

phthalates in the urban or contaminated area, the concentrations in the atmosphere over the North Sea are 1–2 orders of magnitude lower. This level of phthalates determined in the North Sea, therefore, appears to represent a regional background.

As shown in Fig. 3, the particle-associated fractions were calculated as 2%, 46%, 75% and 78% for DEP, DBP, BBP and DEHP. Compared to the values of 43% for DEHP, 32% for DBP reported by Giam et al. (1980), these values are factor of 1.4–1.8 higher. The difference may be determined by the temperature difference of the sampling period or by the velocity of the sampling units. The distribution of phthalates in air between vapour and particles have been estimated by Staples et al. (1997), based on the Junge model (Eisenreich et al., 1981). The estimated fractions of phthalates on the particles were 0.019%, 0.039%, 1.4%, 7.2%, and 80%, at ambient temperature. The estimated value of DEHP agrees with that determined in this study although the temperatures were different. However, the estimated values of DEP, DBP and BBP are 1–2 orders of magnitude lower than those determined by Giam et al. (1978) and in this work. It suggests that temperature significantly determines the partition of phthalates between the vapour and particle phases, especially for the lighter phthalates. Consequently, both vapour and particle phases are important media for the transport of these phthalates from contamination sources to the coastal margins.

3.3. Washout ratio

The washout ratio (W) is defined as the dimensionless ratio of chemical concentrations in precipitation to that in air. Considering both vapour and particle scavenging mechanism, washout can be expressed as (Bidleman, 1988)

$$W = (1 - \phi) \frac{RT}{H} + \phi W_p, \quad (1)$$

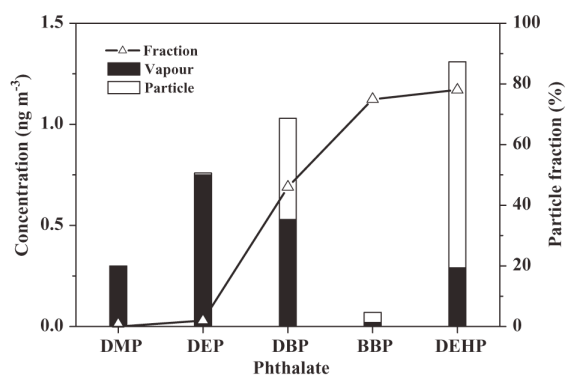


Fig. 3. Total concentrations of phthalates in air and particle fractions.

where ϕ is the fraction of the chemical on the particle, RT/H is the dimensionless Henry's law constant at the ambient temperature, W_p is the particle scavenging coefficient. Based on our experimentally determined ϕ values, using Henry's law constants estimated by Cousins and Mackay (2000), and a representative W_p value of 20,000 (Ligocki et al., 1985), the washout ratio calculated is 9200 for DBP, 15,000 for BBP, and 15,600 for DEHP at average sampling temperature of 5 °C. These values are very comparable to the washout ratios estimated by Staples et al. (1997). Obviously, the washout ratios appear to be temperature dependent, because both Henry's law constant and vapour pressure are determined by the temperature. In fact, this phenomenon has been observed for the atmospheric removal of DBP and DEHP in Sweden (Thurén and Larsson, 1990).

3.4. Air–sea vapour exchange

3.4.1. Air–sea exchange model

In this study, air–sea vapour exchange fluxes were estimated using the modified version of two-film resistance model (Achman et al., 1993; Hornbuckle et al., 1994), which was extensively used for the evaluation of PCBs and PAHs fluxes through air–water interfaces (Nelson et al., 1998; Bamford et al., 1999, 2002a; Gioia et al., 2005; Totten et al., 2004). It assumes that the rate of transfer is controlled by the compound's ability to diffuse across two thin stagnant films at the air–water interface, the water film and the air film. The molecular diffusivity of the compound (dependent on the amount of resistance encountered in the liquid and gas films) describes the rate of transfer while the concentration gradient drives the direction of transfer.

The overall flux calculation is defined by

$$F = K_{OL} \left(C_w - \frac{C_a}{H} \right), \quad (2)$$

where F is the flux ($\text{ng m}^{-2} \text{day}^{-1}$), C_w (ng m^{-3}) and C_a (ng m^{-3}) are the dissolved- and vapour-phase concentrations, $(C_w - C_a/H)$ describes the concentration gradient (ng m^{-3}), H is the dimensionless Henry's law constant, and K_{OL} (m day^{-1}) is mass transfer coefficient comprising resistances to mass transfer in both water (k_w) and air (k_a). Since averages of water temperatures were ranging from 3.8 to 6.7 °C on this cruise, the Schmidt number for CO_2 at 5 °C ($Sc_{\text{CO}_2} = 1395$) was applied for the estimation of k_w (Schwarzenbach et al., 1993). H was corrected with water temperatures (T , K) and averaged salt concentrations (C_s , 0.5 mol L^{-1}) based on following Eqs. (3)–(5) (ten Hulscher et al., 1992; Schwarzenbach et al., 1993):

$$\ln H = \ln H_0 + \frac{\Delta H_v}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right), \quad (3)$$