$$H_{\text{corrected}} = H \times 10^{K_s C_s}, \quad (4)$$

$$H' = \frac{H_{\text{corrected}}}{RT}, \quad (5)$$

where R is the ideal gas constant ($8.314 \times 10^{-3}\,\text{kJ}\,\text{mol}^{-1}\,\text{K}^{-1}$), H ($\text{Pa}\,\text{m}^3\,\text{mol}^{-1}$) is the Henry's law constant at given T, H_0 is Henry's law constant at T_0 (298.15 K), K_s is the salting constant of 0.3 (Schwarzenbach et al., 1993), and $H_{\text{corrected}}$ is the corrected Henry's law constant for salinity. ΔH_v is the enthalpy of vapourization at 298.15 K, which is supposed to be constant over the ambient temperature range (ten Hulscher et al., 1992). ΔH_v values for phthalates (see Table 2) were estimated from their enthalpies of vapourization at boiling point (Schwarzenbach et al., 1993; California EPA, 2001). H_0 values of phthalates estimated using the 'three solubility' approach (Cousins and Mackay, 2000) were used for the calculation.

3.4.2. Uncertainty analysis

The uncertainty in the F (Eq. (2)) was evaluated using a propagation of error analysis derived from Shoemaker et al. (1974), which has been used in previous studies (Nelson et al., 1998; Bamford et al., 2002a). The summation of the various random errors in the flux are described by

$$\sigma^2(F) = \left(\frac{\delta F}{\delta K_{\text{OL}}}\right)^2 (\sigma K_{\text{OL}})^2 + \left(\frac{\delta F}{\delta C_w}\right)^2 (\sigma C_w)^2 + \left(\frac{\delta F}{\delta C_a}\right)^2 (\sigma C_a)^2 + \left(\frac{\delta F}{\delta H}\right)^2 (\sigma H')^2. \quad (6)$$

Total propagated variance $\sigma^2(F)$ is the linear combination of the weighted contribution of the variances (σ^2) of the mass transfer coefficient, H' and measured concentrations. The error in H' was assumed to be zero because it is a systematic and not random error (Nelson et al., 1998; Bamford et al., 2002a). The errors of C_w and C_a were assumed to be 15% including the sampling and analytical errors. The uncertainty in K_{OL} was determined by propagating random errors in the air– and water-side transfer velocities, which was summated to be 40% following Wanninkhof et al. (1990) and Nelson et al. (1998). The overall propagated error in F is thus, 45% (Table 4). It was shown that most of the uncertainty associated with the fluxes was attributed to K_{OL} (78%), which was factor of 7 higher than the uncertainties associated with C_w and C_a (11%). As a source of systematic error, H' has a standard error of prediction that is approximately a factor of 3 on the arithmetic value (Cousins and Mackay, 2000), which can affect either K_{OL} or the overall concentration gradient. Therefore, accuracy of H' is significant for the estimation of air–sea exchange fluxes, which keeps a need for better understanding of their temperature dependences and improvements for the estimation.

3.4.3. Air–sea exchange fluxes

The estimated fluxes of DBP, BBP and DEHP in the North Sea and overall mass transfer coefficients were shown in Table 4. The negative values indicate a net deposition into water; in reverse, the positive values indicate a net volatilization to the atmosphere. Since the water concentrations of DMP and DEP may be underestimated, therefore, their fluxes were not calculated in this work.

The net fluxes of DBP ranged from −60 to $-686\,\text{ng}\,\text{m}^{-2}\,\text{day}^{-1}$ in the North Sea. It indicates that a net deposition dominates the air–sea vapour exchange

Table 4
Air–sea vapour exchange fluxes of DBP, BBP and DEHP in the North Sea. The errors were calculated at 45% level for F and at 40% level for K_{OL}

Sample	DBP		BBP		DEHP	
	$K_{\text{OL}}(10^{-3}\,\text{m}\,\text{day}^{-1})$	Flux($\text{ng}\,\text{m}^{-2}\,\text{day}^{-1}$)	$K_{\text{OL}}(10^{-3}\,\text{m}\,\text{day}^{-1})$	Flux($\text{ng}\,\text{m}^{-2}\,\text{day}^{-1}$)	$K_{\text{OL}}(10^{-3}\,\text{m}\,\text{day}^{-1})$	Flux($\text{ng}\,\text{m}^{-2}\,\text{day}^{-1}$)
W1	4.4±1.8	−686±309	6.6±2.6	−24±11	86±34	+178±80
W2	4.4±1.8	−685±308	6.6±2.6	−25±11	86±34	−58±26
W3	4.5±1.8	−773±348	6.8±2.7	−28±13	—	—
W4	5.0±2.0	−238±107	7.5±3.0	−7±3	98±39	−95±43
W5	4.3±1.7	−173±78	6.5±2.6	−5±2	85±34	−57±26
W6	8.8±3.5	−327±147	13±5.2	−10±4	180±72	+686±309
W7	7.1±2.8	−278±125	11.0 ±4.4	−8±4	140±56	+279±125
W8	3.1± 1.2	−61±27	4.6±1.8	−4±2	60±24	−7±3
W9	3.0±1.2	−60±27	4.4±1.8	−4±2	57±23	−32±14
W10	4.1±1.6	−91±41	6.2±2.5	−5±2	81±32	−60±27
W11	5.8±2.3	−132±59	8.6±3.4	−7±3	110±44	+245±110
Average	4.9±2.0	−338±152	7.4±3.0	−13±6	97±39	+53±24