

Sea spray and the atmospheric transport of nonylphenol ethoxylates. A combined laboratory, field and modeling study

Mark A. McInnes^a, David A. Ellis^{a,b,*}, Eva M. Webster^b, Andrew Peters^c

^aDepartment of Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

^bCentre for Environmental Modelling and Chemistry, Peterborough, Ontario K9J 7B8, Canada

^cBermuda Institute of Ocean Science Ferry Reach, St. George's, Bermuda

HIGHLIGHTS

- ▶ Laboratory-generated spray NPEO concentrations 4 times greater than source water.
- ▶ NPEO entering the gas phase through spray is comparable to direct volatilization.
- ▶ Natural wave action caused 4.3–19.2 NPEO enhancement relative to source water.
- ▶ Spray contributes to atmospheric NPEO burden and subsequent atmospheric transport.

ARTICLE INFO

Article history:

Received 5 June 2012

Received in revised form

27 November 2012

Accepted 29 November 2012

Keywords:

Aqueous spray

Chemical environmental fate

Surfactant

Air–water transfer

Medium-distance transport potential

Atlantic Ocean

ABSTRACT

Nonylphenol ethoxylates (NPEOs) are environmentally ubiquitous non-ionizing surfactants that show a preference for the air–water interface. They are therefore potentially subject to enhanced transport by aqueous aerosols. The extent to which aqueous aerosols affect the overall environmental fate and behavior of NPEOs is investigated with a combination of laboratory and field experiments and mathematical modeling. Aqueous aerosol droplets were generated in a laboratory-based experimental system. Aqueous aerosols were measured to have concentrations of NPEOs at least four times greater than in the bulk source water.

The concentration of nonylphenol and nonylphenol monoethoxylate in aqueous aerosols off the coast of Bermuda were 4.3–19.2 times higher than in coastal water and open water collected from the Bermuda Atlantic Time Series sampling site. Coastal water showed higher concentrations than open water samples ranging from 36 to 51 ng L⁻¹ and 14 to 21 ng L⁻¹ respectively. Depth profiling showed a loss of detection below 300 m. Aqueous aerosol enrichment was demonstrated and relative atmospheric concentrations ranged from 0.28 to 1.8 ng m⁻³. A generic marine model was developed using independent North Sea data to estimate the relative potential for NPEO transfer within spray droplets to the atmosphere and subsequently into the gas phase by volatilization. The results were compared to the estimated direct volatilization from the surface of a natural water body. The upward mass flux of NPEOs by direct volatilization was comparable in magnitude to the fluxes due to spray generation, depending on the wind speed and droplet sizes. The experimental results and the model calculations were illustratively applied to reported NPEO concentrations in the North Sea. Aerosol generation provides a feasible mechanism for atmospheric transport of NPEOs and their degradation products, nonylphenols (NPs).

© 2013 Published by Elsevier Ltd.

1. Introduction

Understanding the mechanisms of chemical transport is essential for predicting the environmental fate of a chemical

* Corresponding author. Department of Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada. Tel.: +1 705 748 1011x7898.

E-mail address: davidellis@trentu.ca (D.A. Ellis).

species and leads to the development and implementation of scientifically defensible regulations to safeguard the environment and ultimately human health. To date there is limited knowledge concerning the mechanisms of transport with regard to a widely used and environmentally significant class of chemicals described as surface-active in physical nature. As such there is a need for better understanding the processes by which these species are disseminated in the environment.

Surface-active chemicals (or *surfactants*) are unique among organic chemicals for their ability to modify their local environment. Their amphiphilicity causes them to distribute preferentially to aqueous interfaces on the molecular level (Royal Society of Chemistry), regardless of the quantity present in the system as a whole. This enrichment at the air–water interface, called the surface micro layer (SML) (Zhang et al., 2003), influences every chemical transfer process taking place at the interface, including spray production. To date, surface enrichment has been largely neglected by researchers seeking to understand the environmental behavior of these organic contaminants.

It has been suggested that aqueous aerosols produced as sea spray in the action of waves may play a significant role in the atmospheric transport of surfactants (Richardson, 2012). The SML is known to have different physical (Zhang et al., 2003), chemical (Zhang et al., 2003; Cincinelli et al., 2001; Aller et al., 2005) and biological (Aller et al., 2005) properties than the sub surface water (SSW). The depth of the SML is reported between 50 μm (Zhang et al., 2003) and 1000 μm (Grammatika and Zimmerman, 2001). The variability of thickness can be attributed to the variation in properties measured in different studies (Zhang et al., 2003; Cincinelli et al., 2001; Aller et al., 2005), the depletion and replenishment that is thought to occur regularly (Zhang et al., 2003), and varying meteorological conditions during sampling. Enrichment of aqueous aerosols in comparison to the bulk water from which they were generated has been documented for bacteria, viruses, lipids, various surfactants, and metals (Aller et al., 2005; McMurdo et al., 2008; Oppo et al., 1999). The SML is reported to have chemical and location specific dissolved phase enrichment factors (EF) of 0.1–950 (Cincinelli et al., 2001), and bacteria and virus enrichment of 6–7 (Aller et al., 2005). A similar air water interface is created by bubbles traveling through the water column creating an environment in which surface-active species are scavenged from the SSW and carried to the surface. Bubble bursting at the waters surface is believed to release aqueous aerosols that are enriched when compared to the SSW (McMurdo et al., 2008). The production of aqueous aerosols in the marine environment is also caused by both breaking waves and wind shear on the surface of the water. Wind shear is considered to be the predominant mechanism and attempts have been made to relate volume flux of aqueous aerosols to wind speed (Andreas, 1998). Aqueous aerosols produced at the sea surface are known to reach altitudes in excess of 600 m (Woodcock, 1953) and to contribute to marine cloud contamination (Oppo et al., 1999) where they are subject to advection due to air currents resulting in a mechanism of atmospheric transport of contaminants contained within the droplet. Communities that experience high levels of spray (i.e., coastal communities, communities near waterfalls, etc.) may have increased exposure to these potentially infectious and toxic substances (Aller et al., 2005). Aqueous aerosols may also contribute to the vertical distribution of contaminants such as deposition to mountain lakes at various altitudes including those in high areas remote from urban or industrialized centers. Aerosols may also act as carriers to the atmosphere both directly and by way of increased interface surface area for direct volatilization thus increasing the possibility for long-range transport (McMurdo et al., 2008; Oppo et al., 1999). Consideration of spray production, in the case of a chemical for which it is important, may assist in explaining observed environmental concentrations especially in locations remote from sources. It may also be important for chemical assessments and categorizations such as those conducted by government regulators such as Environment Canada (Environment Canada, 2003) that may include a model-generated estimate of long-range transport from a standard model, e.g., the TaPL3 model (Beyer et al., 2000).

Nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) are ideal test candidates for the investigation of the role of aqueous aerosol generation as a chemical transfer mechanism for non-ionic surfactants in general. They are chemicals of concern and have suitable physical chemical properties; therefore, it has been suggested that this process may be important for them. As NPEOs do not dissociate in water their environmental behavior is less dependent on pH and aqueous surface charge than is the case for ionizing surfactants (Kissa, 2001). However, in saline solutions, such as the ocean, aqueous phase NPEOs, as with any other chemical, may be subject to a “salting” effect. This phenomenon can generally be described as a change in the aqueous solubility of the species due to the ionic strength of the solution (Perez-Tejeda et al., 1990). To our knowledge, the extent and direction of the salting effect for NPEOs has not yet been determined.

Standard environmental fate models that describe and encode our understanding of chemical behavior typically do not include aqueous aerosols, but rather a solid particulate phase ‘aerosol’ at equilibrium with the surrounding gas in the atmosphere (e.g., Beyer et al., 2000; Mackay et al., 1996; Arnot et al., 2006; Vermeire et al., 2005; Mackay, 2001). An associated water component was added to this dry ‘aerosol’ phase to address the behavior of chemicals with higher water solubilities (Arnot and Mackay, 2008). These models were developed for, and are typically only applicable to, neutral, non-ionizing, non-surfactant organics (e.g., Beyer et al., 2000; Mackay et al., 1996; Arnot et al., 2006; Vermeire et al., 2005; Mackay, 2001) and do not account for the unique properties of surfactants. Only recently was a model developed that included a preliminary representation of aqueous aerosols as a separate environmental compartment not at equilibrium with the atmosphere (Webster et al., 2010). It is noteworthy that for models of chemical fate in indoor environments, the two-resistance film theory will also underestimate the effect of such domestic water uses as showering (Webster et al., 2010).

There is a clear need for field measurements to address the question of the degree of enrichment of sea spray aqueous aerosol with surfactants and hence their importance in this class of chemicals with regard to atmospheric transport. The results of earlier field studies have been modeled with conflicting conclusions where some researchers suggest a net upward and others a net downward air–water flux of NP (Dachs et al., 1999; Van Ry et al., 2000; Xie et al., 2004). Field observations that air concentrations were strongly dependent upon wind speed could be a result of increased spray production; however, terrestrial sources were suggested as more likely to be responsible for the observed air concentrations (Xie et al., 2006). Based on atmospheric sampling in and around a sewage treatment plant that found elevated concentrations of NP and NPnEO ($n = 1–3$) downwind, Cincinelli et al. (2003) concluded that, there is an upward flux of NP and NPnEO. These concentrations were likely predominantly associated with aqueous aerosols generated from the aeration process (Lepri et al., 2000).

The objectives of the present study were to a) quantify the potential enrichment of NPEOs in aqueous aerosols in a laboratory setting using tap water as a proof of concept that enrichment occurs under simple conditions and, if enrichment is indeed observed, to conduct similar measurements in the more increased complex and increased variable marine field setting, b) determine the size of the droplets produced in the laboratory experiment, c) to develop a model for the potential of upward flux of NPEOs to the atmosphere by spray droplets using the independent literature supported well defined system of the North Sea and compare this flux to that predicted to occur by direct volatilization, and d) discuss the potential contribution of spray-mediated transfer to the environmental fate and behavior of NPEO.

2. Materials and methods

2.1. Chemicals and reagents

Nonylphenol ethoxylates technical mixture IGEPAL-CO210™ (CAS: 68412-54-4), reagent grade acetone (CAS: 67-64-1), and SUPLECO™ SPME fiber assemblies with 100 µm polydimethylsiloxane coatings were all purchased from Sigma Aldrich (Oakville, Ontario). Unfiltered tap water was used in all laboratory trials. NP-d standard: 4-n-nonylphenol-2,3,5,6-d4, 99.3 atom% D, 1.0 mg mL⁻¹ in acetone, cat. # 2414.15-K-5AC, supplied by Chiron AS, Trondheim, Norway. All chemicals were used as received without modification or purification.

2.2. Laboratory aerosol experiments

A stock NPEO solution of 960 mg L⁻¹ IGEPAL CO-210™ in acetone was prepared and used as a spiking solution throughout the experiments. Aqueous solutions were prepared by the addition of 6 L of tap water to an 18-L polyethylene container spiked with 3.125 mL of the stock NPEO solution. The aqueous solution was slowly magnetically stirred for the duration of the experiment. The aqueous aerosol generating system employed was that previously described (McMurdo et al., 2008). A piezoelectric aerosol generator (Manchester Products, Cambridge, ON) operating at 60 Hz was suspended from the center of the container and immersed approximately 3 cm below the surface of the water. The temperature of the water was continuously monitored during the experiment and remained constant at 23 °C ± 1 °C. Prior to sampling, the system was closed and aerosols were generated for 72 h to allow the chemical to achieve equilibrium between all phases present (i.e., bulk water, air-borne droplets, and the gas phase). After equilibration, a vacuum line leading to a condensing vessel was connected through an adapter in the top of the experimentation container. Bulk water samples were drawn through septa in the wall of the container just below the surface of the water and at a constant depth of 2.5 cm. A sample was drawn from the bulk water to determine the initial equilibrium concentration and hourly thereafter for the duration of the 10-h experiment. Aerosol samples were collected continuously throughout the experiment and the condensing vessel was emptied and cleaned each hour, on the hour, throughout the experimental period.

2.3. Field sample collection

Samples were collected from April 24th to Jun 20th 2010 in the BATS deployment area (Fig. 1). Samples were taken using a vacuum pump running at 3 L min⁻¹ drawing air over a round bottom flask in an ice bath acting as a condenser. An identical secondary condenser was used in series to detect blow by from the primary condenser flask. The sampling end of the apparatus consisted of LDPE (low density polyethylene) tubing connected to a HDPE (high density polyethylene) funnel 12 cm in diameter. The funnel was positioned so that the opening was facing the ground to avoid collecting rain. To avoid contamination from the exhaust pipe on the ship samples were only drawn when the boat was into a head wind. At the end of the 10-h sampling period, the water from the condenser was collected and analyzed. Aerosol samples were collected simultaneously with the source water samples from condensers both at the bow (5.4 m above the water surface) of the boat and on fly deck (10.8 m above the water surface) when possible.

Surface water samples were taken by skimming the water surface with an open LDPE bottle. All efforts were made to take surface samples in a consistent way based on what was possible with the sea conditions at the time. Sub surface water samples were collected from Niskin flasks.

2.4. Extraction and analysis

2.4.1. Laboratory extraction and analysis

The following method is similar to that developed by Diaz et al. (2002). Aqueous aerosol samples were collected (20 mL) and extracted using solid phase microextraction (SPME) with an automated sampling system (COMBIPAL™). Sample vials were placed in the extraction manifold and mixed at 500 rpm for 5 min. The SPME fiber was then placed in the sample for 30 min with continued mixing at 250 rpm and then desorbed in the injection port of a Varian 3800™ gas chromatogram with a split/splitless liner at 180 °C for 10 min with a continuous flow of helium at 1 mL min⁻¹. The system was set with a split ratio of 5:1 and the port injected onto a 30 m VF-5 column 0.25 mm external diameter and 0.25 µm internal diameter. The column oven was set on a thermal gradient beginning at 120 °C for 1 min ramping to 180 °C at 5 °C min⁻¹ where it was maintained for 1 min followed by a final 2 °C min⁻¹ ramping to 225 °C that was maintained for 8 min. Detection was

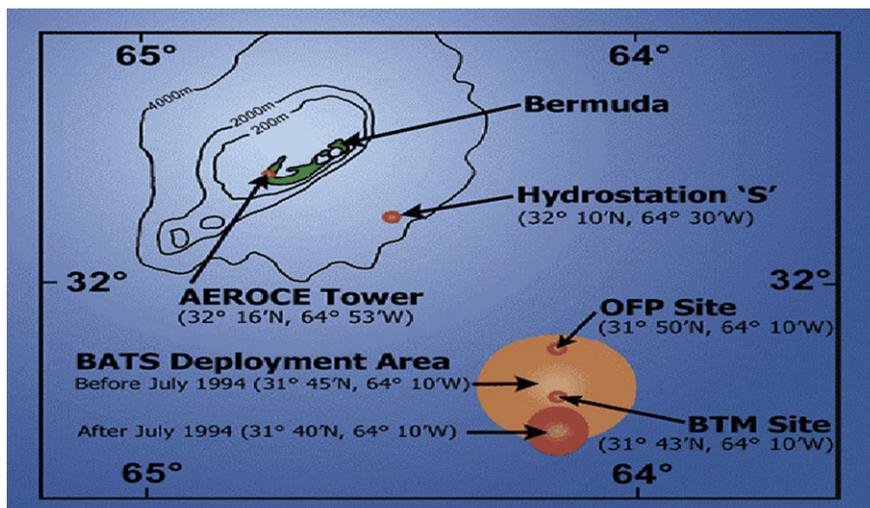


Fig. 1. Map of BATS deployment area location and proximity to Bermuda (Bermuda Institute of Ocean Sciences, <http://www.bios.edu/research/cintoomap.html>).

performed using a Varian 4000 Titan MSTM ion trap in total ion chromatogram (TIC) mode. A set of external analytical standards, ranging from 10 $\mu\text{g L}^{-1}$ to 3000 $\mu\text{g L}^{-1}$, were made from the IGEPAL-CO210TM technical mixture and used to quantify NP1EO, and NP2EO. Each compound was quantified as the sum of the detectable isomers. Method error was determined to be 11.6% by relative standard deviation of 3 replicates. Limits of quantification for NP1EO and NP2EO were established to be 1 ng L^{-1} and 10 ng L^{-1} respectively based on a minimum integrated signal of 500 counts. Detection limits were 0.5 ng L^{-1} and 1 ng L^{-1} defined by concentration at an integrated signal of 100 counts. Isomeric isolation showed 10 isomers for NP1EO and 7 for NP2EO. No difference in isomeric ratio was observed nor was any preferential transport observed for NP1EO or NP2EO in these experiments.

2.4.2. Field study extraction and analysis

All samples were extracted using solid phase microextraction (SPME). The SPME fiber was placed in the sample for 30 min with continuous mixing by a stir bar on medium speed. The SPME fiber was then desorbed in the injection port of a HP 6890TM gas chromatogram with a split/splitless liner at 250 °C for 10 min with a continuous flow of helium at 1 mL min^{-1} . The system was set in splitless mode and the port injected onto a 30 m HP-5ms column 0.25 mm external diameter and 0.25 μm internal diameter. The column oven was set on a thermal gradient beginning at 90 °C for 4 min ramping to 325 °C at 7 °C min^{-1} where it was maintained for 13 min. Detection was performed using an HP 5973TM quadrupole in total ion chromatogram (TIC) mode mass range 40–550 amu. Nonylphenol and NP1EO were quantified based on response ratios with the internal standard deuterated nonylphenol (4-nonylphenol-2,3,5,6-d4). Both compounds were quantified as the sum of the detectable isomers and had quantification limits of 1 ng L^{-1} defined as the concentration at an integrated signal of 500 counts. Limits of detection for both compounds were 0.5 ng L^{-1} established as integrated signals with 100 counts. Method error was determined to be 10.8% by relative standard deviation of 3 replicates.

2.5. Droplet sizing

Droplet sizing was performed using a PCO 4000TM cooled digital 14 bit CCD camera system at 4008 \times 2672 pixels resolution (Optikon Corp) and an Infinity K2/S long distance microscope system with CF-1 (close focus) objective lens. The droplets were illuminated using a solid state Nd:YAG laser with 1 W maximum output, Wavelength – 532 nm Visible color – green (CNI optoelectronics) using a Modified Fiber Coupled Laser System (FCLS) (ILA) and hyperterminal pulse frequency and period control software.

2.6. Modeling method

The potential impact of the experimentally observed enrichment within aqueous aerosols on the environmental fate of NPEOs was assessed by the comparison of results from mathematical models of the flux due to direct volatilization from the surface of the water body (Mackay, 2001) and the flux due to aqueous aerosol generation (Webster and Ellis, 2010) as described in the Supplementary information.

The flux due to volatilization was calculated using the two-resistance film theory (Mackay, 2001) as

$$N_v = k_{ov} A_W E C_W \quad (1)$$

where k_{ov} is the overall diffusion mass transfer coefficient (m h^{-1}) given by $k_{ov} = 1/(1/(k_A K_{AW}) + 1/k_W)$, k_A is the air-side air–water

mass transfer coefficient (m h^{-1}), k_W is the water-side air–water mass transfer coefficient (m h^{-1}), K_{AW} is the air–water partition coefficient (m^3 of water (m^3 of air) $^{-1}$), A_W is the surface area of the water body (m^2), E is the enrichment factor, and C_W is the chemical concentration in the water body ($\mu\text{g m}^{-3}$). The chemical flux in aerosol droplets was calculated as

$$N_s = S A_W C_d \quad (2)$$

where S is the spray generation rate ($\text{m}^3 \text{h}^{-1}$) and C_d is the average concentration ($\mu\text{g m}^{-3}$) in the droplets and is assumed equal to $E C_W$. The ratio of these two fluxes from the water body into the atmosphere, $R_{s/v}$, is given by

$$R_{s/v} = S/k_{ov} \quad (3)$$

The diffusion flux from the spray droplets to the gas phase, N_d , is given by

$$N_d = k_{ov} A_d C_d \quad (4)$$

where A_d is the total surface area of all droplets (m^2) or $\rho_n 4\pi r_0^2 A_W h$ where ρ_n is the number density of droplets, r_0 is the radius of formation of the droplet (m), and $A_W h$ is the total volume of air (assumed h is the air height at constant pressure). Because the processes of spray production and volatilization from the droplets occur in series, the overall flux of chemical from the water body to the gas phase of the atmosphere via aqueous aerosol production, N_{sg} , is

$$N_{sg} = 1/(1/N_s + 1/N_d)$$

or

$$N_{sg} = A_W C_W E / \left(1/S + 1 / \left(k_{ov} \rho_n 4\pi r_0^2 h \right) \right) \quad (5)$$

Thus, the ratio of the direct volatilization flux, N_v , to aerosol-dependent flux, N_{sg} , to the gas phase, $R_{sg/v}$, is

$$R_{sg/v} = 1 / \left(\left(1/S + 1 / \left(k_{ov} \rho_n 4\pi r_0^2 h \right) \right) k_{ov} \right) \quad (6)$$

These ratios are independent of the chemical concentration in the water body, the droplet and water body area. They provide a measure of the relative contribution of each upward transfer route that depends only upon the chemical's K_{AW} and properties of the spray as determined by wind speed and were therefore calculated first and individual fluxes were calculated subsequently for the specific case example of NP1EO in the North Sea.

Standard accepted values of the air-side air–water mass transfer coefficient (3 m h^{-1}) (Mackay, 2001) and water-side air–water mass transfer coefficient (0.03 m h^{-1}) (Mackay, 2001) were used.

In the absence of an air–water partition coefficient, K_{AW} , for NP1EO, that of NP9EO was used ($9.69 \times 10^{-8} \text{ m}^3 \text{ m}^{-3}$ ($\log K_{AW}$ of -7.01)) calculated from the reported Henry's law constant of 0.00024 $\text{Pa m}^3 \text{ mol}^{-1}$ (Environment Canada and Health Canada). For comparison, based on the K_{OW} and K_{OA} reported for NP1EO (Salapavidou et al., 2011), a $\log K_{AW}$ of -6.7 is implied. Also, Henry's law constants for NP have been reported as $3-4 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1}$ or $\sim 1.5 \times 10^{-3} \text{ m}^3 \text{ m}^{-3}$, estimated from a vapor pressure and water solubility (Dachs et al., 1999) and $\sim 0.2 \text{ Pa m}^3 \text{ mol}^{-1}$ or a K_{AW} of $\sim 8 \times 10^{-5} \text{ m}^3 \text{ m}^{-3}$, from measurements for the two stereoisomers of 4(3',5'-dimethyl-3'-heptyl)-phenol of 483 ± 169 and $551 \pm 193 \text{ M atm}^{-1}$ (Xie et al., 2004).

The spray generation rate, droplet size and the number density of droplets are all dependent upon wind speed. The spray rate has

been experimentally determined in the field at various heights above the ocean surface with droplet radii ranging from approximately 1 μm –1000 μm as described by Andreas (1998). From empirical observations, mathematical flux functions were derived to account for the flux of aerosols as a function of droplet radii (Andreas, 1998). The flux of a chemical to the atmosphere via aqueous droplets can be calculated from the concentration of the chemical at the air–water interface and the enrichment of that chemical in the aqueous aerosols (Webster and Ellis, 2010). The naturally occurring film and jet droplets produced at low wind speeds are similar in size and mechanism of production to those in the experimental system of the present study with radii at formation, r_0 , of 3–50 μm (Andreas, 1998). In keeping with the experimental system, the droplet flux for radii of 2–10 μm was considered initially prior to consideration of the contribution of larger droplets.

As a case example, the individual chemical fluxes were calculated for the North Sea. The North Sea has a surface area of $7.5 \times 10^{11} \text{ m}^2$ (Management Unit of the North Sea Mathematical Models) and an average U_{10} wind speed (i.e., the wind speed at a height of 10 m) of 9.6 m s^{-1} (Windfinder). In the present study wind speeds of 5 m s^{-1} and 15 m s^{-1} are used as upper and lower boundaries for the North Sea with a flux of fine aerosols ($r_0 = 2\text{--}10 \mu\text{m}$) of approximately $0.09 \text{ L m}^{-2} \text{ y}^{-1}$ or $6.8 \times 10^{10} \text{ L year}^{-1}$ for a U_{10} wind speed of 5 m s^{-1} , and $0.74 \text{ L m}^{-2} \text{ y}^{-1}$ or $5.6 \times 10^{11} \text{ L year}^{-1}$ for a U_{10} wind speed of 15 m s^{-1} (Andreas, 1998). However, it is to be noted that using the water flux for only fine droplets ($r_0 \leq 10 \mu\text{m}$) provides a conservative estimate of the importance of aerosol production on chemical fate because it does not include the larger spume droplets produced at the higher wind speeds. Over the North Sea, water concentrations were reported at 90–1400 pg L^{-1} for NP in total water (dissolved and particle-associated) and 17–1660 pg L^{-1} for NP1EO in the dissolved phase (Xie et al., 2006). These water concentrations are consistent with measurements for two estuaries emptying into the North Sea, the Rhine and Scheldt estuaries where concentrations of 31–934 ng L^{-1} of NP, 4.6–1029 ng L^{-1} of NPnEO ($n = 1$ and 2), and 31–934 ng L^{-1} of NPnEO ($n = 3\text{--}15$) were reported for 1999 (Jonkers et al., 2003). Similar NP concentrations of 12–95 ng L^{-1} dissolved in the water have also been reported for the Hudson River estuary region (Dachs et al., 1999; Van Ry et al., 2000). This consistency of observed concentrations suggests that the results obtained in the present study will be broadly relevant. The observed enrichment in laboratory-produced droplets measured in the present study was applied to the case of the North Sea.

Larger droplets were not included in any calculation of water-to-gas phase transfer because, it is thought they will re-deposit before any significant chemical transfer has taken place (Armitage et al., 2009). For this reason it is also important to estimate the chemical half-life in a droplet due to volatilization. The half-life for this process, i.e., the chemical's half-life in a droplet, τ , assuming this is the only removal mechanism is given by

$$\tau = \ln(2)V_d/(A_d k_{ov})$$

where V_d is the droplet volume and A_d and k_{ov} are defined as above. For a spherical droplet this can be written as

$$\tau = \ln(2)(r_0/3)/k_{ov}. \quad (7)$$

If the half-life is short relative to the average time a droplet is likely to remain suspended in the air, significant transfer to the gas phase can be expected. If the half-life is long relative to the average suspension time of the droplet, it can be expected that the chemical's fate will be determined by the fate of the droplet, either carried in the atmosphere or re-deposited to the water body.

While it is recognized that that temperature will play a potential role in the transfer of the model sensitively is at least an order of magnitude less than any such effect.

3. Results and discussion

3.1. Laboratory-based aerosol enrichment

The generation of aqueous aerosols increased the water–air transport of NPEOs.

Over a 10-h period, aerosol samples were consistently enriched with respect to temporally coincident bulk water samples. The average enrichment was a factor of 4.4 which was consistent with previous observations for an ionizing surfactant in lake water (5.6 times) (McMurdo et al., 2008). Blank samples consistently showed no detectable levels of NPEO's. The increased ionic strength of natural waters from rivers and lakes to oceans are expected to increase enrichment of organic contaminants, such as NPEOs, in the aerosols. This was observed by McMurdo et al. (2008) who reported an order of magnitude greater enrichment of an ionizing surfactant in aerosols produced from ocean water than from fresh waters. Enrichment was also confirmed in studies using alternate techniques (Reth et al., 2011; Psillakis et al., 2009). Thus, the enrichment in this study is consistent with expectations for the water used but is regarded as a lower limit to the enrichment expected for environmental systems where there is a higher salinity.

3.2. Laboratory droplet sizing

Using high-speed photography, the size of the aerosols was determined (Fig. 2). The aerosol generator was found to be remarkably consistent with respect to droplet size producing droplets with radii of $10 \mu\text{m} \pm 0.5 \mu\text{m}$. The droplet generating system employed was that previously used and described in McMurdo et al. (2008). Similarly, realistic sizes of aerosols were produced in an independent study using a significantly different method of droplet generation (Reth et al., 2011). This droplet size is very representative of film and jet droplets observed in natural environments at low wind speeds (Andreas, 1998).

3.3. Field study water concentrations

Bermuda coastal waters showed concentrations of nonylphenol (Table 1) ranging from 36 to 51 ng L^{-1} which is notably higher than concentrations measured in the BATS deployment area which ranged from 14 to 21 ng L^{-1} (Table 2). The distribution of concentrations in the coastal samples and comparison with samples from the BATS site suggest that Bermuda is releasing nonylphenol into the marine environment. The data does not support a specific point source on the island, but does suggest a more uniform release likely caused by ground water diffusion and the wide spread usage of septic tanks on the island. Nonylphenol ethoxylates are degradable by multiple mechanisms including biodegradation resulting in less ethoxylated compounds and eventually NP (Environment Canada and Health Canada, Chiu et al., 2010; Soares et al., 2008). It is reasonable that degradation is the reason only 2 of 6 coastal samples showed the presence of NPEO (Table 1). If septic systems are the primary source of NP and NP1EO to coastal waters, the relatively long route to marine waters and the bioactive nature of the septic environment provide ideal conditions for degradation. It is also probable that NP1EO concentrations were under the method quantification limit of 1 ng L^{-1} .

Open water concentrations of NP from the BATS deployment area are comparable in concentration to samples from the North Sea between 0.09 and 63 ng L^{-1} (Xie et al., 2006; Heemken et al.,



Fig. 2. High speed photograph of water droplets (the fine, nearly horizontal lines) being blown along with 200 μm reference particles (the wide, more vertical lines).

2001). Comparison to the North Sea is necessary because no such measurements have been taken in the area of this study. It has been suggested that the range of values for NP in previous studies can be attributed to the nature of the currents at the time of sampling (Xie et al., 2006). Seasonal changes in concentrations have also been reported (Heemken et al., 2001). Nonylphenol monoethoxylate was included in the analysis but was not detected in any open water samples. Previous studies in the North Sea have found NP1EO in open water in similar concentrations to NP 0.017–14 ng L^{-1} . It is likely that levels in this study were below the method quantification limit for NP1EO (1 ng L^{-1}). The reduction of use in the years since the previous studies may also contribute to the low levels of NP1EO with NP as its legacy. Depth samples taken at the BATS deployment area show a decrease in concentration with depth with a loss of detection at below 300 m (Table 3).

3.4. Field study aqueous aerosols

Bow aerosol samples showed consistently higher concentrations of NP than fly deck samples with concentrations ranging from

Table 1

Surface concentrations of nonylphenol, NP, and nonylphenol ethoxylate, NPEO, with a 10% method uncertainty, at sampling sites in the Bermuda coastal region.

	NP, ng L^{-1}	NPEO, ng L^{-1}
Summerset Island	41	nd
South Channel	39	1
South Shore Park	40	nd
Harrington Sound	49	3
Bermuda International Airport	36	nd
Castle Harbour	51	nd

nd = below the detection limit.

Table 2

Surface water and aqueous aerosol nonylphenol, NP, concentration with a 10% method uncertainty and enrichment at Bermuda Atlantic Time Series (BATS) deployment area.

NP concentration, ng L^{-1}			Wind/weather conditions	NP enrichment factor	
Bow aerosols	Fly deck aerosols	Surface waters		Bow	Fly
232	70	16	6.7 m s^{-1} NE, Clear 20.1 °C, RH = 50%	14.5	4.3
270	79	14	8.2 m s^{-1} NE, Clear 20.0 °C, RH = 78%	19.2	5.6
217	84	19	6.7 m s^{-1} NE, Clear 23.3 °C, RH = 86%	11.4	4.4
69	n/a	19	2.6 m s^{-1} NE, Rain, 22.4 °C, RH = 98%	3.6	n/a
134	n/a	21	7.2 m s^{-1} NE, Rain, 21.9 °C, RH = 90%	6.3	n/a
116	n/a	16	7.7 m s^{-1} NE, Rain, 20.6 °C, RH = 93%	7.25	n/a

n/a = Not available.

0.72 to 1.8 ng m^{-3} during sampling periods with no rain and 0.57–1.0 ng m^{-3} during rain events. For safety reasons, fly deck samples were only taken during non-rain events and ranged from 0.28 to 0.54 ng m^{-3} . Atmospheric NP has not been reported for the study area but similar concentrations have been reported for both the North Sea (Xie et al., 2006) and the lower Hudson River estuary (Van Ry et al., 2000; Dachs et al., 1999). Quartz fiber filters (QFF), polyurethane foam (PUF) and XAD-2 solid phase extraction cartridges were used in the previous studies and concentrations were reported as particulate bound and vapor phase individually (Xie et al., 2006; Van Ry et al., 2000; Dachs et al., 1999). High volume sampling through PUF or XAD-2 cartridges would not distinguish true gas phase NP from aqueous aerosol bound NP. As a result, it is not surprising that the data from the present field study is similar to the previous work despite different collection apparatus. Field control samples were drawn 400 m inland in a sheltered area at ground level and showed no detectable level of NP. If gas phase chemicals were present at the control site the apparatus was not effectively collecting it.

Aerosols showed some variation in enrichment compared with surface water with bow enrichment ranging from 11.4 to 19.2 and fly deck enrichments from 4.3 to 5.6. This data is comparable to nonylphenol ethoxylate enrichment of 4.4 times the water concentration seen in the laboratory component of the present study that was conducted under low ionic strength conditions. Similar work conducted with perfluorooctanoic acid (CAS 335-67-1) also showed comparable results and reported increased aerosol enrichment when the ionic strength of the bulk solution was increased (McMurdo et al., 2008). The data describes a clear trend of enrichment in each of the samples despite exact quantitation being difficult due to humidity collected in the apparatus. Although the exact proportion of sea spray to vapor phase water is unknown,

Table 3

Concentration depth profile for nonylphenol, NP, with a 10% method uncertainty, at Bermuda Atlantic Time Series, BATS, deployment area.

Depth, m	NP, ng L ⁻¹
0	19
50	8
160	10
200	9
230	6
300	5
400+	nd

nd = below detection limit.

the collection of pure water could only dilute the samples resulting in higher enrichments than are being reported.

3.5. Modeling the sea-to-air flux of NPEOs due to aqueous aerosol spray

The relative contributions of the water-to-air flux processes were calculated for NPEOs using Equations (5) and (6) with results shown in Table 4. Due to the scarcity of measured or reported physical chemical properties for low EO NPEOs the properties of NP9EO were used. When only small droplet sizes are considered, as shown in Table 4, the spray-to-direct volatilization ratio, $R_{s/v}$, is nearly identical to the volatilized from spray-to-direct volatilization ratio, $R_{sg/v}$. Including the larger droplets (i.e. spume droplets) that are produced at higher wind speeds, volatilization from the droplets is much less effective. None-the-less, the contribution to the gas phase due to sea spray, when large droplets are included, exceeds that of direct volatilization by an order of magnitude while the in-droplet flux is nearly three orders of magnitude greater than direct volatilization.

These results are consistent with modeling of the ionizing surfactant, perfluorooctanoate (PFO) in equilibrium with its acid, perfluorooctanoic acid (PFOA) in the Lake Ontario watershed (Webster et al., 2010). It was concluded that at low wind speed, the spray generation rate would be insufficient for the flux to the gas phase via aqueous aerosols to be significant relative to the direct volatilization flux (Webster et al., 2010) but at higher wind speeds, the relative contribution could be much greater, as is seen in the present study.

The flux by each process can also be calculated using the measured NPEO enrichment of 4.4 in aqueous aerosols with respect to the source water as a lower limit of aerosol enrichment in higher ionic strength sea water, the reported observed concentration in a water body, and the total area of the water body. The model results for the case example of the North Sea are shown in Table 5. Calculation details are given in the Supplementary information.

The gross upward flux due to solely direct volatilization of NPEOs from the North Sea was calculated to be approximately 0.14–14 kg y⁻¹. The upward flux to the air in fine ($r_0 = 2–10 \mu\text{m}$) spray droplets at the upper and lower limits of reported bulk

water concentrations of 17–1660 pg L⁻¹ for NP1EO in the dissolved phase of the North Sea (Xie et al., 2006) was calculated to be approximately 5–500 g year⁻¹ and 40–4000 g year⁻¹ at U₁₀ wind speeds of 5 m s⁻¹ and 15 m s⁻¹, respectively. When larger droplets, up to an r_0 of 410 μm , are included, the flux of NP9EO to the atmosphere via spray production increases approximately three to four orders of magnitude depending on the wind speed and initial concentration in the bulk water.

It must be noted that we have here considered and compared only the ‘upward’ transfer processes and there are also similar compensatory ‘downward’ transfer processes, including sorption into the droplets from the gas phase that are not considered in this study. Clearly aqueous aerosol generation is responsible for the movement of a significant mass of NPEO as compared to volatilization even by this conservative estimate that neglects the higher ionic strength of sea water and the contribution of larger spray droplets.

3.6. Environmental relevance of spray-generated aqueous aerosols

Chemical movement between environmental media is an essential component of chemical fate in the environment. The direction of the net movement of NPs between the water and air compartments has been linked to the value of Henry’s law constant or air–water partition coefficient (K_{AW}) used to model the observed field concentrations. Two studies measuring NP concentrations in water and gaseous air samples in the coastal region of the New York-New Jersey Bight reported a net upward flux (Dachs et al., 1999; Van Ry et al., 2000) but a re-analysis of the Van Ry et al. (2000) data with a revised K_{AW} suggested no net flux or even a net downward flux (Xie et al., 2004). Specifically, Dachs et al. (1999) converted their measured concentrations to fugacities and concluded that there was a net upward flux that they attributed to direct volatilization (Dachs et al., 1999). Van Ry et al. (2000) calculated a net upward flux by volatilization using a multimedia model developed for the same region. With their air–water partition coefficient, K_{AW} , measured at approximately 20 times lower than that used by either Dachs et al. (1999) or Van Ry et al. (2000), Xie et al. (2004) concluded that there was a net deposition of NP in the Lower Bay and no net flux in the Upper Bay of the Lower Hudson River estuary (Xie et al., 2004). Similarly, the North Sea was reported by Xie et al. (2006) to be an important sink for NP and NPEOs using their previously published (Xie et al., 2004) Henry’s law constant and temperature correction.

Van Ry et al. (2000) suggested that in addition to direct volatilization, terrestrial sources could be contributing to the observed atmospheric concentrations in their field study. This was extended by Xie et al. (2004) with a net downward flux of NP in their model which attributed the observed atmospheric concentrations to a significant terrestrial source for the Hudson River estuary. Over the North Sea, a net downward flux again required terrestrial sources (Xie et al., 2006) but it was noted by the authors that the potential for chemical movement due to aerosol generation over

Table 4

Ratios of chemical flux to the atmosphere.

Range of radii r_0 , μm	Wind speed U ₁₀ , m s ⁻¹	Spray rate S, L m ⁻² y ⁻¹	$R_{s/v}$ (Eq. (5))	$R_{sg/v}$ (Eq. (6))	1/ $R_{sg/v}$	Dominant flux process
2–10	5	0.09	0.036	0.035	28.6	Direct volatilization
2–10	15	0.74	0.289	0.283	3.5	Direct volatilization
2–410	15	1900	752.24	12.35	0.08	Spray

$R_{s/v} = N_s/N_v$; $R_{sg/v} = N_{sg}/N_v$; N_s = chemical flux in aerosol droplets; N_v = direct volatilization; N_{sg} = flux to the gas phase via spray.

Table 5The calculated flux of NPEO (kg y^{-1}) by each process.

r_0 , μm	U_{10} , m s^{-1}	N_v	N_s	N_{sg}
		0.14–14.0		
2–10	5		0.005–0.50	0.005–0.49
2–10	15		0.04–4.0	0.04–3.94
2–410	5		1.7–165.4	0.87–85.1
2–410	15		107.5–10,497	1.76–172.4

r_0 = droplet radius of formation; U_{10} = wind speed at 10 m above sea level; N_v = flux by direct volatilization; N_s = chemical flux in aerosol droplets; N_d = diffusion flux from the spray droplets; N_{sg} = flux to the gas phase via spray.

the North Sea was unclear (Xie et al., 2006). Van Ry et al. (2000) reported that volatilization accounted for 37% of the total removal of NP from the water column and was the most important removal process. They also note that the absence of such processes as spray generation from their model adds to the overall uncertainty in their results (Van Ry et al., 2000). The modeling in the present study suggests that this omission likely under-estimates the total upward fluxes in their system thus over-estimating removal by advection in the water. Taking the modeling result of no net flux as predicted by Xie et al. (2004) for the Hudson estuary and adding the additional 3.5% contribution of spray production (at $U_{10} = 5 \text{ m s}^{-1}$ and for fine spray only) to the direct volatilization as calculated in this study, a slight upward flux to the gas phase is predicted for the Upper Bay of the Lower Hudson River estuary. Although Cincinelli et al. (2003) and Lepri et al. (2000) appear to be considering particulate released during aeration at sewage treatment plants, their results are consistent with and support the observations for aqueous aerosols in the present study.

The environmental consequences of spray-mediated transfer of contaminants from a water body to the atmosphere depend on the fate pathways available to the aqueous droplets upon entering atmosphere. For chemical remaining in the droplets, the fate of the droplets themselves is of importance as has been observed for various contaminants (e.g., Gill and Graedel, 1983; Oppo et al., 1999; Lepri et al., 2000; Tervahattu et al., 2002). Some droplets, especially the larger droplets, may return rapidly to the water surface with little overall effect while smaller droplets may move into the upper atmosphere and contribute directly to marine cloud contamination (Oppo et al., 1999). The height achieved by the droplet will control the horizontal travel distance and thus the magnitude of the long-range transport (LRT) potential of the associated chemical. It has been suggested that large droplets will return to the water quickly and thus should not be considered when looking at routes to the atmosphere (Armitage et al., 2009). Increased NP concentrations at lower elevation in the field data supports the theory that aqueous aerosols are acting as carriers for NP and provide some evidence to support the loss of large droplets even with small variations in elevation but it is still unknown what proportion and what size of droplets are reaching the heights greater than that of the fly deck sampler at 10.8 m. Furthermore during rain events, a drop in concentration was seen in the collection vessels. This also might be evidence that rain acts to return aqueous aerosols to the water below. Contaminant that is released from the spray droplets into the gas phase will have the greatest potential for transport. The model for chemical spray flux developed in this study suggests that the aerosol mechanism could provide NPEOs to the lower air compartment at a rate that is at least comparable to the volatilization mechanism. It is therefore suggested that omission of this mechanism in any calculation of LRT potential will result in under-estimation for NPEOs. Indeed, support for the mechanisms presented herein could be obtained if these compounds are found in remote regions at distance from their use or at altitude, for example in high altitude lakes.

4. Conclusions

The present study strongly supports the theory that aqueous aerosols are enriched in NP and NPEO's when compared to the bulk source water. Future research is necessary to increase the scope of the study and better understand the implications for long-range transport and fate modeling. Additional studies should include other organic chemicals, specifically species with surfactant properties. Based on previous work with bacteria and inorganics these effects may be relevant to a wide array of chemicals (Zhang et al., 2003; Cincinelli et al., 2001; Aller et al., 2005; McMurdo et al., 2008). The present study demonstrates that the water-to-air transport of NP and NPEOs is significantly influenced by the generation of aqueous aerosols. Thus, current environmental fate models will underestimate the mobility of NP and NPEO's due to their omission of spray generation and the potential for subsequent droplet-gas phase exchange in the atmosphere. Inclusion of the aerosol mass transfer function developed in the present study is expected to yield a more accurate representation of the fate of NPEOs in the environment. There are also areas and scenarios with potential significance for human exposure specifically areas with specialized water features such as coastal regions, waterfalls, and sewage treatment plants where there is a constant spray in addition to the regular and intimate exposure that occurs while showering in the home. Further investigation is required to establish the distribution of NP and NPEO within a water droplet and the effect of droplet size on mass transfer. The environmental impacts of this mechanism, including the potential for medium-distance and long-range transport, warrant further investigation.

Acknowledgments

We thank Procter and Gamble and the Natural Sciences and Engineering Council (NSERC) of Canada for their financial support of this work, and Dr. Cheryl McKenna Neuman and the staff at the Trent Environmental Wind Tunnel for the use of their facilities.

Appendix A. Supplementary information

Supplementary information related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2012.11.066>.

References

- Aller, J.Y., Kuznetsova, M.R., Jahns, C.J., Kemp, P.F., 2005. The sea surface microlayer as a source of viral and bacterial enrichment in marine aerosols. *J. Aerosol Sci.* 36 (5–6), 801–812.
- Andreas, E., 1998. A new sea spray generation function for wind speeds up to 32m/s. *J. Phys. Oceanogr.* 28 (11), 2175–2184.
- Armitage, J.M., MacLeod, M., Cousins, I.T., 2009. Modeling the global fate and transport of perfluorooctanoic acid (PFOA) and perfluorooctanoate (PFO) emitted from direct sources using a multispecies mass balance model. *Environ. Sci. Technol.* 43 (4), 1134–1140.
- Arnot, J.A., Mackay, D., 2008. Policies for chemical hazard and risk priority setting: can persistence, bioaccumulation, toxicity, and quantity information be combined? *Environ. Sci. Technol.* 42 (13), 4648–4654.
- Arnot, J.A., Mackay, D., Webster, E., Southwood, J.M., 2006. A screening level risk assessment model for chemical fate and effects in the environment. *Environ. Sci. Technol.* 40 (7), 2316–2323.
- Beyer, A., Mackay, D., Matthias, M., Wania, F., Webster, E., 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.* 34 (4), 699–703.
- Chiu, T.Y., Paterakis, N., Cartmell, E., Scrimshaw, M.D., Lester, J.N., 2010. A critical review of the formation of mono- and dicarboxylated metabolic intermediates of alkylphenol polyethoxylates during wastewater treatment and their environmental significance. *Crit. Rev. Environ. Sci. Technol.* 40 (3), 199–238.
- Cincinelli, A., Stortini, A.M., Perugini, M., 2001. Organic pollutants in sea-surface microlayer and aerosol in the coastal environment of Leghorn–Tyrrhenian Sea. *Mar. Chem.* 76 (1–2), 77–98.

- Cincinelli, A., Mandorlo, S., Dickhu, R.M., Lepri, L., 2003. Particulate organic compounds in the atmosphere surrounding an industrialised area of Prato (Italy). *Atmos. Environ.* 37 (22), 3125–3133.
- Dachs, J., Van Ry, D.A., Eisenreich, S.J., 1999. Occurrence of estrogenic nonylphenols in the urban and coastal atmosphere of the lower Hudson River estuary. *Environ. Sci. Technol.* 33 (15), 2676–2679.
- Diaz, A., Ventura, F., Galceran, M., 2002. Development of a solid-phase micro-extraction method for the determination of short-ethoxy-chain nonylphenols and their brominated analogs in raw and treated water. *J. Chromatogr. A* 1-2 (963), 159–167.
- Environment Canada and Health Canada: Priority Substances List Assessment Report for Nonylphenol and its Ethoxylates. www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl2-lsp2/nonylphenol/index-eng.php (accessed 31.10.12.).
- Environment Canada, June 2003. Guidance Manual for the Categorization of Organic and Inorganic Substances on Canada's Domestic Substances List: Determining Persistence, Bioaccumulation, and Inherent Toxicity to Non-human Organisms. Existing Substances Branch, Environment Canada, Gatineau, Canada.
- Gill, P.S., Graedel, T.E., 1983. Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes. *Rev. Geophys.* 21 (4), 903–920.
- Grammatika, M., Zimmerman, W.B., 2001. Microhydrodynamics of flotation processes in the sea surface layer. *Dyn. Atmos. Oceans* 34 (2–4), 327–348.
- Heemken, O.P., Reincke, H., Stachel, B., Theobald, N., 2001. The occurrence of xenoestrogens in the Elbe River and the North Sea. *Chemosphere* 45 (3), 245–259.
- Jonkers, N., Laane, R.W.P.M., De Voogt, P., 2003. Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. *Environ. Sci. Technol.* 37, 321–327.
- Kissa, E., 2001. Fluorinated Surfactants and Repellents, second ed., vol. 97. Marcel Dekker Inc, New York, 10 pp.
- Lepri, L., Del Bubba, M., Masi, F., Udisti, R., Cini, R., 2000. Particle size distribution of organic compounds in aqueous aerosols collected from above sewage aeration tanks. *Aerosol Sci. Technol.* 32 (5), 404–420.
- Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E., 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* 15 (9), 1627–1637.
- Mackay, D., 2001. Multimedia Environmental Models: the Fugacity Approach. Lewis Publishers, New York.
- Management Unit of the North Sea Mathematical Models: North Sea Facts. <http://www.mumm.ac.be/EN/NorthSea/facts.php> (accessed 31.10.12.).
- McMurdo, C.J., Ellis, D.A., Webster, E., Butler, J., Christensen, R.D., Reid, L.K., 2008. Aerosol enrichment of the surfactant PFO and mediation of the water–air transport of gaseous PFOA. *Environ. Sci. Technol.* 42 (11), 3969–3974.
- Oppo, C., Bellandi, S., Degli Innocenti, N., Stortini, A.M., Loglio, G., Schiavuta, E., Cini, R., 1999. Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols. *Mar. Chem.* 63 (3–4), 235–253.
- Perez-Tejeda, P., Maestre, A., Delgado-Cobos, P., 1990. Single-ion Setschenow coefficients for several hydrophobic non-electrolytes in aqueous electrolyte solutions. *Can. J. Chem.* 68 (2), 243–246.
- Psillakis, E., Cheng, J., Hoffmann, M.R., Collussi, A.J., 2009. Enrichment factors of perfluoroalkyl oxoanions at the air/water interface. *J. Phys. Chem. A* 113 (31), 8826–8829.
- Reth, M., Berger, U., Broman, D., Cousins, I.T., Nilsson, E.D., McLachlan, M.S., 2011. Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray generator. *Environ. Chem.* 8 (4), 381–388.
- Richardson, S.D., 2012. Environmental mass spectrometry: emerging contaminants and current issues. *Anal. Chem.* 84, 747–778.
- Royal Society of Chemistry: Surfactants: the Ubiquitous Amphiphiles. <http://www.rsc.org/chemistryworld/issues/2003/July/amphiphiles.asp> (accessed 31.10.12.).
- Salapatsidou, M., Samara, C., Voutsas, D., 2011. Endocrine disrupting compounds in the atmosphere of the urban area of Thessaloniki, Greece. *Atmos. Environ.* 45, 3720–3729.
- Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., Lester, J.N., 2008. Nonylphenol in the environment: a critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environ. Int.* 34 (7), 1033–1049.
- Tervahattu, H., Juhanoja, J., Kupiainen, K., 2002. New evidence of an organic layer on marine aerosols. *J. Geophys. Res.* D 107 (4053), AAC1–AAC9.
- Van Ry, D.A., Dachs, J., Gigliotti, C.L., Brunciak, P.A., Nelson, E.D., Eisenreich, S.J., 2000. Atmospheric seasonal trends and environmental fate of alkylphenols in the lower Hudson River estuary. *Environ. Sci. Technol.* 34 (12), 2410–2417.
- Vermeire, T., Rikken, M., Attias, L., Boccardi, P., Boeije, G., Brooke, D., de Bruijn, J., Comber, M., Dolan, B., Fischer, S., Heinemeyer, G., Koch, V., Lijzen, J., Müller, B., Murray-Smith, R., Tadeo, J., 2005. European union system for the evaluation of substances: the second version. *Chemosphere* 59 (4), 473–485.
- Webster, E., Ellis, D.A., 2010. Potential role of sea spray generation in the atmospheric transport of perfluorocarboxylic acids. *Environ. Toxicol. Chem.* 29 (8), 1703–1708.
- Webster, E., Ellis, D.A., Reid, L.K., 2010. Modeling the environmental fate of perfluorooctanoic acid and perfluorooctanoate: an investigation of the role of individual species partitioning. *Environ. Toxicol. Chem.* 29 (7), 1466–1475.
- Windfinder: Wind & Weather Forecast Forties North Sea Platform. http://www.windfinder.com/forecast/forties_north_sea_platform (accessed 31.10.12.).
- Woodcock, A.H., 1953. Salt nuclei in marine air as a function of altitude and wind force. *J. Meteor.* 10, 362–371.
- Xie, Z., Le Calve, S., Feigenbrugel, V., Preuß, T.G., Vinken, R., Ebinghaus, R., Ruck, W., 2004. Henry's law constants measurements of the nonylphenol isomer 4(3',5'-dimethyl-3'-heptyl)-phenol, tertiary octylphenol and γ -hexachlorocyclohexane between 278 and 298K. *Atmos. Environ.* 38 (29), 4859–4868.
- Xie, Z., Lakaschus, S., Ebinghaus, R., Caba, A., Ruck, W., 2006. Atmospheric concentrations and air sea exchanges of nonylphenol, tertiaryoctylphenol and nonylphenol monoethoxylate in the North Sea. *Environ. Pollut.* 142 (1), 170–180.
- Zhang, Z., Liu, L., Liu, C., Cai, W., 2003. Studies on the sea surface microlayer: II. The layer of sudden change of physical and chemical properties. *J. Colloid Interface Sci.* 264 (1), 148–159.