

# INVESTIGATION ON THE DISTRIBUTION AND AIR-SEA EXCHANGE OF ALKYLPHENOLS AND PHTHALATES IN THE GERMAN BIGHT

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**Abstract**

Phthalates are a group of organic chemicals used mainly as plasticizers. Due to their widespread use and their ability to leach from various products, phthalates are ubiquitously considered as environmental contaminations. Tertiary octylphenol (*t*-OP), nonylphenol (NP) and nonylphenol monoethoxylate (NP1EO) are anaerobic breakdown products of widely used nonionic surfactant alkylphenol polyethoxylates (APEOs). The phthalates and alkylphenols (APs) are currently of environmental concern because of their toxicity, and endocrine disrupting effects. The moderately persistent ability of APs and the phthalates suggests there is a continuing for an understanding of their transport and distributions in the environment. This study has been designed to improve our understanding of the distribution pattern and transport mechanisms of APs and the phthalates in the coastal margins, especially the roles of the air-sea exchanges in these processes.

Henry's Law Constants (HLC) were determined for the diastereomeric mixture of NP and *t*-OP in artificial seawater over given temperature range using a dynamic equilibrium system. The reassessment of the air/water vapour exchange based on experimentally derived HLC made for NP in the Lower Hudson River estuary (New York, USA) shows that the atmosphere is both a sink and a source of APs in the coastal regions.

The comprehensive studies on the analytical methodology demonstrate that the large volume sampling methods with PAD-2 column for sea water and PUF/XAD-2 column for air are powerful and suitable for the collection of trace APs and the phthalates in the environment. The field blanks were significantly eliminated with modifications for the in-situ pump and active carbon cartridge for the soxhlet extractor and the rotation evaporator. Although the large volume sampling and soxhlet extraction procedures are time consuming and labour – intensive, they eliminate the matrix, feature high enrichments 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, NP1EO and the phthalates have been simultaneously determined in the surface sea water and atmosphere of the North Sea. A decreasing concentration profile of NP, *t*-OP, NP1EO and the phthalates appeared as the distance from the coast increased to the central part of the North Sea. Air-sea exchanges of *t*-OP, NP, DBP, BBP, and DEHP were estimated using the two-film resistance model based upon relative air-water concentrations. The average of air-sea exchange fluxes 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 and the phthalates in the North Sea.

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## 1. Introduction

A new hypothesis concerning the biological significance of certain chemicals on wildlife was formulated in 1991, now known as the endocrine disruptor hypothesis (Colborn and Clement 1992; Colborn et al., 1993; Johnson 2004). In the last two decades, a great number of studies have demonstrated that there are several classes of chemicals that can behave as biologically relevant signals, capable of alternating the control of gene expression at the molecular level and interfering with homeostatic feedback loops at the development and function level (Mclachlan 2001; Myers et al., 2003). Among these chemicals, many, including PCBs, DDT, HCH and dioxins, are semi-volatile, persistent, and are capable of long distance travel through atmospheric circulation (Atlas and Giam 1981; Bidleman 1988; Eitzer and Hites 1989; Bright et al., 1995; Kalantzi et al., 2001). However, some of these chemicals, e.g. phthalates and alkylphenols (APs) are still manufactured and consumed worldwide even though they have been clearly proved to be toxic to aquatic organism and as an endocrine disruptors. Since 1978, phthalates have been detected from marine environment and remote regions such as in the Arctic, with concentrations comparable to that over land (Giam and Atlas 1978). As for alkylphenols, they typically are not released directly into the environment, but rather are formed as the anaerobic biological breakdown products of widely used nonionic surfactants, alkylphenol ethoxylates (APEOs) (Giger et al., 1984). Concentrations of APs and its parent compounds have been measured worldwide in all compartments of the environment and even in food products for human consumption (Dachs et al., 1999; Kolpin et al., 2002; Guenther et al., 2002; Rudel et al., 2003). The similarities among APs, phthalates and classical persistent organic pollutants (POPs) such as PCBs and PAHs suggested a need for understanding their transport and distributions in the environment.

### *1.1. Sources of alkylphenols and phthalates as environmental pollutions*

Phthalates are manufactured worldwide on a large scale, being mainly produced for use as plasticisers 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 (Peakall, 1975). In the early 1980s, world production of phthalates was estimated to be 2 million t yr<sup>-1</sup> (Schmitzer et al., 1988). 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 plasticisers, 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 plasticiser compounding, and during the production of adhesives and coatings; from the use and disposal of materials containing phthalates or landfilling of 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 EU are not available. However, it was estimated that 3-5% of the market volume of the phthalates released into the environment.

Alkylphenol ethoxylates (APEOs) are nonionic surfactants with a worldwide production of approximately 700,000 t yr<sup>-1</sup> and used in a wide range of applications (Jonkers et al., 2005). 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 was used in many other industrial applications, e.g. as wetting agents, emulsifiers of pesticides, dispersants, solubilizers, foaming agents and polymer stabilizers (Ying et al., 2002). 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 (James, 1999). It was estimated that NP and NPEOs enter into the air and water at a rate of 850 t yr<sup>-1</sup>.

### *1.2. Environmental fate and persistence*

#### *1.2.1. Environmental distribution of the phthalates*

The release of phthalates directly to the atmosphere is believed to be the most important means of entry into the environment (Staples et al., 1997). As based on their physicochemical properties (see Tab. 1), they could redistribute to different media, e.g. air, water and soil or sediment. The level I calculation of the EQC fugacity model predict that when the phthalates are released into environment, approximately 0.1-0.4% are found in air, 0.1-96.3% in soil, 3.5-97.8% in water and 0.5-2.2% in sediment (Cousins et al. 2003). DMP and DEP are more present in air and water as a result of high vapour pressure and high solubility in water. DBP is moderately adsorbed to soil (Howard, 1989; Zurmühl et al., 1991; EHC 189, 1997). But it

forms complex with water-soluble fulvic acid that might increase its mobilization and reactivity in soil to some degree (Matsuda and Schnitzer, 1971). As compared to the low molecule phthalates, DEHP has a strong tendency to be absorbed by the soil. However, it can form a complex with water-soluble fulvic acid that may increase its mobilisation and reactivity in soil. Moreover, the phthalates may enter the water system via wastewater treatment plants, rainfall, runoff and atmospheric deposition. In Canada, Eisenreich et al. (1981) reported that atmospheric transport is a significant source of the phthalates in the Great Lakes, with a calculated total deposition of 48 t yr<sup>-1</sup> to the five Great Lakes.

**Table 1.** Physicochemical properties of the phthalates

Phthalate	DMP	DEP	DnBP	BBP	DEHP	DOP
<b>Formula</b>	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>
<b>Molecular weight</b>	194.2	222.2	278.4	312.4	390.6	390.6
<b>Boiling point (°C)</b>	282.4 <sup>a</sup>	297.8 <sup>a</sup>	340.0 <sup>b</sup>	387.45 <sup>b</sup>	384.0 <sup>b</sup>	-
<b>Le Bas Molar volume (mL mol<sup>-1</sup>)<sup>c</sup></b>	206.4	254.0	342.8	364.8	520.4	520.4
<b>Melting point (°C)</b>	5.5	-40	-35	-35	-46	-
<b>S<sub>w</sub> (mg L<sup>-1</sup>)<sup>c</sup></b>	5200	591	9.9	3.8	0.0025	0.0025
<b>V<sub>P</sub> (Pa)<sup>c</sup></b>	0.263	6.48 × 10 <sup>-2</sup>	4.73 × 10 <sup>-3</sup>	2.49 × 10 <sup>-3</sup>	2.52 × 10 <sup>-5</sup>	2.52 × 10 <sup>-5</sup>
<b>H<sub>0</sub> (Pa m<sup>3</sup> mol<sup>-1</sup>)<sup>c</sup></b>	9.78 × 10 <sup>-3</sup>	2.44 × 10 <sup>-2</sup>	0.133	0.205	3.95	3.95
<b>Log K<sub>OW</sub><sup>c</sup></b>	1.61	2.54	4.27	4.70	7.73	7.73
<b>Log K<sub>OA</sub><sup>c</sup></b>	7.01	7.55	8.54	8.78	10.53	10.53
<b>ΔH<sub>V,B</sub> (kJ mol<sup>-1</sup>)<sup>* b</sup></b>	-	-	61.95	58.80	67.20	-
<b>ΔH<sub>V</sub> (kJ mol<sup>-1</sup>)<sup>d</sup></b>	-	-	84.13	84.32	92.47	-

\* Enthalpy of vaporization at boiling point.

<sup>a</sup> Buckingham and Donaghy, (1982).

<sup>b</sup> California EPA, (2001).

<sup>c</sup> Cousins and Mackay, (2000).

<sup>d</sup> Estimated Enthalpy of vaporization at 25 °C.

### 1.2.2. Environmental fate of the phthalates

The phthalates have several degradation pathways, e.g. photo degradation in the atmosphere, bio-degradation in water, and anaerobic degradation in sediments and soil (Staples et al. 1997). The contributions of hydrolysis to the overall environmental degradation of the phthalates are expected to be low. Photo-oxidation by OH radicals contributes more to the elimination of the phthalates from the atmosphere. Reaction with OH radicals is generally

the most important photo degradation process for organic chemicals pollutants in the atmosphere. As presented in Tab. 2, 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 indicated that susceptibility to photo degradation of phthalates increases as alkyl chain length increasing. The photo degradation half-lives presented in Tab. 2 are calculated with air oxidation program (AOP) (Staples et al., 1997) developed by Atkinson and recalculated (the blankets) with an updated version of (AOP, AOPWIN 1.89) (Peterson and Staples 2003). 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. (1987) 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 absorbed 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 vapour phase. It seems that sorption to atmospheric particles have no significant effect on the overall rate of indirect photo degradation of the phthalates.

**Table 2.** 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)

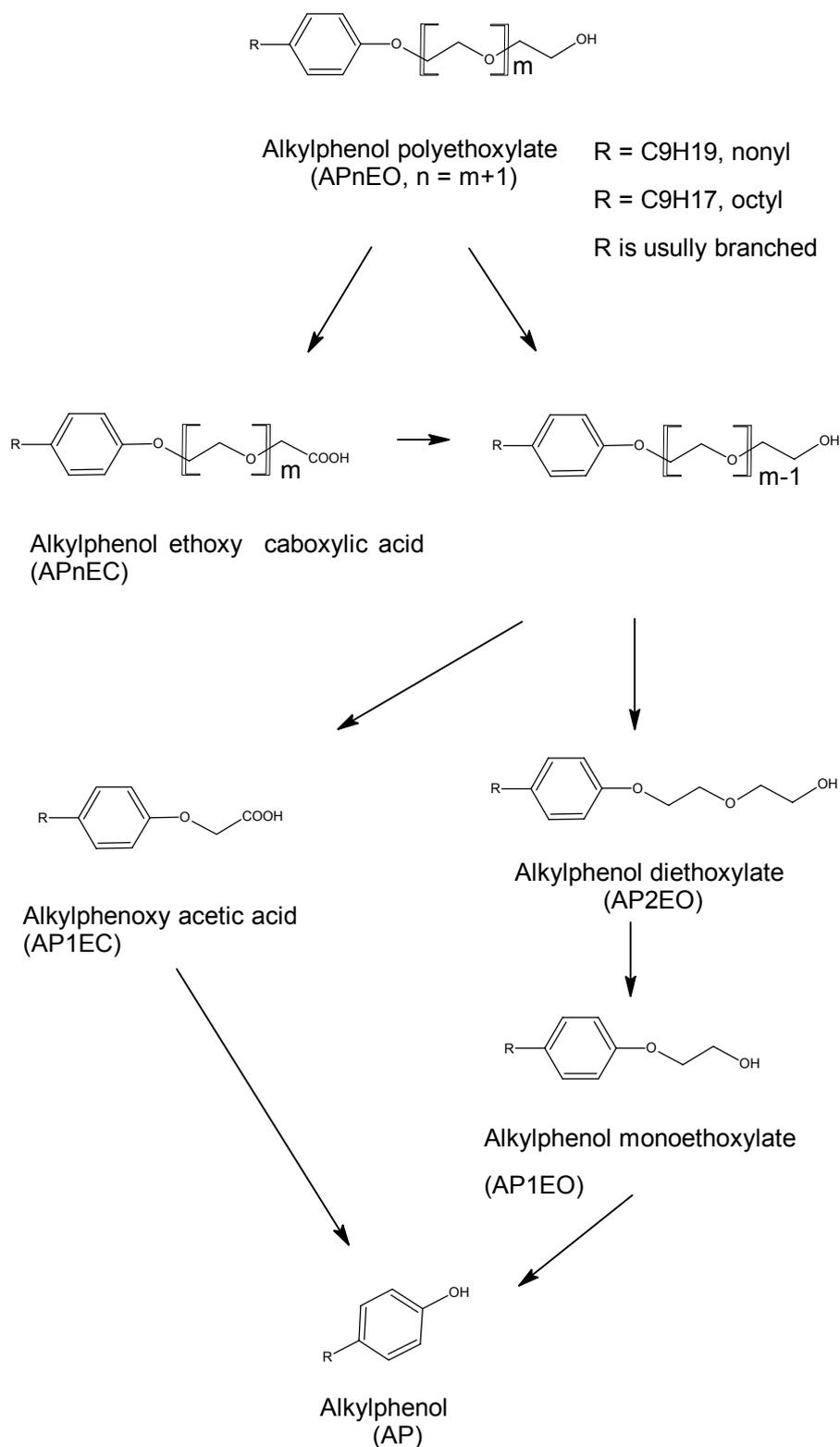
<sup>e</sup> Staples et al., 1997.

<sup>f</sup> Yuan et al., 2002.

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

Many studies have been performed on the primary degradation for different phthalates in aerobic aquatic environments (Staples et al., 1997; Peterson and Staples 2003). The pseudo-first-order rates of primary biodegradation under environmentally realistic conditions are in a range of 0.2-2.0 d<sup>-1</sup> for most of phthalates, suggesting that the phthalates will rapidly degrade in the aquatic environment. The aerobic biodegradation half-lives of the phthalates are summarized in Tab. 2, which ranges from 0.3 to 30 days. As for the biodegradation occurring in sediment, Tagatz et al. (1986) reported primary biodegradation rates in sediments of 3-4 weeks for DBP. In an anaerobic test system, Madsen et al., (1995) found that ultimate biodegradation of DMP and DIBP added to either a freshwater swamp or marine sediment was <30% after 56 days. Recently, Yuan et al. (2002) studied the microbial degradation rates of eight phthalates under aerobic and anaerobic conditions in river water and sediments. Respective average half-lives were measured from 2.5 to 14.8 days under aerobic conditions and from 14.4-34.7 days under anaerobic conditions (See Tab. 2). Both laboratory experiments and field studies proved that primary degradation of the phthalates in water, sediment, and soil compartments is expected to be controlled by biodegradation rather than abiotic loss mechanisms, which suggests that the phthalates are not expected to be highly persistent in most environments. However, longer half-lives are likely under anaerobic conditions, and in cold and nutrient poor environments. Furthermore, their biodegradation rates may be reduced by low bioavailability. Furtmann (1993) has found that the degradation stops if the phthalates concentrations low, down to a level of several ng L<sup>-1</sup>. One suggested explanation is that bacteria are unable to produce the necessary degradative enzymes either because a minimum substrate concentration is necessary to induce them or because the substrate is at too low a level to be transported into the cell (Peterson and Staples, 2003). It implies that low phthalate concentrations may be persistent in the aquatic environment.

The persistence of the phthalates was predicted with EQC level II modeling (Cousins et al., 2003). 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 ambient conditions. These facts suggest it is necessary for a detailed investigation of phthalates in the cold regions.



**Figure 1.** Degradation pathways of Alkylphenol ethoxylates (Ying et al., 2002)

### 1.2.3. Environmental fates of nonylphenol ethoxylates 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 Fig. 1. It was suggested that under aerobic conditions, NPEOs degrades to 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 (Giger et al., 1984). The three most common groups of intermediates reported were summarized as follows (Ying et al., 2002): (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, are persistent and toxic in the environment (Soto et al., 1991; Renner, 1997). Previous investigations showed that NPEOs metabolites degraded more easily under aerobic, than under anaerobic conditions (Brunner et al., 1988). 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 (Nasu et al., 2001).

In the US, the measured removal rates from STPs were from 93% to 99%, with an average of 97% (Naylor, 1995). In Italy, removal of NPEOs during sewage treatment was estimated as  $93 \pm 4\%$  (DiCorcia et al., 2000). Swiss sewage plants performed less well, ranging from 47% to 89% with an average rate of 74%. The different removal rates reported perhaps are due to the design or operating efficiency of different treatment plants. However, in the US case, effluent concentrations of NP ranged from  $<1$  to  $15 \mu\text{g L}^{-1}$ , and those of NPEOs varied from  $<5$  to  $260 \mu\text{g L}^{-1}$  (Naylor, 1995).

Investigations have been performed for the degradation of NPEOs and their metabolites in river water, sea water, and sediment, as well as in soil. Wide ranges of degradation rates were reported based on the means of the test system and conditions. Yoshimura (1986) and Manzano et al. (1999) reported that half-lives of 4 days in river water and  $<10$  days in sediments for primary degradations of NPEOs. Over an ambient temperature range, metabolites, e.g. NP2EO, NP1EO, NP2EC and NP1EC were generated during the biodegradation process, and did not disappear even after 30 days. Similar results were obtained from a static die-away test of NPEOs in estuary water in the dark at  $28 \text{ }^\circ\text{C}$  for 183 days (Potter et al., 1999).

Laboratory studies have shown the possible degradation steps for NPEOs under aerobic environmental conditions. Jonkers et al. (2001) showed that NPEOs with long ethoxylate chains degrades first to NP with carboxylated ethoxylate chains, forming long chained carboxylated NPEOs and that the ethoxylate chains were degraded next. Oxidation of the nonyl-chain was determined to occur at the same time as carboxylation of the ethoxylate chain. In fact, although they found that greater than 99% of the NPEOs were degraded after 4 days, metabolites were still present in the reactors for 31 days after the experiment began. This demonstrates that NPEOs are not very easily and ultimately biodegradable, although the initial NPEOs are quickly degraded (Porter and Hayden, 2004). Maki et al. (1996) studied the biodegradation product of NPEOs with river microbial consortia, and identified those NPECs as the final breakdown products under aerobic conditions. Moreover, many studies proved that NP seems not to be the end product or primary degradation product of NPEOs under aerobic conditions (John and White, 1998; Snyder et al., 1999; Johnson and Sumpter et al., 2001; Jonkers et al., 2001).

Understanding NPEOs degradation in anaerobic environment is very important because these conditions are common during wastewater transport and treatment (Porter and Hayden, 2004). Anaerobic conditions are purposely created during certain wastewater treatment process such as anaerobic sludge digestion. Anaerobic zones may also occur in sewage lines, storm drains, and pipes as the wastewater is in transit to the treatment facility. Thus, NP may be produced during wastewater treatment and transport. Brunner et al. (1988) Previously detected NP did not accumulate during aerobic digestion, however, significant NP accumulation occurred during anaerobic sludge digestion. It was estimated that 50% of NPEOs in the sewage were transformed to NP. In addition, Dicorcia et al. (2000) have shown that under aerobic conditions, 66% of the influent NPEOs were converted to NPEC. As the intermediate degradation products are not easily mineralized (Lee and Peart, 1998), it is possible that these intermediates can be converted to NP if the conditions become anaerobic (Maki et al., 1996; Thiele et al., 1997; Potter et al., 1999; Ejlertsson et al., 1999).

Under anaerobic conditions, NP was regarded as a significant final product of NPEOs biodegradation (Giger et al., 1984). Ejlertsson et al. (1999) found that NP is very resistant to further anaerobic conditions, and might be considered as a persistent degradation product of NPEOs. Lalah et al. (2003) investigated the fate of NP with  $^{14}\text{C}$  labeled isomers. It was found that NP isomers should be resistant to biodegradation in both lake water and sediment. Hesselsoe et al. (2001) found that NP added to soil samples was not biodegraded after three months under anaerobic conditions. Shang et al. (1999) studied the persistence of NPEOs and

their metabolites in the sediments in the Strait of Georgia, British Columbia, Canada. There was very little evidence of a shift from higher NPnEO to lower NPnEO on going from the surface to deep in the core that would indicate sequential breakdown of the ethoxy groups with time. Peak concentrations were observed at NP, NP1EO and NP9EO-NP11EO. A half-life time was then calculated to be about 60 years in the sediment. However, many studies showed that the purported metabolites of NPEOs, e.g. NP, NP1EO and NP2EO can be biodegraded in aerobic situations. Ekelund et al. (1993) found that under aerobic conditions, microorganisms had mineralized 50% of the NP added to a sea water /sediment sample after a 58-day trial. Moreover, Hesselsoe et al. (2001) reported the half-life of NP in soil under aerobic conditions was 3 to 6 days. Additionally, Yuan et al. (2004) investigated the biodegradation of NP1EO and NP by aerobic microbes in river sediment. Half-lives for NP and NP1EO added ranged from 13.6 to 99.0 days and 69.3 to 115.5 days, respectively.

In anaerobic conditions, it was found that NP is not effectively degraded. Ying et al. (2003) reported that 4-n-NP showed no degradation within 70 days under anaerobic conditions in groundwater. Besides, NP is preferentially adsorbed into the solids in the wastewater stream and the system. Sekela (1999) found significant accumulation of NP on the solids near wastewater treatment plant (WWTP) discharge points. It was estimated that 70% of NP in the WWTP was removed by the application of sludge and the rest was discharged into the river. In fact, concentrations of NP were often detected in some microgram per liter in the effluents (Gehring et al., 2004). In Switzerland, it was estimated that  $0.3 \text{ g m}^{-2} \text{ y}^{-1}$  of NP are applied with sewage sludge to Swiss soil (Brunner et al., 1988).

Knowledge of 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 (CSF 01/12; 2001). Pelizzetti et al. (1989) studied photocatalytic degradation of NPEOs with  $\text{TiO}_2$  particulates as photocatalyst. They found that a competitive attack of OH radicals on the ethoxy chain and on the aromatic ring. As a result, complete conversion to  $\text{CO}_2$  has been demonstrated. Therefore, it indicates that photodegradation of NPEOs may quantitatively minimize the accumulation of NP during the treatment.

#### *1.2.4. Degradation of *t*-OP*

As shown in Fig. 1, octylphenol ethoxylates (OPEOs) undergo the similar degradation pathway as NPEOs. Because OPEOs and *t*-OP takes only 15% of the production of APEOs, they have not been given as much attention as NP. Nevertheless, some studies on the

degradation of *t*-OP have been done together with NP and NPEOs. Ball et al. (1989) studied the biotransformation of octylphenol polyethoxylate residues under aerobic and anaerobic conditions. Data from 24-h activated sludge inoculation showed no OPEOs (1-5) in the control, however, OPnEC ( $n > 2$ ) were formed. These results confirmed that those OPEOs could be precursors to the OPECs found in the wastewater treatment plant effluent (Ahel et al., 1987) and indicated that OPEOs can be rapidly transformed into OPECs under these conditions. Moreover, due to the chemical synthesis procedure, no OPEOs biotransformation intermediates with a modified octyl groups were observed. Octyl groups are predominantly 1,1,3,3-tetramethylbutyl (tertiary octyl) (Ahel et al., 1987), therefore tertiary octylphenol (*t*-OP) is the typical biodegradation products of OPEOs and their intermediates (Hawrelak, et al., 1999). Ying et al. (2003) reported that *t*-OP in the aquifer material showed no degradation under both aerobic and anaerobic conditions within 70 days.

### *1.3. Environmental impact and endocrine disrupting effects*

#### *1.3.1. Environmental impact and endocrine disrupting effects of phthalates*

Toxicities of the phthalates have been a subject of discussion and public concern. Some phthalates have been linked to liver and kidney damage, and characterized as endocrine disruptors (Petrovic et al., 2001; Gomez-Hens and Aguilar-Caballos, 2003). Experimental evidence has shown that certain phthalates can disrupt endocrine function and induce reproductive and developmental toxicity (Adibi et al., 2003; Gray et al., 2000; Heindel et al., 1989). DBP, BBP and DEHP have been found to act as antiandrogens and can cause decreased testosterone production in the male fetus resulting in malformations in the external genitalia, degeneration of the seminiferous tubules and reduced sperm production (Gray et al., 2000; Sharpe, 2001). Studies on effects of DEHP on sexual differentiation in juvenile Atlantic salmon have shown that DEHP and its metabolites may affect the metabolism of steroid hormones thus resulting in skewed sex ratios (Norrgrén et al., 1999).

Many studies have been performed for carcinogenic effects of the phthalates. Without doubt, evidence suggests that the phthalates do indeed induce cancer, mostly in the liver of rats and mice (Gray et al., 1977; Schmezer et al., 1988). Concerning reproductive and developmental toxicity studies, Nakamura et al. (1979) found that the non-effective maximum levels of DEHP in mice were 0.065, 0.8, and 0.68 mL kg<sup>-1</sup> for death, and size and skeletal abnormalities. Arcadi et al. (1998) reported that DEHP damaged offspring kidney, liver and testes in reproductive toxicity study. DEHP and DBP have been proved to affect enzymes that

are involved in catalysing the hydroxylation of fatty acids in the electron transport chain, which may cause alternations of physiological processes in the cells (Okita et al., 1992). Another study showed that DEHP could cause morphological changes in the cell and cause decreased levels of gap junction intercellular communication. These changes could potentially contribute to the development of cancer (Melnick, 2001). As regarding to the reproductive and neurobehavioral toxicity of the phthalates, Tanaka (2002; 2003; 2005) reported that no significant effects on the offspring sex ratios of mice in a cross-mating method. Nevertheless, James (2003) mentioned that to guard against the possibility that DEHP treatment has opposite effects on the sex ratios of offspring of male and female mice, one need to know the offspring sex ratios of mating of treated females with untreated males, and of treated males with untreated females. There is also still a need for a better understanding the reproductive effects of material illness, e.g. phthalates.

American scientists, for the first time, documented human exposure to phthalates by determinations of the monoester metabolites in human urine (Blount et al. 2000). Austria, Denmark, Finland, France, Germany, Norway and Sweden have unilaterally banned the phthalates in PVC toys for children under three years old. In December of 1999, the EU placed an emergency ban on six of the phthalates, including DBP, BBP, DEHP, dioctyl phthalate (DOP), diisononyl phthalate and diisodecyl phthalates, in soft PVC toys and children products meant to be placed in the mouths of children under the age of three (European Commission, 1999). Canadian Environmental Protection Act (CEPA) has concluded that DEHP may enter the environment in a quantity or concentration or under conditions that may constitute a danger in Canada to human health (Canadian Environmental Protection Act, 1994). Although the environmental level of the phthalates is likely lower than the level leading to a risk, there remains a need for better information to adequately characterise the risk to plants exposed via the atmosphere (EU Risk Assessment Report, 2003).

### *1.3.2. Environmental impact and endocrine disrupting effects of NP, t-OP and NPEOs*

Because of worldwide spread of alkylphenol and alkylphenol ethoxylates in huge quantity, interests have been increasing in understanding if alkylphenols present a significant risk to humans or environmental health. Laboratory studies have shown alkylphenols are toxic to fish and interfere with reproductive mechanism of animals. Acute toxicity of NPEO to fish typically ranges from 1 to 1000 mg L<sup>-1</sup> with toxicity increase with ethoxylate chain length

decreasing, whereas, acute toxicity of NP ranges from 0.1 to 1.0 mg L<sup>-1</sup> (Macek and Kreminski, 1975; Mcleese et al., 1981; Yoshimura, 1986). It were reported that during chronic exposure to NP in fish and invertebrates at levels as low as 6 and 3.7 µg L<sup>-1</sup> there were no effects (Servos, 1999). However, Nice et al. (2000) demonstrated that NP has effects on oyster embryos beginning with concentration of 100 ng L<sup>-1</sup>. Billinghamurst (1998) from the same group reported that NP shows effect on barnacles at 10 ng L<sup>-1</sup>. These concentrations in fact are lower than those reported in the effluents of WWTP in 1-3 orders of magnitude, and very comparable to the concentrations determined in the estuary of Rhine (Jonkers et al., 2003) and the German Bight (Bester et al., 2001).

Alkylphenols have also been implicated as an endocrine disrupter in animals and fish (White et al., 1994). The effect of endocrine disrupting chemicals on human health and wildlife is receiving growing attention from the scientific community, regulatory agencies, and the public as large. Exposure to endocrine disrupting chemicals can mimic or interfere with mechanisms of natural occurring hormones responsible for regulating reproductive and developmental bodily processes (Colborn et al., 1996; Keith, 1997). It was reported that NP could bind to the estrogen receptor and exerts estrogenic actions on piscine, avian, mammalian cells and human breast tumor cells (Mueller and Kim, 1978; Soto et al., 1991; Jobling and Sumpter, 1993; White et al., 1994). Although many studies showed that environmental concentrations of NP and *t*-OP below the threshold of No Observed Effect Concentrations (NOEC) and might be of no significant effect to the rat, fish or human being, Silva et al. (2002) have proved that weak estrogenic chemicals combined at concentrations below NOECs could produce significant mixture effects.

### *1.4. Environmental concentrations*

#### *1.4.1. Environmental concentrations of the phthalates*

Since 1970s, the phthalates have been found in various environmental media and biota (Williams, 1973; Giam et al., 1975; Giam et al., 1978). Residues have been also detected in food and in rats (Ishida et al., 1981; Albro, 1986). In many cases it is not clear whether the phthalates measured in samples is maturely occurring or is exogenous (Mathur, 1974a; 1974b; Peakall, 1975; Chen, 2004). Manandhar et al. (1979) and Pare et al. (1981) reported residues of the phthalates in biological samples where the source seemed to be natural. Peterson and Freeman (1984) suggested that some of the phthalates found in older samples (from the 1920s and 1930s) of sediment cores from Chesapeake Bay, USA, might have been of natural origin. However, it seems to be clear that high levels of DEHP are anthropogenic in origin (EHC

131, 1992). The concentrations of DEHP and DBP in air, rivers and oceans were summarized in Tab. 3, 4.

**Table 3.** Concentrations of DEHP in atmospheric and aquatic environment

Location	Country	Concentration	Reference
<b>Sea water (<math>\mu\text{g L}^{-1}</math>)</b>			
Northern Atlantic		0.0001-0.006	Giam et al. (1978)
Gulf of Mexico		0.006-0.316	Giam et al. (1978)
Estuaries	Germany	ND-0.3	Weber and Ernst (1983)
Nueces Estuary	USA	0.2-0.77	Ray et al. (1983)
Estuaries	UK	0.058-0.078	Waldock (1983)
	Singapore	0.012-0.148	Basheer and Lee (2002)
<b>Freshwater</b>			
Various rivers	Japan	ND-3.1	Kodama et al. (1975)
River Meuse	Netherlands	>0.1-3.5	Wams (1987)
River Rhine	Netherlands	ND-4.0	Wams (1987)
River Rhine	Netherlands	ND-1.2	Wams (1987)
Rivers	Germany	0.33-97.8	Fromme (2002)
Rivers in Taiwan	China	ND-18.5	Yuan (2002)
<b>Air (<math>\text{ng m}^{-3}</math>)</b>			
North Atlantic		1.4-4.1	Giam et al. (1978)
Gulf of Mexico		0.4-2.3	Giam et al. (1978)
North Pacific		0.32-2.68	Giam et al. (1980)
Great Lakes	Canada	0.5-5.0	Eisenreich et al. (1981)
Portland	USA	0.06-0.94	Ligocki et al. (1985a)
Sweden	Sweden	0.28-77.0	Thuren et al. (1990)
New York city	USA	28.6	Bove et al. (1978)
Lyngby	Denmark	22	Lokke and Rasmussen (1983)
Antwerp	Belgium	29-132	Cautreels et al. (1977)
Antwerp	Belgium	126	Cautreels et al. (1978)
Paris	France	18.9	Teil et al. (2005)
	Canada	300	Thomas (1973)
	Japan	38-790	EPA of Japan (1989)
	Singapore	0.70-4.3	Basheer and Lee (2002)

ND: not detectable

**Table 4.** Concentrations of DnBP in water and air

Location	Country	Concentration	Reference
<b>Sea water (<math>\mu\text{g L}^{-1}</math>)</b>			
<b>Gulf of Mexico</b>		0.47	Chan, 1975
<b>Open Gulf</b>		0.097	Giam et al., 1978
<b>Kiel Bight (Baltic Sea)</b>	Germany	0.203	Ehrhardt and Derenbach, 1980
<b>Nueces Estuary</b>	USA	0.230	Ray et al., 1983
<b>Estuaries</b>	UK	4.8	Law et al., 1991
	Singapore	0.023	Basheer and Lee, 2002
<b>Freshwater</b>			
<b>Rivers</b>	Netherlands	0.1-2.8	Schouten et al., 1979
<b>Rivers in Manchester</b>	UK	12.1-33.5	Fatoki and Verson, 1990
<b>Rhine</b>	Germany	0.18	Furtmann, 1994
<b>Rivers</b>	Japan	0.013-36	Environment Agency, Japan, 1995
<b>Rivers</b>	Gemany	0.12-8.80	Fromme, 2002
<b>Air (<math>\text{ng m}^{-3}</math>)</b>			
<b>North Atlantic</b>		1.0	Giam et al., 1978
<b>Gulf of Mexico</b>		0.3	Giam et al., 1978
<b>North Pacific Ocean</b>		0.40-1.80	Giam et al., 1980
<b>Pigeon Key, Florida</b>	USA	18.5	Atlas and Giam, 1981
<b>Great Lakes</b>	Canada	0.50-5.0	Eisenreich et al., 1981
	Sweden	0.23-49.9	Thuren et al., 1990
<b>New York</b>	USA	3.28-5.69	Bove et al., 1978
<b>Niagara River</b>		4.5	Hoff and Chan, 1987
	Japan	17-370	Environmental Agency of Japan, 1995
	Singapore	1.41-200.98	Basheer and Lee, 2002
<b>Paris</b>	France	22.2	Teil et al., 2005

Concentrations of BBP in the environment reported before 1990s were summarized in a concise international chemical assessment document (WHO, 1999). In air samples, concentrations ranging from 0.38 to 1.78  $\text{ng m}^{-3}$  were determined from Greater Vancouver, British Columbia, Canada (WHO, 1999). Ligocki and coworkers (1985a,b) reported concentrations of BBP up to 9.6  $\text{ng m}^{-3}$  in the aerosol phase at Portland, Oregon, USA. In Europe, BBP has been detected in ambient air in Barcelona, Spain, with concentrations of 1.0 and 8.0  $\text{ng m}^{-3}$  in winter and 0.25 and 2.0  $\text{ng m}^{-3}$  in summer associated with coarse ( $>7.2 \mu\text{m}$ ) and fine ( $<0.5 \mu\text{m}$ ) aerosol fractions, respectively (Aceves and Grimalt, 1993).

In the aquatic environment, BBP was detected at concentrations up to 1  $\mu\text{g L}^{-1}$  in Canadian surface water (WHO, 1999). In central Italy, BBP was detected at concentrations up to 6.6  $\mu\text{g}$

L<sup>-1</sup> in Lae Scandarello (Vitali et al., 1997). In the Rhine and its tributaries, BBP levels were up to 5.5 µg L<sup>-1</sup> (ECPI, 1996). In a survey for the phthalates in German rivers, BBP was only detected in 22% of the surface water samples with concentrations up to a maximal 2.95 µg L<sup>-1</sup> (Fromme et al., 2002).

Concerning DEP, environmental data are very poor compared to the other phthalates, e.g. DBP and DEHP. DEP was determined in Newark (USA) in the indoor air and outdoor air, with concentrations ranging from 1.60 to 2.03 µg m<sup>-3</sup>, and from 0.40 to 0.52 µg m<sup>-3</sup> (Shields and Weschler, 1987). Basheer and Lee (2002) reported concentrations ranging from 0.21 to 4.36 ng m<sup>-3</sup> in Singapore, which is significantly lower than the concentrations of DBP. They have also studied concentrations of DEP in seawater. The concentrations ranged from 14 to 121 µg L<sup>-1</sup> in the mid depth and ranging from below the detection limit to 48 µg L<sup>-1</sup> in the bottom layer. These values are approximately 1-2 orders of magnitude higher than that found in river surface waters in Taiwan (Yuan et al., 2002). In a compilation of concentrations (1984-1997) of DEP in North American and western European surface waters (USA, Canada, United Kingdom, Germany, Netherlands, Sweden) geometric mean concentrations ranged from about 0.01 µg L<sup>-1</sup> to 0.5 µg L<sup>-1</sup> (Staples et al., 2000).

Although the physicochemical properties indicated that DMP is likely partitioning to the atmosphere and staying in the vapour phase, there are very few data available for atmospheric DMP. In surface water, concentrations of DMP were in a range from 0.001 to 1 µg L<sup>-1</sup> which adopted from the compilation of concentrations (1984-1997) of DMP in North American and western European surface waters (Staples et al., 2000).

#### *1.4.2. Environmental concentrations of APs and their ethoxylates*

Concentrations of APs and their ethoxylates have been determined worldwide in the influent and effluent of sewage, surface water, sea water, rain, snow, soil, sediment, the atmosphere and in aquatic organisms (see Tab. 5). Discharges of sewage and wastewater treatment plants are the main sources of environmental occurrence of APs and their ethoxylates in the surface water. Soil system is contaminated mainly via bio-solids and sludge application. Atmospheric occurrence of APs has not yet attracted enough attention even was it indicated the significance of atmospheric transport by Duchs and coworkers since 1999 (Dachs et al., 1999). Mostly, it is due to that the existing knowledge of the physicochemical properties of APs does not support the significance of volatilization of and long-range transport of APs in the environment. However, as shown in (Xie et al., 2004), the basic knowledge used for these estimates are in fact very different among the reported values.

Obviously, studies have shown that volatilization should also be considered as a mechanism when determining the environmental fate of APs. As the data are very rare concerning atmospheric concentrations of APs, more studies are necessary for a better understanding of the significance of atmospheric transport mechanisms. In addition, method of atmospheric sampling, sources of atmospheric APs, the distribution of APs and atmospheric degradation mechanisms require further study. This is especially true for the volatilization of APs during traditional aerated water treatment processes. In addition, further study is necessary to investigate the impacts in harbors and estuaries, terrestrial areas with sludge cover and highly contaminated agricultural areas and their role in long range atmospheric transport.

NPEOs and their metabolites have been detected in a variety of large rivers and in a few coastal waters and sediments (See Tab. 5). A recent study by Kolpin et al. (2002) screened 139 U.S. streams in 1999 – 2000 for 95 contaminants including NP, NP1EO and NP2EO, pharmaceutical compounds, detergents, fragrances and other commonly used chemicals. NP and NP1EO were found in 85% of the streams surveyed with average concentrations ranging from 0.5 to 1.0  $\mu\text{g L}^{-1}$ . In Japan, Isobe and co-workers (2001) studied the distribution and behavior of NP, OP and NP1EO in Tokyo Metropolitan area. Concentrations of NP in the river water samples ranged from 0.01 to 1.08  $\mu\text{g L}^{-1}$ , comparable concentrations of NP1EO found were in the range of 0.04 – 0.16  $\mu\text{g L}^{-1}$ , and concentrations of OP were 1 order of magnitude lower than that of NP and NP1EO. The particulate associated fractions were  $23 \pm 15\%$  for NP and  $8 \pm 8\%$  for OP, respectively. Based on the pair concentrations in the dissolved and particular phases, the organic carbon-normalized apparent partition coefficients ( $K'_{oc}$ ) of NP and OP were estimated respectively to be  $10^{5.22 \pm 0.38}$  and  $10^{4.65 \pm 0.42}$ , which were 1 order of magnitude higher than those expected from their octanol–water partition coefficient ( $K_{ow}$ ), indicating strong affinity of APs to aquatic particles.

NP, OP and NPEOs were determined in the Elbe and the North Sea in 1990s (Heemken et al., 2001). In the Elbe River, APs showed concentrations ranging from below 1 to 84  $\text{ng L}^{-1}$ , the highest concentrations being measured for NP. The NPEOs had concentrations between 0.1 and 111  $\text{ng L}^{-1}$ . Bester et al. (2001) reported that the concentrations of NP varied from 0.7 to 4.4  $\text{ng L}^{-1}$  in seawater from the German Bight of the North Sea, while in the Elbe estuary about 33  $\text{ng L}^{-1}$  were found. Stachel (2003) and co-workers re-investigated APs in the Elbe and its tributaries in 2000. Concentrations of OP ranged from <0.5 to 3.3  $\text{ng L}^{-1}$  in the River Elbe with a maximum of 5  $\text{ng L}^{-1}$  at the mouth of the River Scharze Elster. NP concentrations ranged from 13 to 53  $\text{ng L}^{-1}$  in the River Elbe with a maximum of 87  $\text{ng L}^{-1}$  at the mouth of the Saale. It was found that concentrations of NP are generally higher than that of OP by a

factor of 10. As compared to the concentrations reported by Heemken et al. (2001), they were just slightly lower. Nevertheless, these investigations show that the River Elbe and Rhine represent a significant source of input for APEO and AP into the North Sea.

**Table 5.** Levels of NP, t-OP and NP1EO in different environments and literature data

Media	NP	t-OP	NP1EO	Location	Reference
WWTPs ( $\mu\text{g l}^{-1}$ )	<0.01-37.0	<0.005-0.67	<0.05-332	USA	Snyder et al. (1999)
	3.0	-	45.0	UK	Lye et al. (1999)
	0.025-0.77	0.0022-0.073	-	Germany	Kuch et al. (2001)
	0.14-0.24	0.008-0.02	0.07-0.18	Germany	Jahnke et al. (2004)
Freshwaters	<LOD-5.4	-	-	UK	Blackburn et al. (1995)
	<0.1-7.2	-	0.1-3.4	Switzerland	Ahel et al. (1996)
	<0.010-0.92	<0.005-0.084	<0.020-7.8	Canada	Bennie et al. (1997)
	<0.01-1.19	<0.002-0.081	<0.05-17.8	USA	Snyder et al. (1999)
	<0.2-30	<0.5	<0.6-46	UK	Blackburn et al. (1999)
	<LOD-0.644	-	-	Spain	Sole et al. (2000)
	0.11-3.08	ND-0.09	-	Japan	Tsuda et al. (2000)
	0.006-0.135	0.0008-0.054	-	Germany	Kuch et al. (2001)
	0.013-0.087	<0.0005-0.005	<0.0005-0.120	Germany	Stachel et al. (2003)
	0.10-0.50	-	0.016-0.6	USA	Rice et al. (2003)
	0.051-1.08	0.01-0.18	0.04-0.81	Japan	Isobe et al. (2001)
	0.11-0.30	0.018-0.20	-	China	Jin et al. (2004)
Sea water	<LOD-5.8	<0.5	<0.6-76	UK	Blackburn et al. (1999)
	0.15-0.42	0.0016-0.0083	0.06-0.22	USA	Ferguson et al. (2001)
	0.0007-0.033	-	-	Germany	Bester et al. (2001)
	0.17-1.90	-	-	UK	Smith et al. (2001)
Vapor ( $\text{ng m}^{-3}$ )	0.15-1.0	0.02-0.16	-	Germany	Berkner et al. (2004)
	<LOD-81	<LOD-2.5	-	Coast (US)	Van Ry et al. (2000)
Particle ( $\text{ng m}^{-3}$ )	0.005-0.015	0.0003-0.0042	-	Germany	Berkner et al. (2004)
	0.020-51	<LOD-0.073	-	Coast (US)	Van Ry et al. (2000)

<sup>a</sup> Dry weight.

<sup>b</sup> Wet weight.

As APs are both lipophilic and resistant to biodegradation there is a potential for accumulation in the tissues of animals and human being (Porter and Hayden, 2004). Recently, Ferrara et al. (2005) investigated APs and their ethoxylates in 8 marine species from the

Adriatic Sea. NP was detected in fish from 9.5 to 1431 ng g<sup>-1</sup>, and OP was found in a range of 0.2-21.1 ng g<sup>-1</sup>. It was estimated respectively daily intakes for NP and OP are 12 and 0.1 µg day<sup>-1</sup> for an Italian adult living along the Adriatic Coast. Lalah et al. (2003) investigated the dissipation and distribution of NP in lake water and sediment with <sup>14</sup>C labeled NP isomer. It was found that NP rapidly partition to sediment with a concentration factor of 1.76 after 28 days.

Dachs et al.(1999) reported the concentration of NPs ranging between 2.2 and 70 ng m<sup>-3</sup> in the coastal atmosphere of the New York-New Jersey Bight in 1999. They stated that the occurrence of the NPs in the atmosphere might be important human and ecosystem health issue in urban, industrial and coastal-impacted areas receiving treated sewage effluents. Van Ry et al. (2000) further studied the season trends of NPs and *t*-OP in the atmosphere of the Lower Hudson River Estuary from June to December 1998. Concentrations of NPs in gas phase at a coastal site (Sandy Hook) ranged from below the detection limit to 56.3 ng m<sup>-3</sup>, while the concentrations at a suburban site (New Brunswick) ranged from 0.13 to 81 ng m<sup>-3</sup>. Gas phase concentration of OP ranged from less than the limit of detection (LOD) to 1.0 ng m<sup>-3</sup> at Sandy Hook and from 0.01 to 2.5 ng m<sup>-3</sup> at New Brunswick. NPs and *t*-OP exhibited seasonal trends with higher gas phase concentrations during summer than during fall and early winter. Berkner et al. (2004) determined NP and *t*-OP in NE-Bavaria Germany. The concentrations of NP and *t*-OP in vapour phase ranged from 0.15-1.0 ng m<sup>-3</sup> and 0.02-0.16 ng m<sup>-3</sup>, respectively. In their study, NP and *t*-OP were also found in particle phases with concentrations in the range of 0.3 – 4.3 pg m<sup>-3</sup> and 1.7 – 117 pg m<sup>-3</sup>, respectively. Consequently, these studies demonstrated that APs do not only occur in the high-contaminated area but also the remote region. In addition, it was suggested that atmospheric transport might be an important media for the re-distribution of APs.

### *1.5. The objectives of this work*

This work has been designed to improve our understanding of the distribution pattern and transport mechanisms of APs and the phthalates in the coastal regions, especially the roles of the air-sea exchanges in these processes. The detailed objectives of this thesis were:

1. To improve the analytical methodology and investigate the spatial concentrations of APs and the phthalates in sea water and the atmosphere of the North Sea.
2. To develop, construct and test the dynamic equilibrium system for determining the Henry's Law Constant (HLC) of NP and *t*-OP over ambient temperature range, and

use the temperature corrected HLCs for the estimations of air-sea vapour exchange of APs and the phthalates

3. To estimate the air-sea vapour exchange fluxes of *t*-OP, NP and the phthalates using the two-film resistance model based upon relative air-water concentrations and temperature and salinity corrected Henry's Law Constants.

The analytical methodology development and validation for the determination of APs and the phthalates using large volume samples, including recovery tests, breakthrough checking, and blank elimination technical terms are presented in Paper 1. The measurements of HLCs of NP isomers and *t*-OP are introduced in detail in Paper 2. Distribution and air-sea vapour exchanges of APs and the phthalates in the North Sea are respectively presented in Paper 3 and Paper 4.

## 2. Summary

The comprehensive studies for the analytical method presented in this dissertation demonstrate that the large volume sampling methods with PAD-2 resin column for sea water and PUF/XAD-2 column for air 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 satisfied. The losses 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 labour intensive, they eliminate matrix, feature high enrichments capacity and allow method detections in the  $\text{pg L}^{-1}$  and  $\text{pg m}^{-3}$  for sea water and air sample.

Henry's Law Constants (HLC,  $\text{M atm}^{-1}$ ) were determined for the diastereomeric mixture of the nonylphenol isomer 4(3',5'-dimethyl-3'-heptyl)-phenol diastereomers (NP353(+)) and NP353(-)), tertiary octylphenol (*t*-OP) and  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH) in artificial seawater over a temperature range of 278-298 K using a dynamic equilibrium system. The HLC values of  $\gamma$ -HCH, which were used as the reference substance, were in good agreement with literature values and its corresponding derived enthalpy of solvation agrees well with the previous values reported in the literature. The reassessment of the air/water vapour exchange based on experimentally derived HLC made for NP in the Lower Hudson River estuary (New York, USA) shows that the atmosphere is both a sink and a source of APs in coastal regions.

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 already reported. NP1EO was detected in both vapour 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 vapour 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 vapour 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, consequently, the open ocean and polar areas will be an extensive sink for APs and the phthalates.

### 3. Prospects for future work

It was found that NP and *t*-OP show different behaviors as compared to their surrogates of 4-*n*-OP and 4-*n*-NP. As a solution, the deuterated *t*-OP and certain NP isomer will be synthesized for method improvement and used as a surrogate to monitor the losses of *t*-OP and NP in the following study. Moreover, it is hypothesized, that degradation may happen during the air sampling that leads to low recoveries for *t*-OP and NP, therefore, it needs further study to make clear the mechanism for the losses of *t*-OP and NP during the air sampling.

Analysis for the compositions of NP and NP1EO isomers showed that NP isomers are relatively stable under aerobic conditions, however, selective degradation among NP1EO isomers might be occurring. 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.

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 the phthalates and the Henry's Law Constants of the phthalates over the ambient temperatures. Knowledge of the transport mechanisms of APs and phthalates via atmosphere and the air-sea exchanges might be significantly increased by an evaluation with high accurate physicochemical properties.

The exchanges of APs and the phthalates between air and terrestrial surface according to seasonal temperature changes would benefit from further research. Furthermore, an investigation on the intermediates of the phthalates, e.g. mono-phthalates in the environment should be undertaken together with the phthalates for the purpose of determining their transformation pattern under different conditions. In addition, the removal of APs and the phthalates by vegetation should be considered for the evaluation of their environmental fates.

As for the transport and distribution of APs and the phthalates in the coastal regions, further studies will be conducted to elucidate the temporal dependences of the distributions of APs and the phthalates in the coastal regions and in the open ocean in order to evaluate the states of APs and the phthalates in the remote region and provide evidence for the evaluation of their potential risk to the polar ecosystem.

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