

liver and kidney damage, and characterized as endocrine disruptors (Petrovic et al., 2001; Gomez-Hens and Aguilar-Caballeros, 2003). 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). 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 phthalates in PVC toys for children under three years of age. In December 1999, the European Union (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).

To date, most research focused on aquatic environments. Phthalates' concentrations have been reported in the range of 0.1–300 $\mu\text{g L}^{-1}$ for surface marine waters (Mayer et al., 1972; Giam et al., 1978; Gledhill et al., 1980; Fatoki and Vermon, 1990), and of 1.0–13.5 $\mu\text{g L}^{-1}$ for freshwater sites (Gledhill et al., 1980; Fromme et al., 2002; Yuan et al., 2002). Phthalate concentrations in the river and marine inlet sediments were reported in the range of 0.1–100 $\mu\text{g g}^{-1}$ (Thurén, 1986; Tan, 1995; Yuan et al., 2002; Lin et al., 2003). Data concerning concentrations of phthalates in ambient air are extremely limited. Giam et al. (1978) reported mean DBP concentrations of 0.3 ng m^{-3} over the Gulf of Mexico and 1.0 ng m^{-3} over the North Atlantic. The concentrations of DEHP in air have been investigated in the North Atlantic, the Gulf of Mexico, and on Enewetak Atoll in the North Pacific and found from below the detection limit to 4.1 ng m^{-3} (Giam et al., 1978, 1980; Atlas and Giam, 1981).

Obviously, these chemicals have reached even the remote areas since 1970s (Giam et al., 1978, 1980; Weschler, 1981). However, very few data regarding environmental distribution and fate for phthalates in the North Sea are available. The purpose of this study was to determine concentrations of selected phthalates in different media of the North Sea in order to evaluate their distributions in different compartments. The second goal of this research was to estimate the direction of the air–sea vapour exchange of selected analytes. The selected phthalates were DMP, DEP, DBP, BBP, DEHP and DOP.

2. Experimental

2.1. Air and water sampling

The air and water samples in the North Sea (German Bight) were collected during the cruise no. 414 with the research vessel 'Gauss' from 29th February to 10th March in 2004. Integrated water samples were collected at 4.5 m depth during the ship steaming. The air samples were collected on the upper deck of 'Gauss' about 9 m above sea level. Detailed information on the sampling stations, temperatures, wind speeds, salinities and sample volumes, are given in Fig. 1 and in Table 1.

As described previously (Petrick et al., 1996; Lakaschus et al., 2002), total suspended matter (TSM) and water were collected using a glass fibre filter (GF/F 52, diameter: 142 mm, Schleicher and Schuell, Dassel, Germany) and a PAD-2 resin column (50 g PAD-2, 22 cm \times 3 cm i.d.), respectively. The in situ pump was placed in the wet lab and directly connected to the sea water supplied by an assembly stainless steel pipeline (o.d. 10 mm). Hundred to 400 L sea water passed through the PAD-2 column at a flow rate ranging from 0.5 to 1 L min^{-1} in terms of the amount of TSM. Shipboard air samples (494–1147 m^3) were taken using a high-volume pump (ISAP 2000, Schulze Automation & Engineering, Asendorf, Germany) operating at a constant flow rate of 200 L min^{-1} . The particles were collected using a glass fibre filter (GF/F 8, diameter: 155 mm, Schleicher and Schuell, Dassel, Germany), and the vapour phthalates were collected on the PUF/XAD-2 column. In order to escape the emissions from the ship's funnel, air sampling was performed on headwind, and was stopped while wind speed was lower than 3 m s^{-1} . Samples were stored as described by Lakaschus et al. (2002).

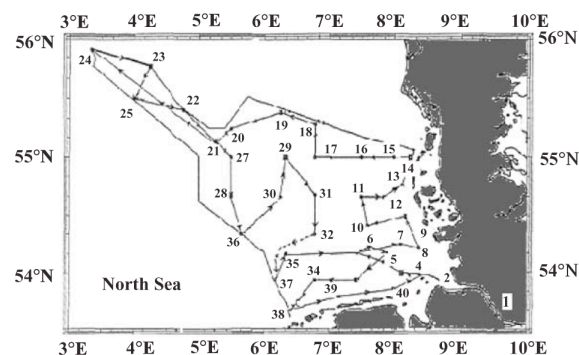


Fig. 1. Sampling stations in the North Sea during the cruise 414 with research vessel "Gauss", 29 February–10 March 2004.