flow rate of $0.41 \, \text{min}^{-1}$. The airborne substances of interest at equilibrium concentrations were then trapped by tandem Amberlite XAD-2 cartridges (ca. 5 g) at the exit of the reactor. The loaded cartridges were immediately stored in a freezer before treating with modified soxhlet extraction.

2.3. Gas generating and trapping experiments

In the present experiment, the inner chamber was approximately filled with 600 ml of artificial seawater spiked with 40–100 μl of the stock solutions in acetonitrile. This gave concentrations in artificial seawater of 0.086–$0.107 \, \text{mg} \, \text{l}^{-1}$ for γ-HCH, 0.080–$0.100 \, \text{mg} \, \text{l}^{-1}$ for *t*-OP and 0.091–$0.114 \, \text{mg} \, \text{l}^{-1}$ for NP353. During the preparation of the solution as well as the trapping experiment, flasks and bottles were wrapped with aluminum foil to prevent substantial photodegradation of NP and *t*-OP. Experiments were conducted at the following temperatures: 278, 283, 288, 293 and 298 K. Two parallel experiments with different concentrations have been performed at each selected temperature. Experiments were running for 116–140 min at 283, 288, 293 and 298 K. It was considered that the selected substances have very low gas phase concentrations at the lowest temperature tested (278 K), therefore, the gas trapping was running over night (938 and 940 min) to ensure a detectable mass trapped on the XAD-2 cartridge. Breakthroughs of the selected substances were tested with a purge in–out set-up. The substances were purged out with nitrogen (99.999%) at a flow rate of $0.41 \, \text{l} \, \text{min}^{-1}$, and the nitrogen stream passed three XAD-2 cartridges connected in series for 3 h. The results showed that more than 99.3% of the total mass of all selected substances was trapped by the first cartridge. 0–0.6% of the total mass was found on the second cartridge, and <0.2% on the third cartridge. This indicated that there is no significant breakthrough occurring during the enrichment of substances selected on XAD-2 cartridges. Consequently, for HLC measurements, two tandem cartridges were used to minimize the risk of artefacts by potential breakthrough.

2.4. Analytical procedure

2.4.1. Extraction, clean-up, and derivatization

The XAD-2 cartridges were spiked with 50 μl of $0.20 \, \text{mg} \, \text{l}^{-1}$ 4-*n*-NP d8 as internal standard and then extracted with a soxhlet extractor using 150 ml of solvent of hexane and diethyl ether (9:1, v/v) for 8 h. The solvent was evaporated to 1–2 ml with rotatory evaporator and then purified with a 1 g silica gel column (1 cm i.d. × 15 m). The silica gel (100–200 mesh) was baked out at 450°C to remove organic contaminations, and then deactivated by adding 5% (w/w) of milli-Q water prior to use. Purification of the sample extracts was accomplished by eluting the column with 20 ml of hexane and diethyl ether (3:1, v/v). The eluate was evaporated to 1 ml and then transferred to a 2 ml scaled glass vial. After addition of 50 μl of dichloromethane and 100 μl of acetonitrile (as keeper), the solvent volume in the vial was reduced to 100 μl under a gentle stream of nitrogen (99.999%).

BSTFA 100 μl were added to the vial containing the extracts, and the mixture was allowed to react for 1 h at 70°C. After cooling for 5 min, the final sample volume was adjusted to 200 μl using acetonitrile. The solution was subsequently applied to the GC-MS without further treatment.

2.4.2. Quantification, recovery and limit of detection

The quantification of the trimethylsilyl (TMS) derivatives of NP, *t*-OP, NP353, and γ-HCH was performed with an Agilent 6890 N capillary gas chromatograph coupled to an Agilent 5973 quadrupole mass spectrometer (GC-MS, Agilent Technologies). Ions detected were generated by electron impact ionisation and monitored in the selective ion mode (EI-SIM). A $30 \, \text{m} \times 0.25 \, \text{mm}$ fused silica capillary column (95%-dimethyl-5%-diphenylpolysiloxan, HP-5ms) with 0.25 μm film thickness was used for the separation. The flow rate of the carrier gas He was kept constant at $1.0 \, \text{ml} \, \text{min}^{-1}$. The temperature program was as follows: 80°C for 1 min, $30°\text{C} \, \text{min}^{-1}$ to 130°C, $3°\text{C} \, \text{min}^{-1}$ to 240°C, $10°\text{C} \, \text{min}^{-1}$ to 300°C, then 300°C for 5 min. The transfer line and the ion source temperature were maintained at 280°C and 150°C, respectively. 1 μl of the sample in acetonitrile was injected into GC-MS with an inlet temperature program of 80°C for 1 min, $100°\text{C} \, \text{min}^{-1}$ to 250°C, and 250°C for 10 min.

Fig. 3 shows that 13 peaks of technical NP with higher concentration were resolved using GC-MS in the selective ion mode after derivatization with BSTFA. Isomeric technical NP concentrations were calculated by accounting for the relative contribution of the ions 207, 221, and 235 to the total spectra for each individual isomer based on their characteristic mass and retention time. NP353(+) and NP353(–) were quantified using the ion mass 221. Both diastereomers are present in the technical NP standard (fraction of 10%) as well as in some air and water samples representing the peaks NP 4 and NP 6. TMS-*t*-OP, γ-HCH and TMS-4-*n*-NP d8 were quantified using the ion masses of 207 (13.68 min), 181 (17.06 min), and 185 (21.85 min), respectively.

The recovery for the extraction and clean-up was obtained as $80.1\% \pm 8.0\%$, $73.5\% \pm 9.0\%$, and $70.0\% \pm 7.4\%$ for technical NP, *t*-OP and γ-HCH, respectively. The quoted errors are given at the 2σ (standard deviation) level from the triplicate experiments. The instrumental limit of detection (LOD) was determined by the signal-to-noise ratio ($\geqslant 3:1$), which
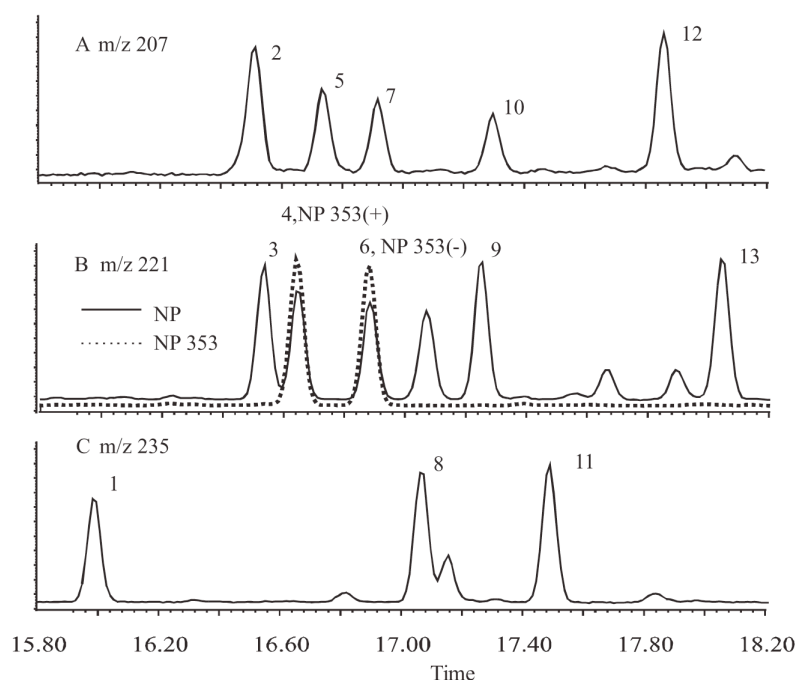
Fig. 3. Reconstructed ion current chromatograms of TMS derivatives of technical NP $(250\,\text{ng}\,\text{ml}^{-1})$ (A-C) and NP353 $(53\,\text{ng}\,\text{ml}^{-1})$ (B) using the three ions masses (m/z): 207, 221, and 235.

was 0.2 pg for the NP353 diastereomers and 1 pg for *t*-OP and γ-HCH.

3. Results and discussion

The experimental results of the dynamic equilibrium system experiments for NP353(+), NP353(–), *t*-OP and γ-HCH are given in Table 1 where the quoted uncertainties is 35%. This value corresponds to the sum of the uncertainties on the calibration curve (approximately 5% for the studied compounds), on the extraction and purification processes (determined to be of the order of 20%), on the flow rates (negligible in our conditions) and on the aqueous concentration (about 10% due to the small volume (40–100 μl) used for preparation of aqueous solutions).

The HLCs were determined by the mass balance equation: $\text{HLC} = 101.325\,C_{w,\,eq}/C_{a,\,eq}/RT$, where $C_{w,\,eq}$ and $C_{a,\,eq}$ are the aqueous and air concentrations of the selected substances. The absolute amounts of NP353(+), NP353(–), *t*-OP and γ-HCH detected on the cartridges ranged from 53 to 1550 ng, and were <1% of the total mass of the substances in the water phase. Thus, $C_{w,\,eq}$ or $C_{a,\,eq}$ can be supposed as constant values for subsequent calculations. All samples have been checked for breakthrough. Less than 10 ng NP353(+) and 8 ng *t*-OP were detected on the second

cartridges, and there is no detectable mass for NP353(–) and γ-HCH. Furthermore, parallel measurements were conducted with different concentrations of the analytes, thus it can be shown that the HLCs determined in this work are independent on the concentration and reliable. However it should be noted that the values at 283 K show fairly high standard deviations. The effect of the air flow rate on HLC has been previously tested for the experimental set-up with some other phenols and pesticides (Gautier et al., 2003; Feigenbrugel et al., 2004a, b). There is no significant difference when the set-up was working with an airflow rate in the range 0.2–0.5 l min^{-1}.

The HLC values of γ-HCH, the reference substance used in this work, have been previously determined using bubble stripping (BS) and dynamic headspace (DHS) (Sahsuvar et al., 2003; Jantunen et al., 2000) as well as wetted wall column (WWC) (Altschuh et al., 1999; Fendinger et al., 1989) techniques. Kucklick et al. (1991) has also determined HLCs of γ-HCH in artificial seawater over a temperature range 273.6–318 K. The HLC values of γ-HCH in deionized water or artificial seawater determined by varied methods are reported in Table 2 and plotted together with our values versus inverse temperature (Fig. 4). Within the experimental errors, our data obtained in artificial seawater are in very good agreement with those determined in pure water by Feigenbrugel et al. (2004c); Sahsuvar et al.