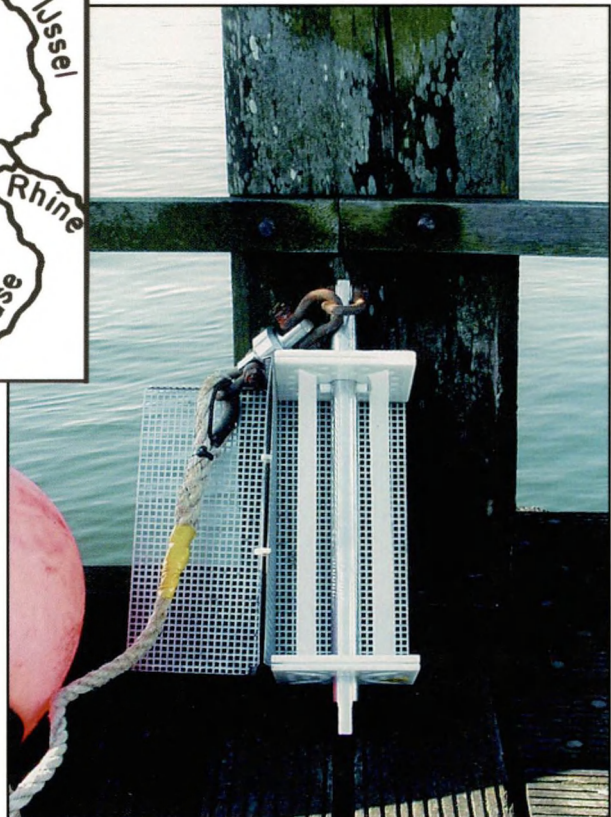
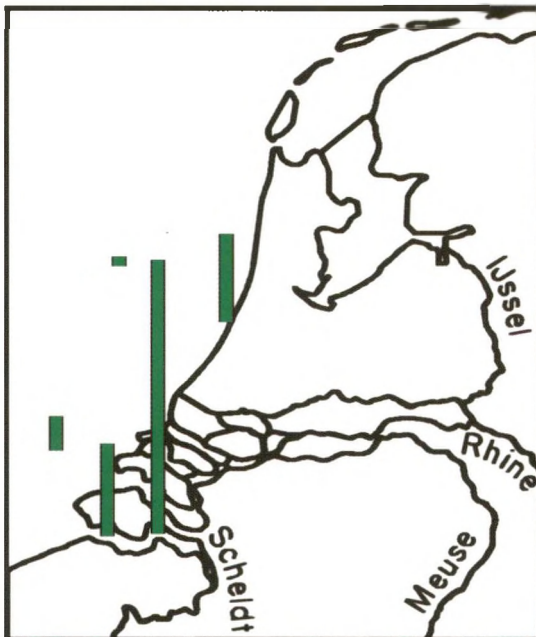


PASSIVE SAMPLING OF ORGANIC CONTAMINANTS IN THE WATER PHASE

Kees Booij, Evaline M. van Weerlee,
Coen V. Fischer, José Hoedemaker



©2000

This report is not to be cited without the
acknowledgement of the source:

Netherlands Institute for Sea Research (NIOZ)
P.O. Box 59, 1790 AB Den Burg, Texel
The Netherlands

ISSN: 0923 - 3210

PASSIVE SAMPLING OF ORGANIC CONTAMINANTS IN THE WATER PHASE

Final report

Kees Booij, Evaline M. van Weerlee,
Coen V. Fischer, José Hoedemaker

NETHERLANDS INSTITUTE FOR SEA RESEARCH

SUMMARY

The exchange kinetics between artificial sea water and three passive samplers (Semipermeable Membrane Devices (SPMDs), Low-Density PolyEthylene (LDPE) membranes, and silicone tubing) was studied in an experimental set-up using three controlled flow techniques, and three temperatures between 2 and 30 °C. Aqueous concentrations of chlorobenzenes, PCBs and PAHs were maintained by continuous circulation of the water over a C18 generator column. The effect of temperature on the sampling rates amounted to a factor of two to three. Differences between the uptake kinetics of organic contaminants by LDPE tubing using three forced flow techniques amounted to a factor of two. Sampling rates of SPMDs and LDPE membranes were the highest reported so far in the literature.

Performance Reference Compounds (PRCs) were spiked into LDPE membranes and silicone tubing by incubation in aqueous-methanolic PRC solutions. During the spiking procedure all PRCs reached equilibrium within a few hours. Best results were obtained with a methanol/water volume ratio of 80/20. The precision of the PRC spiking was 1-6% depending on the compound.

In February and October 1999 field deployments of SPMDs and LDPE membranes were made under ambient flow conditions in the Scheldt estuary (two stations) and in the Southern North Sea (three stations) along with mussel exposures by the National Institute for Coastal and Marine Management /RIKZ. Inter-site differences in absorbed contaminant amounts were more pronounced in SPMDs and LDPE membranes than in mussels. The dissipation rates of PRCs from SPMDs and LDPE membranes indicated that the sampling rates were constant within a factor of 1.3 for all stations.

SPMDs and LDPE membranes were exposed under ambient and forced flow conditions in the Marsdiep (Western Wadden Sea). In addition, silicone tubing was tested as a passive sampler of organic contaminants. The silicone tubing sampler was much more efficient in sampling low K_{ow} compounds when compared to sampling by SPMDs, due to a larger phase volume for the silicone sampler.

This study was carried out within the framework of project TNW*MILLAB of the National Institute for Coastal and Marine Management /RIKZ, under contract RKZ 583.

INTRODUCTION

Passive sampling of dissolved organic contaminants by Semi-Permeable Membrane Devices (SPMDs) has received great deal of attention during the previous decade (Huckins *et al.*, 1990; Prest *et al.*, 1995a). SPMDs consist of a low-density polyethylene (LDPE) lay-flat tubing, filled with either natural lipids or the model lipid triolein (1,2,3-tri[*cis*-9-octadecenoyl]glycerol). Typically, SPMDs are 10 to 230 cm long and 2.5 to 5 cm

wide, with a wall thickness of 50 to 90 μm . A wide range of non-polar to moderately polar contaminants has been sampled successfully with SPMDs: PAHs (Lebo *et al.*, 1992; Huckins *et al.*, 1993), organochlorine pesticides (Prest *et al.*, 1992; Ellis *et al.*, 1995; Herve *et al.*, 1995; Petty *et al.*, 1995; Prest *et al.*, 1995b; Prest *et al.*, 1995c), PCBs (Prest *et al.*, 1992; Petty *et al.*, 1993; Prest *et al.*, 1995b; Prest *et al.*, 1995c), dioxins/dibenzofurans (Prest *et al.*, 1992) and chlorophenols/anisols/veratols (Ellis *et al.*, 1995; Herve *et al.*, 1995). When SPMDs are exposed to the water phase organic contaminants initially are absorbed at a constant rate (linear uptake phase, Fig. 1).

$$N = C_w R_s t \quad (1)$$

with N the absorbed amount, C_w the aqueous concentration, and R_s the sampling rate. For low K_{ow} compounds water-SPMD sorption equilibrium may be approached, causing the uptake curve to level off at the equilibrium amount N_{eq} (Fig. 1, equilibrium phase).

$$N_{eq} = V_s K_{Sw} C_w \quad (2)$$

with V_s the SPMD volume and K_{Sw} the SPMD-water partition coefficient. Equations 1 and 2 indicate that contaminant amounts absorbed by SPMDs are linearly proportional to their concentration in the water phase, regardless of the degree of equilibrium that has been attained between SPMD and water. In principle this means that for each individual compound a higher absorbed amount indicates a higher aqueous concentration. Comparison of absorbed amounts for different compounds is more complicated, because both the

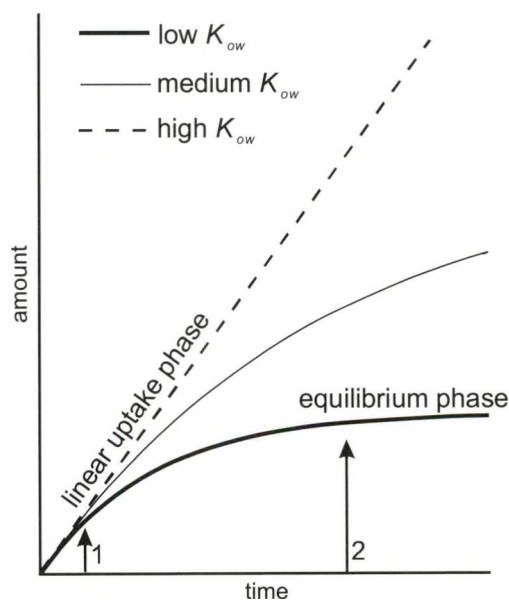


Fig. 1. Uptake curves for three compounds that differ in hydrophobicity: low K_{ow} (thick), medium K_{ow} (thin) and high K_{ow} (dashed). At sampling time 1 all compounds are in the linear uptake phase. At sampling time 2 the low K_{ow} compound has reached equilibrium, the high K_{ow} compound still is in the linear uptake phase, and the medium K_{ow} compound is in an intermediate phase.

sampling rates (R_s in eq. 1) and the SPMD-water partition coefficients (K_{sw} in eq. 2) are dependent on the compound properties. A complicating factor in the inter-site comparison of contaminant amounts is that the sampling rates increase with increasing water flow rates (Booiij *et al.*, 1998). The flow effect can in principle be accounted for by measuring the dissipation rates of Performance Reference Compounds (PRCs) that are spiked into the triolein phase prior to exposure (Prest *et al.*, 1992; Huckins *et al.*, 1993; Booiij *et al.*, 1998).

When PRCs are chosen that do not occur in the environment their dissipation can be described by

$$N = N_0 \exp(-k_e t) \quad (3)$$

where N_0 is the PRC amount at $t=0$ and k_e is the exchange rate coefficient, or the dissipation rate constant. Comparison of k_e values obtained at different exposure sites therefore allows for estimating the effect of inter-site differences in flow on the absorbed amounts. Suitable PRCs are isotopically labelled compounds and a number of polychlorinated biphenyls or other compounds that do not occur in the environment in appreciable amounts (e.g. CB29, CB155).

Another complicating factor in the field application of SPMDs is that both the sampling rates and the SPMD-water partition coefficients may be temperature dependent. This may cause problems in the interpretation of SPMD results obtained at different temperatures.

In a previous laboratory study we showed that the effect of differences in flow velocity on the sampling rates could be accounted for by changes in the dissipation rate constants of the PRCs (Booiij *et al.*, 1998). It also appeared that for high K_{ow} ($>10^6$) compounds the LDPE membranes were just as efficient in sampling organic contaminants as were (triolein filled) SPMDs. In the present study we aim to evaluate the effect of temperature on the sampling rates and the PRC dissipation rates for SPMDs, LDPE membranes and silicone tubing, using laboratory experiments under controlled conditions. For a number of field experiments in the Dutch coastal waters we assessed the merits of these passive samplers compared to mussel exposures for monitoring programmes. In addition we investigated whether or not the application of a forced flow regime during the sampler exposures would facilitate the interpretation of the results. We also developed a method for spiking PRCs into LDPE membranes and silicone tubing.

MATERIAL

Internal standards and Performance Reference Compounds (PRCs). Prior to the exposure of LDPE membranes and SPMDs, the samplers were spiked with a number of PRCs: perdeuterated PAHs (acenaphthene-D10, phenanthrene-D10, chrysene-D12) and PCBs (CB 4, CB 29, CB 155 and CB 204). For SPMDs the PRCs were spiked into the triolein. For LDPE membranes and silicone tubing, the PRCs were loaded by equilibrating the polymers in PRC spiked methanol/water mixtures (80/20 v/v) overnight. Details of the polymer spiking are discussed below. Analytical internal standards were added to the samples prior to extrac-

tion. For the lab experiments CB112, pyrene-D10 and perylene-D12 were used. For the field samples a total of six internal standards were used: CB53, CB112, CB198, pyrene-D10, $^{13}C_6$ -chrysene, and perylene-D12.

LDPE membranes and SPMDs. Low-density polyethylene tubing (2.5 cm wide, wall thickness 70 μ m) that contained no additives was supplied by Brentwood Plastics Inc. (Brentwood, Missouri, USA). Prior to use the membranes were extracted twice by soaking in pentane for 24 hours. After exposure the membranes were extracted 24 hours with 100 mL pentane. SPMDs were prepared following the method described earlier (Booiij *et al.*, 1998) After exposure SPMDs were extracted twice with 100mL pentane for 24 hours. Both LDPE membranes and SPMDs had a length of about 30 cm. SPMDs contained 300 μ L triolein, corresponding to the standard design value of 1 mL m^{-1} .

Silicone tubing. Silicone tubing was purchased from Fischer Scientific ('s Hertogenbosch, The Netherlands; 6 mm id, 9 mm o.d.), Cole-Palmer (Niles, IL, USA; Masterflex 96410-18, 8 mm id, 11 mm o.d.), Rubber BV (Hilversum, The Netherlands, 2 mm id, 6 mm o.d.). The method development for silicone tubing extraction and clean-up is described in the Results and Discussion I section. The Fisher Scientific tubing was selected for the exposure experiments.

MeOH/Acetonitrile/water mixtures. Contaminant concentrations in mixtures of water and methanol or acetonitrile were determined by bringing the water content to $> 80\%$ using hexane extracted bidistilled water, and extracting twice with pentane after addition of the internal standard solutions and about 1 mL 2,2,4-trimethylpentane (TMPE). The extracts were transferred to a round bottom flask equipped with a micro Snyder column, and were concentrated to about 5 mL. After transferring the concentrates to a 20 mL graduated test tube the samples were further concentrated to about 0.5 mL. The final sample volume was 1 mL in TMPE prior to injection.

Water samples. Water volumes from the exposure system (4.8 L) were siphoned off through a stainless steel tubing into a 5 L volumetric flask. The water was extracted with about 100 mL pentane for 30 min using a magnetic stirrer and a stirrer bar from which the Teflon coating had been stripped off. After a clean-up step using 2 g silica (6% water, elution with 40 mL pentane) the sample volumes were concentrated to 100 μ L prior to injection.

Sample clean-up. The raw concentrated extracts were passed over a 6 mm id LC column that contained 2 g silica (6 % water, elution with 40 mL pentane). For the lab experiments the eluate was concentrated to 0.1 or 1 mL followed by analysis for PCBs/chlorobenzenes and PAHs. After analysis for PAHs the field samples were passed again over a silica column (elution with 10 mL pentane) prior to analysis for PCBs/chlorobenzenes.

GC-analysis. Samples were analysed for PCBs and chlorobenzenes on a Carlo-Erba 5160 equipped with an A200S autosampler, a CP-Sil8 capillary column (50m, 0.25 mm id, film thickness 0.25 μ m, carrier gas H_2) and an ECD-80 model electron capture detector (constant-current mode, 340 $^{\circ}C$), injection mode splitless, temperature program 90 $^{\circ}C$ (hold 2 min), increase

with $10\text{ }^{\circ}\text{C min}^{-1}$ to $215\text{ }^{\circ}\text{C}$ (hold 10 min) increase with $8\text{ }^{\circ}\text{C min}^{-1}$ to $275\text{ }^{\circ}\text{C}$ (hold 17 min). For the lab experiment samples a faster temperature program was used: $90\text{ }^{\circ}\text{C}$ (4 min), increase with $15\text{ }^{\circ}\text{C min}^{-1}$ to $300\text{ }^{\circ}\text{C}$ (15 min). Samples were quantified using logarithmic interpolation (internal standard method). PAHs were analysed on a HP5890 GC equipped with a HP7673 autosampler and a CP-Sil 8 capillary column (50 m, 0.25 mm id, film thickness 0.25 μm , carrier gas He), injection mode splitless, temperature program $100\text{ }^{\circ}\text{C}$ (0 min), increase with $15\text{ }^{\circ}\text{C min}^{-1}$ to $200\text{ }^{\circ}\text{C}$, increase with $6\text{ }^{\circ}\text{C min}^{-1}$ to $320\text{ }^{\circ}\text{C}$ (0 min). Analytes were detected with a Fisons Auto-Spec Ultima mass spectrometer, ionisation mode EI (70 eV, source temperature $250\text{ }^{\circ}\text{C}$), detection mode Selected Ion Recording of the molecular ions (dwell time 80 ms, equilibration 10 ms). Samples were quantified using linear interpolation of the responses (internal standard method).

Preparation of the generator column. About one kg of silica bonded C18 (Polygoprep 100-30 C18, Machery-Nagel, Düren, Germany) was loaded in a 1 L pressure filtration unit, using a 25 μm nylon gauze as a filter. The column was pre-flushed three times by circulating about one litre of acetonitrile through the column for 0.5 hour. Between the successive flushings the excess acetonitrile was removed as far as possible. Then 600 mL of a spike solution containing three chlorobenzenes, seven PCBs and ten PAHs in acetonitrile (100 μg - 5 mg) was circulated through the column for one hour. The water content of the solution was increased to 90% in steps of 10-20% by adding bidistilled water, fol-

lowed by equilibration for at least one hour. After reaching a water content of 90% the column was flushed four times by circulating 1L of Milli-Q water. Initial experiments showed that the volume rate of flow through the column was insufficient. Therefore, the C18 material was removed, homogenised and distributed over two identical column systems.

Forced flow exposure apparatus. Three techniques for exposing LDPE membranes under forced flow conditions were tested for mechanical strength and ease of operation (Fig. 2). One system consisted of an LDPE disk (14 cm diameter, thickness 70 μm) rotating at a speed of 180 min^{-1} . A first try with an unsupported disk (Fig. 2A) showed that the membrane was wrapped up around the main shaft. Therefore the disk was positioned between two support disks (gap width 5 mm) with 102 holes with a diameter of 8 mm (Fig. 2B). An assembly with four supported disks was used in the exposure experiments. The second system was a two-toothed fork rotating at 60 min^{-1} (Fig. 2C). The distance between the teeth was 30 cm. On each of the teeth a total of five LDPE membranes or SPMDs could be clamped. In the third system water was pumped through a 1 m lay-flat tubing at a rate of 25 L h^{-1} (Fig. 2D). A metal rod was used to prevent the empty tubing to be wrapped up in the simultaneously exposed rotating disk assembly. The temperature and flow dependence of the sampling rate for LDPE membranes and SPMDs was studied using the fork sampler (Fig. 2C). The exchange kinetics between silicone tubing and water were studied at $13\text{ }^{\circ}\text{C}$ by pumping water through a 1

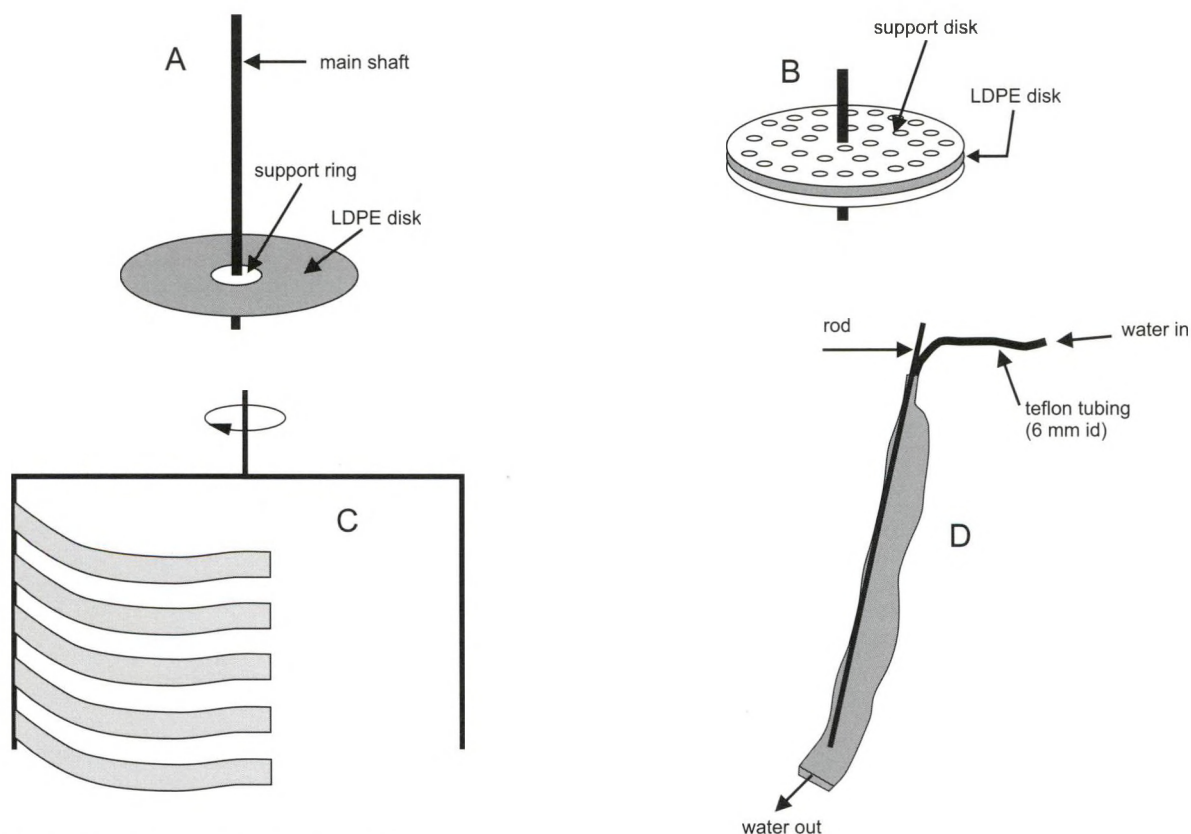


Fig. 2. Forced flow sampling set-ups used.

m long silicone tubing. For the exposures at 2 and 30 °C two 20 cm long silicone tubings were mounted on a 14 cm diameter disk that rotated at 60 min^{-1} , with one end opposed to the flow direction, and the other end extending 5 mm through the disk as a chimney.

Exposure set-up. A 200 L round bottom flask was placed in a 750 L insulated temperature controlled water bath (Fig.3). A volume of 200 L Milli-Q water was circulated through the C18 columns at a rate of 900 L d^{-1} . Six kg sodium chloride was added to bring the salinity at about 30. Sodium azide (400 g) was added in order to inhibit bacterial growth and subsequent DOC production during the exposures. The exposure experiments started after an equilibration period of 20 h.

Method development for spiking PRCs on empty membranes and silicone tubing. Two series of experiments were carried out to optimise the spiking of organic contaminants in LPDE. In each experiment 100 mL of a methanol-water mixture was prepared in a 250 mL erlenmeyer flask by mixing the appropriate volumes of water, methanol and 1 mL of a spike solution in methanol. Five pieces of LDPE membrane (5x2.5 cm, single layer) were added, and the flask was placed on a table shaker operated at 100 min^{-1} . At regular time intervals one of the membranes was removed. The solution sticking to the membranes was removed by wiping the membranes with a paper tissue. Consequently the membranes were extracted 24 h with 100 mL pentane in a round bottom flask. One series of experiments was carried out with technical PCB mixtures (Clophen-A30 and Clophen-A60). In the second experiment a number of PRCs was used. The spiking of silicone tubing with PRCs was studied by incubating five 1 cm long tubings in a MeOH/water mixture (80/20 v/v) on a table shaker. After incubation the tubings were extracted by soaking in pentane for 24 h.

Field exposure. LDPE membranes and SPMDs (2 each) were exposed in the Western Scheldt estuary (2 stations) and at the southern North Sea (3 stations) for

6-8 weeks in January-March 1999 (Fig. 4). A second field survey was made in October-November 1999. Due to bad weather conditions during the second survey only the stations in the Scheldt estuary and the location west of Schouwen could be sampled. The Katwijk and Noordwijk stations could only be visited in January 2000, but then it was observed that the membranes and SPMDs were lost. From October 1999 until February 2000 a number of field exposures was made in the Marsdiep. The purpose of this field study was to assess the merits of forced flow versus passive exposures and to test the merits of passive sampling using silicone tubing in the field. A total of five simultaneous exposures were started for the three methods. Due to repeated leakage of the engine house of the forced flow apparatus two exposures were unsuccessful and one was only partly successful. Two parallel exposures under ambient and forced flow conditions could be finalised without technical difficulties. Analysis of the samples from the second successful parallel exposure could not be finalised before completion of this report.

RESULTS AND DISCUSSION I : LAB EXPERIMENTS

Testing three forced flow techniques for LDPE membranes. A typical example of the uptake kinetics for the three samplers (Fig. 2) is shown in Fig. 5 for CB153. The differences between the three methods are limited to a factor of 2. We decided to use the rotating fork sampler (Fig. 2C) for studying the temperature effect on the uptake rates because this sampler could support both SPMDs and empty LDPE tubing.

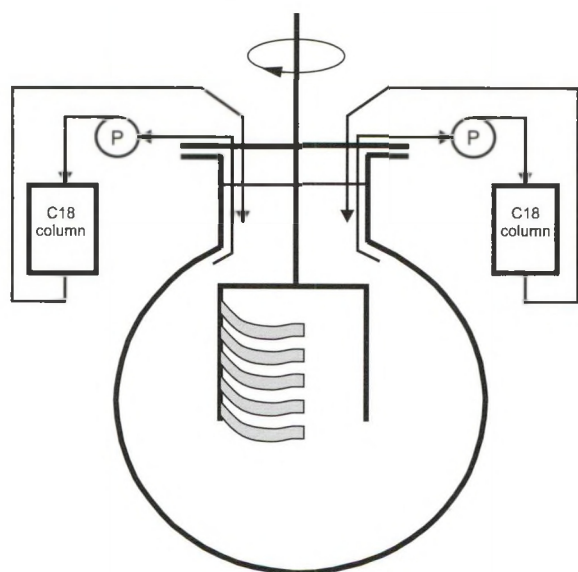


Fig. 3. Exposure set-up used in the laboratory experiments

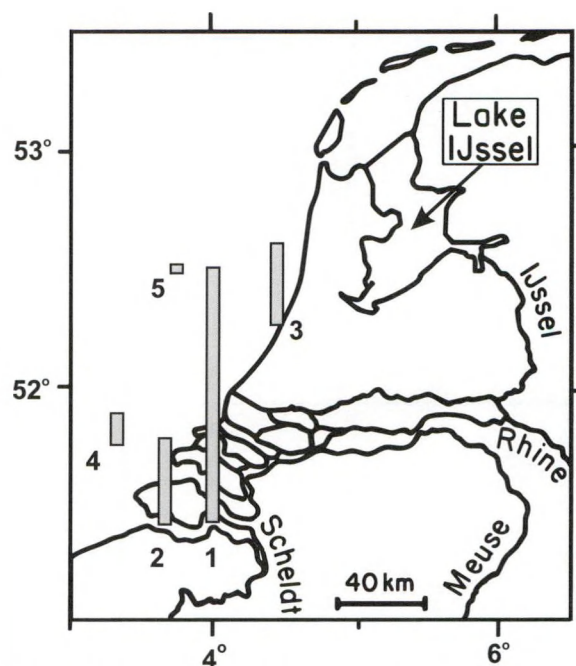


Fig. 4. Pyrene amounts absorbed by SPMDs during the January-March 1999 field exposure. 1: Hansweert, 2: Vlissingen, 3: Katwijk6, 4: Schouwen25, 5: Noordwijk60. The bar for station 1 represents an amount of 1802 ng pyrene.

Silicone tubing pre-treatment. Synthetic polymers commonly contain large amounts of additives and low-molecular weight polymer units that may cause significant problems during sample clean-up and GC analysis. A number of experiments were carried out to eliminate these co-extracts.

As a first step samples of the three brands of silicone tubing (length 1-3 cm, mass 1-2 g) were extracted overnight using pentane, toluene and DCM as extraction fluids. Volumetric polymer swell factors and extractable mass were evaluated. The largest swelling was observed for pentane (~ factor of 3.5). Dichloromethane caused the smallest swelling (~ a factor of 2.0). Differences between the various tubing brands were insignificant (~10%). Approximately the same extractable mass was found for the three solvents used. The highest extractable mass was found for the Masterflex tubing (25 mg g^{-1}), followed by the Fischer Scientific tubing (22 mg g^{-1}) and the Rubber BV tubing (18 mg g^{-1}). The extracted amounts had an oily appearance, and probably mainly consisted of silicone oil. These quantities can be expected to give large problems in sample clean-up and GC analysis. Amounts of 10 mg and 34 mg extracted residue of the Masterflex tubing were passed over an LC column filled with 2 g silica that was deactivated with 6% water. The samples were eluted with 40 mL pentane, followed by elution with 10 mL DCM. About 90% of the residue was retained by the column during 40 mL elution with pentane, both for the 10 mg and for the 34 mg loading.

The pre-extracted tubings were extracted a second time with pentane. The concentrated extracts were passed over silica using the same procedure. The eluate was split in two parts. The first part was used for determining GC blanks, the second part was used for determining extractable mass residues in the LC column eluate. For the Masterflex tubing a small residue was found in the eluate (0.16 mg g^{-1} tubing). For the other tubings and for a pentane control no residue was found (detection limit 0.02 mg g^{-1}). Therefore we concluded

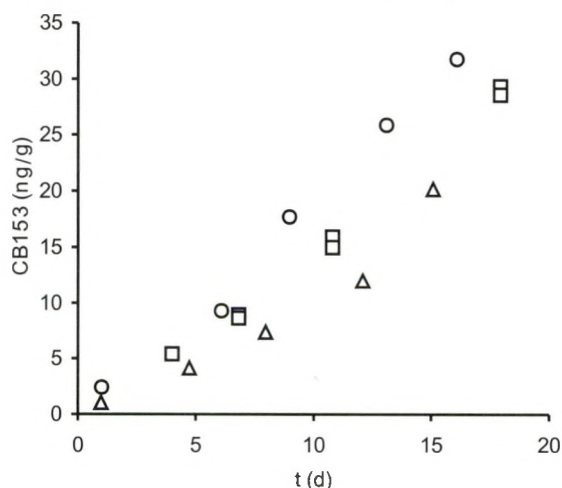


Fig. 5. CB153 uptake by LDPE membranes for three forced flow exposure methods: rotating disk (circles), rotating fork (squares) and pumping through empty tubing (triangles). Absorbed amounts were normalised on the sampler mass (1, 0.5 and 0.4 g respectively)

that the Masterflex tubing was not suitable for passive sampler construction. In addition, we concluded that for the other two tubing brands a double pre-extraction with pentane is sufficient as a tubing pre-treatment, and that a single silica clean-up removes remaining co-extracts that may be hazardous for the GC.

Polymer PRC loading. Figure 6 shows the uptake curves for PRC spiking of LDPE and silicone respectively. Both sampling phases can be rapidly spiked with PRCs by incubation in 80/20 (v/v) methanol-water mixtures. Equilibrium is generally attained within a few hours. The within-batch coefficient of variation amounted to 2-6 % for PRC spiking of LDPE, as determined for five series of four control membranes prepared over a time period of about a year. For SPMDs (spiking via addition to the triolein) the variability amounted to 6-10 %. For silicone tubing not enough series have been prepared so far to assess the within batch variability, but the results of the first series are promising (1-4 %)

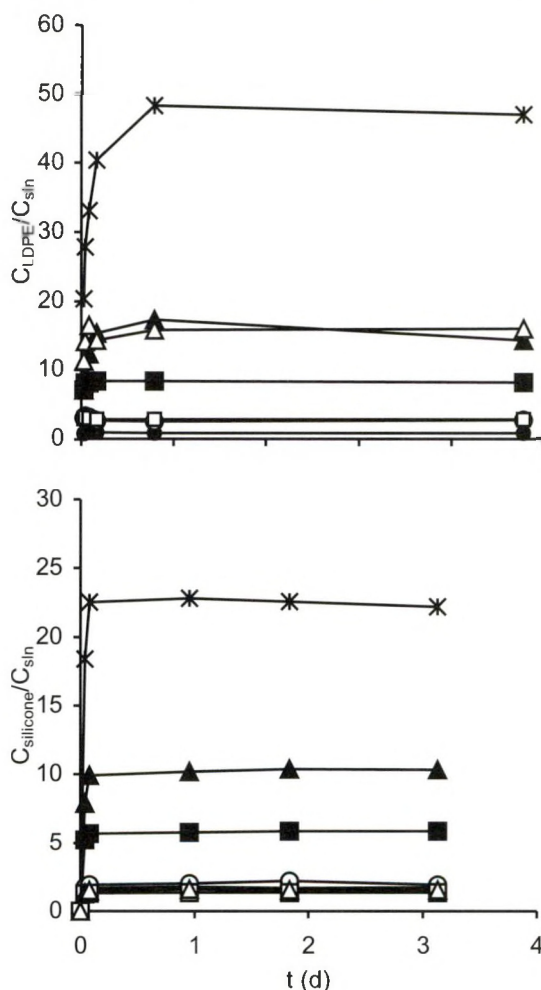


Fig. 6. Uptake kinetics of Performance Reference Compounds by LDPE membranes (upper panel) and silicone tubing (lower panel) from 80/20 (v/v) methanol-water mixtures. CB4 (closed circles), CB29 (closed squares), CB155 (closed triangles), CB204 (asterisks), acenaphthene-D10 (open circles), phenanthrene-D10 (open squares) and chrysene-D12 (open triangles).

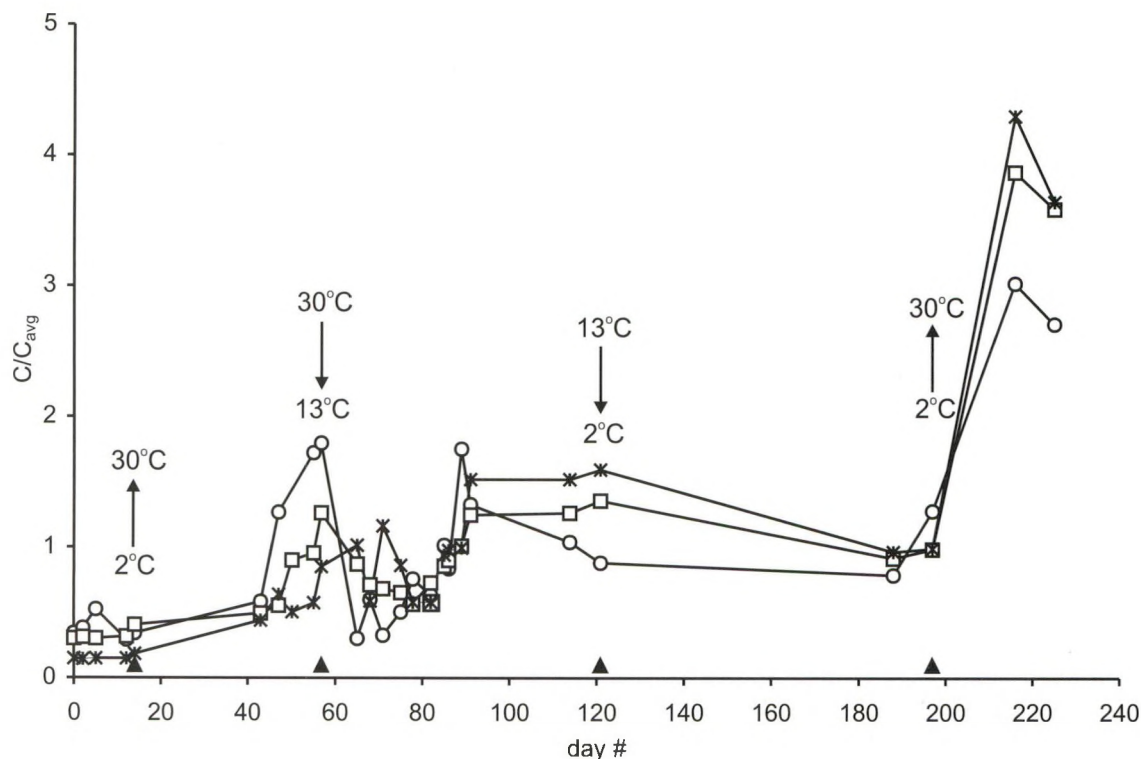


Fig. 7. Time evolution of aqueous concentrations during the laboratory experiments for pentachlorobenzene (circles), CB153 (squares), and CB194 (asterisks). All concentrations were normalised on the average concentration during the laboratory experiments.

Stability of the aqueous concentrations. The evolution of aqueous concentrations during the lab incubations is shown for pentachlorobenzene, CB153 and CB194 in Fig. 7. The triangles near the x-axis indicate the temperature changes from 2-30, 30-13, 13-2 and 2-30 °C respectively. The first temperature change from 2 to 30 °C caused a slight increase in concentrations over a one month period, followed by a large increase during the first experiment at 30 °C. Following the temperature change from 30 to 13 °C the concentrations first dropped rapidly, then increased steadily, and finally stabilised. The temperature drop from 13 to 2 °C induced a small decrease in concentrations to a level that was much higher than at the start of the experiments. The temperature rise from 13 to 30 °C caused a large and rapid increase. One reason for the unstable concentrations may be that the uptake rate of the samplers was of the same order as the delivery rate of the generator column. The volume rate of flow from the generator column was about 900 L d⁻¹. The sampling rate of the SPMDs and the LDPE membranes during the 30 °C experiment was about 60 L d⁻¹ for each device. During the first day a total of 10 devices was present in the set-up, which means that the total sampling rate was about 600 L d⁻¹. During the course of the experiments the number of samplers in the set-up decreased from 10 to 2, thereby enabling the generator column to better keep up with the contaminant removal by the samplers. This conclusion is supported by the observation that the apparent sampling rates for the first day of the 30 °C experiment were much higher than for the later time periods. The sampling rate for day 1 was based on the concentration

measured at this moment, but the average concentration during day one most likely was much higher. The decrease in concentrations following the temperature drop from 30 to 13 °C is caused in the first place by lower exit concentration levels from the generator column. The concentration of pentachlorobenzene showed a steady increase, probably caused by a decrease in sampling rate from about 300 to 40 L d⁻¹. The initially steady decrease in concentration for CB153 and CB194 is probably caused by a longer equilibration time for these (more hydrophobic) compounds in the generator column. For the experiments with silicone tubing (from day 110 onwards) the total sampling rates were smaller than 40 L d⁻¹, which allowed the generator column to efficiently stabilise the aqueous concentrations. The overall conclusion should be that the generator column method as such is suitable for stabilising the aqueous concentrations, but that the total volume rate of flow from the columns should have been much higher. A second conclusion is that column equilibration periods following temperature changes should be at least three weeks.

Sampling rates. A summary of observed sampling rates is shown in figures 8 to 11. Sampling rates of LDPE membranes and SPMDs at a flow of 90 cm s⁻¹ do not depend on log K_{ow} (Fig. 8, Table 1). For LDPE membranes a temperature increase from 2 to 13 °C has no effect on the sampling rate (18.9 ± 3.9 L d⁻¹ versus 18.6 ± 4.6 L d⁻¹). A further increase to 30 °C causes an increase in sampling rate by a factor of two (36.4 ± 8.1 L d⁻¹). Sampling rates for SPMDs continuously increase with temperature (18.5 ± 5.8, 25.7 ± 8.0, and 56.2 ±

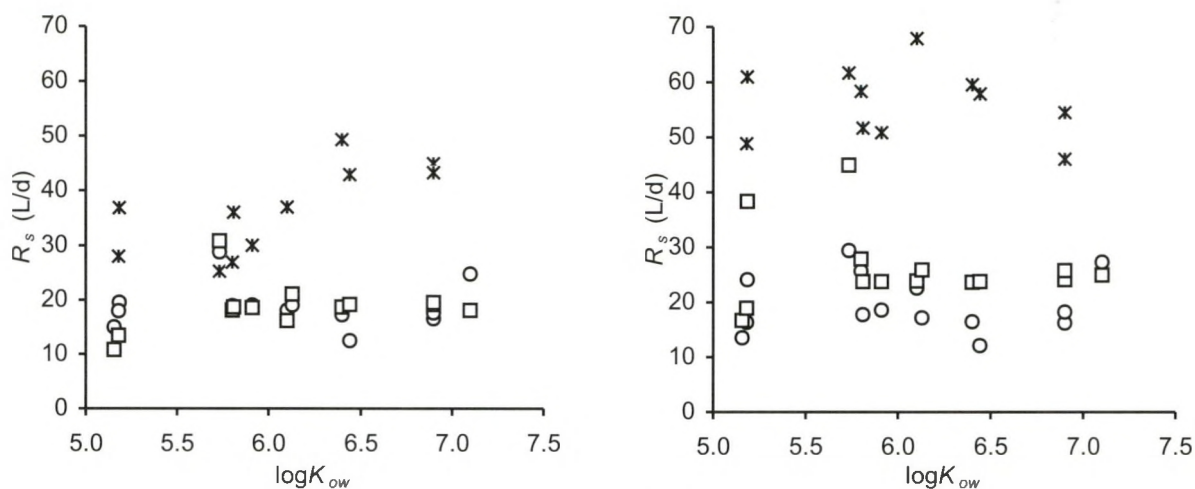


Fig 8. Sampling rates (R_s) of LDPE membranes (left panel) and SPMDs (right panel) at 2°C (circles), 13°C (squares) and 30°C (asterisks).

6.5 L d⁻¹ at 2, 13 and 30 °C respectively), but the effect of a temperature increase from 2 to 13 °C is quite small (~ factor of 1.4). For PAHs sampling rates of about 3.8 L d⁻¹ for 100 cm long SPMDs have been reported at water flow velocities of 1 cm s⁻¹ (Huckins *et al.*, 1999). The present SPMD sampling rates at 13 °C are higher by a factor of 23 when converted to a 100 cm SPMD length (multiply by 100/30). The present values are also considerably higher than PAH/PCB sampling rates of about 7 L d⁻¹ at 13 °C at a flow rate of 30 cm s⁻¹ for 30 cm long SPMDs (Booij *et al.*, 1998). These observations once again stress the importance of water flow velocities for the observed sampling rates.

The observed sampling rates at higher flows (225 cm s⁻¹) are shown in Fig. 9. Increased sampling rates of about 40 L d⁻¹ are observed for the log K_{ow} range 5 to 5.8. At higher log K_{ow} values sampling rates decrease to about 6 L d⁻¹ at log K_{ow} = 7. During the high flow experiments the LDPE membranes were ripped to several parallel strips that often extended up to the mounting loop seal. No damage was observed for the SPMDs. The only explanation for the decreasing sampling rates at higher K_{ow} we can think of is that the very high shear stresses induce a change in the molecular structure of the membrane, which causes a sharp decrease in membrane permeability for higher molecular weight compounds.

Sampling rates for silicone tubing are slightly dependent on contaminant hydrophobicity (Figs. 10 and 11). During the 13 °C silicone experiment water was pumped through the tubing at a rate of about 25 L d⁻¹.

Sampling rates decreased from 3 L d⁻¹ at log K_{ow} = 4 to 1.6 L d⁻¹ at log K_{ow} = 7. For the 2 °C and the 30 °C silicone experiment the tubing was mounted on a rotating disk that rotated at 60 RPM, with one end directed towards the flow and the other end extending perpendicularly through the disk, as a chimney. For these experiments the observed sampling rates were virtually independent of log K_{ow} , with average values of 4.1 ± 0.6 and 9.3 ± 1.3 L d⁻¹ at 2 °C and 30 °C respectively. The difference in sampling rates between the silicone tubing and the SPMDs and LDPE membranes is largely caused by differences in surface area and flow rates. The smaller surface area (70 versus 150 cm²) accounts for a factor of two difference in sampling rates. The tubing rotated at a radius of 14 cm whereas the SPMDs and LDPE membranes rotated at a 30 cm radius (~ factor 4 difference in flow rate). Although there is no simple relationship between ambient flow rates and sampling rates the effect of a decrease in ambient flow by a factor of four would be substantial. The higher mechanical strength of silicone tubing compared to LDPE most likely allows for exposing these samplers under much higher forced flow regimes.

PRC dissipation rates. Dissipation rate constants (Table 2) are shown as a function of K_{ow} in Fig. 12. Values for LDPE membranes are higher than for SPMDs by a factor of 9.5 ± 1.5. Each 11 to 17 °C temperature increase causes an increase in dissipation rates by a factor of 2.3 ± 1.7, both for SPMDs and LDPE membranes, with no apparent relation with

Table 1. Summary of sampling rates (R_s) for SPMDs and LDPE membranes (30x2.5 cm), and silicone tubing (15cm, 6 mm id, 9 mm id) obtained during the lab experiments

	2 °C	13 °C	30 °C
	R_s (L d ⁻¹)	R_s (L d ⁻¹)	R_s (L d ⁻¹)
SPMD	19 ± 6	26 ± 8	56 ± 6
LDPE	19 ± 4	19 ± 5	36 ± 8
silicone tubing	4.3 ± 1.0		9.9 ± 1.2

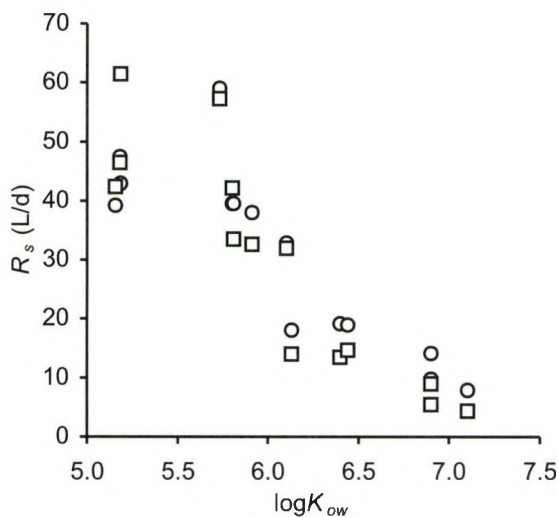


Fig. 9. Sampling rates of LDPE membranes (circles) and SPMDs (squares) at 13°C at conditions of increased flow (225 cm s⁻¹)

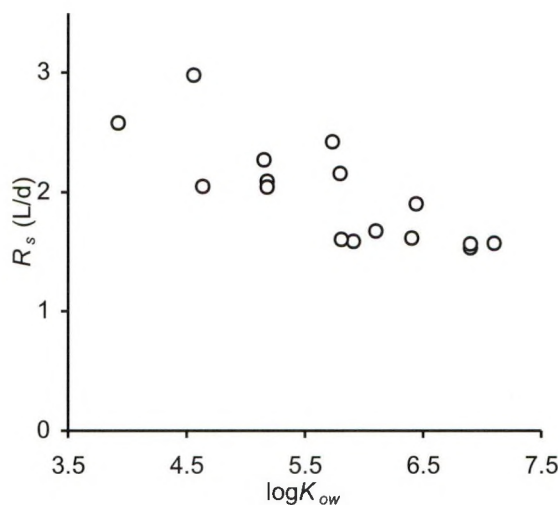


Fig. 10. Sampling rates of silicone tubing at 13°C. Water was sucked through the tubing at a rate of 25 L d⁻¹.

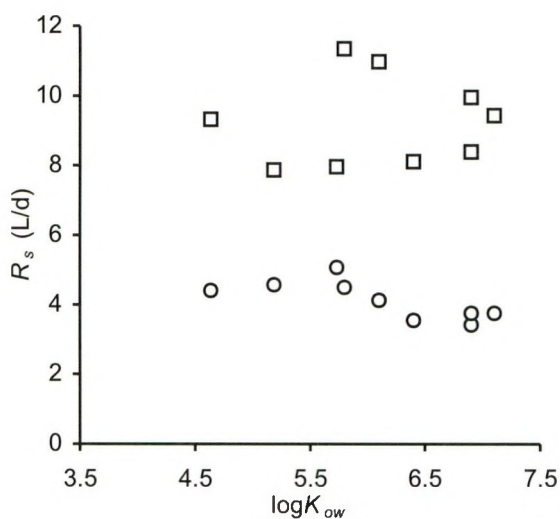


Fig. 11. Sampling rates of silicone tubing at 2°C (circles) and 30°C (squares). The tubings were mounted on a 15 cm diameter disk that rotated at 60 RPM.

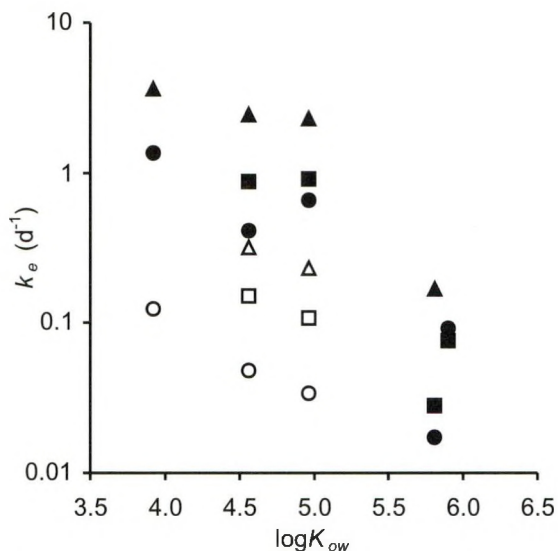


Fig. 12. Dissipation rate constants (k_e) of the Performance Reference Compounds for LDPE membranes (filled symbols) and SPMDs (open symbols) at 2°C (circles), 13°C (squares) and 30°C (triangles)

$\log K_{ow}$. In a previous study we showed that the effect of flow on sampling rates and on PRC dissipation rate constants is the same (Booij *et al.*, 1998). The value of PRC dissipation for accounting for differences in sampling rates as a result of temperature differences is limited, however. For LDPE membranes no difference in sampling rates is found between 2 and 13 °C, whereas PRC dissipation rate constants increase by a factor of 2. For the 13 to 30 °C temperature range the increase in R_s by a factor of 2 is indeed matched by an increase in PRC dissipation rate constants by a factor of about 2. For SPMDs increased sampling rates by a factor of 1.4 and 2.1 are reasonably matched by increased dissipation rates by a factor of two. It does not seem wise,

however, to rely on PRC dissipation to account for the effect of temperature on the sampling rates, since the exposure temperature generally is known with reasonable accuracy. The temperature correction in the dissipation rate constants is therefore easily made, which allows for estimating the pure flow effect on the sampling rates from the PRC dissipation rate constants.

RESULTS AND DISCUSSION II : FIELD EXPERIMENTS

Field survey Scheldt estuary and Southern North Sea. The amounts absorbed by SPMDs and LDPE

Table 2. Summary of dissipation rate constants (k_e) of the Performance Reference Compounds obtained during the lab experiments for SPMDs and LDPE membranes (30x2.5 cm).

		2 °C	13 °C	30 °C
		k_e (d ⁻¹)	k_e (d ⁻¹)	k_e (d ⁻¹)
SPMD	ACE-D10	0.124		
	PHEN-D10	0.048	0.151	0.317
	CB004	0.034	0.108	0.231
	CHR-D12			
	CB029			
LDPE	ACE-D10	1.35		3.63
	PHEN-D10	0.41	0.87	2.45
	CB004	0.66	0.91	2.30
	CHR-D12	0.017	0.028	0.168
	CB029	0.092	0.076	

membranes during the February/March survey are shown in Fig. 13. These graphs reflect the intuitively expected geographical trend in the contamination of the water phase: Hansweert > Vlissingen ~ Katwijk6 > Schouwen25 > Noordwijk60. A typical example of the geographical distribution of the contaminant amounts absorbed by SPMDs is shown for pyrene in Fig. 4.

PRC dissipation data are shown in table 3. Amounts of CB155 and CB204 retained during the exposures averaged 97% and 100% of the amounts in the controls, with standard deviations of 8 %. Reliable dissipation rate constants could be estimated for CB4, CB29 and chrysene-D12, both for SPMDs and for LDPE membranes. We did not consider the dissipation rate constants for phenanthrene-D10 to be very reliable, because of a phenanthrene-D10 contamination in the pyrene-D10 batch that was used to prepare the PAH analytical internal standard solution. The chemical noise in the acenaphthene-D10 trace on the MS, combined with the short dissipation time scale (~ 6 days) prevented the calculation of a reliable dissipation rate constant for this compound. Dissipation rate constants were virtually the same for all locations, with coeffi-

cients of variation of 7 to 20 %, with the exception of CB4 for the SPMDs which had a CV value of 42% due to an exceptionally high value for the Schouwen25 location (Table 3). This high value is most likely due to storage of the Schouwen25 sample at room temperature for several months instead of storage at -20 °C. The high similarity of dissipation rate constant for the different locations means that the uptake rate constants also were the same for all locations within a small error margin. The half life times for the attainment of equilibrium can be estimated as 11 days for CB4 ($\log K_{ow}=5.0$), 58 days for CB29 ($\log K_{ow}=5.9$) and 102 days for chrysene-D10 ($\log K_{ow}=5.8$).

Results for LDPE membranes and for SPMDs are quite similar. The SPMD/LDPE amount ratio is shown as a function of $\log K_{ow}$ in Fig. 14. For HCB, tri- and tetrachlorobiphenyls, and three- to four ring PAHs the amounts absorbed by SPMDs are much higher than for LDPE membranes. For larger PCBs and five-ring PAHs this difference is negligible, which indicates that the sorption capacity of both samplers is sufficient to keep the sampling in the linear uptake phase for these compounds.

Table 3. Dissipation rate constants of the Performance Reference Compounds for the February-March field survey (average and coefficient of variation).

	$\log K_{ow}$	Hansweert		Vlissingen		Katwijk		Schouwen		Noordwijk	
		$k_{e,SPMD}$ (d ⁻¹)	CV (%)	$k_{e,SPMD}$ (d ⁻¹)	CV (%)	$k_{e,SPMD}$ (d ⁻¹)	CV (%)	$k_{e,SPMD}$ (d ⁻¹)	CV (%)	$k_{e,SPMD}$ (d ⁻¹)	CV (%)
SPMDs											
CB004	4.97	0.0495	13	0.0529	2	0.0510	-	(0.1131)	-	0.0579	2
CHR-D12	5.81	0.0070	6	0.0064	4	0.0052	-	0.0066	-	0.0088	8
CB029	5.90	0.0109	9	0.0120	0	0.0104	-	0.0127	-	0.0133	1
LDPE membranes											
		$k_{e,LDPE}$ (d ⁻¹)	CV (%)	$k_{e,LDPE}$ (d ⁻¹)	CV (%)	$k_{e,LDPE}$ (d ⁻¹)	CV (%)	$k_{e,LDPE}$ (d ⁻¹)	CV (%)	$k_{e,LDPE}$ (d ⁻¹)	CV (%)
CB004	4.97	0.164	2	0.174	8	0.182	-	-	-	0.196	7
CHR-D12	5.81	0.025	6	0.021	6	0.019	-	-	-	0.017	24
CB029	5.90	0.066	0	0.094	4	0.081	-	-	-	0.084	12

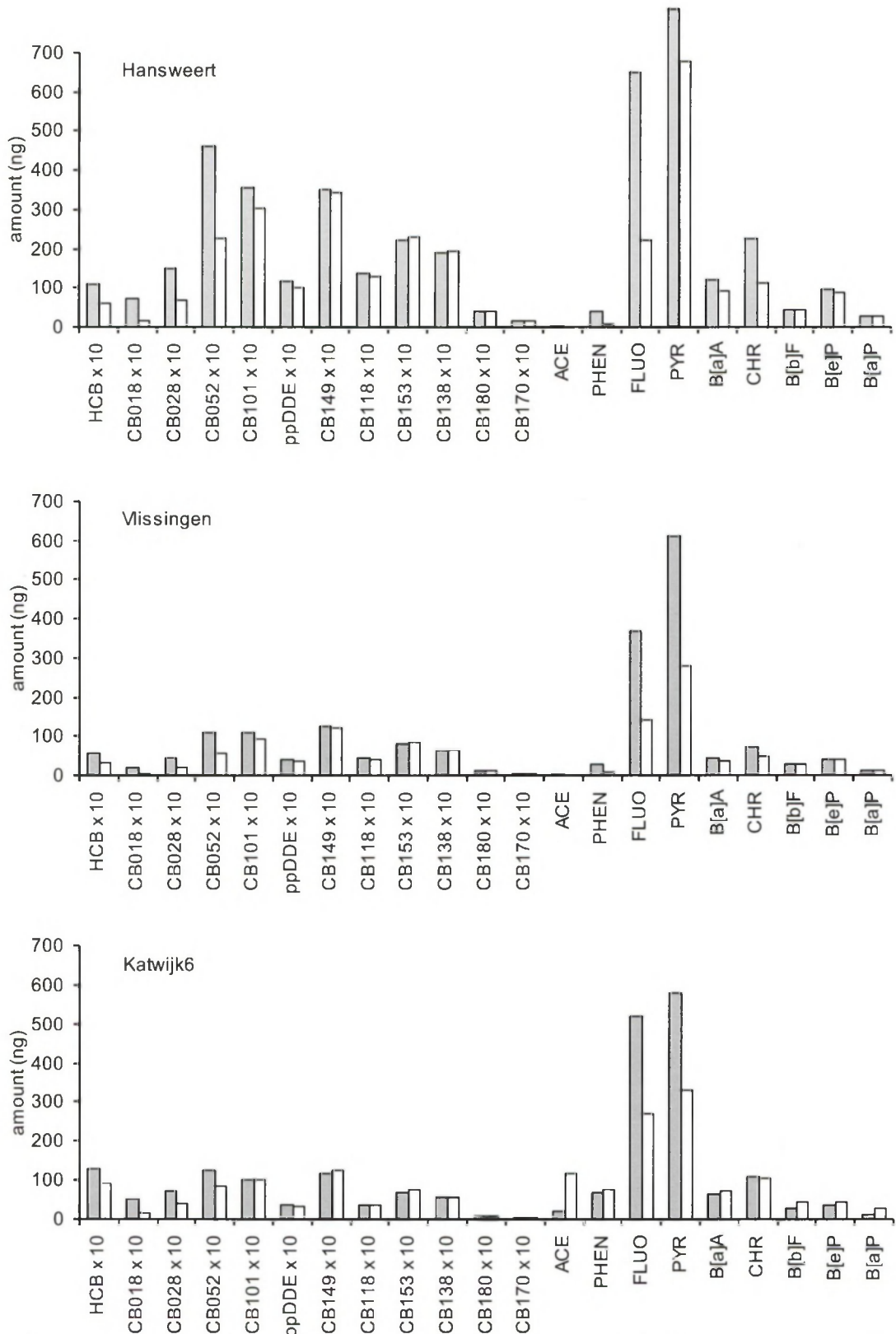


Fig. 13. Amounts absorbed by SPMDs (hatched) and LDPE membranes (white) during 38 - 43 days exposures in February-March 1999 in the Scheldt estuary and the Southern North Sea at locations Hansweert (top), Vlissingen (middle), Katwijk6 (bottom) (continued on next page)

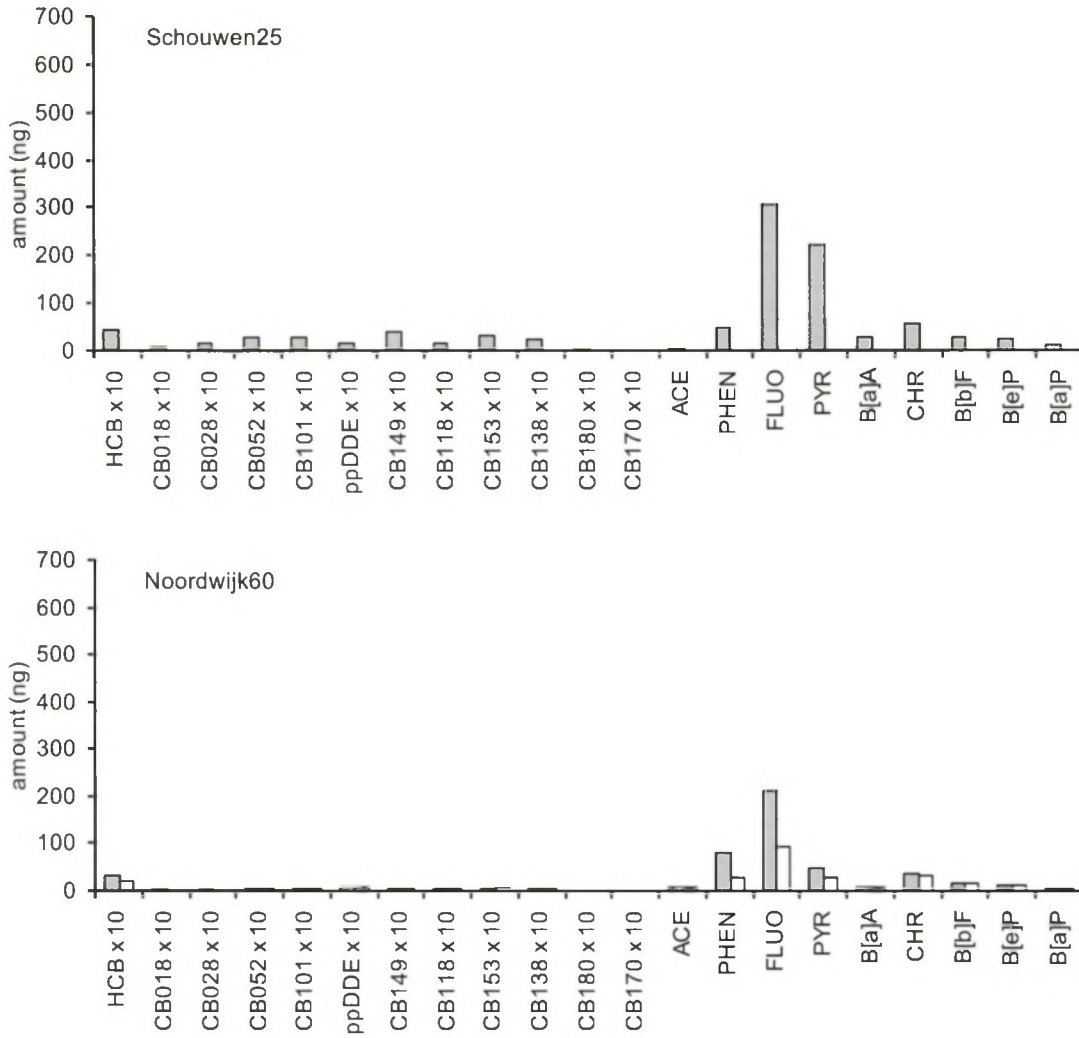


Fig. 13 (continued). Amounts absorbed by SPMDs (hatched) and LDPE membranes (white) during 38 - 43 days exposures in February-March 1999 in the Scheldt estuary and the Southern North Sea at locations Schouwen25 (top), and Noordwijk60 (bottom).

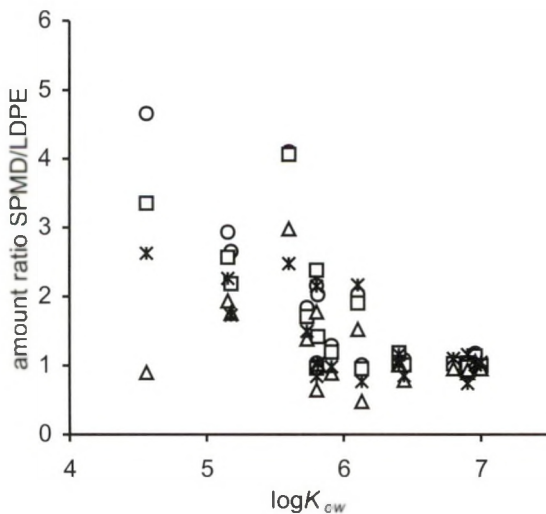


Fig. 14. Ratio of amounts absorbed by SPMDs and LDPE membranes during the February-March 1999 field survey as a function of $\log K_{ow}$ for the locations Hansweert (circles), Vlissingen (squares), Katwijk6 (triangles) and Noordwijk60 (asterisks).

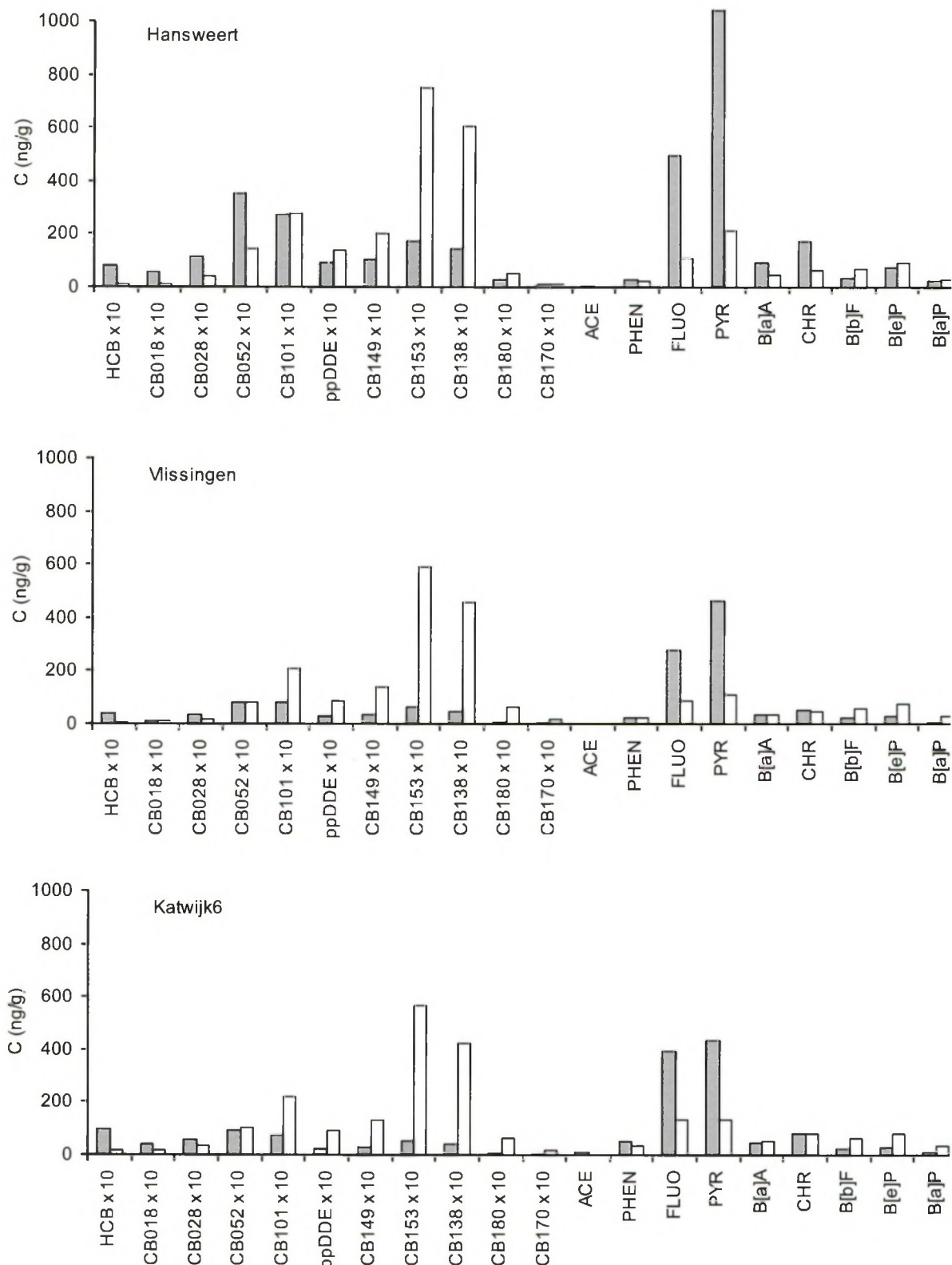


Fig. 15. Contaminant concentrations in SPMDs (hatched) and mussels (white) during 38 - 43 days exposures in February-March 1999 in the Scheldt estuary and the Southern North Sea at locations Hansweert (top), Vlissingen (middle), and Katwijk6 (bottom).

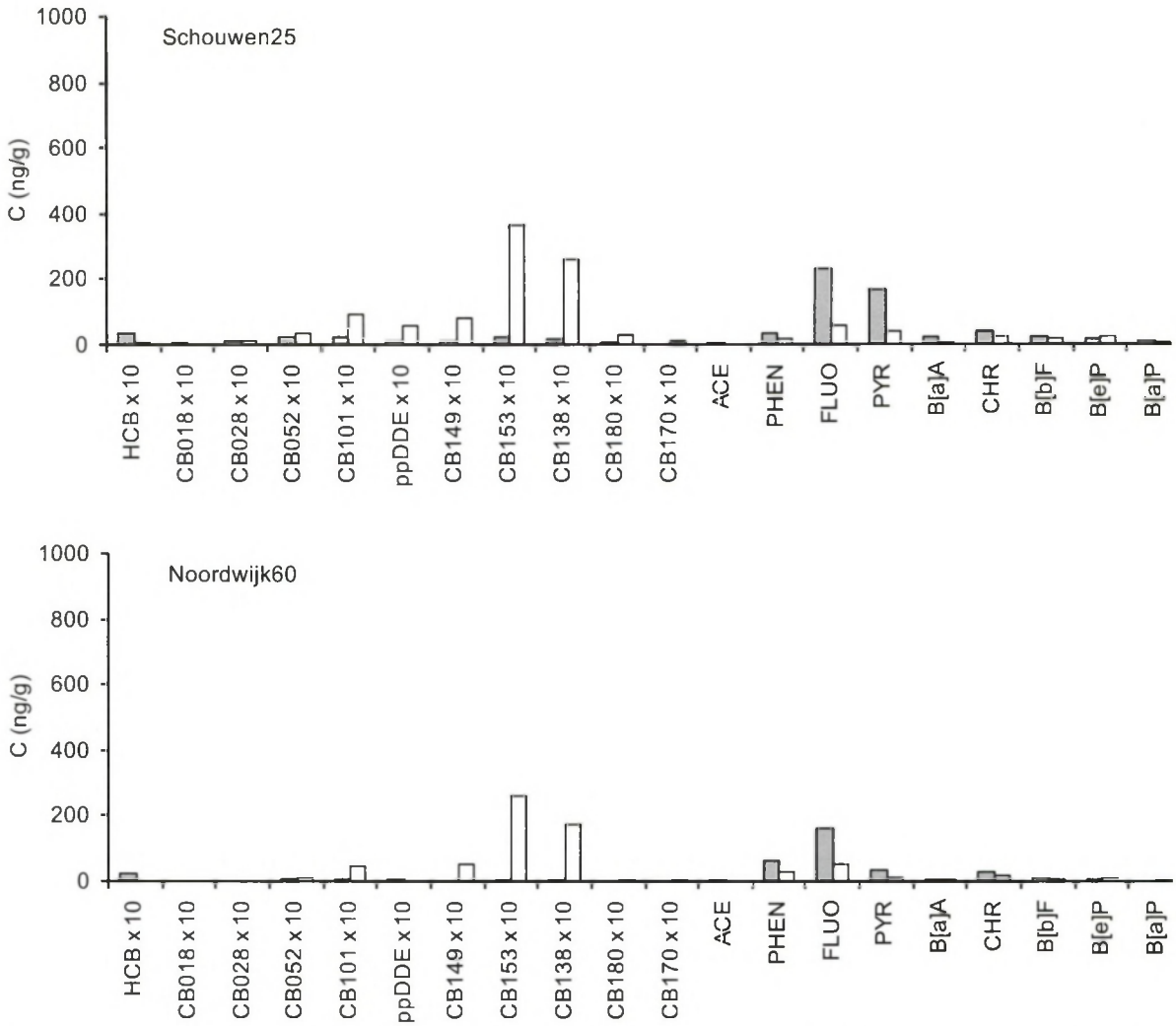


Fig. 15 (continued). Contaminant concentrations in SPMDs (hatched) and mussels (white) during 38 - 43 days exposures in February-March 1999 in the Scheidt estuary and the Southern North Sea at locations Schouwen25 (top), and Noordwijk60 (bottom).

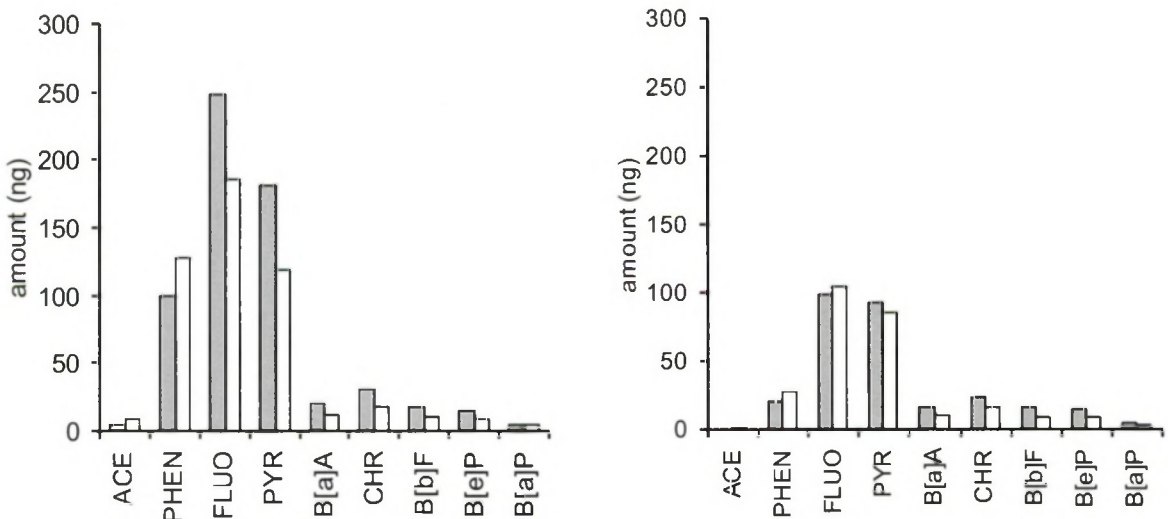


Fig. 16. Amount absorbed by SPMDs (left panel) and LDPE membranes (right panel) exposed under forced flow (hatched) and ambient flow conditions (white) during the 07/10/99 to 28/10/99 Marsdiep experiment.

A comparison between contaminant absorption by mussels and by SPMDs is shown in Fig. 15. All absorbed amounts were normalised on dry weight in order to express data for mussels and SPMDs on the same scale. Geographical trends in contaminant concentrations are more pronounced in SPMDs than in mussels. The concentrations of CB153 in mussels, for example, are lower at Schouwen25 than at Hansweert by a factor of two. SPMDs indicate a difference in exposure concentrations by a factor of seven. CB153 concentration differences between Noordwijk60 and Hansweert are a factor of three for mussels and a factor of 48 for SPMDs.

Marsdiep field experiments. The first purpose of the Marsdiep experiments was to assess the merits of exposing SPMDs and LDPE membranes under a forced flow regime, as opposed to exposures under ambient flow conditions. The amounts absorbed for the 07/10/1999 to 28/10/1999 period are shown in Fig. 16. For the three and four-ring PAHs the amounts absorbed by SPMDs under forced flow conditions is higher than for LDPE membranes, indicating that equilibrium has been attained for these compounds. For the five-ring PAHs no difference was observed. The amounts absorbed by SPMDs under forced flow conditions were higher than for the ambient flow exposures, with the exception of acenaphthene and phenanthrene. The difference increases with the hydrophobicity of the compound and levels off to a factor of 1.8 for the compounds with the highest K_{ow} . For LDPE membranes no difference in absorbed amounts is observed up to pyrene and fluoranthene, which indicates that these compounds have attained equilibrium both for the ambient flow and the forced flow conditions. The difference between ambient and forced flow exposures is also reflected in the dissipation rate constants (k_e) of the PRCs (table 4). For SPMDs and LDPE membranes the k_e estimates are higher for the forced flow conditions by a factor of 2.5 \pm 1.2 and 1.2 \pm 1.1 respectively. It should be borne in mind, however, that the purpose of the forced flow exposures was to gain better control over the sampling rates, rather than to increase the sampling rates.

The second aim of the Marsdiep experiments was to test passive sampling by silicone tubing in the field. Figure 17 shows a large difference between the amounts of low K_{ow} compounds absorbed by the silicone sampler compared to the LDPE forced flow sampler. This is caused by the higher sorption capacity of the silicone sampler. The silicone-LDPE amount ratio decreases with compound hydrophobicity, and levels off to a value of 0.5 in the high K_{ow} range (Fig. 18). On the basis of the laboratory experiments a somewhat lower ratio was expected for the high K_{ow} compounds. With a temperature of about 8 °C sampling rates of about 6 L d⁻¹ are expected for the silicone tubing, compared to 19 L d⁻¹ for the LDPE membranes, which would result in an ratio of absorbed amounts of 6/19 \approx 0.3. The higher ratios observed in the field may indicate that the silicone sampler was insufficiently shielded off from the ambient flow. This also indicates that much higher sampling rates for the silicone sampler can be realised.

CONCLUSIONS AND OUTLOOK

- Sampling rates attained by SPMDs and LDPE membranes are dramatically increased at a flow rates of about 1 m s⁻¹, compared to literature values obtained at 1 and 30 cm s⁻¹.
- CB4, CB29 and chrysene-D12 ($\log K_{ow}$ = 5.0, 5.9, 5.8) are suitable Performance Reference Compounds for six week exposures of SPMDs and LDPE membranes in the Dutch coastal waters. Perdeuterated fluoranthene ($\log K_{ow}$ =5.2) may be used in the future to supplement this set of PRCs.
- PRC dissipation rate constants for these compounds in the field could be estimated with a precision of 6-25%.
- The temperature effect on the PRC dissipation rate constants amounts to a factor of about 2 for each 10°C temperature change.
- The effect of a temperature increase from 2 to 13°C on the sampling rates is limited to a factor of 1.0 and 1.3 for LDPE membranes and SPMDs respectively. For the 13 to 30 °C temperature increase the change in sampling rates amounts to a factor of 2 for both samplers.
- Passive sampling with silicone tubing has a great potential for monitoring organic contaminants in the Dutch coastal waters, particularly in the low K_{ow} range ($<10^4$).
- Passive sampling by SPMDs and LDPE membranes is quite suitable for monitoring PCBs, chlorobenzenes and PAHs in the Dutch coastal waters. The differences in dissipation rate constants for the field stations in the Scheldt estuary and the southern North Sea were limited to a factor of 1.3, indicating that the sampling rates attained for ambient flow exposures are sufficiently similar. Therefore the application of forced flow samplers at these locations is not worth the effort.

RECOMMENDATIONS

It is useful to initiate a follow-up study on monitoring PCBs and PAHs in the Dutch coastal waters using passive samplers. We recommend that this study be structured along the following main lines.

- The programme covers a period of five years in which the stations Hansweert, Vlissingen, Schouwen25, Katwijk6 and Noordwijk60 are sampled twice each year.
- Sampling is done using silicone tubing and SPMDs. The use of silicone tubing facilitates the detection of low K_{ow} compounds, and also allows for time integrative sampling of these compounds. It seems wise to also include SPMDs in the programme, in order to link the results for silicone tubing to the results obtained by the more generally accepted SPMD method.
- Performance Reference Compounds are used to assess differences in sampling rates. Suitable PRCs for SPMDs that are exposed for six weeks are CB4, CB29, phenanthrene-D10, fluoranthene-

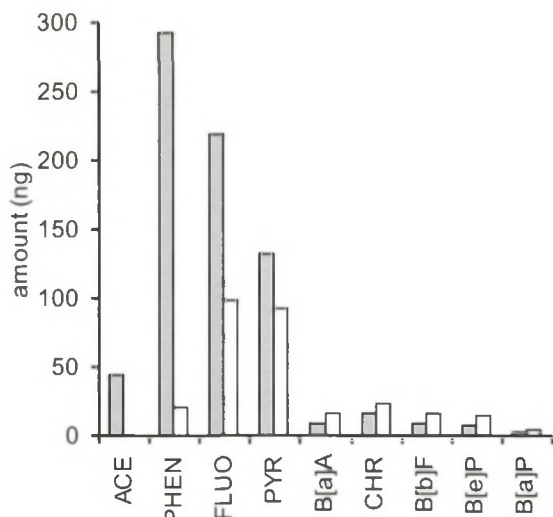


Fig. 17. Amounts absorbed by silicone tubing sampler (hatched) and LDPE membranes (white) under forced flow conditions during the 07/10/99 to 28/10/99 Marsdiep experiment.

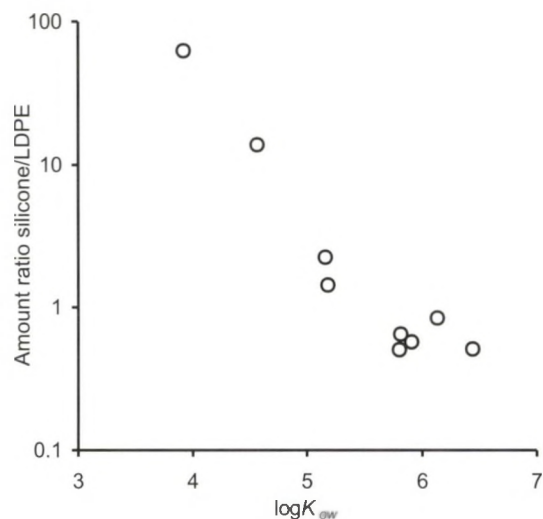


Fig. 18. Ratio of amounts absorbed by silicone tubing sampler and LDPE membranes exposed under forced flow conditions during the 07/10/99 to 28/10/99 Marsdiep experiment.

10 and chrysene-D12. We suggest that also CB155 and/or CB204 be included as PRCs. The recoveries of these compounds can be used as control parameters for extraction efficiency and analytical stability. For exposures using silicone tubing we suggest that less hydrophobic PRCs are included, such as naphthalene-D8 ($\log K_{ow}=3.35$)

- At the beginning of the programme an operating procedure is formulated that describes in detail the sampler construction, storage, exposure, extraction, clean-up, and analysis. Special attention should be given to minimise sample handling outside the laboratory, particularly when use is made of vessels that lack clean analytical facilities.
- Internal Reference Material (IRM) samples are prepared that are analysed at regular time intervals in order to assess the overall stability of the method.

REFERENCES

- Booij, K., Sleiderink, H.M., and Smedes, F., 1998. Calibrating the uptake kinetics of semi-permeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* 17: 1236-1245.
- Ellis, G.S., Huckins, J.N., Rostad, C.E., Schmitt, C.J., Petty, J.D., and MacCarthy, P., 1995. Evaluation of lipid-containing semipermeable membrane devices for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* 14: 1875-1884.
- Herve, S., Prest, H.F., Heinonen, P., Hyötyläinen, T., Koistinen, J., and Paasivirta, J., 1995. Lipid-filled semipermeable membrane devices and mussels as samplers of organochlorine compounds in lake water. *Environ. Sci. Pollut. Res. Int.* 2: 24-29.
- Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., and Lebo, J.A., 1993. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* 27: 2489-2496.
- Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., and Echols, K.R., 1999. Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* 33: 3918-3923.
- Huckins, J.N., Tubergen, M.W., and Manuweera, G.K., 1990. Semipermeable membrane devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 20: 533-552.

Table 4. Dissipation rate constants of the Performance Reference Compounds for the 07/10/99 to 28/10/99 Marsdiep exposure (average and coefficient of variation).

	ambient flow SPMDs			forced flow SPMDs		ambient flow LDPE membranes		forced flow LDPE membranes	
	$\log K_{ow}$	k_e (d^{-1})	CV (%)	k_e (d^{-1})	CV (%)	k_e (d^{-1})	CV (%)	k_e (d^{-1})	CV (%)
CB004	4.56	0.062	10	0.135	12	0.285	0	0.336	25
PHEN-D10	4.97	0.093	7	0.202	9	0.275	1	0.261	3
CHR-D12	5.81	0.006	16	0.017	30	0.032	3	0.041	4

- Lebo, J.A., Zajicek, J.L., Huckins, J.N., Petty, J.D., and Peterman, P.H., 1992. Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere* 25: 697-718.
- Petty, J.D., Huckins, J.N., Martin, D.B., and Adornato, T.G., 1995. Use of semipermeable membrane devices (SPMDs) to determine bioavailable organochlorine pesticide residues in streams receiving irrigation drainwater. *Chemosphere* 30: 1891-1904.
- Petty, J.D., Huckins, J.N., and Zajicek, J.L., 1993. Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* 27: 1609-1624.
- Prest, H.F., Huckins, J.N., Petty, J.D., Herve, S., Paasivirta, J., and Heinonen, P., 1995a. A survey of recent results in passive sampling of water and air by Semipermeable Membrane Devices. *Mar.Pollut.Bull.* 31: 306-312.
- Prest, H.F., Richardson, B.J., Jacobson, L.A., Vedder, J., and Martin, M., 1995b. Monitoring organochlorines with Semi-Permeable Membrane Devices (SPMDs) and mussels (*Mytilus edulis*) in Corio Bay, Victoria, Australia. *Mar.Pollut.Bull.* 30: 543-554.
- Prest, H.F., Jacobson, L.A., and Huckins, J.N., 1995c. Passive sampling of water and coastal air via semipermeable membrane devices. *Chemosphere* 30: 1351-1362.
- Prest, H.F., Jarman, W.M., Weismuller, T., Martin, M., and Huckins, J.N., 1992. Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joaquin river delta. *Chemosphere* 25: 1811-1823.

CONTENTS

Summary	1
Introduction	1
Material	2
Results and discussion I : Lab experiments	4
Results and discussion II : Field experiments	8
Conclusions and outlook	14
Recommendations	14
References	15