

The derived enthalpies of solvation are -72.6 ± 7.9 , -71.6 ± 7.6 , -75.1 ± 11.5 and $-51.3 \pm 9.0 \text{ kJ mol}^{-1}$ for NP353(+), NP353(-), *t*-OP, and γ -HCH, respectively. The errors on the enthalpies were calculated using the errors of the slopes of the regression functions. As shown in Table 2, the calculated value of ΔH_{sol} for γ -HCH agrees very well with the values found in the literature that range from -45.6 to $-61.4 \text{ kJ mol}^{-1}$ (Feigenbrugel et al., 2004c; Sahsuvar et al., 2003; Jantunen et al., 2000; Kucklick et al., 1991).

4. Application: air/water exchange of NP in coastal regions

Air/water exchange of NP has been previously estimated for the Lower Hudson River estuary in 1999 (Dachs et al., 1999) and 2000 (Van Ry et al., 2000). Since the HLC value of NP353 in this work is significantly different from the estimated HLC value from vapor pressure and water solubility that was employed for the calculations in these publications, reevaluations have been done with our experimental HLC values of NP for those areas.

The ratio of the fugacities in water (f_w) and air (f_a) has often been employed to assess the state of equilibrium of semi-volatile organic compounds between the air and water phase (Jantunen and Bidleman, 1997). Fugacities (partial pressure, Pa) of f_a and f_w were calculated from

$$f_a = C_a \frac{RT_a}{M}, \quad (9)$$

$$f_w = C_w \frac{H}{M}, \quad (10)$$

where C_a and C_w are gaseous and dissolved concentrations of NP in air and surface water (g m^{-3}), M is the molecular mass (g mol^{-1}), $R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$, T_a (K) is air temperature and H is the Henry's law constant ($\text{Pa m}^3 \text{ mol}^{-1}$) at the water temperature ($H = 101.325/\text{HLC}$) (Schwarzenbach et al., 1993; Gaudier et al., 2003). In this work, we took the average of the HLC values of both diastereomers of NP353 as the HLC value of NP. We normalized the fugacity of water and

air, thus

$$Ff_w = \frac{f_w}{(f_w + f_a)}, \quad (11)$$

$$Ff_a = \frac{f_a}{(f_w + f_a)}, \quad (12)$$

when $Ff_w = Ff_a = 0.5$, it implies that deposition and volatilization of the compound is balanced. When $Ff_w < 0.5$, it indicates that the direction of air/water exchange of the compound deposits from air into water, in the reverse case, the compound volatilizes (Lakaschus et al., 2002).

Uncertainties in the fugacity calculations were estimated by propagation of the uncertainties in C_w , C_a and H . A detailed analysis of the uncertainties associated with the determination of air/sea gaseous exchange fluxes of organic chemicals was given by Hoff (1994). Following Hoff and assuming that the errors in R , T and M were negligible, Bruhn et al. (2003) deduced

$$\varepsilon^2 f_w = \varepsilon^2 C_w + \varepsilon^2 H. \quad (13)$$

A reasonable estimate of ε_{C_w} and ε_{C_a} that considers random sampling and analytical measurement uncertainty is 15%. Therefore, the uncertainty is 38% and 15% for f_w and f_a of NP, respectively.

The calculations were made using concentrations of NP in the air and water phase in the Lower Hudson River estuary taken from the publication (Van Ry et al., 2000). Table 3 shows Ff_w for NP in the Lower Bay and the Upper Bay calculated with the HLC determined in this work and the one used by Van Ry et al. (2000). Differences in the net gas exchange directions for NP in the Lower Hudson River Estuary were predicted using the HLC values determined in this work and that estimated with vapor pressure and solubility (Van Ry et al., 2000). In both Upper Bay and Lower Bay in the Lower Hudson River, a net volatilization of NP could be predicted employing the estimated HLC value. However, the reversed direction of the net gas exchange of NP could be resulted from the HLC values determined in this work. The Ff_w value (0.46) suggested that the gas exchange of NP almost reaches the equilibrium in the area of the Upper Bay (at the mouth

Table 3
Reassessment for the air/water exchange of nonylphenol (NP) in the Lower Hudson River Estuary

Sample date	Lower Bay			Av	Upper Bay		
	7/5/98	7/6/98	7/7/98		7/10/98 A	7/10/98 B	av
C_w (NP) (ng l^{-1})	12	24	49	28	61	94	78
C_a (NP) (ng m^{-3})	2.6	1.5	69	24	21	2.2	12
Ff_w (Van Ry)	0.87	0.96	0.52	0.64	0.81	0.98	0.91
Ff_w (This work)	0.37	0.68	0.08	0.13	0.27	0.85	0.46

C_w (NP), C_a (NP) = concentration of NP in the water phase and the air.