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## Occurrence and air/sea-exchange of novel organic pollutants in the marine environment

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**Abstract.** A number of studies have demonstrated that several classes of chemicals act as biologically relevant signalling substances.

Among these chemicals, many, including PCBs, DDT and dioxins, are semi-volatile, persistent, and are capable of long-range atmospheric transport via atmospheric circulation. Some of these compounds, e.g. phthalates and alkylphenols (APs) are still manufactured and consumed worldwide even though there is clear evidence that they are toxic to aquatic organisms and can act as endocrine disruptors.

Concentrations of NP, *t*-OP and NP1EO, DMP, DEP, DBP, BBP, and DEHP have been simultaneously determined in the surface sea water and atmosphere of the North Sea. Atmospheric concentrations of NP and *t*-OP ranged from 7 to 110 pg m<sup>-3</sup>, which were one to three orders of magnitude below coastal atmospheric concentrations already reported. NP1EO was detected in both vapor and particle phases, which ranged from 4 to 50 pg m<sup>-3</sup>. The concentrations of the phthalates in the atmosphere ranged from below the method detection limit to 3.4 ng m<sup>-3</sup>. The concentrations of *t*-OP, NP, and NP1EO in dissolved phase were 13-300, 90-1400, and 17-1660 pg L<sup>-1</sup>. DBP, BBP, and DEHP were determined in the water phase with concentrations ranging from below the method detection limit to 6.6 ng L<sup>-1</sup>.

This study indicates that atmospheric deposition of APs and phthalates into the North Sea is an important input pathway. The net fluxes indicate that the air-sea exchange is significant and, consequently the open ocean and polar areas will be an extensive sink for APs and phthalates.

### 1. INTRODUCTION

In the last two decades, a number of studies have demonstrated that several classes of chemicals exist that can act as biologically relevant signalling substances, capable to influence the control gene expression at the molecular level and interfering with homeostatic feedback loops at the development and function level [1, 2]. These substance features are known as endocrine disruption potential, a hypothesis which was first described in the early 1990s [3].

Among these chemicals, many, including PCBs, DDT and dioxins, are semi-volatile, persistent, and are capable of long-range atmospheric transport via atmospheric circulation [4-8]. Some of these compounds, e.g. phthalates and alkylphenols (APs) are still manufactured and consumed worldwide even though there is clear evidence that they are toxic to aquatic organisms and can act as endocrine disruptors. Since 1978, phthalates have been detected in the marine environment and in remote regions such as the Arctic, with concentrations comparable to terrestrial environments [9]. Phthalates are a group of chemicals that are primarily used as plasticizers in huge quantities. Since they are not chemically bound they can be liberated from the consumer products into the environment. Alkylphenols are typically not directly released but are rather formed as anaerobic biological breakdown products of widely used non-ionic surfactants, alkylphenol ethoxylates (APEOs) [10]. Concentrations of APs and their parent compounds have been measured worldwide in all compartments of the environment and even in food products for human consumption [11-14].

International conventions aiming at the protection of the marine environment (such as OSPAR) have listed phthalates and APs together with more persistent compound classes, such as brominated flame retardants (BFRs), musk compounds and chlorinated paraffines as emerging organic pollutants of priority concern. Concentrations of nonylphenol (NP), tertiary octylphenol (*t*-OP) and nonylphenol monoethoxylate (NP1EO) and a number of phthalates have been simultaneously determined in the surface seawater and atmosphere of the North Sea. Air-sea exchange of these compounds was estimated using the two-film resistance model based upon relative air-water concentrations [15].

## 2. SOURCES OF ALKYLPHENOLS AND PHTHALATES AS ENVIRONMENTAL POLLUTANTS

Phthalates are manufactured worldwide on a large scale, being mainly produced for use as plasticizers in resins, polymers and especially as a softener in polyvinylchloride (PVC). Other industrial applications include the manufacturing of cosmetics, insect repellents, insecticide carriers, and propellants [16]. In the early 1980s, world production of phthalates was estimated to be 2 million t yr<sup>-1</sup> [17]. A market volume of phthalates in European Union (EU) was estimated around 1000,000 t yr<sup>-1</sup> in 1990s, of which approximately 480,000 t yr<sup>-1</sup> was for DEHP and 45,000 t yr<sup>-1</sup> for BBP. The production volume of DBP in the EU was estimated at 49,000 t yr<sup>-1</sup> in 1994, and 26,000 t yr<sup>-1</sup> in 1998, showing clear decreasing trends in production. As plasticizers, phthalates are not physically bound to the polymer and can thus migrate out of plastic and leach into the environment. Phthalates can enter the environment via emission from household and industrial products; from wastewater from production and processing activities, including losses during phthalates synthesis, resin and plasticizer compounding, and during the production of adhesives and coatings; from the use and disposal of materials containing phthalates or landfills with refuse and other waste. In the United States, it was estimated that in 1989, 500 t of DEHP were released into the environment through manufacturing facilities. Recent data on releases of phthalates in the EU are not available. However, it was estimated that 3-5% of the market volume of the phthalates are released into the environment.

Alkylphenol ethoxylates (APEOs) are non-ionic surfactants with a worldwide production of approximately 700,000 t yr<sup>-1</sup> and are used in a wide range of applications [18]. In mid of 1990s, the EU had a market volume of 79,000 t yr<sup>-1</sup> for technical nonylphenol (NP) and nonylphenol ethoxylates (NPEOs). In 1995, Germany had an alkylphenols (APs) consumption of 20,000 t, of which approximately 14,000 t was nonylphenol (NP). The rest of 6,000 t was made up of octyl-, butyl- and other alkylphenols. The main application was in industrial and household detergents. Moreover, APEOs were used in many other industrial applications, e.g. as wetting agents, emulsifiers of pesticides, dispersants, solubilizers, foaming agents and polymer stabilizers [19]. APEOs are discharged in high quantities in sewage or industrial wastewater treatment plants. They can also directly enter the environment in areas without wastewater treatment [20]. It was estimated that NP and NPEOs enter into the air and water at a rate of 850 t yr<sup>-1</sup>.

### 2.1 Environmental fate and distribution of phthalates

The release of phthalates directly into the atmosphere is believed to be the most important input pathway into the environment [21]. Following release they will distribute between different environmental compartments according to their physicochemical properties. Dimethylphthalate (DMP) and diethylphthalate (DEP) are more present in ambient air and water as a result of high vapor pressure and high solubility in water. Dibutylphthalate (DBP) is moderately adsorbed to soil [22-24], but forms complexes with water-soluble fulvic acids that might increase its mobilization and reactivity in soil to some degree [25]. A similar effect can be observed with diethylhexylphthalate (DEHP) that has a strong tendency to be adsorbed by soil however, this effect can be less pronounced in the presence of fulvic acids.

Additionally, phthalates as a group may enter the aquatic environment via wastewater treatment plants, rainfall, runoff and atmospheric deposition. The latter has shown to be a significant input pathway for the Great Lakes in Canada [26].

Several degradation pathways have been described for phthalates, e.g. photo degradation in the atmosphere, bio-degradation in water, and anaerobic degradation in sediments and soils [21]. Contribution of hydrolysis to the overall environmental degradation of phthalates is expected to be low, whereas photo oxidation by OH-radicals contributes more to the elimination of phthalates from the atmosphere.

As presented in Table 1, reported half-lives are specified as a range to indicate differences that are expected due to the OH radical concentrations between pristine ( $3 \times 10^5$  radical  $\text{cm}^{-3}$ ) and polluted ( $3 \times 10^6$  radical  $\text{cm}^{-3}$ ) air. Results are indicating that susceptibility to photo degradation of phthalates increases as alkyl chain length is increasing. The photo degradation half-lives presented in Table 1 are calculated with air oxidation program (AOP) [21] developed by Atkinson and recalculated (the brackets) with an updated version of (AOP, AOPWIN 1.89) [27]. Obviously, the recalculated values are at the lower level as compared to the previous calculation. These values may significantly influence the prediction for the persistence and transport of the phthalates in the atmosphere. Concerning the photo degradation half-lives of particle-associated phthalates, Behnke et al. [28] have investigated the photo degradation rate for DEHP adsorbed to various particulate aerosols. They reported a first-order rate constant of  $1.4 \times 10^{-11}$   $\text{cm}^3$  molecule  $\text{s}^{-1}$  for the reaction of DEHP with hydroxyl radicals when adsorbed as a monolayer on  $\text{Fe}_2\text{O}_3$  or  $\text{SiO}_2$  aerosols. This rate for inert particle adsorbed photo degradation corresponds to a half-life of 0.6 d, using the global average hydroxyl radical concentrations of  $9.7 \times 10^5$  molecule  $\text{cm}^{-3}$ , which is not much longer than that calculated for the vapor phase. It seems that sorption to atmospheric particles have no significant effect on the overall rate of indirect photo degradation of the phthalates.

**Table 1.** Half-lives of phthalates for aqueous hydrolysis, microbial degradation and atmospheric photo degradation.

Phthalate	DMP	DEP	DnBP	BBP	DEHP	DOP
<b>Aqueous hydrolysis (years)<sup>e</sup></b>	3.3	8.8	22	<0.3	2000	107
<b>Biodegradation (aerobic) (days)</b>	-(1.4-3.0) <sup>g</sup>	2.5 (0.39-4.33)	2.9 (0.87-5.78)	3.1 (0.32-5)	14.8 (0.4-30)	-(1.0)
<b>Biodegradation (anaerobic) (days)</b>	-(21.0) <sup>g</sup>	33.6 (-)	14.4 (2.2-19.3)	19.3 (9.1-13.6)	34.7 (1.0-53.3)	-
<b>Atmospheric photo degradation (days)</b>	9.3-93 (14.41) <sup>g</sup>	1.8-118 (2.39)	0.6-6.0 (0.89)	0.5-5.0 (0.75)	0.2-2.0 (0.38)	0.3-3.0 (0.40)

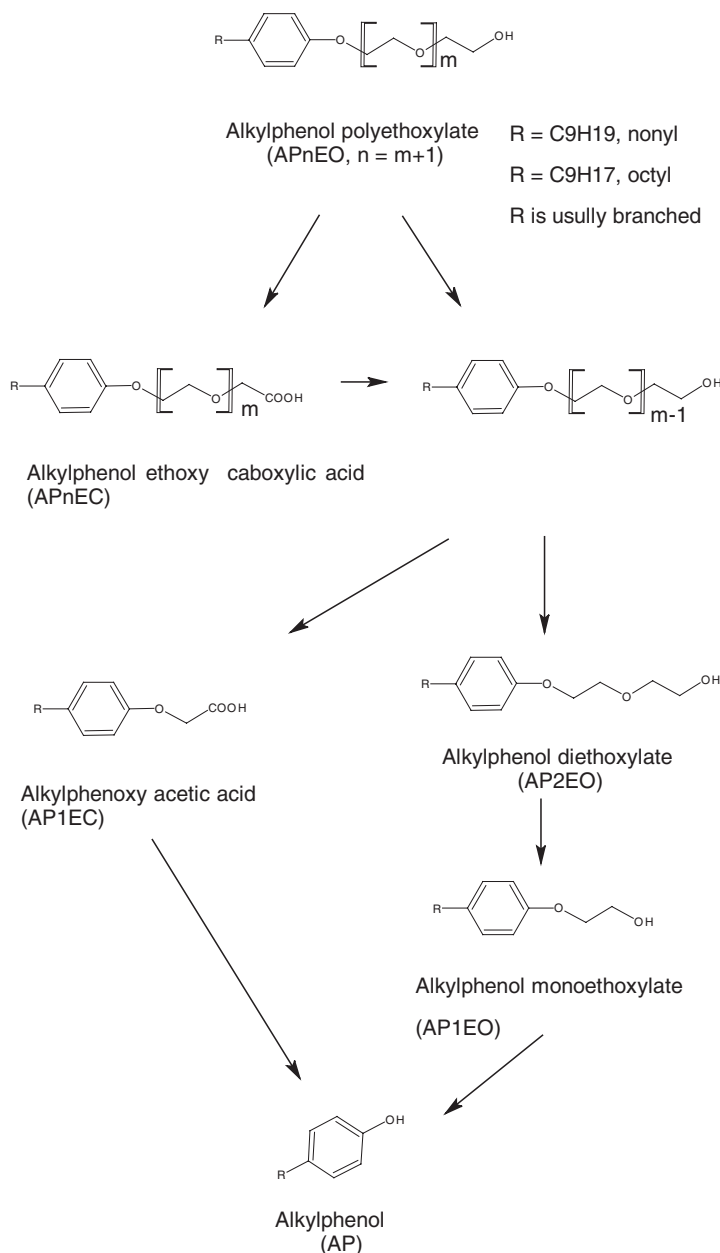
<sup>e</sup> [21]<sup>f</sup> [29]

<sup>g</sup> the values in the brackets are recalculated with an updated version of AOP. Peterson, D. and Staples, C.A.2003.

The persistence of phthalates was predicted with EQC level II modeling [30]. Increasing half-lives and tendency could be expected with increasing alkyl chain length, which ranges from 9.9 to 34 days for the phthalates. It seems the phthalates are not as persistent as the well-known POPs, e.g.  $\alpha$ -HCH and PCBs. However, based on the estimated overall persistence for emission to air, travel distances ranging from 220 km for DEHP to 1000 km for DEP were predicted, which is beyond or close to the distance from the European continent to the North Atlantic ocean and Arctic circle. In these cold areas, the phthalates will undergo a slow degradation processes as compared to that predicted with temperate conditions. These facts suggest the need for a detailed investigation of the occurrence and turnover of phthalates in the cryosphere.

## 2.2 Environmental fate and distribution of nonylphenoethoxylates and their metabolites

NPEOs are produced by the base-catalyzed reaction of NP with ethylene oxide (EO). During the production, a mixture of NP isomers with branched hydrocarbon chains is typically used to form the NPEOs. Biodegradation of NPEOs results in a series of transformations that shorten the ethoxylate chain. The proposed aerobic and anaerobic biological degradation mechanism for NPEOs is shown in Figure 1. It was suggested that under aerobic conditions, NPEOs degrade to



**Figure 1.** Degradation pathways of Alkylphenol ethoxylates [19].

nonylphenol ethoxylates with short-chained ethoxylates groups or to nonylphenol ethoxycarboxylates with carboxylated ethoxylate and carbon chains, e.g. nonylphenol diethoxylates (NP2EO), nonylphenol monoethoxylate (NP1EO). Complete deethoxylation with formation of NP has been observed under anaerobic conditions [10]. The three most common groups of intermediates reported were summarized as follows [19]: (a) NP, (b) short chain NPEOs having one to four EO unites; (c) a series of ether carboxylates including alkylphenoxy acetic acid and alkylphenoxy ethoxy acetic acid. NP tends to be formed as the final product. Studies have shown that the metabolites of NPEOs, e.g. NP, NP1EO and NP2EO are more hydrophobic, persistent and toxic in the environment [31, 32]. Previous investigations showed that NPEOs metabolites degraded more easily under aerobic, than under anaerobic conditions [33]. The removal rates of NPEOs through sewage treatment plants (STPs) were from 86% to 99% in autumn and from 66% to 99% in winter in Japan, indicating the temperature dependence of degradation of NPEOs [34].

Knowledge on the photo-degradation of APs is very poor. However, it is supposed that photo-degradation dominates the atmospheric fate of NP and NPEOs. A half-life for NP was estimated as 0.3 day [35]. Pelizzetti et al. [36] studied photocatalytic degradation of NPEOs with TiO<sub>2</sub> particulates as photocatalyst. They found that a competitive attack of OH radicals on the ethoxy chain and on the aromatic ring occurs. As a result, complete conversion to CO<sub>2</sub> has been demonstrated. Therefore, photodegradation of NPEOs may quantitatively minimize the accumulation of NP during the sample handling.

This work has been designed to improve our understanding of the distribution pattern and transport mechanisms of APs and phthalates in the coastal and marine environment, with special emphasis on the air-sea exchange to derive flux estimates between the atmosphere and the North Sea/North Atlantic.

### 3. EXPERIMENTAL

#### 3.1 Reagent preparation

The solvents (methanol, acetone, hexane, dichloromethane, acetonitrile, diethyl ether (Promochem GmbH, Germany) used were residue analysis or HPLC grade, and were distilled prior to use. Milli-Q water (18.2 M $\Omega$ cm) was generated by a Millipore Ultra-pure water system (Millipore S.A., Molsheim France) and additionally purified with XAD-2 or PAD-2 resins. All glassware was rinsed with Milli-Q water and acetone and then baked at 450°C for at least 8 hours before use.

Analytical standards (*t*-OP, technical NP and NP1EO, dimethyl phthalate (DMP) diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), di-*i*-butyl phthalate (DiBP), butylbenzylphthalate (BBP), DEHP and dioctyl phthalate (DOP)), internal standards (4-*n*-NP *d*8 and dibenzylphthalate) and the surrogates (4-*n*-OP, 4-*n*-NP, technical NP1EO *d*2 (NP1EO *d*2), DMP *d*4, DEP *d*4, DBP *d*4, DEHP *d*4) were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Stock solutions of each chemical or mixture of chemicals were made by dissolving approximately 5-10  $\mu$ g of the neat chemicals in liquid, solid or in solution into 10 mL of hexane. The standard solutions used in these experiments were made from appropriate dilutions of these stock solutions. Calibration solutions for preparing GC-MS calibration curves were made by diluting 1-200  $\mu$ l of the standard solutions in hexane (final volume 200  $\mu$ L). Stock solutions were prepared every half-year; internal standards and surrogates were prepared for the entire sampling campaign and the measurements.

#### 3.2 PUF/XAD-2 column, PAD-2 column and glass fiber filter (GF/F) preparation

Amberlite XAD-2 resins (particle size: 20-60 mesh) were obtained from Supelco Germany. PAD-2 resins (particle size: 0.3-1.0mm) were obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). To prepare the PUF/XAD-2 column, 30 g of XAD-2 resin were packed into a glass column with a glass frit. A piece of polyurethane foam (PUF, 2 cm x 5 cm  $\emptyset$ ) was placed on the top to cover

the XAD-2 resin. The packed column was cleaned with methanol, acetone and hexane (twice with each solvent) in turn using a modified soxhlet extractor for 72 hours. The residue solvent was removed using purified N<sub>2</sub> (300 mL for 20 min).

To prepare the PAD-2 resin column, 50 g of PAD-2 resin were first rinsed with 500 mL Milli-Q water, and then, the water was replaced with acetone. The PAD-2 resins and acetone were packed into a glass column with a glass frit. The column was filled to about 2/3 with PAD-2 resin. The PAD-2 column was rinsed with 200 mL acetone and then cleaned with acetone and DCM (twice with each solvent) using a modified soxhlet extractor for 72 h. Finally, DCM was replaced by purified milli-Q water (200 mL).

Glass fiber filters (GF/F 8 and GF/F 52) were obtained from Schleicher and Schuell Corporation (Dassel, Germany). GF/F 8 (diameter: 155 mm, pore size: 0.45  $\mu\text{m}$ ) was used for atmospheric particles and GF/F 52 (diameter: 142 mm, pore size: 0.7  $\mu\text{m}$ ) was used for total suspended matter (TSM) in sea water. Filters were wrapped in a single layer of aluminium foil that was sealed around the filter to create a 'bag'. The filters and the aluminium bag were then baked for 12 h at 450°C in a muffle furnace.

After purification, the PUF/XAD-2 and PAD-2 columns were covered by a pair of pan-like and ball-like caps and sealed by sliding clips. Columns were stored before and after sampling in heat-sealed airtight polypropylene/aluminium/polyethylene bags (PP/AL/PE, Tesseraux, Germany) at 7°C for water samples and at -20°C for air samples, respectively. Cleaned filters were wrapped between aluminium foil in PP/AL/PE bags and used filters were closed in fused test tubing and stored at -20°C.

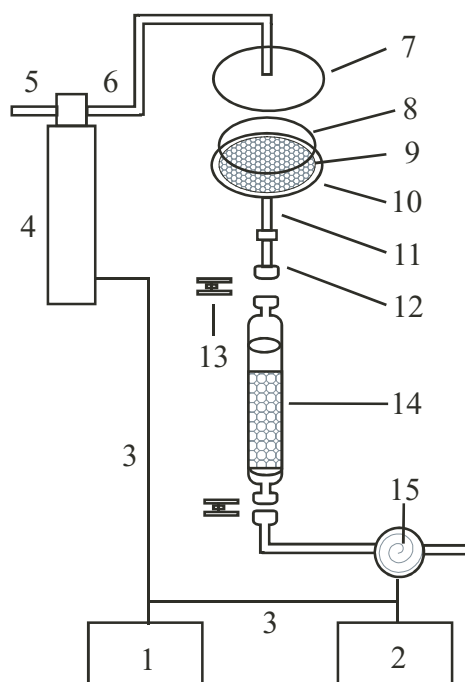
### 3.3 Sampling and sample preparation

#### 3.3.1 Water and air sampling

Water sampling was conducted with a modified Kiel In-Situ Pump (KISP) which has been widely applied to the extraction of marine trace organic chemicals [37-39]. Petrick et al [40] described the technical design and principle and tested its performance in the Atlantic Ocean. Although low blanks and extremely low detection limits obtained from KISP samples could satisfy the demands for reliably detecting PCBs and HCHs, the system still presents a blank risk for the determination of trace APs and phthalates as several parts of the KISP are manufactured with or contained PVC material. Therefore, modifications were made to the frame of KISP. All plastic parts were removed and replaced with parts made from stainless steel or glass.

As shown in Figure 2, the in-situ pump includes a filter holder, a PAD-2 column, a pump and a flow meter. The pump and the flow meter were operated on board. The pumping rate can be selected from 0.01-2 L min<sup>-1</sup> by adjusting the power supply. The glass fiber filter (GF/F 52) was placed on the glass filter holder. Stainless steel tubing was used to connect the pump to the filter plate. Glass tubing connects the filter plate to the PAD-2 resin column. Sea water samples were taken from beneath the bottom of the ship. In the North Sea, typical water sample volumes were from 20 to 100 L in the area near the coast and from 200 to 400 L in the open sea. In the Atlantic Ocean, up to 1000 L of sea water can be extracted due to the low concentration of total suspended matter (TSM).

Air samples were collected using a high-volume air sampler that was operated at a constant flow rate of 200 L min<sup>-1</sup>. As shown in Fig 3. (left), the high volume air sampler consists of a high volume pump (ISAP 2000, Schulze Automation & Engineering, Asendorf, Germany), a digital flow meter, a metal filter holder and a PUF/XAD-2 column. The filter holder and the PUF/XAD-2 were linked with a Teflon connector that could protect the glass column while it works under stormy weather. To eliminate the blank risk from the Teflon, the connector was cleaned ultrasonically, three times with acidified water (pH: 2.0) and three times with acetone, respectively. All parts of the filter holder were washed with a washing machine and rinsed with acetone. The pump and the flow meter were set up separately in metal boxes. All electronic plugs were wrapped with waterproof stick film for work outside. GF/F 8 was used to collect atmospheric particles. The filter was changed in the laboratory with tweezers pre-cleaned by thermal treatment. The ship-borne air samples were collected on the upper deck of the research vessel



**Figure 2.** Schematic of the in-situ pump. 1: flow meter controller; 2: flow meter; 3: cable connections; 4: pump; 5: pump inlet; 6: pump outlet; 7: stainless steel deck of filter holder; 8: GF/F 52 filter; 9: glass plate; 10: filter holder; 11: stainless steel tubing; 12: glass connect; 13: adjustable clip; 14: PAD-2 resins column; 15: counter of flow meter.

(see Figure 3, right). Typical air sample volumes were from 400 to 1000 m<sup>3</sup>. As reported by Lohmann et al. [41], there is always the potential for contamination by air from ship-board samples. In order to avoid emissions from the ship's funnel, therefore, air sampling was performed on headwind and was halted at station or wind speeds lower than 3 m s<sup>-1</sup>.

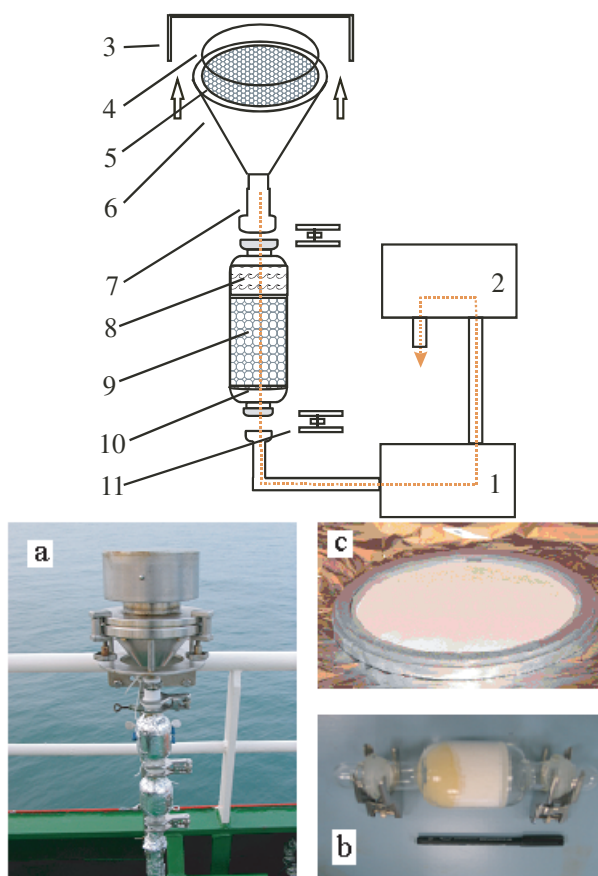
### 3.3.2 Extraction

The PUF/XAD-2 columns were spiked with the internal standards (50  $\mu\text{L}$  of 200 ng mL<sup>-1</sup> 4-n-NP d8 50  $\mu\text{L}$  of 1.0  $\mu\text{g mL}^{-1}$  NP1EO d2) and extracted for 16 h using 300 mL of 10% (v/v) diethyl ether in hexane solution with the modified Soxhlet extractor. The PAD-2 columns were extracted for 16 h using 250 mL DCM with the modified Soxhlet extractor after spiking with the internal standards (50  $\mu\text{L}$  of 200 ng mL<sup>-1</sup> 4-n-NP d8 50  $\mu\text{L}$  of 1.0  $\mu\text{g mL}^{-1}$  NP1EO d2). Both air and water filter samples were spiked with surrogate standards (50  $\mu\text{L}$  of 200 ng mL<sup>-1</sup> 4-n-NP and 4-n-OP, 50  $\mu\text{L}$  of 1.0  $\mu\text{g mL}^{-1}$  NP1EO d2, 50  $\mu\text{L}$  of 0.5-1.25  $\mu\text{g mL}^{-1}$  deuterated phthalates) and extracted for 16 h using 150 mL of DCM with the Soxhlet extractor. After Soxhlet extraction, the samples were stored in the freezer for rotation evaporation. Several PUF/XAD-2 columns, PAD-2 columns and filters were extracted for a second time in order to check the extraction efficiency.

### 3.3.3 Evaporation

The inner system of the rotation evaporator was cleaned with 100 mL of acetone prior to and after use. A self-designed adaptor was used to connect the round flask to the evaporator. The special design prevents condensate solvent flow backward into the round flask to eliminate potential contamination from inner tubing of the evaporator. The volume of the extracts were reduced to  $\sim 20$  mL using rotation evaporator





**Figure 3.** Schematic of the air sampler and operation on board. 1: high volume pump; 2: flow meter; 3: filter shelter; 4: GF/F 8 filter; 5: metal frame for holding up glass filter 6: stainless steel filter holder; 7: teflon connector; 8: PUF sheet; 9: XAD-2 resins; 10: glass frit; 11: adjustable clip; a: air sampler; b: PUF/XAD-2 column; c: filter and particles.

at 30°C under reduced pressure (500-600 mPa for DCM, 220-290 mPa for the mixture of hexane and diethyl ether, 340 for acetone). 20 mL hexane was added to the flask and the solution was continually evaporated to 10-20 mL. The extracts were transferred to another 25 mL pear-bottom flask. The volume of the extracts was further reduced to 1-2 mL before clean-up. In order to remove small residues of water that might be present, the extracts were stored overnight in the freezer at -20°C prior to clean-up.

### 3.3.4 Silica gel clean-up

All the extracts were purified through a 5% H<sub>2</sub>O deactivated silica gel column (2.5 g silica gel packed in a 15 cm × 1 cm i.d. glass column). The silica gel (0.063-0.200 mm, Merck, Darmstadt, Germany) was prepared as follows: extracted using acetone and baking out at 450°C for 12 h to remove organic contamination and deactivation by addition of 5% (w/w) of milli-Q water (purified by PAD-2 resin). After the extracts were transferred into the column, purification was performed by passing 10 mL of hexane through the column in order to remove non-polar compounds. The column was then eluted with 30 mL of hexane and diethyl ether (3:1 v/v) for the APs and phthalates fraction. It was followed with a 25 mL hexane and diethyl ether (1:1 v/v) fraction for NP<sub>2</sub>EO. Eluates were reduced in volume in a rotatory evaporator and subsequently concentrated in a nitrogen evaporator to 100 μL.

### 3.3.5 Derivatization

The extracts were derivatized in a glass vial by the addition of N,O-bis(trimethylsilyl)trifluoroacetamide and 1% trimethylchlorosilane (TMCS) (BSTFA +1% TMCS) (Part No. 701 490.201, Macherey-Nagel GmbH, Dueren, Germany). 40  $\mu\text{L}$  of 500 ng mL<sup>-1</sup> surrogate standard mix 5 were spiked as internal standard (if it is not spiked before extraction). The volume was reduced to 100  $\mu\text{L}$  under a gentle stream of nitrogen (99.999%). 100  $\mu\text{L}$  of BSTFA + 1% TMCS was added to the glass vial. The mixture was allowed to react for 1 h at 70°C. After cooling for 5 min, the final sample volume was adjusted to 200  $\mu\text{L}$  using hexane. After derivatization, the extracts were ready for GC-MS without further treatment.

### 3.4 GC-MS analysis

Quantification of APs and phthalates was performed with an Agilent system consisting of a 6890 N gas chromatograph equipped with an Agilent 7683 series autosampler, a 7683 split-splitless temperature and pressure-programmed injector, and an Agilent 5973 quadrapole mass selective detector (GC-MS). Chemstation Software (2000 version) was used for data processing. The injector was equipped with a deactivate PTV multi-baffle liner. Ions detected were generated by electron impact ionization and monitored in the selective mode (EI-SIM) and total ion scan mode by two injections. A 30 m  $\times$  0.25 mm fused silica capillary column (5%-phenyl-95% methylpolysiloxane, HP-5ms) with 0.25  $\mu\text{m}$  film thickness was used for the separation. General conditions for GC-MS analysis are shown in Table 2.

**Table 2.** GC-MS conditions for the determination of APs and phthalates.

GC-MS	APs	Phthalates
<b>Column</b>	HP-5ms (30 m $\times$ 0.25 mm i.d., 0.25 $\mu\text{m}$ film thickness; J&W Scientific, Folsom, CA, USA)	HP-5ms (30 m $\times$ 0.25 mm i.d., 0.25 $\mu\text{m}$ film thickness; J&W Scientific, Folsom, CA, USA)
<b>Injection</b>	1 $\mu\text{L}$	1 $\mu\text{L}$
<b>Injector temperature</b>	280°C (pulse splitless mode, 20 psi for 2 min) (Program 1) 80°C (1min), 300°C min <sup>-1</sup> to 250°C (10 min) <sup>b</sup> (Program 2)	300°C (pulse splitless mode, 20 psi for 2 min)
<b>Carrier gas</b>	Helium, 1.0 mL min <sup>-1</sup>	Helium, 1.0 mL min <sup>-1</sup>
<b>Purge gas</b>	Helium, 250 mL min <sup>-1</sup>	Helium, 250 mL min <sup>-1</sup>
<b>Oven program</b>	80°C (1 min), 30°C min <sup>-1</sup> to 130°C, 3°C min <sup>-1</sup> to 240°C, 10°C min <sup>-1</sup> to 300°C, then 300°C (5 min)	80°C (1 min), 30°C min <sup>-1</sup> to 150°C, 5°C min <sup>-1</sup> to 300°C (5 min)
<b>Ionization energy</b>	70 eV	70 eV
<b>Interface temperature</b>	280°C	290°C
<b>Ion source temperature</b>	230°C	230°C
<b>Quadrapole</b>	150°C	150°C

### 3.5 Calibration and quantification

Stock solutions containing all the analytes at accurately defined concentrations were prepared in hexane by dilution in the peak-bottom glass vials. The solvent was removed under a gentle nitrogen stream to 100  $\mu\text{L}$ . These solutions were derivatized as described above. Quantification was carried out using calibration curves based on the peak area of the internal standards 4-n-NP d8 and the surrogate standard mix 5. NP and NP1EO were quantified by each of the isomer peaks. Calibration curves were made with concentrations from 12.5 to 500 ng mL<sup>-1</sup> for *t*-OP, NP and NP1EO and from 5 to 5000 ng mL<sup>-1</sup> for the phthalates. The limits of detection (LODs) were set as 3 times the signal to noise ratio. The detection limits of the method (MDLs) were derived from the blanks and quantified as mean field blanks plus

**Table 3.** Instrumental limit of detection (LOD) and method detection limits obtained in this method.

Compound	LOD (pg)	Sea water (200 L) (pg L <sup>-1</sup> )		Air (500 m <sup>3</sup> ) (pg m <sup>-3</sup> )	
		Dissolved	TSM	Vapor	Particle
<i>t</i> -OP	0.4	5	5	5	5
NP	3.5	40	5	15	5
NP1EO	3.7	25	10	5	5
DMP	0.8	65	15	5	5
DEP	1.2	75	125	10	10
DiBP	0.3	40	15	5	5
DnBP	0.3	25	30	5	5
BBP	1.8	5	5	2	2
DEHP	1.8	200	150	100	40
DOP	1.4	5	5	2	2

three times the standard deviation ( $3\sigma$ ) of field blanks according to the sample volumes (typically, sea water: 200 L, air: 500 m<sup>3</sup>). The LODs and MDLs calculated for the analytes are listed in Table 3.

As compared to those reported in the literature, the instrument detection limits for *t*-OP, NP and NP1EO were quite comparable to those obtained with GC-MS [42, 43] GC-MS/MS [44, 45], LC-MS and LC-MS/MS [46]. For phthalates, it was found that GC-MS provided LODs from 0.03 to 0.5 pg, which are 1-3 orders of magnitude lower than those obtained with LC-ESI-MS. The detection limits of the method were found to be comparable between GC-MS and LC-ESI-MS [47]. In this work, coupling GC-MS analysis with large volume sampling, except for DEHP, the detection limits for APs and phthalates could reach a few pg L<sup>-1</sup> in sea water and a few pg m<sup>-3</sup> in the atmosphere, which are 1 - 2 orders of magnitude lower than the reported MLDs [42, 46, 48-51].

#### 4. THEORETICAL CONSIDERATIONS ON AIR/SEA GAS EXCHANGE AND WASH-OUT RATIOS

##### 4.1 Washout ratio

The washout ratio ( $W$ ) is defined as the dimensionless ratio of chemical concentrations in precipitation to that in air. Considering both vapor and particle scavenging mechanism, washout can be expressed as [5]:

$$W = (1 - \phi) \frac{RT}{H} + \phi W_P \quad (1)$$

where  $\phi$  is the fraction of the chemical on the particle,  $RT/H$  is the dimensionless Henry's law constant at the ambient temperature,  $W_P$  is the particle scavenging coefficient. Based on our experimentally determined  $\phi$  values (see section 5), using Henry's law constants estimated by Cousins and Mackay [52], and a representative  $W_P$  value of 20,000 [53], the washout ratio calculated is 9,200 for DBP, 15,000 for BBP, and 15,600 for DEHP at average sampling temperature of 5°C. These values are very comparable to the washout ratios estimated by Staples et al. [21]. Obviously, the washout ratios appear to be temperature dependent, because of both Henry's law constant and vapor pressure are determined by the temperature. In fact, this phenomenon has been observed for the atmospheric removal of DBP and DEHP in Sweden [54].

##### 4.2 Air-sea vapor exchange model

In this study, air-sea vapor exchange fluxes were estimated using the modified version of two-film resistance model [55, 56] which was extensively used for the evaluation of PCBs and PAHs fluxes through air-water interfaces [57-61]. 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

$$F = K_{OL} \left( C_w - \frac{C_a}{H'} \right) \quad (2)$$

where  $F$  is the flux ( $\text{ng m}^{-2} \text{ day}^{-1}$ ),  $C_w$  ( $\text{ng m}^{-3}$ ) and  $C_a$  ( $\text{ng m}^{-3}$ ) are the dissolved- and vapor-phase concentrations,  $(C_w - C_a/H')$  describes the concentration gradient ( $\text{ng m}^{-3}$ ),  $H'$  is the dimensionless Henry's law constant, and  $K_{OL}$  ( $\text{m day}^{-1}$ ) is mass transfer coefficient comprising resistances to mass transfer in both water ( $k_w$ ) and air ( $k_a$ ). Since averages of water temperatures were ranging from 3.8 to 6.7°C on this cruise, the Schmidt number for  $\text{CO}_2$  at 5°C ( $Sc_{\text{CO}_2} = 1395$ ) was applied for the estimation of  $k_w$  [62].  $H'$  was corrected with water temperatures ( $T$ , K) and averaged salt concentrations ( $C_s$ , 0.5 mol  $\text{L}^{-1}$ ) based on following equations (3-5) [62, 63]

$$\ln H = \ln H_0 + \frac{\Delta H_v}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad (3)$$

$$H_{corrected} = H \cdot 10^{K_s C_s} \quad (4)$$

$$H' = \frac{H_{corrected}}{RT} \quad (5)$$

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  $T$ ,  $H_0$  is Henry's law constant at  $T_0$  (298.15 K),  $K_s$  is the salting constant of 0.3 [62], and  $H_{corrected}$  is the corrected Henry's law constant for salinity.  $\Delta H_v$  is the enthalpy of vaporization at 298.15 K, which is supposed to be constant over the ambient temperature range [63].  $\Delta H_v$  values for phthalates (see Table 2) were estimated from their enthalpies of vaporization at the boiling point [62, 64].  $H_0$  values of phthalates estimated using the 'three solubility' approach [52] were used for the calculation.

#### 4.2.1 Uncertainty analysis

The uncertainty in the  $F$  (Equation 2) was evaluated using a propagation of error analysis derived from Shoemaker et al. [65], which has been used in previous studies [57, 59]. The summation of the various random errors in the flux are described by

$$\sigma^2(F) = \left( \frac{\delta F}{\delta K_{OL}} \right)^2 (\sigma K_{OL})^2 + \left( \frac{\delta F}{\delta C_w} \right)^2 (\sigma C_w)^2 + \left( \frac{\delta F}{\delta C_a} \right)^2 (\sigma C_a)^2 + \left( \frac{\delta F}{\delta H'} \right)^2 (\sigma H')^2 \quad (6)$$

Total propagated variance  $\sigma^2(F)$  is the linear combination of the weighted contribution of the variances ( $\sigma^2$ ) of the mass transfer coefficient,  $H'$  and measured concentrations. The error in  $H'$  was assumed to be zero because it is a systematic and not random error [57, 59]. The errors of  $C_w$  and  $C_a$  were 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. [66] and Nelson et al. [57]. The overall propagated error in  $F$  is thus, 45% (Table 4). It was shown that most of the uncertainty associated with the fluxes was attributed to  $K_{OL}$  (78%), which was a factor of 7 higher than the uncertainties associated with  $C_w$  and  $C_a$  (11%). As a source of systematic error,  $H'$  has a standard error of prediction that is approximately a factor of 3 on the arithmetic value [52], which can affect either  $K_{OL}$  or the overall concentration gradient. Therefore,

**Table 4.** Water and air sampling.

Sample	Date	Station	Volume (L)	Temperature(°C)	Wind speed (m s <sup>-1</sup> )	Salinity (‰)
<b>Water</b>						
W1	29/2/2004	3 – 4	38	4.3	9.0	28.5
W2	1/3/2004	4 – 6	174	4.5	8.7	30.4
W3	1/3/2004	6 – 8	82	3.8	10.0	27.8
W4	2/3/2004	10 – 13	175	4.5	10.0	30.1
W5	3/3/2004	16 – 19	254	6.0	6.8	34.1
W6	4/3/2004	23 – 25	410	6.7	14.0	34.9
W7	5/3/2004	22 – 36	381	6.3	11.6	34.6
W8	6/3/2004	29, 30, 36	335	6.2	4.3	34.5
W9	7/3/2004	35 – 37	201	6.0	4.2	34.5
W10	8/3/2004	33 – 34	162	5.3	7.2	32.2
W11	9/3/2004	34 – 39	81	4.8	11.4	31.6
<b>Air</b>						
A1-1*			(m <sup>3</sup> )			
A1-2*	29/2 – 2/3/2004	1 – 11	494			
A2-1			549			
A2-2	2/3 – 6/3/2004	11 – 25 – 36	1147			
A3-1			927			
A3-2	6/3 – 9/3/2004	33 – 39	670			
			589			

accuracy of H' is significant for the estimation of air-sea exchange fluxes, which keeps a need for better understanding of their temperature dependences and improvements for the estimation.

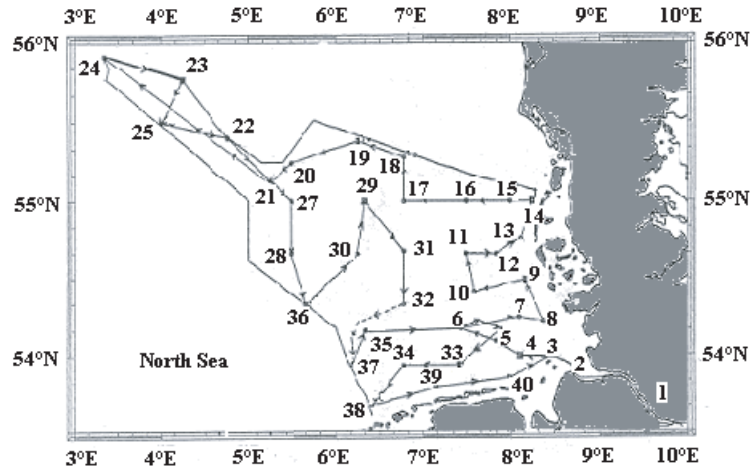
## 5. AQUEOUS AND ATMOSPHERIC CONCENTRATIONS OF PHTHALATES AND ALKYLPHENOLS AND DERIVED AIR/SEA GAS-EXCHANGE IN THE NORTH SEA

The air and water samples in the North Sea (German Bight) for both phthalates and alkylphenols were collected during the cruise no. 414 with the research vessel 'Gauss' from February 29<sup>th</sup> to March 10<sup>th</sup> in 2004. Integrated water samples were collected at 4.5 m depth during the ship steaming. The air samples were collected on the upper deck of 'Gauss' about 9 m above sea level. Detailed information on the sampling stations, temperatures, wind speeds, salinities and sample volumes, are given in Figure 4 and Table 4.

### 5.1 Concentrations of phthalates in sea water

The concentrations of phthalates in dissolved and TSM phases together with air concentrations are given in Table 5. The results showed that DEHP and DBP dominated phthalates' concentrations in the water phase of the North Sea. The concentrations were in the range of 0.45 – 6.6 ng L<sup>-1</sup> for DBP and 0.52 – 5.3 ng L<sup>-1</sup> for DEHP. DMP and DEP were detected in more than 80% water samples with concentrations ranging from 0.02 to 4.0 ng L<sup>-1</sup>. Due to the artefacts of high volume sample collection and their high water solubility, the concentrations of DMP and DEP might be under-estimated. BBP was unexpectedly found in most of the water samples, with concentrations ranging from below MDL to 0.26 ng L<sup>-1</sup>, although it is released in lower quantities as compared to those of DBP and DEHP. Since DOP concentrations were lower than the method detection limits ( $\leq 0.01$  ng L<sup>-1</sup> in water and  $\leq 0.002$  ng m<sup>-3</sup> in air) in all the samples, this compound is not discussed in this paper.

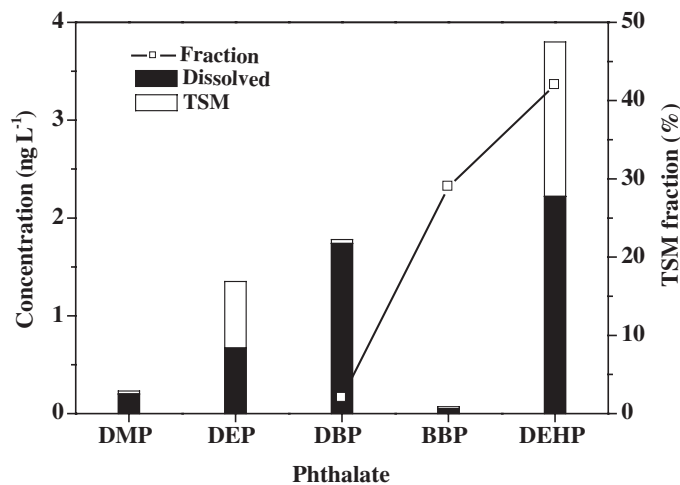
Fromme et al. [67] investigated phthalates in the surface water of various rivers in Germany (Rhine, Elbe, Ruhr, Mosel, Havel, Spree, Oder), and reported that the concentrations were ranging from 0.33 to 97.8  $\mu\text{g L}^{-1}$  for DEHP and from 0.12 to 8.80  $\mu\text{g L}^{-1}$  for DBP, respectively. They were 2 or 3 orders of magnitude higher than the concentrations determined in the North Sea in our study. Moreover, the



**Figure 4.** Sampling stations in the North Sea during the cruise 414 with research vessel “Gauss”, February 29–March 10, 2004.

**Table 5.** Field blanks (ng) and the concentrations of phthalates in the sea water and in the atmosphere of the North Sea. (The averages of field blanks were subtracted before calculating the concentrations of the samples.)

Water	Dissolved					TSM				
	DMP	DEP	DBP	BBP	DEHP	DMP	DEP	DBP	BBP	DEHP
Mean blank (ng)	9.7	10.2	3.7	0	43.7	2.8	9.0	2.5	0	30.8
SD (n = 3)	4.1	2.4	0.7	0	8.0	0.4	0.9	0.4	0	9.0
W1 (ngL <sup>-1</sup> )	0.68	4.0	6.6	0.26	4.4	0.07	0.49	0.2	0.03	5.8
W2	0.18	0.60	2.0	0.03	1.6	0.05	0.53	0.04	ND	1.0
W3	0.26	0.71	2.2	0.02	NA	NA	NA	NA	NA	NA
W4	0.25	0.71	2.2	0.02	0.93	0.01	0.05	0.01	ND	0.56
W5	0.08	0.17	1.4	0.01	0.88	0.01	4.1	0.01	ND	0.16
W6	ND	0.03	0.94	0.01	5.3	0.01	0.13	0.01	ND	4.0
W7	ND	0.05	0.67	ND	3.4	NA	NA	NA	NA	NA
W8	0.02	0.08	0.52	0.01	0.99	ND	0.02	0.01	ND	0.27
W9	0.05	0.14	0.45	ND	0.58	ND	0	0.01	ND	0.34
W10	0.19	0.51	0.78	0.01	0.52	ND	ND	0.02	0.01	0.64
W11	0.1	0.35	1.4	0.08	3.5	0.01	0.09	0.04	0.02	1.4
Average	0.2	0.67	1.7	0.05	2.2	0.03	0.68	0.04	0.02	1.6
Air	Vapor					Particle				
Mean blank (ng)	5.1	17.1	4.6	0.3	63.1	4.0	17.6	3.2	0	11.6
SD (n = 3)	0.3	1.0	0.4	0.05	12.4	0.8	5.6	0.6	0	2.0
A1 (ng m <sup>-3</sup> )	0.54	3.4	1.1	0.04	0.36	ND	0.18	1.2	0.05	0.95
A 2	0.16	0.64	0.34	0.01	0.30	ND	ND	0.10	0.05	0.97
A 3	0.19	0.75	0.17	0.01	0.22	ND	0.01	0.32	0.06	1.1
Average	0.30	1.6	0.53	0.02	0.29	ND	0.06	0.53	0.05	1.0



**Figure 5.** Total concentrations of phthalates in sea water and TSM fractions.

concentrations of DBP and DEHP in the samples collected in the plume of Elbe were one order of magnitude higher than that in the central part of the North Sea. It was suggested that the river-carried contaminations are a significant input source of phthalates into the North Sea.

DBP and DEHP were also detected in most of TSM samples. The concentration ranged from 0.01 to 0.20 ng L<sup>-1</sup> for DBP, and from 0.16 to 5.8 ng L<sup>-1</sup> for DEHP. BBP was found in three samples with concentrations ranging from 0.01 to 0.03 ng L<sup>-1</sup>. As shown in Figure 5, TSM-associated DBP, BBP and DEHP fractions were 2%, 29% and 42%, respectively. DMP and DEP were also found in some TSM samples. Considering the underestimated water concentrations (see above), the TSM fractions were not calculated for DMP and DEP.

TSM associated phthalate fractions were examined previously in surface water samples. Germain and Langlois [68] reported a TSM fraction of 14% for DBP and 53% for DEHP. No other phthalate was detectable in TSM associated fractions. Preston and Al-omran [69, 70] studied the distribution of phthalates in the River Mersey Estuary in UK. 14–34% of DBP was found to be TSM bound (TSM = 1524 mg L<sup>-1</sup>). Furtmann [71] reported that 15–17% of the low molecular weight phthalates DMP and BBP were TSM bound. Ritsema et al. [72] estimated that 2% of DBP and 67% of DEHP was TSM bound in the Lake Yssel and the Rhine River (Netherlands). As compared to the reported values, our results are in the lower part of the ranges. The differences might be result from the sampling device and separation techniques, especially the TSM concentrations in aquatic phase. In the North Sea, TSM concentrations ranging from 1.36 to 12.69 mg L<sup>-1</sup> were recorded during another cruise in April 2003. Moreover, the organic matter fraction in the TSM phase is also an important factor for the partitioning of phthalates in the aquatic phase. In addition, the water temperature significantly influences the partition of phthalates between aquatic and TSM phases. Finally, the effect of the salinity should be taken into account for the salting out effect. Nevertheless, these results provided evidence that high molecular phthalates likely partition to suspended matter either in river or the open sea. Particularly, DEHP has a very low solubility in water and high TSM binding affinity, consequently, it was expected to be accumulated in the sediment and to undergo degradation processes only slowly.

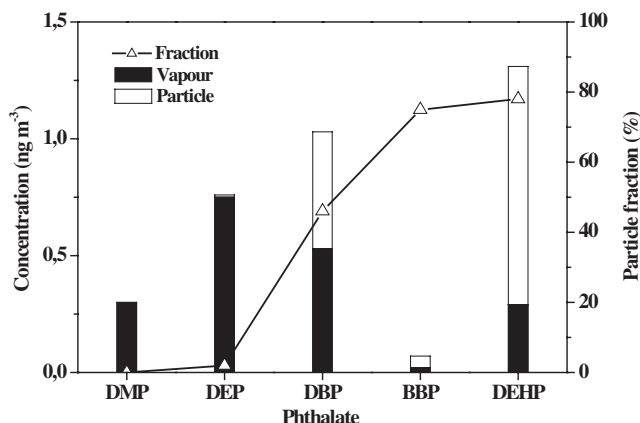
## 5.2 Air concentrations of phthalates

Phthalates concentrations in the atmosphere were shown in Table 5. The average concentrations were 0.30, 1.6, 0.53, 0.02, 0.29 ng m<sup>-3</sup> for DMP, DEP, DBP, BBP and DEHP in the vapor phase, respectively.

In the particle phase, average concentrations were 0.06, 0.53, 0.05 and 1.0  $\text{ng m}^{-3}$  for DEP, DBP, BBP and DEHP. DMP concentration in the particle phase was below the detection limit in all air samples. The low level of particle associated DMP fractions is likely to be the result of its high vapor pressure.

Atlas and Giam [4] reported that DBP and DEHP mean concentrations at Enewetak Atoll in the North Pacific Ocean, which were 0.9  $\text{ng m}^{-3}$  for DBP and 1.4  $\text{ng m}^{-3}$  for DEHP, can be considered as background data for selected organic pollutants. Giam et al. [9, 73] reported the total vapor and particle concentrations of phthalates in marine atmosphere of the North Atlantic and the Gulf of Mexico. The average concentrations were 1.30 and 1.16  $\text{ng m}^{-3}$  for DBP and DEHP in the Gulf of Mexico and 1.0 and 2.9  $\text{ng m}^{-3}$  for DBP and DEHP in the North Atlantic. Weschler [74] reported DBP in the Arctic aerosol at Barrow, Alaska, at a concentration of 1  $\text{ng m}^{-3}$  indicating that phthalates are ubiquitous in the marine atmosphere. The total concentrations of DBP and DEHP in the atmosphere over the North Sea were determined as 1.0 and 1.3  $\text{ng m}^{-3}$ , which agree well to those previously reported values. Similar DEHP concentrations from 0.5 to 5  $\text{ng m}^{-3}$  have been detected in the Great Lakes [26] and in the Swedish atmosphere [54]. Moreover, DEHP were detected in relatively high concentrations near contaminated areas with levels of 29 – 132  $\text{ng m}^{-3}$  in Antwerp, Belgium [75, 76], 300  $\text{ng m}^{-3}$  in City of Hamilton and Ontario, Canada [77], and 38-790  $\text{ng m}^{-3}$  in Japan [78]. Hoff and Chan [79] reported mean DBP concentrations of  $1.9 \pm 1.3 \text{ ng m}^{-3}$  in the vapor phase and  $4.0 \pm 2.2 \text{ ng m}^{-3}$  in the particle phase along the Niagara River in Ontario, Canada. DBP has also been detected in ambient air in Barcelona, Spain, with a concentration ranging from 3.0 to 17  $\text{ng m}^{-3}$  in winter and 1.1-10  $\text{ng m}^{-3}$  in summer for coarse ( $>7.2 \mu\text{m}$ ) and fine particulate ( $<0.5 \mu\text{m}$ ), respectively [80]. Cautreels et al. [75] reported the concentrations of DBP from 24 to 74  $\text{ng m}^{-3}$  in the particulate phase of the air in a residential area of Antwerp, Belgium, and 19 to 36  $\text{ng m}^{-3}$  in a rural area in Bolivia. BBP have been also previously determined in the ambient air in Barcelona, Spain, with a concentration ranging 0.25 – 8.0  $\text{ng m}^{-3}$ , associated with coarse ( $>7.2 \mu\text{m}$ ) and fine particulate ( $<0.5 \mu\text{m}$ ), respectively [80]. DEP was determined in Newark (USA) in the indoor air and outdoor air, with concentrations ranging from 1.60 to 2.03  $\mu\text{g m}^{-3}$ , and from 0.40 to 0.52  $\mu\text{g m}^{-3}$  [81], respectively. As compared to the concentrations of phthalates in urban or contaminated area, the concentrations in the atmosphere over the North Sea are 1-2 orders of magnitude lower. This level of phthalates determined in the North Sea, therefore, appears to represent a regional background concentration.

As shown in Figure 6, the particle-associated fractions were calculated as 2%, 46%, 75% and 78% for DEP, DBP, BBP and DEHP. Comparing to the values of 43% for DEHP, 32% for DBP reported by Giam et al. [73], these values are factor of 1.4 to 1.8 higher. The difference may be a result of the temperature difference of the sampling period or by the velocity of the sampling units. The distribution



**Figure 6.** Total concentrations of phthalates in air and particle fractions.



of phthalates in air between vapor and particles have been estimated by Staples et al. [21], based on the Junge model [26]. The estimated fractions of phthalates on the particles were 0.019, 0.039, 1.4, 7.2, and 80%, at ambient temperature. The estimated value of DEHP agrees with that determined in this study although the temperatures were different. However, the estimated values of DEP, DBP and BBP are 1-2 orders of magnitude lower than those determined by Giam et al. [9] and in this work. It suggests that temperature significantly determines the partition of phthalates between the vapor and particle phases, especially for the lighter phthalates. Consequently, both vapor and particle phases are important media for the transport of these phthalates from contamination sources to the coastal margins and the open sea.

### 5.3 Air/sea gas-exchange fluxes of phthalates

The estimated fluxes of DBP, BBP and DEHP in the North Sea and overall mass transfer coefficients were shown in Table 6. The negative values indicate a net deposition into water; in reverse, the positive values indicate a net volatilization to the atmosphere. Since the water concentrations of DMP and DEP may be underestimated, therefore, their fluxes were not calculated in this work.

**Table 6.** Air-sea vapor exchange fluxes of DBP, BBP and DEHP in the North Sea. The errors were calculated at 45% level for F and at 40% level for  $K_{OL}$ .

Sample	DBP		BBP		DEHP	
	$K_{OL}$ ( $10^{-3} \text{m day}^{-1}$ )	Flux ( $\text{ng m}^{-2} \text{day}^{-1}$ )	$K_{OL}$ ( $10^{-3} \text{m day}^{-1}$ )	Flux ( $\text{ng m}^{-2} \text{day}^{-1}$ )	$K_{OL}$ ( $10^{-3} \text{m day}^{-1}$ )	Flux ( $\text{ng m}^{-2} \text{day}^{-1}$ )
W1	$4.4 \pm 1.8$	$-686 \pm 309$	$6.6 \pm 2.6$	$-24 \pm 11$	$86 \pm 34$	$+178 \pm 80$
W2	$4.4 \pm 1.8$	$-685 \pm 308$	$6.6 \pm 2.6$	$-25 \pm 11$	$86 \pm 34$	$-58 \pm 26$
W3	$4.5 \pm 1.8$	$-773 \pm 348$	$6.8 \pm 2.7$	$-28 \pm 13$	–	–
W4	$5.0 \pm 2.0$	$-238 \pm 107$	$7.5 \pm 3.0$	$-7 \pm 3$	$98 \pm 39$	$-95 \pm 43$
W5	$4.3 \pm 1.7$	$-173 \pm 78$	$6.5 \pm 2.6$	$-5 \pm 2$	$85 \pm 34$	$-57 \pm 26$
W6	$8.8 \pm 3.5$	$-327 \pm 147$	$13 \pm 5.2$	$-10 \pm 4$	$180 \pm 72$	$+686 \pm 309$
W7	$7.1 \pm 2.8$	$-278 \pm 125$	$11.0 \pm 4.4$	$-8 \pm 4$	$140 \pm 56$	$+279 \pm 125$
W8	$3.1 \pm 1.2$	$-61 \pm 27$	$4.6 \pm 1.8$	$-4 \pm 2$	$60 \pm 24$	$-7 \pm 3$
W9	$3.0 \pm 1.2$	$-60 \pm 27$	$4.4 \pm 1.8$	$-4 \pm 2$	$57 \pm 23$	$-32 \pm 14$
W10	$4.1 \pm 1.6$	$-91 \pm 41$	$6.2 \pm 2.5$	$-5 \pm 2$	$81 \pm 32$	$-60 \pm 27$
W11	$5.8 \pm 2.3$	$-132 \pm 59$	$8.6 \pm 3.4$	$-7 \pm 3$	$110 \pm 44$	$+245 \pm 110$
Average	$4.9 \pm 2.0$	$-338 \pm 152$	$7.4 \pm 3.0$	$-13 \pm 6$	$97 \pm 39$	$+53 \pm 24$

The net fluxes of DBP ranged from  $-60$  to  $-686 \text{ ng m}^{-2} \text{ day}^{-1}$  in the North Sea. It indicates that a net deposition dominates the air-sea vapor exchange process of DBP. The net fluxes of BBP were in a range from  $-4$  to  $-28 \text{ ng m}^{-2} \text{ day}^{-1}$ , which indicate also a net deposition. The results obtained for DEHP were ranging from  $-95$  to  $+686 \text{ ng m}^{-2} \text{ day}^{-1}$ , indicating a more complex pattern of the air-sea vapor exchange for DEHP.

As shown in Table 6, the averages of  $K_{OL}$  values were  $0.0049$ ,  $0.0074$  and  $0.097 \text{ m day}^{-1}$  for DBP, BBP and DEHP, respectively. Similar effects of wind speeds on  $k_w$  as indicated by Wanninkhof [82] and Bamford et al. [59] can be seen in air-sea exchange fluxes (Table 6). Besides, although water temperatures were only varying from  $3.8$  to  $6.7^\circ\text{C}$  during this cruise, the  $H'$  values estimated at higher temperatures were higher by factor of approximately 1.5 than the average value. Both impacts from temperature and wind speed significantly increased  $K_{OL}$  values for water samples W6, W7, and by a factor of 1.5 compared to 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 rather improve the estimation of the vapor exchange fluxes than a higher accuracy of the concentration [58].

Eisenreich et al. [26] have previously estimated total deposition (dry and wet) of DBP and DEHP to the Great Lake as 3.7-16 tons per year, which indicated that the atmosphere is the major contamination source. Because of the absence of  $H$  values and air/water fluxes calculations for phthalates in their

report, it was suitable for comparison to only a limited extent. Therefore, comparison was performed with air-water vapor exchange fluxes of PAHs and PCBs in coastal regions. Nelson et al. [57] studied air-sea exchange of PAHs and PCBs in the Chesapeake Bay. Moreover, the vapor exchange fluxes of PCBs across Baltimore Harbor and the North Chesapeake Bay were well studied by Bamford and co-workers [59]. The high ratios of volatilization fluxes to deposition fluxes indicated the dominance of the water-side concentration of PCBs in the overall concentration gradient. As compared to their results, our findings for DBP indicated that the air-side concentrations dominated the overall concentrations gradients, which were comparable to those of lighter PAHs. As compared to PCBs, the difference for overall concentration gradients can be addressed to their  $H'$  values. For example,  $H'$  values of PCBs estimated by Bamford et al. [59] are 1-3 orders of magnitude higher than that of DBP. It indicates that, besides the effect on  $K_{OL}$ , temperature determined  $H'$  values could change the overall concentration gradients with the interface temperature increasing in warm season. If it is supposed that the concentrations of phthalates were less variable through all the seasons, air-sea exchange fluxes and directions might significantly change in warm season. Consequently, decreasing deposition fluxes for DBP could be expected in summer. BBP might show a similar pattern like Chrysene [57], based upon their comparable  $K_{OL}$  values and their concentration gradients. As for DEHP, it can be expected that increasing temperature in warm season will increase the potential of volatilization based on the significantly increasing  $H'$  value.

## 6. AQUEOUS AND ATMOSPHERIC CONCENTRATIONS OF ALKYLPHENOLS AND DERIVED AIR/SEA GAS-EXCHANGE FLUXES

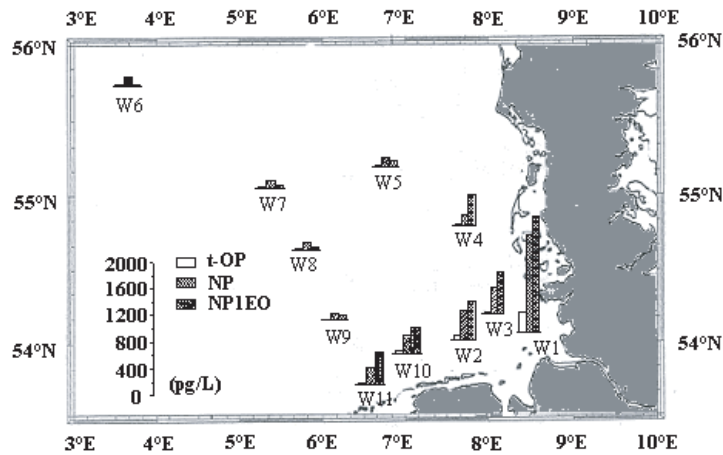
### 6.1 Concentrations of alkylphenols in sea water

Total concentrations of NP in sea water and TSM ranged from 90 to 1400  $\text{pg L}^{-1}$  and less than MDL (10  $\text{pg L}^{-1}$ ) to 86  $\text{pg L}^{-1}$ , respectively. Water-phase  $t$ -OP was determined with concentrations ranging from 13 to 300  $\text{pg L}^{-1}$ . In the TSM-phase,  $t$ -OP concentrations were very close to the level of MDL. NP1EO concentrations ranged between 28 and 1660  $\text{pg L}^{-1}$  in the dissolved phase, and from below the MDL to 68  $\text{pg L}^{-1}$  in the TSM.

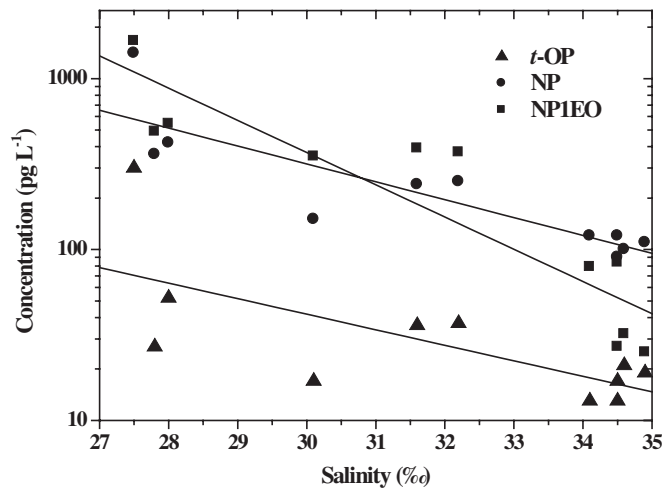
Figure 7 shows that high concentrations occurred in the water samples that were collected near River plumes, and an obviously spatial distribution profile with decreasing concentrations from the coast to the open sea. These results agree well with the distribution pattern determined by Heemken et al. [43] and Bester et al. [83]. 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  $\text{pg L}^{-1}$ , respectively. Compared with other coastal waters and open ocean the concentrations of APs in the North Sea are in a relatively low level. 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.

In Figure 8, 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 origin of the current. Together, with the investigations done by Heemken et al. [43], Bester et al. [83], and Jonkers et al. [85], 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  $\text{pg L}^{-1}$  for  $t$ -OP, 8 – 86  $\text{pg L}^{-1}$  for NP and 7 – 68  $\text{pg L}^{-1}$  for NP1EO. As compared to the dissolved concentrations, TSM bound fractions were  $5 \pm 1\%$  for  $t$ -OP,  $6 \pm 2\%$  for NP and  $3 \pm 1\%$  for NP1EO, which are very comparable to their  $\log K_{OW}$  sequence: NP (4.48) > NP1EO (4.17 - 4.20) >  $t$ -OP (4.12) [86]. However, these fractions were lower by factor of



**Figure 7.** Spatial distributions of *t*-OP, NP and NP1EO in the North Sea. The concentrations are marked on the mean sample locations.



**Figure 8.** Changing of concentrations of *t*-OP, NP and NP1EO with salinity gradients.

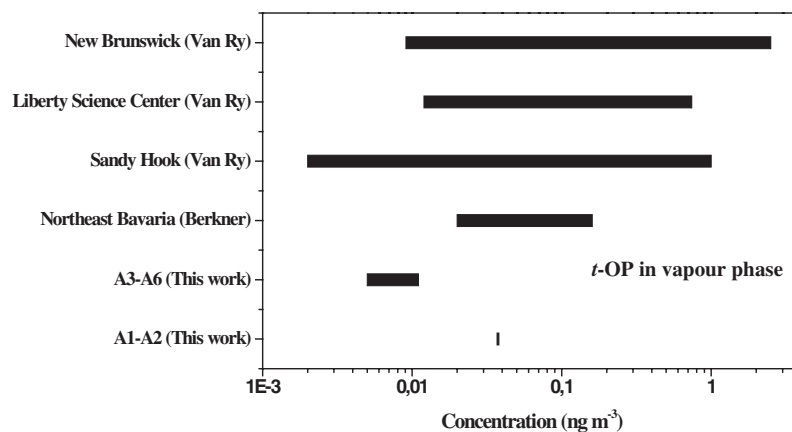
2 – 5 than the reported values found in Tokyo Metropolitan area [87] and in the Lower Hudson River Estuary [88]. The likely reason is the low amount of TSM present in the North Sea as compared to those in rivers and estuaries.

## 6.2 Air concentrations of alkylphenols

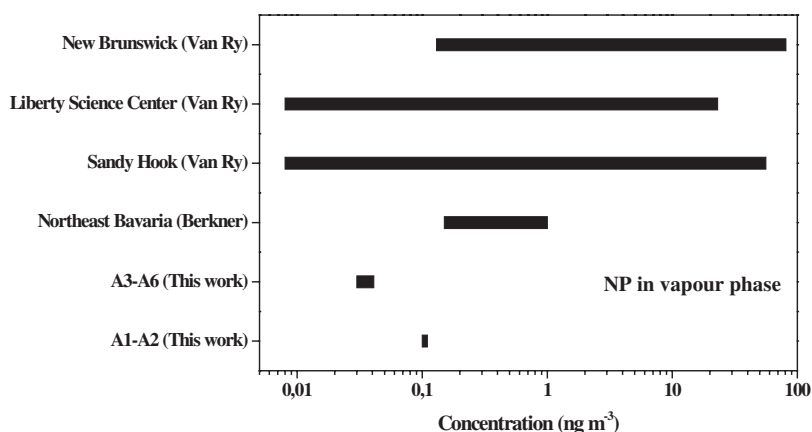
NP, *t*-OP were detected in the vapour phase of the air samples. Relatively high concentrations were present in the air samples A1 and A2, which were collected while the ship was steaming along the Northeast German Coast. The concentrations in the air samples A3-A6 are lower by a factor of 3-5. NP1EO was unexpectedly determined in the particle phase with a concentration range from 14 to 50  $\text{pg m}^{-3}$ . Consequently, we re-examined the NP1EO in the vapour phase. Concentrations of 31 and 14  $\text{pg m}^{-3}$  were found in A1 and A2, and 4 - 9  $\text{pg m}^{-3}$  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 indoor dusts [14] and in the atmosphere surrounding an industrialised area of Prato (Italy) [89]. This was the first time that this particular compound was found in the marine atmosphere. The air samples collected over the sea surface are often influenced by wind pattern. 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  $7 \text{ m s}^{-1}$ , the aerosol formation might be dominated by sea spray and sea salts [90]. Therefore, atmospheric samples were a mixture of land-based, coastal and oceanic air and aerosols. 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.

Comparisons of atmospheric APs concentrations in the North Sea described here have been made with previously reported data in the forest area in Southeastern Germany [42] and urban and coastal sites at the Lower Hudson River Estuary [10, 88]. Figure 9a, 9b shows that atmospheric *t*-OP and NP



**Figure 9a.** Range of measured *t*-OP concentrations in the atmosphere over the North Sea and comparison with other reported values.



**Figure 9b.** Range of measured NP concentrations (in total isomers) in the atmosphere over the North Sea and comparison with other reported values.

in the North Sea were in the lower concentration range. 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 waters, the terrestrial use of APs is also a significant source for atmospheric APs [91].

### 6.3 Air/sea gas-exchange fluxes of alkylphenols

The estimated fluxes of *t*-OP and NP in the North Sea and overall mass transfer coefficients are shown in Table 7. 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 deposition dominate the air-sea vapour exchange process of *t*-OP and NP in the North Sea.

**Table 7.** 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	$11 \pm 4$	$-62 \pm 30$	$14 \pm 6$	$-23 \pm 11$
W2	$11 \pm 4$	$-71 \pm 34$	$14 \pm 6$	$-26 \pm 13$
W3	$12 \pm 5$	$-81 \pm 39$	$15 \pm 6$	$-30 \pm 14$
W4	$13 \pm 5$	$-30 \pm 14$	$16 \pm 6$	$-6 \pm 3$
W5	$11 \pm 4$	$-22 \pm 10$	$13 \pm 5$	$-4 \pm 2$
W6	$22 \pm 9$	$-41 \pm 20$	$27 \pm 11$	$-8 \pm 4$
W7	$18 \pm 7$	$-35 \pm 17$	$22 \pm 9$	$-7 \pm 3$
W8	$8 \pm 3$	$-12 \pm 6$	$10 \pm 4$	$-3 \pm 2$
W9	$7 \pm 3$	$-12 \pm 6$	$9 \pm 3$	$-3 \pm 2$
W10	$11 \pm 4$	$-16 \pm 8$	$13 \pm 5$	$-5 \pm 2$
W11	$15 \pm 6$	$-24 \pm 12$	$18 \pm 7$	$-7 \pm 4$
Average	$13 \pm 5$	$-39 \pm 19$	$16 \pm 6$	$-12 \pm 6$

As shown in Table 7, the averages of  $K_{OL}$  values were  $0.013$  and  $0.016 \text{ m day}^{-1}$  for *t*-OP and NP, respectively. 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. Again it was demonstrated that a better understanding of the mass transfer coefficient would improve the estimation of the vapor exchange fluxes rather than a higher accuracy of the concentrations [58, 92].

Van Ry et al. [88] estimated the air-water exchange fluxes for NP in the lower Hudson River Estuary, which ranged from  $+25$  to  $+67 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$  in the upper bay and from  $+1.2$  to  $+9.5 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$  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 [92]. As estimated by Xie et al. [92], the  $H'$  value of *t*-OP and NP at  $298.15 \text{ K}$  is 8 times higher than that at  $278.15 \text{ K}$ . 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 can be derived 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 a 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  $\text{ng m}^{-3}$  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 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.

## 7. SUMMARY AND CONCLUSIONS

High-volume sampling methods with PAD-2 resin columns for seawater and PUF/XAD-2 column for atmospheric samples are powerful and suitable tools for the collection of trace APs and the phthalates in the environment. The field blanks are partly eliminated with a self-designed glass connector for the in-situ pump and active carbon cartridges for the soxhlet extractor and the rotation evaporator. These developments are not only a benefit for reducing the blanks for APs and the phthalates, but also suitable for controlling the blank levels of other organic pollutants. BSTFA + 1% TMCS was selected for the derivatization of *t*-OP, NP and NP1EO. The instrument detection limits of APs reached picogram in absolute amount. Furthermore, the reagent of BSTFA does not react with the phthalates under the optimized condition, which allows detecting *t*-OP, NP, NP1EO and the phthalates simultaneously. The soxhlet extraction with the modified soxhlet extractor combined with the active carbon cartridge and the distilled solvent is very convenient for the operation and achieves detection of very low contaminations. The recoveries of *t*-OP, NP, NP1EO and the phthalates achieved for the entire procedure are satisfactory. The loss of the phthalates during sampling and laboratory treatments could be fully recovered using the deuterated compounds. Although the large volume sampling and soxhlet extraction procedures are time consuming and labor intensive, they eliminate matrix, feature high enrichment capacity and allow method detections in the  $\text{pg L}^{-1}$  and  $\text{pg m}^{-3}$  for sea water and air samples.

Concentrations of NP, *t*-OP and NP1EO, DMP, DEP, DBP, BBP, and DEHP have been simultaneously determined in the surface sea water and atmosphere of the North Sea. The concentrations of *t*-OP, NP, and NP1EO in dissolved phase were 13-300, 90-1400, and 17-1660  $\text{pg L}^{-1}$ . In total suspended matters (TSM), the analytes were detectable only in the samples collected close to the coast with concentrations ranging from 1 to 84  $\text{pg L}^{-1}$ . DBP, BBP, and DEHP were determined in the water phase with concentrations ranging from below the method detection limit to 6.6  $\text{ng L}^{-1}$ . 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 and the phthalates present in the North Sea.

Atmospheric concentrations of NP and *t*-OP ranged from 7 to 110  $\text{pg m}^{-3}$ , which were one to three orders of magnitude below coastal atmospheric concentrations reported before. NP1EO was detected in both vapor and particle phases, which ranged from 4 to 50  $\text{pg m}^{-3}$ . The concentrations of the phthalates in the atmosphere ranged from below the method detection limit to 3.4  $\text{ng m}^{-3}$ .

Air-sea vapor exchanges of *t*-OP and NP, DnBP, BBP and DEHP were estimated using the two-film resistance model based upon relative air-water concentrations. The average of air-sea exchange fluxes was  $-12 \pm 6 \text{ ng m}^{-2} \text{ day}^{-1}$  for *t*-OP,  $-39 \pm 19 \text{ ng m}^{-2} \text{ day}^{-1}$  for NP,  $-338 \text{ ng m}^{-2} \text{ day}^{-1}$  for DBP and  $-13 \text{ ng m}^{-2} \text{ day}^{-1}$  for BBP which indicates a net deposition is occurring. The air-sea exchange fluxes

of DEHP were ranging from  $-95$  to  $+686 \text{ ng m}^{-2} \text{ day}^{-1}$ . The average value of  $+53 \text{ ng m}^{-2} \text{ day}^{-1}$  for DEHP suggested a net volatilisation from the North Sea. These results suggest that the air–sea vapor exchange is an important process that intervenes in the mass balance of alkylphenols and the phthalates in the North Sea.

The concentrations of *t*-OP, NP and NP1EO present over land and the North Sea suggested that apart from the emission of a highly contaminated water body, terrestrial applications of NPEOs and APs are significant sources for their atmospheric occurrence. Consequently, via atmosphere, both APs and the phthalates may undergo a long distance transport and accumulate in the cold region. Air-sea exchange fluxes of *t*-OP and NP and the phthalates 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 the phthalates. The net fluxes indicate that the air–sea exchange is significant and, consequently the open ocean and polar areas will be an extensive sink for APs and the phthalates.

As many physicochemical properties governing the environmental fate of organic pollutants are temperature dependent, there is a need to determine the gas-particle partitioning coefficients of APs and phthalates and the Henry's Law Constants of the phthalates over the range of ambient temperatures. Knowledge of the transport mechanisms of APs and phthalates via the atmosphere and the air-sea exchanges might be significantly increased by a re-evaluation with improved data of physicochemical properties.

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