Fig. 1. Chemical structure of the target substances. *Optic active carbons.

In this work, the HLCs of the defined NP isomer 4(3′,5′-dimethyl-3′-heptyl)-phenol (Vinken et al., 2002) and of tertiary octylphenol were measured between 278 and 298 K using a dynamic equilibrium system. This experimental set-up offers the significant advantage to be able to trap the trace compounds in the gas phase and to preconcentrate them subsequently before analysis. γ-HCH was selected as a reference substance due to its similar solubility and vapor pressure compared to NP and because its HLC value has been previously determined by many groups using different experimental set-up. The chemical structures of the studied substances are shown in Fig. 1. The experiments were conducted with artificial seawater in order to obtain realistic HLC values for the estimation of air/water exchange of NP and OP in coastal regions.

2. Experimental section

2.1. Chemicals and material

Analytical standards of technical NP (CAS: 25154-52-3), *t*-OP, 4-*n*-NP d8 (Cat. No. XA15630010AC), and γ-HCH were supplied by Dr. Ehrensdorfer GmbH (Augsburg, Germany). The individual NP isomer 4(3′,5′-dimethyl-3′-heptyl)-phenol (diastereomeric mixture, NP353(+), NP353(−); 91% in ethanol) was synthesized in the laboratories of the RWTH Aachen in Germany. Standard solutions of technical NP $(0.50\,mg\,l^{-1})$, NP353 $(1.08\,mg\,l^{-1})$, *t*-OP $(1.00\,mg\,l^{-1})$, γ-HCH $(1.07\,mg\,l^{-1})$, and 4-*n*-NP d8 $(0.20\,mg\,l^{-1})$ were prepared in hexane for calibration. Additionally, stock solutions used for the HLC determination experiments containing NP353 $(2.28\,g\,l^{-1})$, OP $(2.00\,g\,l^{-1})$ and γ-HCH $(2.14\,g\,l^{-1})$ were prepared in acetonitrile. A mixture of the derivatization reagents BSTFA and TMCS (99:1; Part No. 701 490.201) was obtained from Macherey-Nagel GmbH (Dueren, Germany). The solvents (*n*-hexane, diethyl ether, acetonitrile, acetone, methanol and dichloromethane) were of super grade quality. Artificial seawater used for HLC measurements consisted of a solution of 35 g NaCl in 1 l Milli-Q water $(18\,m\Omega\,cm)$. The NaCl and all used glass vials and pipettes were baked out at 450°C in a muffle furnace for 12 h. Amberlite® XAD-2 resins (Supelco) were purified
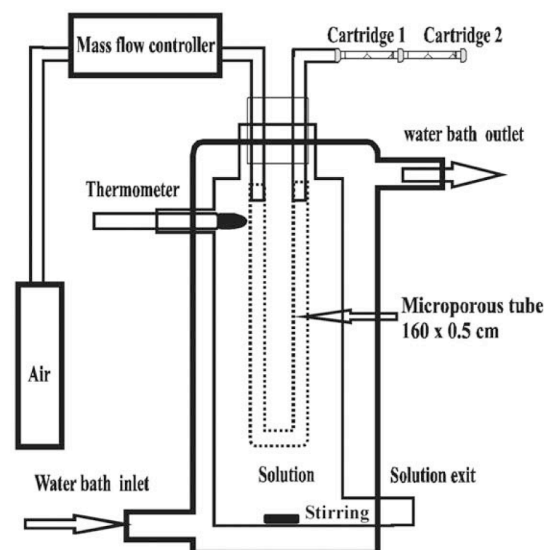

Fig. 2. Scheme of the dynamic equilibrium system used to determine Henry's law constant (HLC) as a function of the temperature.

prior to use by soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h), and then dried with nitrogen stream at room temperature.

2.2. Apparatus

The dynamic equilibrium system (Fig. 2) is similar to those used in recent studies (Shepson et al., 1996; Treves et al., 2000), and detailed descriptions were previously given by Gautier et al. (2003) and Feigenbrugel et al. (2004a, b). In brief, the air/water equilibrium apparatus consists of two chambers and one piece of microporous PTFE membrane tubing with a length of 160 cm and an inner diameter of 0.5 cm (Sumitomo Corporation, Tokyo, Japan). The outer chamber is for water circulation at constant temperature (water bath produced by a thermostat). The tube is immersed into 600 ml of the aqueous solution contained in the inner chamber for air/water equilibrium. A thermometer is inserted into the inner chamber to monitor the actual temperature of the aqueous solution. Air (Air Liquid, 99.99%) was passed through the tube at a controlled