Monitoring of polycyclic aromatic hydrocarbons in the Portsmouth Harbour, United Kingdom, using the Chemcatcher® passive sampling devices

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Abstract

The use of passive sampling techniques to monitor water quality offers a number of advantages over conventional grab or spot sampling methods. Recently, a passive sampling device - Chemcatcher® has been developed for the measurement of a broad range of priority organic and inorganic pollutants. The device uses a common design with interchangeable receiving phases and membranes, depending upon application. There are two designs of housing available for the Chemcatcher®. The samplers were deployed at two sites in Portsmouth Harbour (Portsmouth, UK) for several 14-day periods. Three replicates of the Chemcatcher® sampler were deployed at each site. Two different designs of sampler housing were used and compared in the trial. During the whole exposure time the water chemistry was carefully monitored. Spot samples were collected regularly during the deployment period and the uptake of selected organic priority pollutants in the passive samplers was compared to the levels found in the spot samples. The samplers provided time-weighted average concentrations of the bioavailable (truly dissolved) fraction of monitored pollutants. Sampling rates at Site 1 (outside the harbour basin) were are almost three times higher than those at Site 2, which was probably caused by the more intense turbulence of water. In comparison with

the concentrations of truly dissolved analytes measured by passive samplers, higher concentrations of pollutants were determined in filtered spot water samples. The difference was likely caused by the elevated content of colloidally bound contaminants present in water samples. In contrast, passive samplers measure the concentrations of truly dissolved fractions. Concentrations of pollutants at Site 1 determined in passive samplers were lower compared to Site 2. Concentrations in water samples at the two sites did not differ significantly, although slightly higher PAH concentrations were determined at Site 1.

Keywords: Chemcatcher[®], passive sampling, water monitoring, hydrophobic organic pollutants, polycyclic aromatic hydrocarbons

Introduction

Several methods are available for monitoring of organic pollutants in water. Conventional spot sampling has several limitations. For example, spot sampling is always associated with definite place and time and thus the obtained data are not representative for the whole area. When the pollutants are present at ultra-trace levels, large volumes of water are necessary to be processed. With grab sampling, it is also not possible to asses the truly dissolved (bioavailable) fraction, which is relevant for prediction of the risk of the chemicals in the environment. More representative ways of monitoring needs to be used to assess the time weighted average concentration. Commonly used methods are sampling with an increased frequency, automatic sequential sampling, biomonitoring, continuous on-line monitoring systems, and passive sampling which can be expensive, especially in remote areas. Biomonitoring, which is based on a direct accumulation of lipophilic compounds into living organisms, offers only a partial solution. Data obtained from living organisms are difficult to compare, are characteristic for a species and vary depending on temperature, water flow, migration or nourishment and metabolic activity of organisms.

A wide range of passive sampling devices have been developed to overcome the limitations of conventional sampling methods. These include the lipid-filled semi-permeable membrane device (SPMDs) (Huckins et al. 1990), solvent-filled dialysis membrane samplers, the membrane enclosed sorptive coating (MESCO) (Vrana et al. 2001), and Chemcatcher[®] (Kingston et al. 2000) for non-polar compounds. State of the art of the passive sampling

technology has been recently described in several reviews (Seethapathy et al. 2008; Gorecki et al. 2002) and monographs (Greenwood et al. 2007).

Methods of passive sampling of analytes involve the measurement of the concentration of an analyte as a weighted average over the sampling time. The concentration of the analyte is integrated over the whole exposure time, making such a method immune to accidental, extreme variations of pollutant concentrations (Namiesnik et al. 2005). Passive sampling devices consist of a receiving phase and optionally of a diffusion membrane.

Passive samplers find a broad range of applications. They are suitable for screening the presence/absence of pollutants, for investigation of temporal trends in contamination, for assessing toxicity in extracts of bioavailable compounds, for tracing the source of pollution and for monitoring spatial contaminant distribution.

The Chemcatcher®, developed at the University of Portsmouth, is based on the diffusion of target compounds through a membrane and the subsequent accumulation of these pollutants in a sorbent-receiving phase. There is a variety of sorbents and membranes commercially available, so that high and specific affinity for the analytes of interest can be achieved. In the field trial a non-polar version of Chemcatcher® sampling devices were used. A subsequent study confirmed that the values of kinetic parameters for the new housing design are on average two times higher in comparison with the old body design (Lobpreis et al. 2008).

Theory

Mass transfer of a chemical into the sampler involves several diffusion mass transport steps across the various layers. The possible barriers may include: stagnant aqueous boundary layer, possibly a biofilm, the diffusion membrane, the inner priming phase, and the receiving phase, which is in this case a C_{18} Empore® disk saturated with *n*-octanol. Theory of mass transfer for the Chemcatcher® passive sampler has been described in detail (Greenwood et al. 2007). The amount of the chemical accumulated from water in the receiving phase of the sampler can be described by the equation:

$$m_D(t) = m_{D0} + \left(C_W K_{DW} V_D - m_{D0}\right)\left[1 - \exp\left(-\frac{k_o A}{K_{DW} V_D}\right)t\right] \qquad (1)$$

where:

m_D [kg] is the mass of analyte in the receiving phase, m_{D0} [kg] is the analyte mass in the receiving phase at the start of exposure, C_W [kg m^{-3}] represents the water concentration during the deployment period, K_{DW} is the receiving phase/water distribution coefficient, V_D [m^3] is the volume of the receiving phase, k_o [m s^{-1}] is the overall mass transfer coefficient, A [m^2] is the membrane surface area, and t [s] stands for time.

The coefficient in the exponential function (Eq. 1) is referred to as the overall exchange rate constant k_e.

$$k_e = \frac{k_o A}{K_{DW} V_D} \tag{2}$$

At the initial stages of exposure, analyte uptake is expected to be linear or time-integrative after steady-state flux of chemicals into the sampler has been achieved. Under these conditions, the amount of a chemical in the receiving phase is directly proportional to the product of the concentration in the surrounding water (C_W) and the exposure time (t). For practical purposes, uptake in the linear phase can be expressed as:

$$m_D(t) = m_{D0} + C_W k_0 At \tag{3}$$

The product Ak_ot is equivalent to the apparent water volume extracted during the exposure time t. Hence, the product Ak_o can be viewed as an apparent water sampling rate (R_S)

$$R_S = k_o A = k_e K_{DW} V_D \tag{4}$$

Because R_s represents the volume of water extracted per unit time [m^{3}s^{-1}], it forms a conceptual link between traditional batch water extraction methods and passive sampling methods. Equation (4) shows that water sampling rates are linearly proportional to the surface area of the sampler. For this reason, a comparison of sampling rates among different sampler designs only yields meaningful results when differences in surface area are taken into account (Booij et al. 2007). To overcome the effect of environmental variables (water temperature, hydrodynamic conditions, biofouling, etc.) on the kinetic parameters during the field trial, internal chemical standards, so called performance reference compounds (PRCs), were added

to the receiving phase prior to exposure. It was found that the rate of uptake of target analytes from water to the sampler receiving phase is related to the rate at which they offload to the water (Booij et al. 1998). This enables the use of offloading rates of PRCs to be used to adjust uptake rates for the variables in the field. The calibration procedures and data have been previously reported (Vrana et al. 2005). When PRCs are used that are not present in water ($C_W = 0$) and isotropic exchange kinetics applies, Equation 1 is simplified to:

$$m_D = m_{D0} \exp(-k_e t) \tag{5}$$

where the amount of PRCs added to the sampler (m_{D0}) is known.

Materials and Methods

Sampling sites

The passive samplers were deployed at two sites in the Portsmouth Naval Base (one site outside the docks and other inside the non-tidal Basin 3) (Fig. 1 and Table 1) for several 14-day periods from the 19th September to the 14th October 2005. At each site, three replicates of each sampler configuration (old and new housing design) of the non-polar Chemcatcher® configuration were deployed. Both designs of housing were used. In addition, low density polyethylene (LDPE) strips were deployed as samplers of hydrophobic organic compounds.

Fig. 1. Sites of passive sampler deployment and water sampling the UK
  Naval Base in Portsmouth harbour (source: maps.google.com).

Table 1. Sampling sites in the UK Naval Base in Portsmouth Harbour, autumn 2005

Sampling site	Description	Coordinates	
Site 1	Site affected by tide, outside the locks	50°48`26.59`` N	1°06`20.64`` W
Site 2	Site inside a non-tidal basin	50°48`31.08`` N	1.05`45.06`` W

Materials and chemicals

C_{18} Empore® disks (47 mm diameter) were purchased from Varian Inc., Walton-on-Thames, UK. LDPE membrane material (40 mm thick) was obtained from Fisher Scientific, Loughborough, UK. The solvents (HPLC grade quality or equivalent), acetone, ethyl acetate, methanol, *n*-hexane, *n*-octanol, *n*-nonane, 2,2,4-trimethyl pentane, and water were obtained from Fisher Scientific. Certified pure (purity >98% in all cases) reference standards of the test compounds, surrogates, and internal standards were obtained from Qm_X Laboratories, Saffron Walden, UK. Certified external calibration solutions of target analyte mixtures at a concentration of 10 μg mL^{-1} in cyclohexane were obtained from Qm_X Laboratories.

Sampler preparation

Chemcatcher® passive samplers (Fig. 2) were prepared in accordance with a procedure described in Vrana et al. (2005). C_{18} Empore® disks were conditioned by soaking in methanol for at least 20 min or until required. The Empore® disks were prepared in a 47-mm diameter disk vacuum manifold platform (Varian Inc.). Perdeuterated polycyclic aromatic hydrocarbons were utilised as PRCs. For loading the disks with PRCs, 10 mL methanol was slowly passed through the disk, followed by 20 mL ultrapure distilled water. Aqueous solution (500 mL) of PRCs, containing 5 mg L^{-1} of each of the following chemicals: D10-biphenyl, D10-acenaphthene, D10-phenanthrene, D10-pyrene and D12-benzo[a]anthracene was filtered through the disk. Vacuum was applied for 30 min to ensure that the disc was completely dry. The Empore® disk was then put on the sampler housing. One mL solution of *n*-octanol in acetone (45% v/v) was applied and allowed to evaporate for 10 min to resulting *n*-octanol volume of 450 mL. The LDPE membrane (pre-cleaned by soaking for 24 h in *n*-hexane and dried) was carefully put on the top of the Empore® disk and air bubbles were smoothed away from between the two layers. Two variants of sampler housing Chemcatcher®

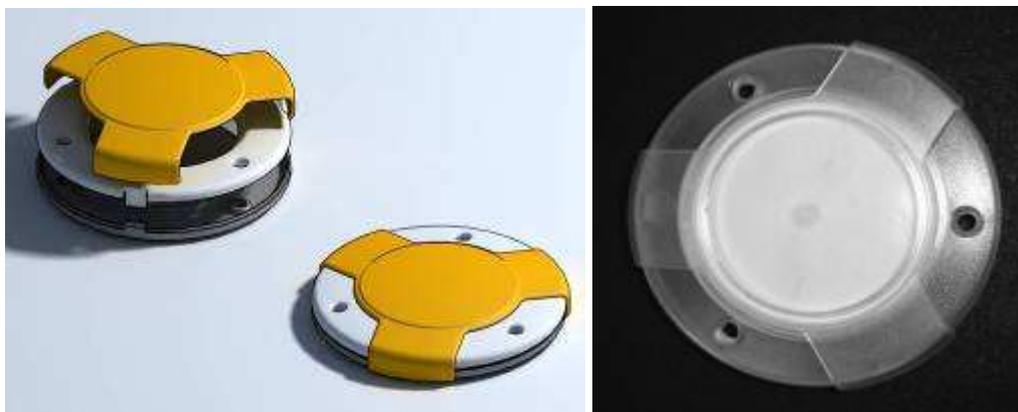passive sampler (made of PTFE and polycarbonate, respectively) were applied to compare their performance in situ.

Fig. 2. New generation of Chemcatcher® passive sampler.

Sampler deployment, exposure and retrieval

On the day of deployment, samplers were transported to the sampling sites in a portable coolbox. At the sampling site, transport lids were removed from the samplers and samplers were tied on plates made of PTFE. The PTFE plates with samplers rope were deployed at the depth of approximately 1 m below surface using a rope and a buoy, and were secured to a waterside using a rope. To prevent floating of the devices due to the current, anchors were attached to the devices.

On day 14, samplers were removed from the water, checked visually for mechanical damage and the extent of biofouling and sealed with their transportation lids. The samplers were transported to the analytical laboratory in a portable coolbox. Part of the samplers deployed outside the docks were unfortunately damaged by a ship, which moved devices with samplers.

The field control samplers were exposed to air while samplers were being deployed and collected. The field control samplers were processed as the deployed samplers and were used to measure contamination during transport and handling. Two sampler fabrication controls were also analyzed to determine contamination arising from the manufacturing process, sampler components, laboratory storage, processing, and analytical procedures, as well as to determine the nominal concentration of PRCs in the samplers before exposure. Field and fabrication controls were stored at 4°C, whilst the rest of the field samplers were in the field.

During samplers exposure, temperature was monitored at trial sites using thermo-logging devices. Spot water samples were taken regularly during the deployment period. Each time, 2×2.5 L of water from each site were taken in amber glass bottles for analysis of organic pollutants. In laboratory, water samples for organic analytes were filtered through a glass fibre filter (Whatman, 0.7 μm pore size).

Extraction and analysis of analytes from passive samplers and water samples

After exposure, the sampler was carefully disassembled and analytes extracted from the Empore® disks and membranes in an ultrasonic bath (5 min) using acetone (5 mL) followed by 5 min in 50 : 50 (v/v) ethyl acetate : 2,2,4-trimethyl pentane (5 mL). The extracts were filtered through a drying cartridge containing 1 g of anhydrous sodium sulfate (Varian Inc.) and gradually reduced in volume under nitrogen to approximately 450 μL of remaining *n*-octanol. The final volume was adjusted to 500 mL with n-octanol. As an internal standard, 50 mL of 10 ng mL^{-1} solution of D10-anthracene was added prior to exposure.

The test analytes in water samples were extracted using solid-phase extraction (SPE) on Bondelut C$_{18}$ LO SPE cartridges (3 mL/ 200 mg sorbent; Varian Inc.). The sorbent was first activated by the passage of 2 mL methanol followed by 10 mL water through the bed. The water sample (500 mL) was passed through the cartridge at 30 mL min^{-1} using low-pressure. After the entire water sample has passed through the cartridge, the sorbent was dried by aspirating air through the bed. Extracted analytes were eluted with 1 mL *n*-hexane. 50 mL of internal standard (10 ng mL^{-1} D10-anthracene in *n*-hexane) was added prior to analysis. Analysis was performed with a 6890A series gas chromatograph (GC) equipped with a mass-selective detector 5973 (Agilent Technologies, Bracknell, UK). The GC oven temperature programme, column type and MS parameters for both *n*-octanol and hexane methods were used according to Vrana et al. (2006).

Results and Discussion

Data processing

To determine the TWA concentration of an analyte in water, substance specific sampling rate (R_S expressed as mL day^{-1}) needs to be known for the conditions in the environment. The mass transfer from the environment into the receiving phase is strongly affected by

hydrodynamic conditions in the vicinity of the membrane (laminar water boundary layer), temperature and biofouling. To eliminate the effect of these environmental variables, sampling rates were calculated using the PRC approach. PRCs are analytically non-interfering compounds added to the sampler prior to exposure. The rate of PRC loss during an exposure and the rate of uptake of the target compound are related and both driven by the 1st Fick's law kinetics. The release of performance reference compounds from the sampler was fitted by non-linear regression analysis using Eq. (5) with $m_D(0)$ and k_e as adjustable parameters. The in situ sampling rates of target analytes were calculated using approach described by Vrana et al. (2005). Briefly, first-order PRC offload rates, k_e, allowed the calculation of uptake rates for PRC (or non-deuterated PRC analogues, assuming similar log K_{OW} values for deuterated and non-deuterated analytes) using Eq. (4). K_{SW} values for the Chemcatcher[®] were obtained from Vrana et al. (2007). The following polynomial relationship was used to calculate R_S values for PAHs and PCBs with log K_{OW} values between 3.7 and 6.8:

$$\log R_S = Pi + 22.755 \log K_{OW} - 4.061 \log^2 K_{OW} + 0.2318 \log^3 K_{OW} \qquad (6)$$

R_S values for PRCs calculated using Eq. (4) were used in Eq. (6) to determine a P_i for each exposure and each PRC. An average P_i value was then determined for each exposure and this allowed to determine R_S for any compound of known log K_{OW}. Eq. (1) was then used to calculate time-weighted average concentrations.

Water samples

Spot water samples were taken regularly during the deployment period. Temperature was monitored at trial sites using thermo-logging devices to take measurements every 15 minutes. The temperature varied from 15.8 to 19.3°C (Fig. 3). In addition, physico-chemical parameters (pH value, conductivity) for both sites were measured (Table 2 and 3).
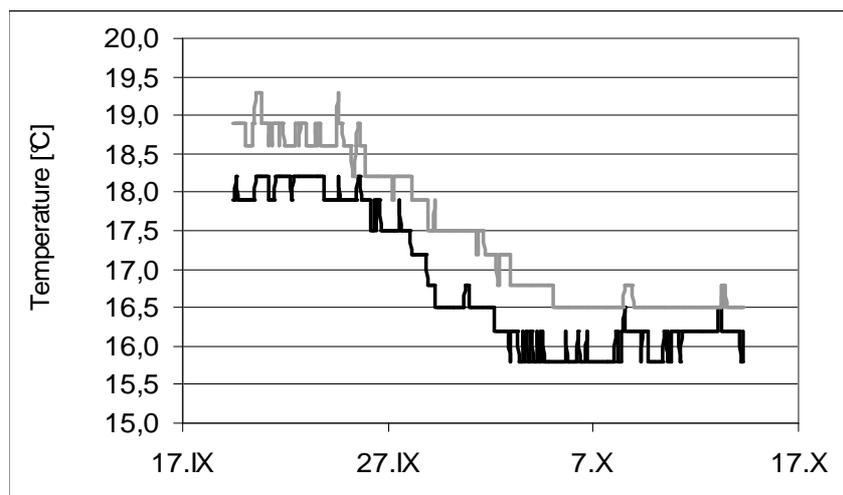
Fig. 3. Water temperature at sampling Site 1 (black) and Site 2 (grey) during field trial using thermo-logging device.

Table 2. Parameters of water at Site 1.

	Site 1				
Date	18/09/05	19/09/05	22/09/05	30/09/05	03/10/05
time of sampling	11:00	10:30	14:30	11:15	15:20
air temperature [°C]	29.0	22.6	25.0	21.0	19.2
water temperature [°C]	20.4	18.2	18.8	16.8	16.4
pH	8.3	8.3	8.3	8.4	8.6
conductivity [mS cm^{-1}]	52.6	52.3	53.1	52.7	53.0

Table 3. Parameters of water at Site 2.

	Site 2				
Date	18/09/05	19/09/05	22/09/05	30/09/05	03/10/05
time of sampling	11:20	11:45	14:50	11:55	15:30
air temperature [°C]	28.0	18.0	25.0	21.0	19.2
water temperature [°C]	21.4	19.3	19.8	18	17.3
pH	8.7	8.65	8.6	8.7	8.6
conductivity [mS cm^{-1}]	51.4	51.8	51.3	51.5	57.7

The concentration of target analytes (PAHs) measured in filtered water samples taken from the two sampling sites are reported in Tables 4 and 5. Measured concentrations at the two sites did not differ significantly, although slightly higher PAH concentrations were

determined at the Site 1. The low ratio of concentrations phenanthrene/anthracene in all samples (<10) indicates a petrogenic (fuel leakage) source as a likely pollution source rather than a pyrogenic (incomplete combustion). The environmental quality standard (EQS) criteria defined by the European Water Framework Directive for the compounds under investigation were not exceeded at neither of the two sampling sites.

Table 4. Concentration of target analytes in water samples at Site 1 (n.d. = not detected).

date	Site 1 – Dissolved PAHs [ng L^{-1}]				
	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene
19/09	n.d.	n.d.	2	n.d.	4
22/09 A	n.d.	13	8	6	4
22/09 B	n.d.	14	8	5	4
30/09 A	n.d.	11	11	10	2
30/09 B	n.d.	13	13	10	3
03/10 A	n.d.	7	11	8	2
03/10 B	n.d.	n.d.	5	4	3

Table 5. Concentration of target analytes in water samples at Site 2 (n.d. = not detected).

date	Site 2 – Dissolved PAHs [ng L^{-1}]				
	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene
19/09	2	n.d.	8	n.d.	4
22/09 A	n.d.	13	9	5	3
22/09 B	18	7	6	2	1
30/09 A	n.d.	7	9	4	5
30/09 B	n.d.	5	10	3	4
03/10	n.d.	7	5	4	3

Passive samplers

The amount of PRCs offloaded from the receiving phase enabled the calculation of sampling rates in water (Eq. 4). For sampling Site 1, the overall exchange rate constant k_e and R_S values obtained using the new design Chemcatcher® samplers (fitted in polycarbonate housing) ranged between 0,1254 day^{-1} and 0,3340 L day^{-1}; for sampling Site 2 between 0,0433 day^{-1} and 0,1152 L day^{-1}. The results show that the exchange kinetics was much faster at Site 1, which was caused by more turbulent hydrodynamic conditions caused by tidal water

movement. In contrary, at Site 2 which is isolated from the open sea, the streaming could be caused by occasional and limited ship passing.

The amount of analytes detected in the fabrication control samplers was subtracted from the amount found in the exposed samplers. These amounts corrected for controls were used to estimate the TWA concentration of target analytes in water using Eq. 3 and 4. The results for both sites are shown in Table 6.

Table 6. Sampling rates and calculated TWA concentration obtained from field exposed passive samplers.

		Site 1			Site 2		
	$\log K_{OW}$	$\log R_S$ [L d^{-1}]	R_S [L d^{-1}]	C_W [ng L^{-1}]	$\log R_S$ [L d^{-1}]	R_S [L d^{-1}]	C_W [ng L^{-1}]
Acenaphthene	4.0	- 0.357	0.440	n.d.	- 0.819	0.152	n.d.
Fluorene	4.2	- 0.127	0.746	1.05	- 0.590	0.257	1.10
Phenanthrene	4.5	0.049	1.119	1.79	- 0.413	0.386	2.93
Anthracene	4.6	0.068	1.171	0.53	- 0.394	0.404	0.91
Fluoranthene	5.1	- 0.064	0.862	1.45	- 0.527	0.297	5.17
Pyrene	5.1	- 0.064	0.862	1.84	- 0.527	0.297	6.14

The comparison of the concentration from spot sampling and TWA concentration obtained from Chemcatcher samplers are shown in Fig. 4 and 5. Concentrations of pollutants at Site 1 determined in passive samplers were lower than the average value of concentration determined from multiple spot samples. Passive samplers reflect the truly dissolved fraction of contaminants. Higher concentrations of contaminants in spot water samples (filtered through a 0.45 µm) may be caused by elevated content of colloidally bound contaminants in water samples collected in the harbour area, affected by strong tidal currents and particulate matter mobilization from the seabed. The TWA concentrations of PAHs at Site 2, estimated using the 2nd generation Chemcatcher® prototype, seem to be overestimated for compounds with higher $\log K_{OW}$. We hypothesize that higher concentrations of PAHs at Site 2 may have been caused by locally elevated PAH concentrations in the aqueous phase, caused by PAH desorption from particles that settled inside the sampler body cavity during deployment.
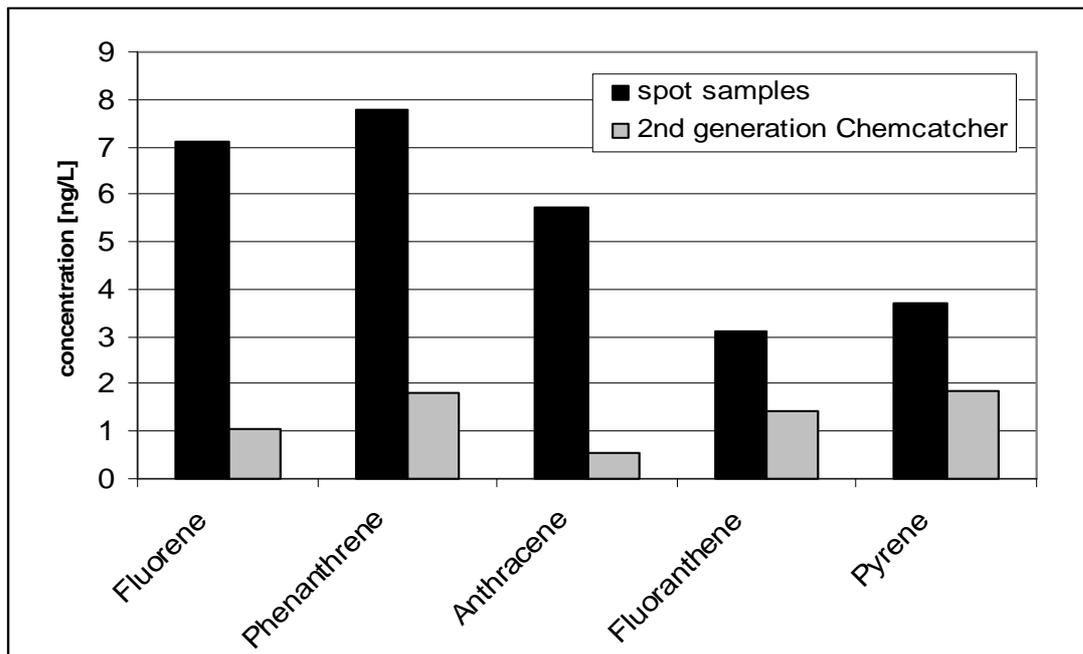
Figure 4. Comparison of TWA concentration of selected PAHs obtained from the levels found in Chemcatchers® and those measured using spot samples at Site 1.
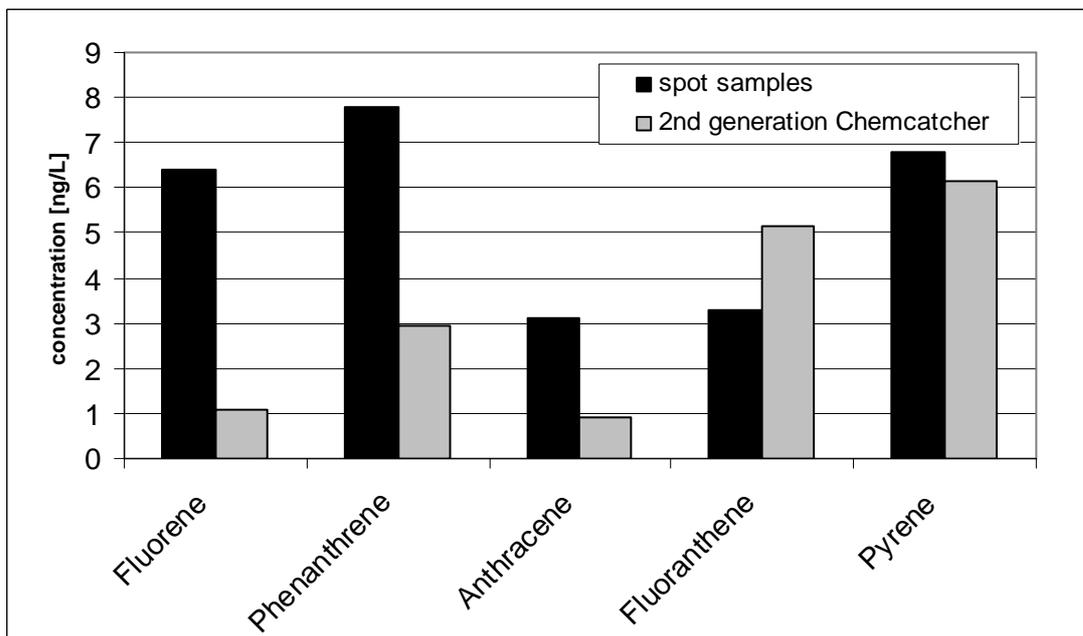

Figure 5. Comparison of TWA concentration of selected PAHs obtained from the levels found in Chemcatchers® and those measured using spot samples at Site 2.

Conclusion

Chemcatcher® passive sampling device was applied for monitoring priority organic pollutants in a marine harbour environment. The 2nd generation sampler prototype is characterized by reduced "cavity" in the sampler body to a minimum which causes higher sampling rates and reduced resistance of aqueous boundary layer in the vicinity of the receiving phase. The results confirmed the ability of the device to be used under real conditions and, in addition, provide further information about the state of the contamination compared to conventional sampling methods, which are accompanied by several limitations. The levels of selected priority organic pollutants in spot samples taken at two sampling sites in the Portsmouth Harbour indicate that the environmental quality standard criteria defined by the European Water Framework Directive were not exceeded.

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