Table 3
Field blanks (ng) and the concentrations of phthalates in the sea water and in the atmosphere of the North Sea

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

NA: sample was not analyzed; ND: Concentration was lower than the MDL; SD: Standard deviation. The averages of field blanks were subtracted before calculating the concentrations of the samples.

to 6 pg. The MDLs were derived from the blanks and quantified as mean field blanks plus three times of the standard deviation (3σ) of field blanks.

3. Results and discussion

3.1. Water concentrations

The concentrations of phthalates in dissolved and TSM phases are given in Table 3. The results showed that DEHP and DBP dominated phthalates' concentrations in the water phase of the North Sea. The concentrations were in the range of 0.45–6.6 ng L^{-1} for DBP and 0.52–5.3 ng L^{-1} for DEHP. DMP and DEP were detected in more than 80% water samples with concentrations ranging from 0.02 to 4.0 ng L^{-1}. Due to the artefacts of high volume sample collection and their high water solubility, the concentrations of DMP and DEP might be under-estimated. BBP was unexpectedly found in most of the water samples, with concentrations ranging from below MDL to 0.26 ng L^{-1}, although it is released in lower quantities as compared to those of DBP and DEHP. Since DOP concentrations were lower than the method detection limits ($\leqslant 0.01$ ng L^{-1} in water

and $\leqslant 0.002$ ng m^{-3} in air) in all the samples, it is not discussed in this paper.

Fromme et al. (2002) investigated phthalates in the surface water of various rivers in Germany (Rhine, Elbe, Ruhr, Mosel, Havel, Spree, Oder), and reported that the concentrations were ranging from 0.33 to 97.8 μg L^{-1} for DEHP and from 0.12 to 8.80 μg L^{-1} for DBP, respectively. They were 2 or 3 orders of magnitude higher than the concentrations determined in the North Sea in our study. Moreover, the concentrations of DBP and DEHP in the samples collected in the plume of Elbe were one order of magnitude higher than that in the central part of the North Sea. It was suggested that the river-carried contaminations are a significant input source of phthalates into the North Sea.

DBP and DEHP were also detected in most of TSM samples. The concentration ranged from 0.01 to 0.20 ng L^{-1} for DBP, and from 0.16 to 5.8 ng L^{-1} for DEHP. BBP was found in three samples with concentrations ranging from 0.01 to 0.03 ng L^{-1}. As shown in Fig. 2, TSM-associated DBP, BBP and DEHP fractions were 2%, 29% and 42%, respectively. DMP and DEP were also found in some TSM samples. Considering the underestimated water concentrations, the TSM fractions were not calculated for DMP and DEP.
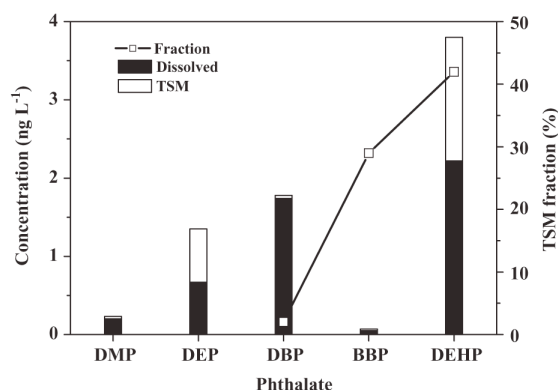
Fig. 2. Total concentrations of phthalates in sea water and TSM fractions.

TSM associated phthalate fractions were examined previously in surface water samples. Germain and Langlois (1988) reported a TSM fraction of 14% for DBP and 53% for DEHP. No other phthalate was detectable in TSM associated fractions. Preston and Al-omran (1986,1989) studied the distribution of phthalates in the River Mersey Estuary in UK. Fourteen to 34% of DBP was found to be TSM bound (TSM = $1524\,mg\,L^{-1}$). Furtmann (1993) reported that 15–17% of the low molecular weight phthalates DMP and BBP were TSM bound. Ritsema et al. (1989) estimated that 2% of DBP and 67% of DEHP was TSM bound in the Lake Yssel and the Rhine River (Netherlands). As compared to the reported values, our results are in the lower part of the ranges. The differences might result from the sampling device and separation techniques, especially the TSM concentrations in aquatic phase. In the North Sea, TSM concentrations ranging from 1.36 to $12.69\,mg\,L^{-1}$ were recorded during another cruise in April 2003. Moreover, the organic matter fraction in the TSM phase is also an important factor for the partitioning of phthalates in the aquatic phase. In addition, the water temperature significantly influences the partition of phthalates between aquatic and TSM phases. Finally, the effect of the salinity should be taken into account for the salting out effect. Nevertheless, these results provided evidence that high molecular phthalates likely partition to suspended matter either in river or the open sea. Particularly, DEHP has very low solubility in water and high TSM bound capability, consequently, it was expected to be accumulated in the sediment and to undergo degradation processes only slowly.

3.2. Air concentrations

Phthalates concentrations in the atmosphere were shown in Table 3. The average concentrations were 0.30, 1.6, 0.53, 0.02, $0.29\,ng\,m^{-3}$ for DMP, DEP, DBP, BBP and DEHP in the vapour phase, respectively. In the particle phase, average concentrations were 0.06, 0.53, 0.05 and $1.0\,ng\,m^{-3}$ for DEP, DBP, BBP and DEHP. DMP concentration in the particle phase was below the detection limit in all air samples. The low level of particle associated DMP fractions may result from its high vapour pressure.

Atlas and Giam (1981) reported that DBP and DEHP mean concentrations at Enewetak Atoll in the North Pacific Ocean, which were $0.9\,ng\,m^{-3}$ for DBP and $1.4\,ng\,m^{-3}$ for DEHP, to be considered as background data for selected organic pollutants. Giam et al. (1978, 1980) reported the total vapour and particle concentrations of phthalates in marine atmosphere in the North Atlantic and the Gulf of Mexico. The average concentrations were 1.30 and $1.16\,ng\,m^{-3}$ for DBP and DEHP in the Gulf of Mexico and 1.0 and $2.9\,ng\,m^{-3}$ for DBP and DEHP in the North Atlantic. Weschler (1981) reported DBP in the Arctic aerosol at Barrow, Alaska, at a concentration of $1\,ng\,m^{-3}$. It was indicated that phthalates were ubiquitous in the marine atmosphere. The total concentrations of DBP and DEHP in the atmosphere over the North Sea were determined as 1.0 and $1.3\,ng\,m^{-3}$, which well agree to those reported values. Similar DEHP concentrations from 0.5 to $5\,ng\,m^{-3}$ have been detected in the Great Lakes (Eisenreich et al., 1981) and in the Swedish atmosphere (Thurén and Larsson, 1990). Moreover, DEHP were detected in relatively high concentrations near contaminated areas with levels of 29–$132\,ng\,m^{-3}$ in Antwep, Belgium (Cautreels et al., 1977; Cautreels and Van Cauwenberghe, 1978), $300\,ng\,m^{-3}$ in City of Hamilton and Ontario, Canada (Thomas, 1973), and 38–$790\,ng\,m^{-3}$ in Japan (Environment Agency of Japan, 1989). Hoff and Chan (1987) reported mean DBP concentrations of $1.9\pm1.3\,ng\,m^{-3}$ in the vapour phase and $4.0\pm2.2\,ng\,m^{-3}$ in the particle phase along the Niagara River in Ontario, Canada. DBP has also been detected in ambient air in Barcelona, Spain, with a concentration ranging from 3.0 to $17\,ng\,m^{-3}$ in winter and 1.1–$10\,ng\,m^{-3}$ in summer for coarse ($>7.2\,\mu m$) and fine particulate ($<0.5\,\mu m$), respectively (Aceves and Grimalt, 1993). Cautreels et al. (1977) reported the concentrations of DBP from 24 to $74\,ng\,m^{-3}$ in the particulate phase of the air in a residential area of Antwerp, Belgium, and 19–$36\,ng\,m^{-3}$ in a rural area in Bolivia. BBP have been also previously determined in the ambient air in Barcelona, Spain, with a concentration ranging 0.25–$8.0\,ng\,m^{-3}$, associated with coarse ($>7.2\,\mu m$) and fine particulate ($<0.5\,\mu m$), respectively (Aceves and Grimalt, 1993). DEP was determined in Newark (USA) in the indoor air and outdoor air, with concentrations ranging from 1.60 to $2.03\,\mu g\,m^{-3}$, and from 0.40 to $0.52\,\mu g\,m^{-3}$ (Shields and Weschler, 1987), respectively. As compared to the concentrations of