 549 | | | | | |
| A3 | 2/3 - 6/3 | 11 – 25 - 36 | 1147 | 6 | | 5 - 16 | SW and NW | 100 |
| A4 | | | 927 | | | | | |
| A5 | 6/3 – 9/3 | 33 - 39 | 670 | 3 | | 4 - 8 | SW and SE | 85 |
| A6 | | | 589 | | | | | |

As described by Petrick et al., (1996), total suspended matter (TSM) and sea water were collected using a glass fibre filter (GF/F 52, 142 mm diameter, Schleicher & Schuell, Dassel, Germany) and a PAD-2 resin column (22 cm x 3 cm i.d.), respectively. The in-situ pump was placed in the wet lab and directly connected to the sea water supplied by an assembly stainless steel pipeline (o.d. 10 mm). 38-400 L sea water passed through the PAD-2 column at flow rate ranging from 0.5 to 1 L min⁻¹ in terms of the amount of TSM. Ship-borne air samples were taken using a high-volume pump (ISAP 2000, Schulze Automation & Engineering, Asendorf, Germany) operated at a constant flow rate of 0.2 m³ min⁻¹. The particles were collected using a glass fibre filter (GF/F 8, diameter: 155 mm, Schleicher and Schuell, Dassel, Germany), and the gaseous analytes were collected on the PUF/XAD-2 column. In order to escape the emissions from the ship's funnel, air sampling was performed on headwind, and was stopped while wind speed was lower than 3 m s⁻¹. Samples were stored as described by Lakaschus et al. (2002).

2.2. Chemicals and materials

All handling of samples was performed under clean-room conditions (positive pressure, filtered air) to minimize contamination. Solvents (acetone, n-hexane, dichloromethane (DCM) and diethyl ether) were pico grade (Promochem GmbH, Germany) and distilled prior to use. The glass pipettes, vials and ampoules were initially rinsed with Milli-Q water and acetone, then baked out at 450 °C in a muffle furnace prior to use.

All glass fibre filters were pre-cleaned by baking out at 450 for 12 h in a muffle furnace. For PAD-2 resin column, 50 g of Serdolit[®] PAD-2 resins (0.3-1.0 mm, analytical grade, SERVA Electrophoresis GmbH, Heidelberg, Germany) were initially rinsed with water and then packed into a glass column. The column was sequentially purified by modified Soxhlet extractor with acetone, n-hexane and DCM for 72 h, and finally conditioned with 200 mL purified Milli-Q water. Each air-sampling column was packed with 25 g of XAD-2 and one piece of PUF slice. The columns were pre-cleaned by sequential Soxhlet extraction with methanol, acetone and n-hexane for 72 h. Residual solvent was removed by nitrogen stream (0.5 L min⁻¹ for 20 min).

2.3. Extraction, clean-up and derivatization

The PUF/XAD-2 columns were spiked with internal standards (50 μL of 200 ng mL^{-1} 4-n-NP and 4-n-OP) and extracted for 16 h using 300 mL of 10% (v/v) diethyl ether in n-hexane solution with modified Soxhlet extractor (Ehrhardt, 1987). The PAD-2 columns were extracted for 16 h using 250 mL DCM with modified Soxhlet extractor. Solvent circulation rate was approximately 5 mL min^{-1} . Both air and water filter samples were extracted for 16 h using 150 mL of DCM with Soxhlet extractor (10-15 min pro circle). Prior to the extraction for PAD-2 columns and filter samples, 50 μL of 4-n-NP and 4-n-OP solution at 200 ng mL^{-1} and 50 μL of deuterated NP1EO (NP1EO D2) solution at 1.0 $\mu\text{g mL}^{-1}$ were added into the solvent as internal standards.

All the extracts were purified by a 5% H_2O deactivated silica gel column (2.5 g silica gel packed in 1cm i.d. x 15 cm glass column). Silica gel (0.063-0.200 mm, Merck, Darmstadt, Germany) was prepared as follows: extracted with acetone for 12 h; dried with nitrogen; baked out at 450 $^{\circ}\text{C}$ for 12 h; deactivated by addition of 5% (w/w) of milli-Q water (purified by XAD-2 resins). The glass column with frit (pore size 0) was first cleaned using 5 mL acetone and hexane in turn, and packed with 2.5 g silica gel, and then conditioned with 20 mL diethyl ether and 10 mL n-hexane, respectively. After the extracts were transferred into the column, purification of the extracts was accomplished by passing 10 mL hexane through the column in order to remove the non-polar compounds. The column was eluted with 30 mL of n-hexane and diethyl ether (3:1 v/v) for the NP, *t*-OP and NP1EO fraction. The elution was rotary evaporated to 1 mL and then transferred into a 2 mL scaled glass vial. 50 μL of 200 ng mL^{-1} deuterated 4-n-NP (4-n-NP D8) was spiked as the performance standard for monitoring the derivatization. The volume was blown-down to 100 μL under a gentle stream of nitrogen (99.999%). 100 μL of N,O-bis(trimethylsilyl)trifluoroacetamide and 1% TMCS (BSTFA) (Part No. 701 490.201, Macherey-Nagel GmbH, Dueren, Germany) was added into the vial. The mixture was allowed to react for 1 h at 70 $^{\circ}\text{C}$. After cooling for 5 min, the final sample volume was adjusted to 200 μl using hexane for analysis.

2.4. Gas Chromatography-Mass Spectrometry

The quantification of analytes was performed with an Agilent 6890 capillary gas chromatograph coupled to an Agilent 5973 quadrupole mass selective detector (GC-MS). Ions detected were generated by electron impact ionisation and monitored in the selective mode (EI-SIM). A 30 m x 0.25 mm fused silica capillary column (95%, Dimethyl-5%-

diphenylpolysiloxan, HP-5ms) with 0.25 μm film thickness was used for the separation. The flow rate of the carrier gas helium was kept constant at 1.0 mL min^{-1} . The temperature program was as follows: 80 $^{\circ}\text{C}$ for 1 min, 30 $^{\circ}\text{C min}^{-1}$ to 130 $^{\circ}\text{C}$, 3 $^{\circ}\text{C min}^{-1}$ to 240 $^{\circ}\text{C}$, 10 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C}$, then 300 $^{\circ}\text{C}$ for 5 min. The transfer line and the ion source temperature were maintained at 280 $^{\circ}\text{C}$ and 230 $^{\circ}\text{C}$, respectively. 1 μL of the sample was injected into GC-MS by pulse splitless mode with a pulse pressure of 20 psi for 2 min and inlet temperature of 280 $^{\circ}\text{C}$.

The GC-MS was operated in the selective ion monitoring mode detecting the following masses: $m/z = 207, 221, 235$ (TMS-NP); $m/z = 207$ (TMS-*t*-OP); $m/z = 251, 265, 279$ (TMS-NP1EO); $m/z = 179$ (TMS-4-*n*-NP, TMS-4-*n*-OP); $m/z = 185$ (TMS-4-*n*-NP D8); $m/z = 253, 267$ (TMS-NP1EO D2). As shown in Fig. SI-1 and Fig. SI-2 (supplementary information), 13 peaks for NP-TMS and NP1EO-TMS with higher proportions were resolved using GC-MS by selective ion mode. NP1EO 3 and NP1EO 4 were integrated together for the quantification. Fig. SI-3 (supplementary information) shows that 4-*n*-NP, 4-*n*-OP were spiked as the internal standards for NP and *t*-OP, and NP1EO D2 was spiked as internal standard for NP1EO. Analytes were quantified by comparing the integrated peak area of each peak to that of the internal standard. The quantification was performed with calibration curves made for individual peaks using standard with concentrations ranging from 12.5 to 500 ng mL^{-1} for NP and *t*-OP, and from 25 to 1000 ng mL^{-1} for NP1EO.

2.5. Quality control

The analytical quality of the data was determined using field blanks, method detection limits (MDLs) and recoveries. The instrumental limit of detection (LOD) was determined by the signal to noise ratio ($\geq 3:1$), which were 0.4 pg for *t*-OP, 0.1 – 0.8 pg for NP isomers and 0.3 – 0.5 pg for NP1EO isomers. MDLs were derived from the blanks and quantified as means of field blanks plus three times the standard deviation (3σ) of field blanks with normalizing average sampling volume of 200 L for water sample and 500 m^3 for air sample, respectively. Therefore, the limit of quantification was 17, 4 and 20 pg L^{-1} for NP, *t*-OP and NP1EO in the water; 7, 3 and 10 pg L^{-1} for NP, *t*-OP and NP1EO in TSM; 5 pg m^{-3} for NP, *t*-OP and NP1EO in the vapor; and 3, 1, 4 pg m^{-3} for NP, *t*-OP, NP1EO in the particle.

Tandem PUF/XAD-2 columns were used to test the breakthrough of air samples at GKSS Research Centre. More than 80% of the total mass of NP and *t*-OP was retained in

the first column, and indicated minimal breakthrough. Extraction recoveries for PAD-2 column, PUF/XAD-2 column and filters were tested by spiking the standards of target compounds and internal standards (IS) in the laboratory, and by spiking the internal standards on the columns prior to the sampling, respectively. The recoveries found were $76 \pm 9\%$ ($n = 5$) for 4-n-OP and $71 \pm 10\%$ ($n = 5$) for 4-n-NP in water samples, and $65 \pm 2\%$ ($n = 3$) for 4-n-NP in air samples. For the water filter extraction, the recoveries (IS, 4-n-OP: $97 \pm 16\%$, 4-n-NP: $86 \pm 10\%$) were $108 \pm 9\%$, $109 \pm 17\%$ and $105 \pm 7\%$ for NP, *t*-OP and NP1EO respectively. Because of very low recoveries of 4-n-NP, and 4-n-OP happened in particle samples, therefore, the particle NP, and *t*-OP concentrations were not presented in this study. On the chromatograms of air sample, NP 4 and NP 10 were totally immersed in two interferences, therefore, their concentrations were not counted. Reported concentrations were subtracted by means of field blanks but not corrected with the recoveries.

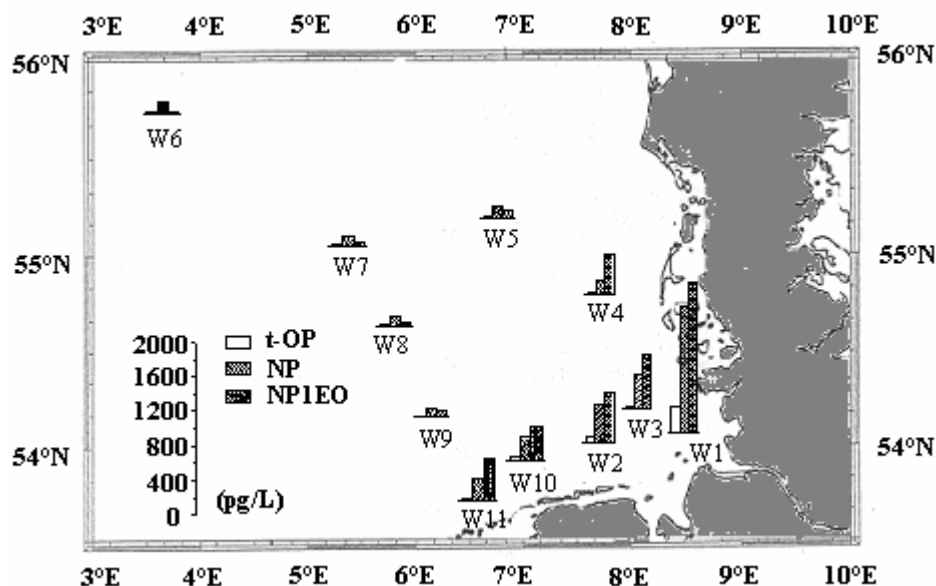


Figure 2. Spatial distributions of *t*-OP, NP and NP1EO in the North Sea. The concentrations are marked on the mean sample locations.

3. Results and discussion

3.1. Concentrations of *t*-OP, NP and NP1EO in sea water

The concentrations of *t*-OP, NP and NP1EO isomers obtained from 11 water samples and 6 air samples are summarized as supplementary information (Tab. SI-1, SI-2, SI-3). Total concentrations of NP in sea water and TSM ranged from 90 to 1400 pg L^{-1} and less

than MDL (10 pg L^{-1}) to 86 pg L^{-1} , respectively. Water-phase *t*-OP was determined with concentrations ranging from 13 to 300 pg L^{-1} . In TSM-phase, *t*-OP concentrations were very close to the level of MDL. NP1EO concentrations ranged between 28 and 1660 pg L^{-1} in the dissolved phase, and from below the MDL to 68 pg L^{-1} in the TSM.

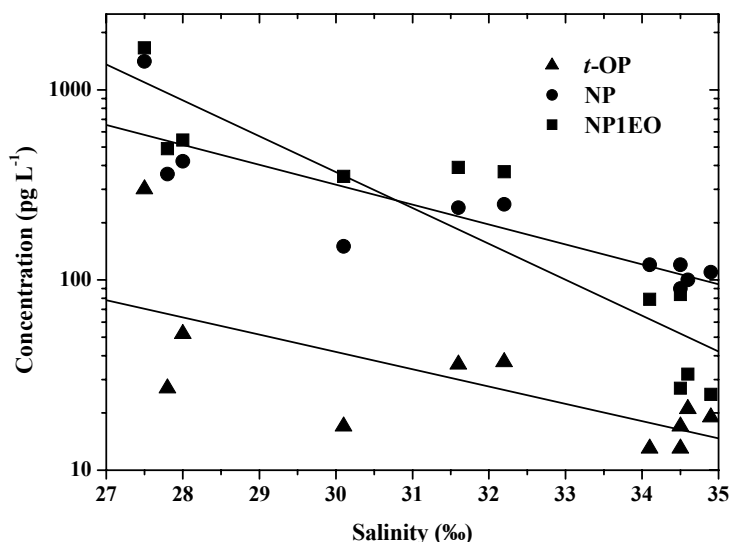


Figure 3. Changing of concentrations of *t*-OP, NP and NP1EO with salinity gradients.

Fig. 2 shows that high concentrations occurred in the water samples that collected near Rive plumes, and an obviously spatial distribution profile from the coast to the open sea. These results agree well with the distribution pattern determined by Heemken et al. (2001) and Bester et al. (2001). W1 was taken from station 2 to station 3, which is located within the plume of the Elbe. The highest concentrations of *t*-OP, NP and NP1EO found in this sample were 300, 1400 and 1660 pg L^{-1} , respectively. Concentrations of *t*-OP, NP and NP1EO determined in other coastal water and open ocean have been summarized in Tab. 2. It shows that the concentrations of APs in the North Sea are in a relatively low level. Concentrations of NP found in the Sea of Japan by Kannan et al. (1998), ranged from $0.002 - 0.093 \text{ ng L}^{-1}$. As compared to these results, concentrations found in the North Sea are one order of magnitude higher. It is reasonable for the sample obtained in the deep water of the Sea of Japan that is actually far away from any local source. As compared to the concentrations of NP and *t*-OP determined in previous sampling campaigns in the North Sea, present results are 8-40 times lower.

Table 2. Range of measured *t*-OP, NP and NP1EO concentrations (in total isomers) in the sea water of the North Sea and comparison with other reported values determined in the North Sea, rivers and coastal waters.

| Sample site | NP (ng L ⁻¹) | <i>t</i> -OP (ng L ⁻¹) | NP1EO (ng L ⁻¹) | Reference |
|--------------------------|--------------------------|------------------------------------|-----------------------------|-----------------------|
| North Sea | 0.09 – 1.4 | 0.013 – 0.3 | 0.017 – 1.66 | This work |
| Sea of Japan | 0.002 – 0.093 | - | - | Kannan, et al. (1998) |
| North Sea (May 1998) | 0.8 – 4.2 | 0.02 - 7 | 2.2 - 14 | Heemken et al. (2001) |
| North Sea (January 1999) | 0.3 - 63 | 0.1 - 16 | 0.7 - 29 | Heemken et al. (2001) |
| Elbe (January 1999) | 367 - 852 | 21 - 77 | 323 - 967 | Heemken et al. (2001) |
| Weise Elster | 78 - 221 | 1.5 - 6 | 30 - 115 | Heemken et al. (2001) |
| Elbe (July 2000) | 13 - 53 | 0.5 – 3.3 | - | Stachel et al. (2003) |
| Rhine Estuaries | 31 - 147 | - | 54 - 471 | Jonkers et al. (2003) |
| Scheldt Estuaries | 35 - 934 | - | 4.6 - 1029 | Jonkers et al. (2003) |
| Hudson River Upper Bay | 61 - 94 | - | - | Van Ry et al. (2000) |
| Hudson River Lower Bay | 12 - 49 | - | - | Van Ry et al. (2000) |
| Sumidagawa River | 80 - 1080 | 10 - 180 | 120 - 810 | Isobe et al. (2001) |
| Tamagawa River | 50 - 170 | 10 - 70 | 40 - 160 | Isobe et al. (2001) |

In Fig. 3, the dissolved concentrations of *t*-OP, NP and NP1EO are plotted against the salinities of the water samples. The salinity changed from 27.5 – 34.9‰ in our sampling area. Typically, the high concentrations were found in the body of water with low salinity, and contrarily, low concentrations were found in the body of water with high salinity. The correlation coefficients between salinity and concentrations of *t*-OP, NP and NP1EO are, 0.70, 0.88, and 0.90, which indicates that changing concentrations could be linked to the origination of the current. Together, with the investigations done by Heemken et al. (2001), Bester et al. (2001), and Jonkers et al. (2003), it shows that the input of River Elbe and Rhine represent a significant source for alkylphenols in the North Sea.

In this study, *t*-OP, NP and NP1EO were also found in TSM in the samples collected near the coast. The concentrations were in a range of 1-11 pg L⁻¹ for *t*-OP, 8 – 86 pg L⁻¹ for NP and 7 – 68 pg L⁻¹ for NP1EO. As compared to the dissolved concentrations, TSM bound fractions were 5 ± 1% for *t*-OP, 6 ± 2% for NP and 3 ± 1% for NP1EO, which are very comparable to their log K_{OW} sequence: NP (4.48) > NP1EO (4.17 - 4.20) > *t*-OP (4.12) (Ahel and Giger, 1993). However, these fractions were lower by factor of 2 – 5 than the reported values found in Tokyo Metropolitan area (Isobe, et al., 2001) and in the Lower Hudson River Estuary (Van Ry et al., 2000). Likely the reason is the low amounts of TSM present in the North Sea as compared to those in rivers and estuaries.

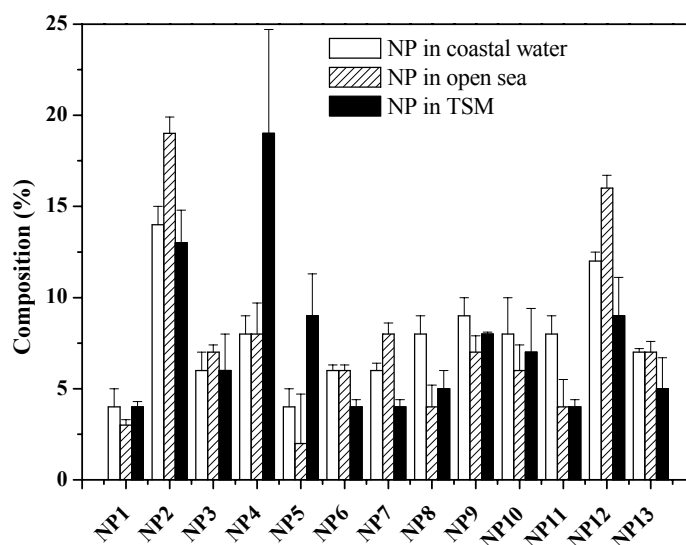


Figure 4. Comparison of compositions of NP isomers in the Coastal water (including W1, W2, W3, W4, W10, W11) in the open North Sea (Including W5, W6, W7, W8, W9) and in the total suspended matters (Including W1, W2, W10, W11). The error bars on the figure are the standard deviation calculated from the compositions in different samples.

3.2. Comment on the degradation of NP and NP1EO

22 and 21 peaks have been isolated from technical NP isomers using a 100 m capillary column GC-MS by Wheeler et al. (1997) and Thiele et al. (2004), respectively. Yamashita et al. (1999) indicated that estrogenic activity might be different among NP isomers, which highlighted the need to probe the state of specific isomers in the environmental samples. Fig. SI-1 shows that NP consists of 13 peaks on the gas chromatogram, and each peak is supposed to represent one isomer. Figure 4 shows that compositions of NP isomers in dissolved phase were fairly constant among the water samples near the coast and in the open sea. Change is mostly within the range of uncertainties. As TSM associated NP were only detectable in the sample near the coast, comparison was done with the NP composition in the dissolved phase. Isomer NP4 and NP5 were found with high proportion, and as a result, all of the other isomers have slightly lower proportions. As the uncertainties of the proportions of NP4 and NP5 are quite large, it is very difficult to conclude that these isomers are selective for the degradation process or have higher particulate partitioning behaviour. The overall results suggested that NP composition in the technical mixture is

relatively identical between dissolved and particulate phases, and constant in the surveyed area. These results agree well with those presented by Isobe et al. (2001).

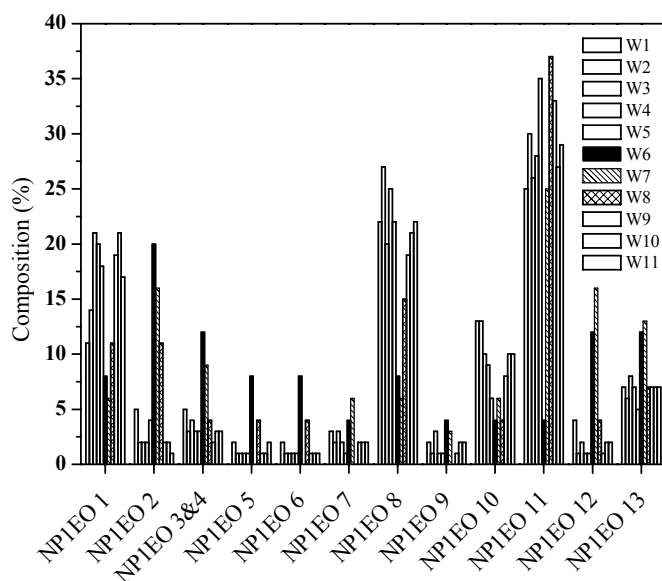


Figure 5. Comparison of compositions of NP1EO isomers in different water samples.

As shown in supplementary information (Fig. SI-2), NP1EO could be identified in 13 peaks (NP1EO 3 and NP1EO 4 were integrated together) with high responses using GC-MS. In this study, we suppose each peak only represents one isomer when probed for their character in the samples from different sites. Fig. 5 shows that the compositions of NP1EO isomers are changing in different samples. Obviously, it is observed in the water sample W6, W7 and W8, which were obtained in the open area. Moreover, Figure 6 shows that NP1EO/NP ratios are ranging from 1.2 to 2.3 in the water near the coast, and ranging from 0.4 to 0.8 in the water samples W5-W8. TSP associated NP1EO/NP ratios are from 0.2 to 0.7. Decreasing NP1EO/NP ratios in the water phase provide further evidence that aerobic degradation of NP1EO is active in the water phase. The relatively constant compositions of NP isomers in all of the water samples content to the conclusions of Jonkers et al. (2001), and the formation of NP in aerobic circumstances does not seem a likely source for the occurrence of NP in the environment. In addition, Isobe et al. (2001) pointed out that anaerobic conversion of NP1EO to NP is a significant process in the river sediment. As there is insufficient information for the NP and NP1EO in the particulate phase and the sediments, the anaerobic degradation of NP1EO is not discussed in this paper. A further investigation on the distribution of NP, *t*-OP and NP1EO in the sediment of the North Sea is still necessary.

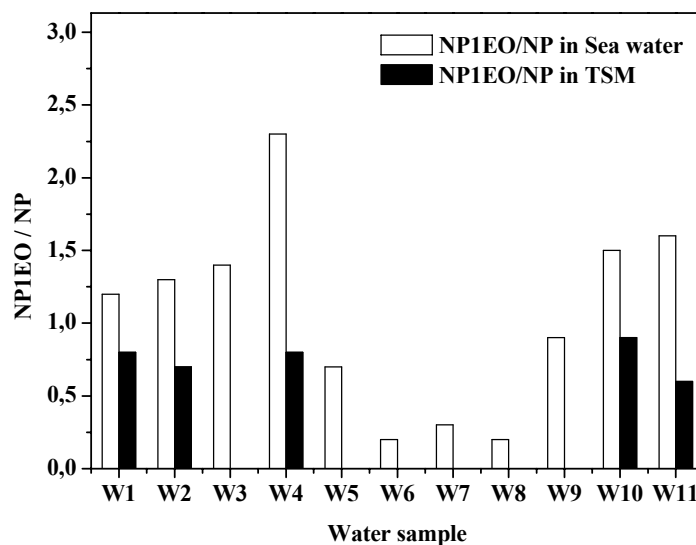


Figure 6. NP1EO/NP ratios in dissolved phase and total suspended matters.

3.3. Atmospheric concentrations of *t*-OP, NP and NP1EO

NP, *t*-OP were detected in the vapour phase of the air samples. As shown in supplementary information (Table SI-2), high concentrations were present in the air sample A1 and A2, which were collected while the ship was steaming along the Northeast German Coast. The concentrations in the air samples A3-A6 are lower by a factor of 3-5. NP1EO was unexpectedly determined in the particle phase with a concentration range from 14 to 50 pg m^{-3} . Consequently, we re-examined the NP1EO in the vapour phase. Concentrations of 31 and 14 pg m^{-3} were found in A1 and A2, and 4 - 9 pg m^{-3} were found in A3 - A6. As a result of the internal standard of NP1EO D2 was not applied for PUF/XAD-2 extraction, therefore, there is considerably uncertainty concerning the vapour concentrations. NP1EO has been detected in the indoor dusts (Rudel et al., 2003) and in the atmosphere surrounding an industrialised area of Prato (Italy) (Cincinelli et al., 2003). This was the first time it has found in the marine atmosphere. The air samples collected over the sea surface are often influenced by wind pattern. The wind speeds and directions over the course were summarized in Tab. 1. During this cruise, Southwest and Southeast winds were dominant. It meant that air masses were originating from the German and Dutch coasts. Furthermore, when the wind speed is higher than 7 m s^{-1} , the aerosols formation might be dominated by sea spray and sea salts (Spiel and De Leeuw, 1996). Therefore, atmospheric samples were a mixture of land-based, coastal and oceanic air and aerosols. As shown in Tab. 1, A1 – A4

were collected always under heavy winds and high humidity conditions. This may be an explanation for the high concentrations present in the samples A1 and A2, especially for the occurrence of NP1EO. As the data of aerosol composition and particle concentrations of *t*-OP and NP was not available, the uptake of APs during the aerosol generation over the North Sea is still not clear.

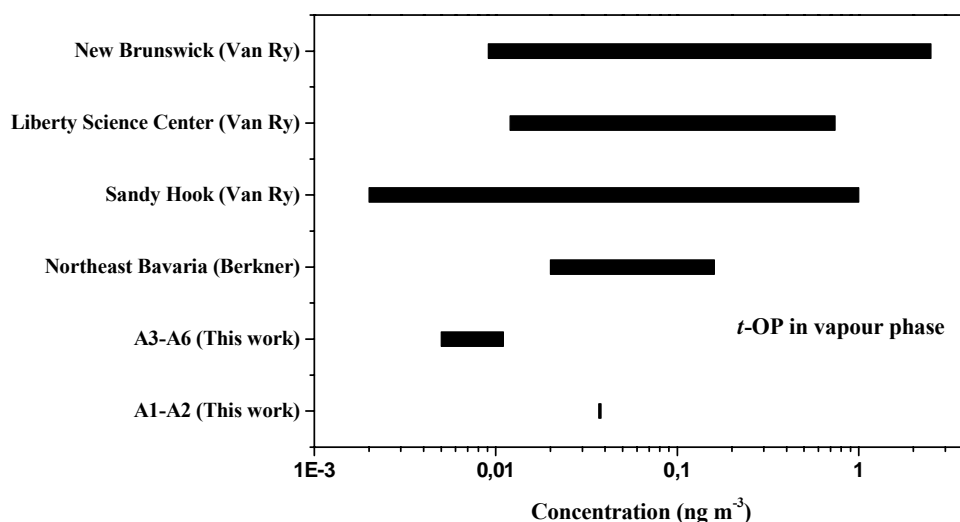


Figure 7a. Range of measured *t*-OP concentrations in the atmosphere over the North Sea and comparison with other reported values.

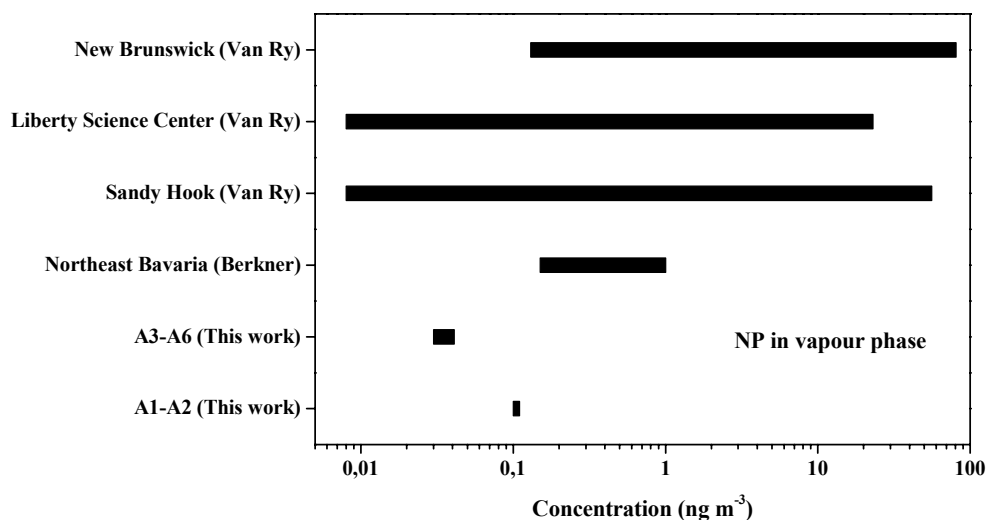


Figure 7b. Range of measured NP concentrations (in total isomers) in the atmosphere over the North Sea and comparison with other reported values.

This work is the first report for atmospheric APs concentrations in the North Sea. Therefore, comparisons have been made with previously reported data in the forest area in Southeastern Germany (Berkner et al., 2004) and urban and coastal sites at the Lower Hudson River Estuary (Dachs et al., 1999; Van Ry et al., 2000). Fig. 7a, 7b shows that atmospheric *t*-OP and NP in the North Sea were in the low concentration level. Concentration of NP and *t*-OP in air samples A1 and A2 were very comparable to reported terrestrial concentrations in southeast of Germany, and lower than those determined at the Lower Hudson River Estuary. These results provide evidence that, apart from the volatilization from surface water, the terrestrial use of APs is also a significant source for atmospheric APs (Gehring et al., 2003).

3.4. Air-sea vapour exchange

3.4.1. Air-sea exchange model

In this study, air-sea vapour exchange fluxes were estimated using the modified version of a two-film resistance model (Achman et al., 1993; Hornbuckle et al., 1994), which was extensively used for the evaluation of PCBs, PAHs and phthalates fluxes through air-water interfaces (Nelson et al., 1998; Bamford et al., 1999; 2002; Totten et al., 2004; Gioia et al., 2005; Xie et al., 2005). It assumes that the rate of transfer is controlled by the compound's ability to diffuse across two thin stagnant films at the air-water interface, the water film and the air film. The molecular diffusivity of the compound (dependent on the amount of resistance encountered in the liquid and gas films) describes the rate of transfer while the concentration gradient drives the direction of transfer.

The overall flux calculation is defined by

$$F = K_{OL} \left(C_w - \frac{C_a}{H'} \right) \quad (1)$$

where F is the flux ($\text{ng m}^{-2} \text{ day}^{-1}$), C_w (ng m^{-3}) and C_a (ng m^{-3}) are the dissolved- and vapour-phase concentrations, $(C_w - C_a/H')$ describes the concentration gradient (ng m^{-3}), H' is the dimensionless Henry's law constant, and K_{OL} (m day^{-1}) is mass transfer coefficient comprising resistances to mass transfer in both water (k_w) and air (k_a). As averages of water temperatures ranged from 3.8 to 6.7 °C on this cruise, the Schmidt number for CO_2 at 5 °C ($Sc_{\text{CO}_2} = 1395$) was applied for the estimation of k_w (Schwarzenbach et al., 1993). H' was corrected with water temperatures (T , K) and averaged salt concentrations (C_s , 0.6 mol L^{-1})

based on following equations (2-3) (ten Hulscher et al., 1992; Schwarzenbach et al., 1993; Xie et al., 2004)

$$\ln H = \ln H_0 + \frac{\Delta H_v}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (2)$$

$$H' = \frac{H}{RT} \quad (3)$$

where R is the ideal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), H ($\text{pa m}^3 \text{ mol}^{-1}$) is the Henry's law constant at given T and salt concentration of 0.6 mol L^{-1} , H_0 is Henry's law constant at T_0 (298.15 K). ΔH_v is the enthalpy of vaporization at 298.15 K, which is 72.1 and 75.1 kJ mol^{-1} for NP and *t*-OP, respectively (Xie et al., 2004).

3.4.2. Uncertainty analysis

The uncertainty in the F (Equation 1) was evaluated using a propagation of error analysis derived from Shoemaker et al. (1974), which has been used in previous studies (Nelson et al., 1998; Bamford et al., 2002; Xie et al., 2005). The summation of the various random errors in the flux are described by

$$\sigma^2(F) = \left(\frac{\delta F}{\delta K_{OL}} \right)^2 (\sigma K_{OL})^2 + \left(\frac{\delta F}{\delta C_w} \right)^2 (\sigma C_w)^2 + \left(\frac{\delta F}{\delta C_a} \right)^2 (\sigma C_a)^2 + \left(\frac{\delta F}{\delta H'} \right)^2 (\sigma H')^2 \quad (4)$$

Total propagated variance $\sigma^2(F)$ is the linear combination of the weighted contribution of the variances (σ^2) of the mass transfer coefficient, H' and measured concentrations. The error in H' was 15% (Xie et al., 2004). The errors of C_w and C_a was assumed to be 15% including the sampling and analytical errors. The uncertainty in K_{OL} was determined by propagating random errors in the air- and water-side transfer velocities, which was summated to be 40% following Wanninkhof et al. (1990) and Nelson et al. (1998). The overall propagated error in F is thus, 48% (Tab. 3). Most of the uncertainty associated with the fluxes was attributed to K_{OL} (69%), which was factor of 7 higher than the uncertainties associated with C_w , C_a and H' (10%).

3.4.3. air-sea exchange fluxes

The estimated fluxes of *t*-OP and NP in the North Sea and overall mass transfer coefficients are shown in Tab. 3. Detail of flux calculations are shown in Tab. SI-4. The

negative values indicate a net deposition into the water; contrarily, the positive values indicate a net volatilization to the atmosphere. The fluxes ranged from -3 to -30 $\text{ng m}^{-2} \text{day}^{-1}$ for *t*-OP and -12 to -81 $\text{ng m}^{-2} \text{day}^{-1}$ for NP, which indicated that net depositions dominate the air–sea vapour exchange process of *t*-OP and NP in the North Sea.

Table 3. Air-sea exchange fluxes of NP and *t*-OP in the North Sea. The errors were calculated at 48% level for F and at 40% level for K_{OL} .

| Sample | NP | | <i>t</i> -OP | |
|---------|--|---|--|---|
| | K_{OL} ($10^{-3} \text{ m day}^{-1}$) | Flux ($\text{ng m}^{-2} \text{ day}^{-1}$) | K_{OL} ($10^{-3} \text{ m day}^{-1}$) | Flux ($\text{ng m}^{-2} \text{ day}^{-1}$) |
| W1 | 11 ± 4 | -62 ± 30 | 14 ± 6 | -23 ± 11 |
| W2 | 11 ± 4 | -71 ± 34 | 14 ± 6 | -26 ± 13 |
| W3 | 12 ± 5 | -81 ± 39 | 15 ± 6 | -30 ± 14 |
| W4 | 13 ± 5 | -30 ± 14 | 16 ± 6 | -6 ± 3 |
| W5 | 11 ± 4 | -22 ± 10 | 13 ± 5 | -4 ± 2 |
| W6 | 22 ± 9 | -41 ± 20 | 27 ± 11 | -8 ± 4 |
| W7 | 18 ± 7 | -35 ± 17 | 22 ± 9 | -7 ± 3 |
| W8 | 8 ± 3 | -12 ± 6 | 10 ± 4 | -3 ± 2 |
| W9 | 7 ± 3 | -12 ± 6 | 9 ± 3 | -3 ± 2 |
| W10 | 11 ± 4 | -16 ± 8 | 13 ± 5 | -5 ± 2 |
| W11 | 15 ± 6 | -24 ± 12 | 18 ± 7 | -7 ± 4 |
| Average | 13 ± 5 | -39 ± 19 | 16 ± 6 | -12 ± 6 |

As shown in Tab. 3, the averages of K_{OL} values were 0.013, 0.016 m day^{-1} for *t*-OP and NP, respectively. Similar effects of wind speeds on k_w , as indicated by Wanninkhof (1992) and Bamford et al. (2002), can be seen in air-sea exchange fluxes (Tab. 3 and Tab. SI-4). In addition, although water temperatures were only varying from 3.8 to 6.7 °C during this cruise, the H' estimated at higher temperatures were higher by a factor of approximately 1.5 than that at lower temperatures (Tab. SI-4). Both impacts from temperature and wind speed significantly increased K_{OL} values for water samples W6, W7, which were higher by a factor of 2 compared to the average values. Consequently, relative higher exchange fluxes were estimated for these samples. It was demonstrated that a better understanding of the

mass transfer coefficient would improve the estimation of the vapour exchange fluxes rather than a higher accuracy of the concentrations (Bamford et al., 1999; Xie et al., 2005).

Van Ry et al. (2000) estimated the air-water exchange fluxes for NP in the lower Hudson River Estuary, which ranged from +25 to +67 $\mu\text{g m}^{-2} \text{day}^{-1}$ in the upper bay and from +1.2 to +9.5 $\mu\text{g m}^{-2} \text{day}^{-1}$ in the lower bay. As compared to these results, the air-sea exchange fluxes of NP in the North Sea are 2 orders of magnitude lower. The large differences of air-sea exchange fluxes of NP present in these two studies, with the exception of those resulting from the differences in the NP concentrations, could be addressed to the H' values used for the estimations and its temperature dependence (Xie et al., 2004). As estimated by Xie et al. (2004), the H value of *t*-OP and NP at 298.15 K is 8 times higher than that at 278.15 K. Assuming the concentrations of *t*-OP and NP are less variable in both water and vapour phases of the North Sea through all the seasons, in warm times, the K_{OL} could significantly change, following the increasing H' . Moreover the concentration gradients ($C_w - C_a / H'$) will significantly decrease and might change in directions. Nevertheless, these results indicated that the air-sea exchange significantly interferes with the process of distributions of *t*-OP and NP in the North Sea.

In conclusion, *t*-OP, NP and NP1EO were studied in different compartments of the North Sea using ship-borne samples. Concentrations in sea water were 1-3 orders magnitude lower than those determined in the River Elbe, Rhine and their estuaries. Dilution profiles were present from the coast to the central part of the North Sea. It indicated that the rivers are main input sources for APs present in the North Sea. Analysis for the compositions of NP and NP1EO isomers showed that NP isomers are relative stable under aerobic conditions, however, selective degradation among NP1EO isomers might be occurring. However, further study of NP and NP1EO isomers in sediment is still needed for better understanding of their behavior under anaerobic conditions in the marine ecosystem. *t*-OP, NP and NP1EO were studied for first time in the atmosphere over the North Sea. Concentrations were in lower ng m^{-3} range and comparable to those found in the rural area of Southeastern Germany. Air-sea exchange fluxes of *t*-OP and NP showed that atmospheric deposition were dominant in the winter. Re-volatilization might happen in the warm seasons due to the increasing H values with the rise of the temperature. Nevertheless, this study indicated that the North Sea is an important sink for the APs, and might be as a potential source for the occurrences of APs in the Oceans and remote area. Therefore, further studies will be conducted to elucidate the spatial and temporal dependences of the distributions of APs in the coastal margins and in the open ocean.

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References

- Achman, D.R., Hornbuckle, K.C., Eisenreich, S.J., 1993. Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environmental Science & Technology* 37, 75-87.
- Ahel, M. and Giger, W., 1993. Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. *Chemosphere* 26, 1471-1478.
- Ahel, M., Giger, W., Schaffner, C., 1994. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment—II. Occurrence and transformation in rivers. *Water Research* 28, 1143-1152.
- Ahel, M., Molnar, E, Ibric, S, Giger, W., 2000. Estrogenic metabolites of alkylphenol polyethoxylates in secondary sewage effluents and rivers. *Water Science and Technology*, 42, 15-22.
- Atienzar, F.A., Billinghamurst, Z., Depledge, M.H., 2002. 4-n-Nonylphenol and 17- β estradiol may induce common DNA effects in developing barnacle larvae. *Environmental Pollution* 120, 735-738.
- Bamford, H.A., Offenber, J.H., Larsen, R.K., Ko, F.C., Baker, J.E., 1999. Diffusive exchange of polycyclic aromatic hydrocarbons across the air-water interface of the Patapsco River, and urbanized subestuary of the Chesapeake Bay. *Environmental Science & Technology* 33, 2138-2144.
- Bamford, H.A., Ko, F.C., Baker, J.E., 2002. Seasonal and annual air-water exchange of polychlorinated biphenyls across Baltimore Harbor and the Northern Chesapeake Bay. *Environmental Science & Technology* 36, 4245-4252.
- Bennie, D.T., Sullivan, C.A., Lee, H.B., Peart, T.E., Maguire, R.J., 1997. Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River. *The Science of the Total Environment* 193, 263-275.

- Berkner, S., Streck, G., Herrmann, R., 2004. Development and validation of a method for the determination of trace levels of alkylphenols and bisphenol A in atmospheric samples. *Chemosphere* 54, 575-584.
- Bester, K., Theobald, N., Schroeder, H.Fr., 2001. Nonylphenols nonylphenol-ethoxylates, linear alkylbenzensulfonates (LAS) and bis (4-chlorophenyl)-sulfone in the German Bight of the North Sea. *Chemosphere* 45, 817-826.
- Blackburn, M.A. and Waldock, M.J., 1994. Concentrations of alkylphenols in rivers and estuaries in England and Wales. *Water Research* 29, 1623-1629.
- Blackburn, M.A., Kirby, S.J., Waldock, M.J., 1998. Concentrations of alkylphenol polyethoxylates entering UK estuaries. *Marine Pollution Bulletin* 38, 109-118.
- Cincinelli, A., Mandorlo, S., Dickhut, R.M., Lepri, L., 2003. Particulate organic compounds in the atmosphere surrounding an industrialised area of Prato (Italy). *Atmospheric Environment* 37, 3125-3133.
- Comber, M.H.I., Williams, T.D., Stewart, K.M., 1993. The effects of nonylphenol on *Daphnia Magna*. *Water Research* 27, 273-276.
- Dachs J., Van Ry Da, Eisenreich S. J., 1999. Occurrence of estrogenic nonylphenols in the urban and coastal atmosphere of the Lower Hudson River estuary. *Environmental Science & Technology* 33, 2676-9.
- Directive 2003/53/EC of European Parliament and of the Council, 2003. Amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol nonylphenol ethoxylate and cement). *Official Journal of the European Union* 178, 24-26.
- Ehrhardt, M., 1987. Lipophilic organic material: An apparatus for extracting solids used for their concentrations from seawater. *ICES Techniques in Marine Environmental Science* 4, 1-14.
- Ferguson, P. L., Iden, C. R., Brownawell, B. J., 2001. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. *Environmental Science & Technology* 35, 2428-2435.

- Gehring, M., Tennhardt, L., Vogel, D., Weltin, D., Bilitewski, B. 2003. Release of Endocrine Active Compounds Including 4-Nonylphenol and Bisphenol A with Treated Wastewater and Sewage Sludge to the Environment in Germany. Poster Joint UK Government/SETAC Conference on Endocrine Disrupters. York, UK.
- Giger, W., Brunner, P. H., Schaffner, C., 1984. 4-nonylphenol in sewage sludge: accumulation of toxic metabolite from nonionic surfactants, *Science N.Y.*, 25: 623-625.
- Giger, W., Stephanou, E., Schaffner, C., 1981. Persistent organic chemicals in sewage effluents: I. Identification of nonylphenols and nonylphenolethoxylates by glass capillary gas chromatography / mass spectrometry. *Chemosphere* 10, 1253-1263.
- Gioia, R., Offenberg, J.H., Gigliotti, C.L., Totten, L.A., Du, S., Eisenreich, S.J., 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. *Atmospheric Environment* 39, 2309-2322.
- Heemken, O.P., Reincke, H., Stachel, B., Theobald, N., 2001. The occurrence of xenoestrogens in the Elbe River and the North Sea. *Chemosphere* 45, 245-259.
- Hill, M., Stabile, C., Kraig Steffen, L., Hill, A., 2002. Toxic effects of endocrine disrupters on freshwater sponges: common developmental abnormalities. *Environmental Pollution* 117, 295-300.
- Hornbuckle, K.C., Jeremlason, J.D., Sweet, C.W., Eisenreich, S.J., 1994. Seasonal variation in air-water exchange of polychlorinated biphenyls in Lake Superior. *Environmental Science & Technology* 28, 1491-1501.
- Isobe, T., Nishiyama, H., Nakashima, A., Takada, H., 2001. Distribution and behaviour of nonylphenol, octylphenol and nonylphenol monoethoxylate in Tokyo Metropolitan area: Their association with aquatic particles and sedimentary distributions. *Environmental Science & Technology* 35, 1041-1049.
- James, M. R., 1999. Review of the persistence of Nonylphenol and Nonylphenol Ethoxylates in aquatic Environments, *Water Quality Research Journal of Canada* 34, 37-38.

- Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P., Sumpter, J.P., 1996. Inhibition of testicular growth in rainbow-trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. *Environmental Toxicology and Chemistry* 15, 194-202.
- Jonkers, N, Knepper, T.P, de Voogt, P., 2001. Aerobic biodegradation studies of nonylphenol ethoxylates in river water using liquid chromatography-electrospray tandem mass spectrometry. *Environmental Science & Technology* 35, 335-340.
- Jonkers, N., Lanne, R.W.P.M., de Voogt P., 2003. Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. *Environmental Science & Technology* 37, 321-327.
- Kannan, N., Yamashita, N., Petrick, G. and Duinker, J.C., 1998. Polychlorinated biphenyls and nonylphenols in the Sea of Japan. *Environmental Science & Technology* 32, 1747-1753.
- Kawahata, H., Ohta, H., Inoue, M., Suzuki, A., 2004. Endocrine disrupter nonylphenol and bisphenol A contamination in Okinawa and Ishigaki Islands, Japan-within coral reefs and adjacent river mouths. *Chemosphere*, 55, 1519-1927.
- Kvestak, R. and Ahel, M., 1994. Occurrence of toxic metabolites from non-ionic surfactants in the Krka River. *Ecotoxicology and Environmental Safety* 28, 25-34.
- Lakaschus, S., Weber, K., Wania, F., Bruhn, R., Schrems, O., 2002. The air-sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctic. *Environmental Science & Technology* 36, 138-145.
- Nelson, E.D., McConnell, L.L., Baker, J.E., 1998. Diffusive exchange of gaseous polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of the Chesapeake. *Environmental Science & Technology* 32, 912-919.
- PARCOM Recommendation 92/8 on nonylphenol-ethoxylates.
<http://www.ospar.org/asp/ospar/dra.asp?id=9>, accessed December 2003.
- Petrick, G., Schuz, D.E., Martens, V., Scholz, K., Duinker, J.C., 1996. An in-situ filtration/extraction system for the recovery of trace organics in solutions and on particles tested in deep ocean water. *Marine Chemistry* 54, 97-105.

- Porter, A.J., and Hayden, N.J., 2004. Nonylphenol in the environment: A critical review. <http://www.emba.uvm.edu/~nhayden/npreview.pdf>.
- Routledge, E.J., Sumpter, J.P. 1996. Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environmental Science & Technology* 15, 241-248.
- Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine – disrupting compounds in indoor air and dust. *Environmental Science & Technology* 37, 4543-4553.
- Shoemaker, D.P., Garland, G.W., Steinfeld, J.I., 1974. Propagation of errors, 3rd ed., McGraw-Hill: New York, pp 51-58.
- Schwarzenbach, R.P., Gschwend, P. M., Imboden, D. M. *Environmental Organic Chemistry*, John Wiley & Sons, New York, 1993.
- Servos, M.R., 1999. Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates. *Water Quality Research Journal of Canada* 34, 123-177.
- Soto, A.M., Justicia, H., Wray, J.W., Sonnenschein, C., 1991. p-Nonylphenol: an estrogenic xenobiotic released from "modified" polystyrene. *Environmental Health Perspectives* 92, 167-173.
- Spiel D.E. and De Leeuw G., 1996. Formation and production of sea spray aerosol. *J. of Aerosol Science* 27, S65-S66.
- Stachel, B., Ehrhorn, U., Heemken, O.P., Lepom, P., Reincke, H., Sawal, G., Theobald, N., 2003. Xenoestrogens in the River Elbe and its tributaries. *Environmental Pollution* 124, 497-507.
- ten Hulscher, T.E.M., Van Der Velde, L.E., Bruggeman, W.A., 1992. Temperature dependence of Henry's Law Constant for selected chlorobenzene, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. *Environmental Science & Technology* 11, 1595-1603.

- Thiele, B., Heinke, V., Einhard Kleist, E., Guenther, K., 2004. Contribution to the structural elucidation of 10 isomers of technical p-nonylphenol. *Environmental Science & Technology* 38, 3405-3411.
- Totten, L.A., Gigliotti, C.L., Vanry, D.A., Offenber, J.H., Nelson, E.D., Dachs, J., Reinfelder, J.R., Eisenreich, S.J., 2004. Atmospheric concentrations and deposition of polychlorinated biphenyls to the Hudson River Estuary. *Environmental Science & Technology* 38, 2568-2573.
- Van Ry D.A., Dachs J., Gigliotti, C. L., Brunciak, P.A., Nelson, E.D., Eisenreich, S.J., 2000. Atmospheric seasonal trends and environmental fate of alkylphenols in the Lower Hudson River estuary. *Environmental Science & Technology* 34, 2410-7.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophysical Research* 97, 7373-7382.
- Wanninkhof, R., Ledwell, J., Crusius, J., 1990. In *Air-Water Mass Transfer*, Wilhelms, S., Gulliver, J., Eds., American Society of Civil Engineers: New York, pp 441-458.
- Wheeler, T.F., Heim, J.R., LaTorre, M.R., Janes, A. B., 1997. Mass spectral characterization of p-nonylphenol isomers using high-resolution capillary GC-MS. *J. of Chromatographic Science* 35, 19-30.
- White R., Jobling, S., Hoare, S.A., Sumpter, J.P., Parker, M.G., 1994. Environmentally persistent alkylphenolic compounds are estrogenic. *Endocrinology* 135, 175-182.
- Xie, Z., Ebinghaus, R., Temme, C., Caba, A., Ruck, W., 2005. Atmospheric concentrations and air-sea exchanges of phthalates in the North Sea (German Bight). *Atmospheric Environment* 39, 3209-3219.
- Xie, Z., Le Calve, S., Feigenbrugel, V., Preuß, T., Vinken, R., Ebinghaus, R., Ruck, W., 2004. Henry's Law Constant measurements of the nonylphenol isomer 4(3',5'-dimethyl-3'.heptyl)-phenol, tertiary octylphenol and γ -hexachlorocyclohexane between 278-298 K. *Atmospheric Environment* 38, 4859-4868.

Yamashita, N., Kannan, K., Hashimoto, S., Miyazaki, A., Giesy, J. P., 1999. Estrogenic potency of individual nonylphenol congeners isolated from technical mixtures. *Organohalogen Compounds* 42, 121-125.

Ying, G.G., Williams, B., Kookana, R., 2002. Environmental fate of alkylphenols and alkylphenol ethoxylates—a review. *Environment International*, 28, 215-22.

Supplementary material

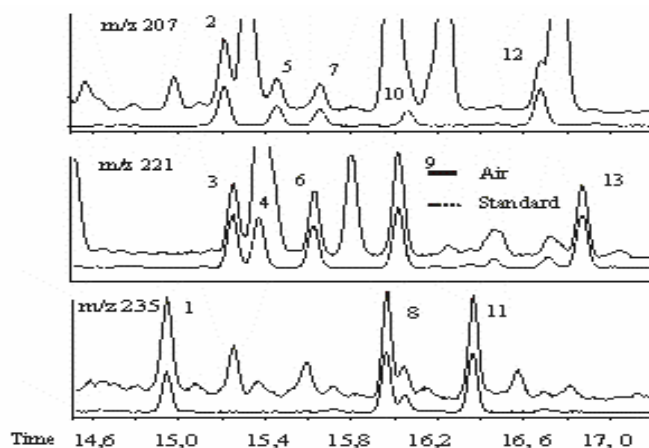


Figure SI-1: GC-MS chromatograms of an air extract showing selected characteristic ion peak clusters 207, 221, 235 m/z for NP (BSTFA derivatives).

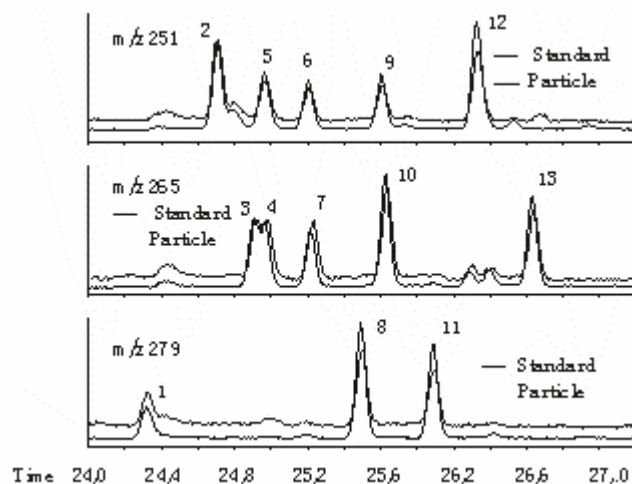


Figure SI-2: GC-MS chromatograms of a particle extract showing selected characteristic ion peak clusters 251, 265, 279 m/z for NP1EO (BSTFA derivatives).

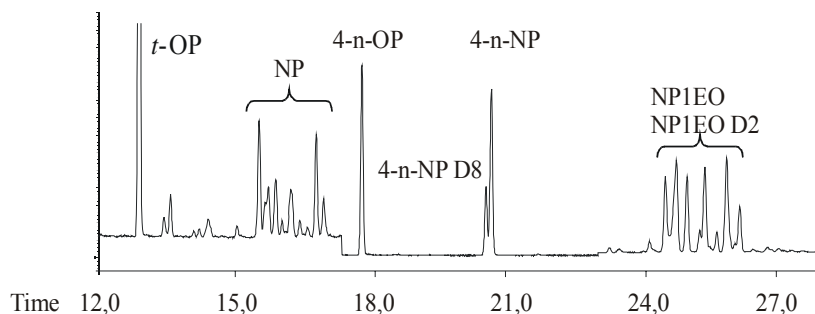


Figure SI-3: Total ion chromatogram (TIC) of standards of *t*-OP, NP, NP1EO and NP2EO and internal standards of 4-n-NP, 4-n-OP, 4-n-NP D8 and NP1EO D2 (BSTFA derivatives).

Table SI-1: Concentrations of *t*-OP, NP isomers and NP1EO isomers (pg L⁻¹) measured in the sea water of the North Sea. (The values in the blankets are the standard deviations calculated based on parallel samples).

| Substance | W1 | | W2 | | W3 | | W4 | | W5 | | W6 | | W7 | | W8 | | W9 | | W10 | | W11 | |
|--------------|------|-----|-----|-----|-----|------|-----|------|-----|------|-----|------|------|------|------|------|----|------|-----|-----|-----|-----|
| | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM | D | TSM |
| NP1 | 55 | 3 | 17 | 1 | 18 | n.a. | 7 | n.d. | 4 | 0 | 3 | n.d. | 3 | n.a. | 4 | n.d. | 3 | n.d. | 9 | 0 | 9 | 1 |
| NP2 | 200 | 13 | 65 | 3 | 49 | n.a. | 22 | 1 | 23 | 1 | 21 | n.d. | 19 | n.a. | 24 | n.d. | 16 | n.d. | 33 | 1 | 33 | 3 |
| NP3 | 90 | 5 | 27 | 1 | 22 | n.a. | 10 | 1 | 9 | 0 | 8 | n.d. | 7 | n.a. | 8 | n.d. | 6 | n.d. | 13 | 1 | 13 | 2 |
| NP4 | 100 | 11 | 29 | 6 | 27 | n.a. | 12 | 3 | 10 | 3 | 7 | n.d. | 8 | n.a. | 9 | n.d. | 10 | n.d. | 19 | 0 | 24 | 5 |
| NP5 | 58 | 7 | 22 | 2 | 10 | n.a. | 5 | 1 | 2 | 1 | 7 | n.d. | n.d. | n.a. | 4 | n.d. | 0 | n.d. | 16 | 1 | 10 | 3 |
| NP6 | 79 | 4 | 24 | 1 | 19 | n.a. | 9 | n.d. | 8 | 0 | 7 | n.d. | 6 | n.a. | 8 | n.d. | 6 | n.d. | 14 | 0 | 15 | 1 |
| NP7 | 91 | 4 | 27 | 1 | 21 | n.a. | 9 | 1 | 10 | 0 | 9 | n.d. | 9 | n.a. | 11 | n.d. | 7 | n.d. | 15 | 1 | 16 | 1 |
| NP8 | 95 | 5 | 28 | 1 | 30 | n.a. | 14 | 1 | 6 | 0 | 3 | n.d. | 3 | n.a. | 5 | n.d. | 5 | n.d. | 19 | 1 | 16 | 1 |
| NP9 | 140 | 7 | 36 | 2 | 34 | n.a. | 14 | 1 | 9 | 0 | 7 | n.d. | 7 | n.a. | 8 | n.d. | 8 | n.d. | 20 | 1 | 22 | 2 |
| NP10 | 140 | 7 | 39 | 2 | 35 | n.a. | 9 | 1 | 8 | 0 | 8 | n.d. | 8 | n.a. | 7 | n.d. | 4 | n.d. | 22 | 1 | 16 | 1 |
| NP11 | 92 | 4 | 27 | 1 | 28 | n.a. | 13 | 1 | 6 | 0 | 3 | n.d. | 3 | n.a. | 5 | n.d. | 6 | n.d. | 20 | 0 | 19 | 1 |
| NP12 | 160 | 10 | 53 | 2 | 41 | n.a. | 18 | 1 | 18 | 1 | 18 | n.d. | 16 | n.a. | 20 | n.d. | 14 | n.d. | 30 | 1 | 29 | 2 |
| NP13 | 100 | 6 | 30 | 1 | 25 | n.a. | 11 | n.d. | 8 | 0 | 7 | n.d. | 6 | n.a. | 8 | n.d. | 7 | n.d. | 18 | 1 | 18 | 1 |
| ΣNP | 1400 | 86 | 420 | 25 | 360 | n.a. | 150 | 12 | 120 | 8 | 110 | n.d. | 100 | n.a. | 120 | n.d. | 90 | n.d. | 250 | 8 | 240 | 24 |
| NP1EO 1 | 190 | 8 | 74 | 2 | 101 | n.a. | 70 | 1 | 14 | n.d. | 2 | n.d. | 2 | n.a. | 3 | n.d. | 16 | n.d. | 76 | 2 | 67 | 4 |
| NP1EO 2 | 76 | 5 | 9 | 1 | 12 | n.a. | 7 | 1 | 3 | n.d. | 5 | n.d. | 5 | n.a. | 3 | n.d. | 2 | n.d. | 7 | 1 | 5 | 0 |
| NP1EO 3&4 | 85 | 7 | 18 | 1 | 21 | n.a. | 11 | 1 | 2 | n.d. | 3 | n.d. | 3 | n.a. | 1 | n.d. | 2 | n.d. | 12 | 1 | 13 | 2 |
| NP1EO 5 | 38 | 4 | 5 | 1 | 4 | n.a. | 2 | 0 | 1 | n.d. | 2 | n.d. | n.d. | n.a. | 1 | n.d. | 1 | n.d. | 4 | 0 | 8 | 0 |
| NP1EO 6 | 27 | 3 | 3 | 1 | 3 | n.a. | 3 | 0 | 1 | n.d. | 2 | n.d. | n.d. | n.a. | 1 | n.d. | 1 | n.d. | 4 | 0 | 4 | 0 |
| NP1EO 7 | 49 | 3 | 9 | 1 | 14 | n.a. | 6 | 0 | 1 | n.d. | 1 | n.d. | 2 | n.a. | n.d. | n.d. | 2 | n.d. | 8 | 0 | 8 | 1 |
| NP1EO 8 | 369 | 9 | 148 | 2 | 99 | n.a. | 87 | 1 | 17 | n.d. | 2 | n.d. | 2 | n.a. | 4 | n.d. | 16 | n.d. | 79 | 1 | 87 | 2 |
| NP1EO 9 | 26 | 2 | 8 | 0 | 14 | n.a. | 5 | 0 | 1 | n.d. | 1 | n.d. | 1 | n.a. | 0 | n.d. | 1 | n.d. | 6 | 0 | 7 | 0 |
| NP1EO 10 | 209 | 6 | 68 | 1 | 47 | n.a. | 33 | 1 | 5 | n.d. | 1 | n.d. | 2 | n.a. | 1 | n.d. | 7 | n.d. | 38 | 1 | 41 | 1 |
| NP1EO 11 | 418 | 13 | 164 | 5 | 130 | n.a. | 98 | 3 | 28 | n.d. | 1 | n.d. | 8 | n.a. | 10 | n.d. | 28 | n.d. | 101 | 1 | 115 | 3 |
| NP1EO 12 | 63 | 6 | 7 | 1 | 8 | n.a. | 5 | 0 | 1 | n.d. | 3 | n.d. | 5 | n.a. | 1 | n.d. | 1 | n.d. | 6 | 0 | 7 | 0 |
| NP1EO 13 | 110 | 4 | 31 | 1 | 39 | n.a. | 24 | 0 | 4 | n.d. | 3 | n.d. | 4 | n.a. | 2 | n.d. | 6 | n.d. | 27 | 0 | 29 | 1 |
| ΣNP1EO | 1660 | 68 | 540 | 17 | 490 | n.a. | 350 | 10 | 79 | n.d. | 25 | n.d. | 32 | n.a. | 27 | n.d. | 84 | n.d. | 370 | 7 | 390 | 14 |
| <i>t</i> -OP | 300 | 11 | 52 | 2 | 27 | n.a. | 17 | 1 | 13 | n.d. | 19 | 1 | 21 | n.a. | 17 | 1 | 13 | n.d. | 37 | 2 | 36 | 3 |

D: Dissolved-phase concentration; TSM: Total suspended matter bund concentration; n.a.: the sample was not analysed; n.d.: the concentration is below the detection limit.

Table SI-2: Concentrations of *t*-OP and NP isomers (pg m^{-3}) measured in the vapor phase over the North Sea. (The values in the blankets are the standard deviations calculated based on parallel samples.)

| Substance | A1 | A2 | Mean | A3 | A4 | Mean | A5 | A6 | Mean |
|-------------|-----|-----|----------|----|----|--------|----|----|--------|
| NP1 | 7 | 4 | 6 (2) | 3 | 2 | 3 (1) | 3 | 2 | 3 (1) |
| NP2 | 24 | 24 | 24 (0) | 9 | 9 | 9 (0) | 6 | 7 | 7 (1) |
| NP3 | 8 | 8 | 8 (0) | 3 | 3 | 3 (0) | 2 | 2 | 2 (0) |
| NP4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NP5 | 13 | 13 | 13 (0) | 4 | 5 | 5 (1) | 4 | 4 | 4 (0) |
| NP6 | 7 | 6 | 7 (1) | 2 | 2 | 2 (0) | 1 | 2 | 2 (1) |
| NP7 | 11 | 12 | 12 (1) | 5 | 5 | 5 (0) | 4 | 5 | 5 (1) |
| NP8 | 4 | 3 | 4 (1) | 2 | 1 | 2 (1) | 1 | 1 | 1 (0) |
| NP9 | 12 | 8 | 10 (3) | 3 | 5 | 4 (1) | 2 | 3 | 3 (1) |
| NP10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NP11 | 5 | 3 | 4 (1) | 1 | 2 | 2 (1) | 1 | 2 | 2 (1) |
| NP12 | 13 | 15 | 14 (1) | 6 | 4 | 5 (1) | 4 | 4 | 4 (0) |
| NP13 | 8 | 6 | 7 (1) | 2 | 3 | 3 (1) | 2 | 2 | 2 (0) |
| ΣNP | 110 | 100 | 110 (10) | 40 | 41 | 41 (1) | 30 | 34 | 32 (3) |
| t-OP | 39 | 37 | 38 (1) | 5 | 11 | 8 (4) | 7 | 11 | 9 (3) |

Table SI-3: Concentrations of NP1EO isomers (pg m^{-3}) measured in the vapor and particle phases over the North Sea. (The values in the blankets are the standard deviations calculated based on parallel samples. V: vapor phase; P: particle phase)

| | A1 | | A2 | | Mean | | A3 | | A4 | | Mean | | A5 | | A6 | | Mean | |
|---------------------------------|----|----|----|----|------|----|----|----|----|----|------|----|----|----|----|----|------|----|
| | V | P | V | P | V | P | V | P | V | P | V | P | V | P | V | P | V | P |
| NP1EO 1 | 1 | 3 | 2 | 3 | 2 | 3 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 1 |
| NP1EO 2 | 3 | 9 | 6 | 8 | 5 | 9 | 2 | 2 | 1 | 4 | 2 | 3 | 1 | 2 | 1 | 2 | 1 | 2 |
| NP1EO 3&4 | 2 | 6 | 3 | 6 | 3 | 6 | 1 | 2 | 1 | 3 | 1 | 3 | 0 | 1 | 1 | 2 | 1 | 2 |
| NP1EO 5 | 1 | 5 | 3 | 5 | 2 | 5 | 1 | 1 | 1 | 2 | 1 | 2 | 0 | 1 | 0 | 2 | 0 | 2 |
| NP1EO 6 | 1 | 3 | 2 | 3 | 2 | 3 | 0 | 1 | 0 | 2 | 0 | 2 | 0 | 1 | 0 | 1 | 0 | 1 |
| NP1EO 7 | 1 | 3 | 1 | 3 | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 1 |
| NP1EO 8 | 1 | 3 | 2 | 3 | 2 | 3 | 0 | 1 | 0 | 2 | 0 | 2 | 0 | 1 | 0 | 1 | 0 | 1 |
| NP1EO 9 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 0 | 1 |
| NP1EO 10 | 1 | 4 | 3 | 3 | 2 | 4 | 1 | 1 | 1 | 2 | 1 | 2 | 0 | 1 | 0 | 1 | 0 | 1 |
| NP1EO 11 | 1 | 3 | 2 | 2 | 2 | 3 | 0 | 2 | 0 | 2 | 0 | 2 | 1 | 3 | 0 | 3 | 1 | 3 |
| NP1EO 12 | 1 | 6 | 4 | 6 | 3 | 6 | 1 | 2 | 1 | 4 | 1 | 3 | 1 | 1 | 0 | 2 | 1 | 2 |
| NP1EO 13 | 1 | 3 | 3 | 3 | 2 | 3 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 0 | 1 |
| ΣNP1EO | 14 | 50 | 31 | 47 | 23 | 49 | 9 | 15 | 8 | 24 | 9 | 20 | 4 | 14 | 5 | 19 | 5 | 17 |

Table SI-4: Temperature and salt concentration corrected Henry's law constants for *t*-OP and NP, water- and air-side mass transfer coefficients, overall mass transfer coefficients and air-sea exchange fluxes for samples collected in the North Sea (29. 02-10. 03 2004). ($Sc_{CO_2} = 1395$. $C_{salt} = 0.6 \text{ mol L}^{-1}$)

| Sample | AP | Temp. (K) | WS (m s^{-1}) | H' (10^{-5}) | k_a (m day^{-1}) | k_w (m day^{-1}) | K_{OL} (10^{-3}m day^{-1}) | C_w (ng L^{-1}) | C_a (ng m^{-3}) | Flux ($\text{ng m}^{-2} \text{ day}^{-1}$) |
|---------|------|--------------|-----------------------------|-----------------------|----------------------------------|----------------------------------|--|---------------------------------|---------------------------------|---|
| W1 | t-OP | 277.45 | 9 | 1.93 | 731.4 | 3.33 | 14 | 0.3 | 0.038 | -23 |
| W1 | NP | 277.45 | 9 | 1.61 | 713.9 | 3.25 | 11 | 1.4 | 0.11 | -62 |
| W2 | t-OP | 277.56 | 8.7 | 1.97 | 710.4 | 3.15 | 14 | 0.052 | 0.038 | -26 |
| W2 | NP | 277.56 | 8.7 | 1.64 | 693.5 | 3.08 | 11 | 0.42 | 0.11 | -71 |
| W3 | t-OP | 276.95 | 10 | 1.82 | 801.0 | 3.95 | 15 | 0.027 | 0.038 | -30 |
| W3 | NP | 276.95 | 10 | 1.52 | 781.9 | 3.87 | 12 | 0.36 | 0.11 | -81 |
| W4 | t-OP | 277.70 | 10 | 1.98 | 801.0 | 3.95 | 16 | 0.017 | 0.008 | -6 |
| W4 | NP | 277.70 | 10 | 1.65 | 781.9 | 3.87 | 13 | 0.15 | 0.041 | -30 |
| W5 | t-OP | 279.15 | 6.8 | 2.34 | 578.1 | 2.10 | 13 | 0.013 | 0.008 | -4 |
| W5 | NP | 279.15 | 6.8 | 1.93 | 564.3 | 2.05 | 11 | 0.12 | 0.041 | -22 |
| W6 | t-OP | 279.85 | 14 | 2.53 | 1079.6 | 6.86 | 27 | 0.019 | 0.008 | -8 |
| W6 | NP | 279.85 | 14 | 2.08 | 1053.9 | 6.71 | 22 | 0.11 | 0.041 | -41 |
| W7 | t-OP | 279.45 | 11.6 | 2.42 | 912.4 | 5.04 | 22 | 0.021 | 0.008 | -7 |
| W7 | NP | 279.45 | 11.6 | 2.00 | 890.7 | 4.93 | 18 | 0.10 | 0.041 | -35 |
| W8 | t-OP | 279.35 | 4.3 | 2.39 | 404.0 | 0.99 | 10 | 0.017 | 0.009 | -3 |
| W8 | NP | 279.35 | 4.3 | 1.97 | 394.3 | 0.97 | 8 | 0.12 | 0.032 | -12 |
| W9 | t-OP | 279.15 | 4.2 | 2.34 | 397.0 | 0.95 | 9 | 0.013 | 0.009 | -3 |
| W9 | NP | 279.15 | 4.2 | 1.93 | 387.6 | 0.93 | 7 | 0.09 | 0.032 | -12 |
| W10 | t-OP | 278.45 | 7.2 | 2.16 | 606.0 | 2.31 | 13 | 0.037 | 0.009 | -5 |
| W10 | NP | 278.45 | 7.2 | 1.79 | 591.5 | 2.26 | 11 | 0.25 | 0.032 | -16 |
| W11 | t-OP | 277.95 | 11.4 | 2.04 | 898.5 | 4.90 | 18 | 0.036 | 0.009 | -7 |
| W11 | NP | 277.95 | 11.4 | 1.70 | 877.1 | 4.79 | 15 | 0.24 | 0.032 | -24 |
| Average | t-OP | 278.46 | 8.8 | 2.16 | 719.9 | 3.23 | 16 | 0.05 | 0.02 | -12 |
| Average | NP | 278.46 | 8.8 | 1.79 | 702.8 | 3.16 | 13 | 0.31 | 0.06 | -39 |