process of DBP. The net fluxes of BBP were in a range from -4 to $-28\,\mathrm{ng\,m^{-2}\,day^{-1}}$, which indicate also a net deposition. The results obtained for DEHP were ranging from -95 to $+686\,\mathrm{ng\,m^{-2}\,day^{-1}}$, shows a very complicated mechanism for the air–sea vapour exchange for DEHP.

As shown in Table 4, the averages of K_{OL} values were 0.0049, 0.0074 and 0.097 m day^{-1} for DBP, BBP and DEHP, respectively. Similar effects of wind speeds on k_w as indicated by Wanninkhof, (1992) and Bamford et al. (2002a) can be seen in air–sea exchange fluxes (Table 4). Besides, although water temperatures were only varying from 3.8 to 6.7 °C during this cruise, the H' estimated at higher temperatures were higher by factor of approximately 1.5 than the average value. Both impacts from temperature and wind speed significantly increased K_{OL} values for water samples W6, W7, and by a factor of 1.5 compared to average values. Consequently, relative higher exchange fluxes were estimated for these samples. It was demonstrated that a better understanding of the mass transfer coefficient would rather improve the estimation of the vapour exchange fluxes than a higher accuracy of the concentrations (Bamford et al., 1999).

Eisenreich et al. (1981) have previously estimated total deposition (dry and wet) of DBP and DEHP to the Great Lake as 3.7–16 tons per year, which indicated that the atmosphere is the major contamination source. Because of the absence of H values and air/water fluxes calculations for phthalates in their report, it was limited to be used for comparison. Therefore, comparison was performed with air–water vapour exchange fluxes of PAHs and PCBs in coastal regions. Nelson et al. (1998) studied air–sea exchange of PAHs and PCBs in the Chesapeake Bay. Moreover, the vapour exchange fluxes of PCBs across Baltimore Harbor and the North Chesapeake Bay were well studied by Bamford and co-workers (2002a). The high ratios of volatilization fluxes to deposition fluxes indicated the dominance of the water-side concentration of PCBs in the overall concentration gradient. As compared to their results, our findings for DBP indicated that the air-side concentrations dominated the overall concentration gradients, which were comparable to those of lighter PAHs. As compared to PCBs, the difference for overall concentration gradients can be addressed to their H' values. For example, H values of PCBs estimated by Bamford et al. (2002b) are 1–3 orders of magnitude higher than that of DBP. It indicates that, besides the effect on K_{OL}, temperature determined H values could change the overall concentration gradients with the interface temperature increasing in warm season. If it is supposed that the concentrations of phthalates were less variable through all the seasons, air–sea exchange fluxes and directions might significantly change in warm season. Consequently, decreasing deposition fluxes for DBP could be expected in summer. BBP might show a similar

pattern like Chrysene (Nelson et al., 1998), based upon their comparable K_{OL} values and their concentration gradients. As for DEHP, it can be expected that increasing temperature in warm season will increase the potential of volatilization based on the significantly increasing H value.

In conclusion, this study showed that the North Sea is an important sink for the phthalates. Re-volatilization of phthalates might be expected in warm season. Since phthalates are continually produced and consumed in huge amounts worldwide, they might predominate environmental contaminations for a relatively long period. The net fluxes indicate that the air–sea exchange is significant, and the open sea even in polar areas will be an extensive sink for phthalates. Considering the particle associated fractions and washout ratios, the dry deposition by descending particles and the wet deposition by rainfall or snow, atmospheric input of phthalates to the aquatic phase might be even higher. Furthermore, since phthalates turn to partition to the suspended matter in the water phase, it will significantly slowdown the photo- or bio-degradation processes and increase their environmental life and potential hazard to marine organisms. Therefore, further studies will be conducted to elucidate the spatial and temporal dependences of the distributions of phthalates in the coastal margins and in the open ocean.

Acknowledgements

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