Measurement of the availability of polycyclic aromatic hydrocarbons (PAHs) in marine sediments and pore-waters from Loch Leven, Scotland using silicone rubber passive samplers

K. Yates, I. M Davies, L. Webster, P. Pollard, L. Lawton, and C. F. Moffat

Abstract

The sediments of Loch Leven, Scotland contain high concentrations of PAHs and have been monitored by Fisheries Research Services since 1999. The contamination has been attributed to the effluent discharged from an aluminium smelter at Kinlochleven, which ceased operation in June 2000. The availability of PAHs in sediments collected from 5 points along the loch in 2006 was assessed using silicone rubber passive samplers, following protocols developed through the ICES Working Group on Marine Sediments. The total (2- to 6-ring, parent and branched) measured PAH concentration in the 5 sediments ranged from 13,282 to 95,158 ng/g dry weight with concentrations in the 3 sediments from the upper basin of the loch a factor of 8 higher than those found in the 2 sediments from the lower basin. The 4- to 6- ring compounds accounted for ~ 95% of the PAHs found in both basins, with a dominance of the 5-ring compounds (~ 45%). Results from the laboratory application of silicone rubber passive samplers provide estimates of the free dissolved concentrations of PAHs in pore water, and also of the fraction of the total concentration of PAHs in the sediment that could potentially be mobilised into the pore water. The method also allowed for the estimation of site specific sediment-water partition coefficients. These information aids in the assessment of environmental risk arising from contamination from smelter discharges.

Keywords: silicone rubber, PAHs, passive sampler, free dissolved concentration

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# 1	Introduction

The sediments of Loch Leven, Scotland contain high concentrations of polycyclic aromatic hydrocarbons (PAHs) and have been monitored by Fisheries Research Services since 1999. The contamination has been attributed to the effluent discharged from an aluminium smelter at Kinlochleven, which ceased operation in June 2000 (McIntosh *et al*., 2002, McIntosh *et al*., 2004 and Webster *et al*., 2004) and enhanced concentrations of PAHs may persist for a considerable time. Loch Leven is also known to support a number of fish farms and elevated PAH concentrations have been found (McIntosh *et al*., 2004) in farmed mussels close to Kinlochleven, with a dominance of the 5-ring PAHs compared to mussels from a reference site in Loch Etive, where 2- to 3-ring compounds were dominant. Electrodes used in some aluminium smelting processes include coal tar pitch, which contains PAHs. However, Naes *et al*. (1999) found that PAHs generated from aluminium production appeared not to have adverse or severe effects on benthic biota, even in areas of very elevated concentrations of PAHs in sediment. This observation supported their hypothesis that PAHs associated with soot-like materials had limited biological availability.

The availability of persistent organic pollutants (POPs) such as PAHs for uptake by organisms has been linked to the freely dissolved concentration in sediment pore waters through equilibrium partition theory (Smedes, 1994; Mayer *et al*., 2000). The pore water concentration is important in the assessment of biological effects as only dissolved concentrations tend to partition into biological membranes (Macrae and Hall, 1998; Huckins *et al*., 1990). Reichenberg and Mayer (2006) identified two complementary parameters of bioavailability as the accessible quantity and the chemical activity of the POP. They identified the accessible quantity as the proportion of the total concentration that can be mobilised and made available for processes such as biodegradation and digestive uptake, and is determinable by strong extractions of sediment, or POP sediment concentration-depletive extraction. The chemical activity, however, determines processes such as partitioning and diffusion and encapsulates concepts such as freely dissolved

concentration and fugacity which are measurable using equilibrium sampling devices. Consequently, passive sampling using a reference phase that equilibrates with the dissolved concentration in the sampling medium is attractive.

The availability of PAHs in sediments from Loch Leven was therefore studied using a silicone rubber passive sampler, following protocols developed through the ICES Working Group on Marine Sediments (ICES WGMS 2003). Determinations were made of the pore water and water extractable (accessible) concentrations of PAHs in the sediments, and also the partition coefficients of PAHs between sediment and water.

2   Sampling Theory

Most equilibrium samplers assume non- or negligible depletion of the sediment phase (Jonker and Koelmans, 2001; Mayer *et al*., 2003; Heringa and Hermens, 2003). However, in this study, no such assumption was made; rather measurements of the pore water concentrations were made at different degrees of sediment depletion (or phase ratios) using equation 1 and also calculating the concentration extracted by the silicone rubber from the sediment from equation 3.

The pore water concentration (C_w) is calculated from the concentration in the silicone rubber using equation **1** below

$$C_w = \frac{C_{sr}}{K_{sr,w}}$$
                                          1

where, C_{sr} = concentration in the silicone rubber / ng g^{-1} SR (sr and SR denoting silicone rubber), $K_{sr,w}$ = silicone rubber-water partition coefficient / l kg^{-1}. Silicone rubber-water partition coefficients for the silicone rubber sampler used were independently determined in an earlier study (Yates *et al*., 2007).

$$C_{sr} = \frac{N_{sr}}{M_{sr}}$$
                                          2

3

N_{sr} = Amount of PAH in the silicone rubber, M_{sr} = mass of silicone rubber

Similarly the concentration extracted from the sediment (C_{SedEx}) is calculated from equation **3** below

$$C_{SedEx} = \frac{N_{sr}}{M_{sed}}$$
$$\qquad\qquad\qquad\qquad\qquad\mathbf{3}$$

M_{sed} = Mass of sediment

Subsequently, a plot of C_w versus C_{SedEx} is made and extrapolated to the axes to yield the freely dissolved concentrations in pore water, and the water extractable concentrations. In a similar regard, sediment-water partition coefficients, $K_{sed,w}$ were calculated from the plots of C_w versus $C_{res}(C_{Sed} - C_{SedEx})$, referred to as residual sediment concentration at each phase ratio with the slope of such plots being equivalent to $1/K_{sed,w}$.

3   Materials and Methods

3.1   Materials

HPLC grade solvents (dichloromethane, ethyl acetate, acetone, methanol and *iso*-hexane) were purchased from Rathburn Chemicals Ltd, Scotland, UK. Certified solid standards for PAHs (including deuterated PAHs) were obtained from QMX Laboratories, Essex, UK and dissolved in *iso*-hexane to obtain the required concentrations of spiking and calibration solutions. To avoid contamination of samples, all glassware and stainless steel forceps were either washed in Decon® 180 solutions and rinsed with distilled water or washed in a CAMLAB GW 4050 glassware washer and dried in an oven at 100 °C. Before use, the glassware was rinsed twice each in dichloromethane and *iso*-hexane, with the latter allowed to evaporate to dryness. Glass Duran® or Schott® (VWR, Leicester, UK) bottles were used for passive extraction of contaminants from sediment, and were

always capped with aluminium-lined PTFE caps to reduce or prevent sorption of POPs by the caps.

AlteSil™ Silicone rubber sheet (600 × 600 mm, 0.5 mm thick) used as the passive sampling material was purchased from Altec Products, Ltd, Cornwall, UK. The silicone rubber sheets used were cut into required dimensions (6 × 4 cm, or 9 × 4 cm) and pre-extracted in hot ethyl acetate using a Soxhlet apparatus for ~ 4 days before use to remove any low molecular weight oligomers or residues that might subsequently be co-extracted with the analytes and could affect instrumental analysis (Gruber *et al*. 2000; Rusina *et al*., 2007). After pre-extraction and cooling, the sheets were removed from the solvent and stored in bulk in glass jars containing methanol until required for use. The weight of the sheets used was determined after extraction of exposed sheets to avoid contamination from the environment.

3.2   Methods

3.3   Sediment Sampling

Samples of sediment (12-14 cm depth of mud) were collected from RV *Seol Mara* using a 0.1 m^2 Day Grab and Van Veen grab at depths between 15 and 40 m at five stations within Loch Leven (Fig **1**). The top 2 cm of the sediment was transferred to a solvent washed aluminium can, thoroughly mixed, labelled and stored at -20 ± 5 ^{o}C until required for analysis. Particle size analysis of sediment samples was determined by laser granulometry using a Malvern Mastersizer E Particle Size Analyser, after freeze drying of the sediments. The precision of the method based on 7 replicate measurements of a laboratory reference material (LRM C100) on the D (4, 3) mean weighted volume fraction equals 2.50 %. Total organic carbon (TOC) was determined on freeze dried sediment using a ThermoQuest Flash EA 1112 elemental analyser, following removal of inorganic carbon by acidification using hydrochloric acid. The method limit of detection is 0.005 mg although the limit of quantification (LOQ) calculated as 0.005 divided by the

sample weight analysed × 100 % is normally reported. E.g. for a sample weight of 16.50 mg, the LOQ is 0.03 %.
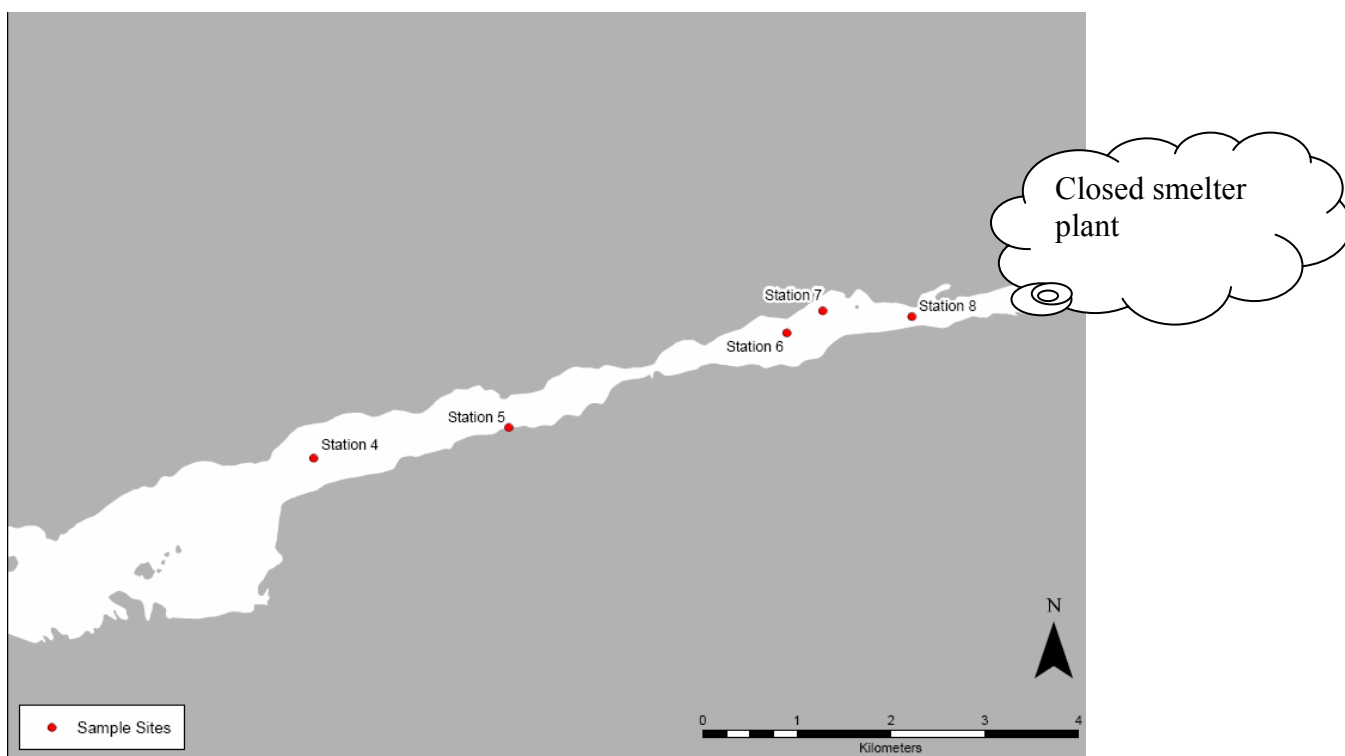

Fig 1: Sediment sampling stations in Loch Leven, September, 2006. The closed Smelter is closer to Station 8. Stations 6-8 lie within the upper basin of the loch while Stations 4 and 5 are in the lower basin. The closed aluminium smelter is towards the right (landwards) of station 8.

3.4   Hydrocarbon analysis of sediment

Sediment samples were thoroughly mixed after thawing and ~ 10 g per sample was removed for determination of moisture content by drying in an oven at 80 ± 5 ^{o}C for 22 ± 2 h (Webster *et al.*, 1997). PAHs were determined as described by Webster *et al.* (2004). Briefly, aliphatic hydrocarbon internal standards, heptamethylnonane and squalane and deuterated aromatic internal standards (D_8-naphthalene, D_{10}-biphenyl, D_8-dibenzothiophene, D_{10}-anthracene, D_{10}-pyrene and D_{12}-benzo[*a*]pyrene (100 or 200 µl; approximately 1 µg ml^{-1} each)) were added to 0.3 ± 0.1 g sub samples of wet sediment. The hydrocarbons were extracted using dichloromethane/methanol with sonication and the halogenated solvent isolated and dried over sodium sulphate prior to solvent exchange

into *iso*-hexane. The aliphatic and aromatic hydrocarbons were separated by isocratic high performance liquid chromatography (HPLC). The aromatic fraction collected and concentrated prior to chromatographic analysis. A laboratory reference material (LRM) and procedural blank were also included in the analyses. Recoveries of ≥ 85 % and precision of ≤ 17 % for individual PAH compounds were obtained with spiked sediment samples.

3.5   Determination of availability parameters

The sediment samples were weighed into 50 ml and 3×250 ml glass Duran$^®$ bottles, and water added, where necessary, to liquefy the sediment so as to ensure proper interaction between the sediment slurry and the silicone rubber sheets that would be added to the bottles. Pre-extracted silicone rubber sheets were loaded with PAH performance reference compounds (PRCs) as described by Booij *et al*. (2002) and a single sheet added to each bottle to obtain different phase ratios (g silicone rubber per g sediment). The bottles were placed on an orbital shaker horizontally and shaken at 200 rpm for 20 days in a light and temperature controlled room. In a preliminary developmental study (data not reported), this time was found to be sufficient for the PAHs to attain equilibrium. After this time, the sheets were removed from the bottles, rinsed with distilled water and gently wiped dry with paper tissue to remove any adhering water.

3.6   Extraction of silicone rubber sheets

The silicone rubber sheets were Soxhlet extracted using 100 ± 5 ml of *iso*-hexane: acetone (3:1$^v/_v$) mixture or methanol for 6 h. Aliphatic hydrocarbon standard (containing heptamethylnonane and squalane) and deuterated PAH aromatic internal standard containing D_8-naphthalene, D_{10}-biphenyl, D_8-dibenzothiophene, D_{10}-anthracene, D_{10}-pyrene and D_{12}-benzo[*a*]pyrene were then added to the cooled extract, concentrated by rotary evaporation followed by nitrogen blow down of the extract to 1 ml. The extract was reduced to 0.5 ± 0.2 ml and an aliquot of the concentrated extract was fractionated using an isocratic, normal phase Genesis metal-free high performance liquid

chromatograph (HPLC) column (25 cm x 4.6 mm) and eluted with *iso*-hexane at a flow rate of 2 ± 0.1 ml/min into aliphatic and aromatic fractions. The aliphatic fraction was discarded and the aromatic fraction collected in 100 ml flasks, concentrated by rotary evaporation and further reduced under nitrogen to 50 ± 10 µl for gas chromatography – mass selective detection (GC-MSD) analysis.

The weights of the silicone rubber sheets were recorded after the extraction to avoid contamination from external sources. A procedural blank (an un-spiked sheet exposed to only the distilled water used to liquefy the sediments) was included and analysed in the same manner as the other samples. The result from the procedural blank was subsequently subtracted from the results of samples. Similarly a spiked sheet was also analysed to obtain the initial amounts of PRCs in the sheets.

3.7   Gas chromatography-mass selective detection (GC-MSD)

The concentrations and composition of the PAHs were determined by GC-MSD using an HP6890 Series Gas Chromatograph interfaced with an HP5973 MSD fitted with a cool on-column injector (Webster *et al.*, 2007). Briefly, a non-polar HP5 (30 m × 0.25 mm id, 0.25 µm film thickness; Agilent Technologies, Stockport, England) column was used for the analyses with helium as the carrier gas, controlled using the constant flow mode at 0.7 ml min^{-1}. The MSD was set for selective ion monitoring (SIM) with a dwell time of 50 ms. Injections were made at 50 ^{o}C and the oven temperature held constant for 3 min. Thereafter, the temperature was raised at 20 ^{o}C min^{-1} up to 100 ^{o}C, followed by a slower ramp of 4 ^{o}C min^{-1} up to a final temperature of 270 ^{o}C. A total of 29 (later 36 with the addition of extra performance reference compounds) ions plus the six internal standard ions were measured over the analysis period, thus incorporating 2- to 6- ring, parent and branched PAHs. Limits of detection based on multiplying the standard deviation of the mean of the lowest standard (0.005 ng ml^{-1}) by 4.65 were found to be < 0.2 ng g^{-1} for chrysene and < 0.1 ng g^{-1} for benzo[*a*]pyrene. The GC-MSD is calibrated using seven different concentrations of a solution containing 33 PAHs.

4   Results and Discussion

The total PAH concentrations in sediment (2- to 6-ring parent and alkylated PAHs, Table
1 and Fig **2**) varied between 13282 ng g^{-1} dry weight (Station 4 which had the lowest %
TOC) to 95158 ng g^{-1} dry weight (Station 7 with the highest % TOC). The 4- to 6-ring
compounds accounting for ~ 96 ± 0.98 % of the total concentrations (Fig **2**) and there was
a strong dominance of the 5-ring compounds, as has been reported for sediments around
aluminium smelters elsewhere (Naes *et al*., 1995 and Naes *et al*., 1999).

Table 1: Sediment bulk properties and total PAH (2- to 6-ring parent and alkylated
compounds) concentration from the five sampling points

Field ID	% TOC	PS % < 63 μm	Total PAH (ng g^{-1} dw)
Station 4	5.09	85.26	13282
Station 5	5.62	78.39	15244
Station 6	7.29	77.50	64305
Station 7	8.04	78.18	95158
Station 8	5.17	54.41	68099
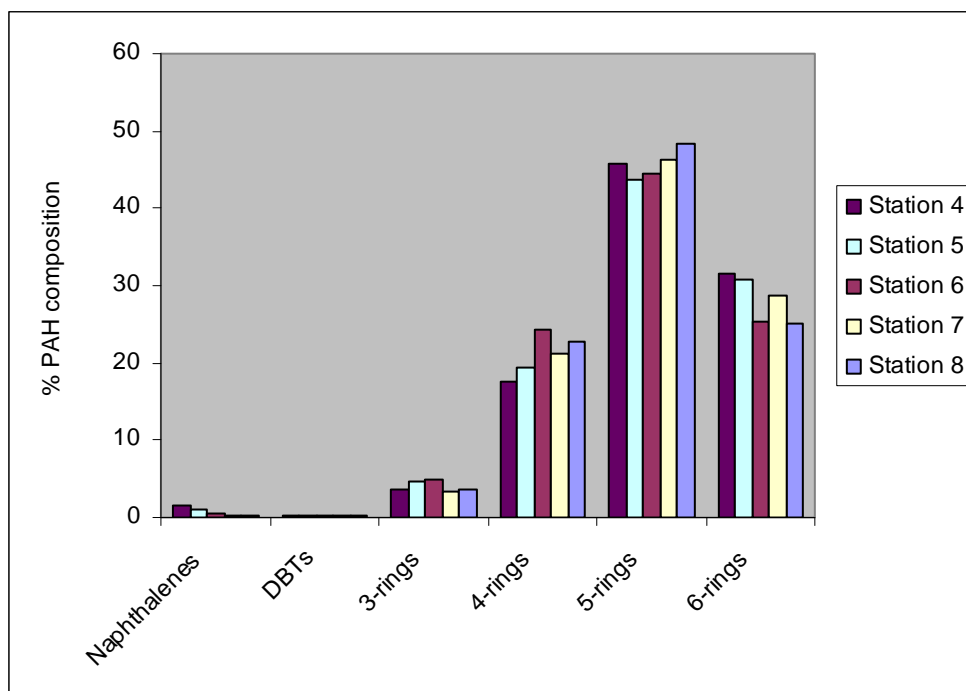
Fig **2**: Sediment PAH composition determined in sediments collected from Loch Leven in September, 2006. Naphthalenes = sum of naphthalene; 1 & 2-methylnaphthalene; C2-, C3- and C4- naphthalenes. 3-rings = sum of phenanthrene; anthracene, C1-178, C2-178, and C3-178; acenapthylene; acenaphthene and fluorene. DBTs = sum of Dibenzothiophene; C1-DBT, C2-DBT, and C3-DBTs. 4 –rings = sum of fluoranthene; pyrene; C1-202, C2-202, and C3-202; benzo[*c*]phenanthrene; benz[*a*]anthracene; benz[*b*]anthracene; chrysene; C1-228; C2-228. 5-rings = sum of benzofluoranthenes; benzo[*e*]pyrene; benzo[*a*]pyrene; perylene; C1-252 and C2-252. Benzofluoranthene is the summation of benzo[*b*] and [*k*]fluoranthene. 6-rings = sum of indeno[1, 2, 3-*cd*]pyrene; benzo[*ghi*]perylene; C1-276 and C2-276

Provisional Oslo and Paris Commission (OSPAR) Background Concentrations (BCs) have been established for ten parent PAHs in sediments (OSPAR, 2006). The Background Concentration has been defined as the concentration of a contaminant at a "pristine" or "remote" site based on contemporary or historical data. Observed concentrations are said to be 'near background' if the mean concentration is statistically significantly below the corresponding Background Assessment Concentration (BAC). In this study, only single measurements of PAH concentrations were made, therefore the individual PAH concentrations for each station were normalized to 2.5 % organic carbon and an approximate 95 % confidence interval calculated using uncertainty values from

validation data at FRS. The normalized concentrations for individual PAHs far exceeded the BACs at the 5 % significance level (Table **2**)

Table **2**: Available OSPAR Background Concentrations and provisional Background Assessment Concentration (both ng g^{-1} dry weight) normalised to 2.5 % organic carbon (OSPAR, 2006) and corresponding concentrations in the sediment samples from Loch Leven, also normalised to 2.5 % organic carbon with 95 % confidence interval expressed as a percentage

				Station				
	BC^1	BAC^2	C.I. (%)	4	5	6	7	8
Naphthalene	5	8	30	440	536	2180	2268	1636
Phenanthrene	17	32	28	7572	10756	60448	60536	45392
Anthracene	3	5	24	1480	2536	12836	13944	11324
Fluoranthene	20	39	25	12780	16244	99776	106060	77652
Pyrene	13	24	25	12352	15488	94428	103616	76144
Benz[a]anthracene	9	16	33	7316	9284	52520	68704	53600
Chrysene	11	20	38	12628	15020	102024	156336	140460
Benzo[a]pyrene	15	30	22	30976	34072	173256	257692	196292
Indeno[1,2,3-cd]pyrene	50	103	19	61012	66612	236480	381444	255576
Benzo[ghi]perylene	45	80	19	67920	72748	258724	430504	277232

[1]Background Concentration; [2]Background Assessment Criteria

4.1   Pore water concentrations

Sorption isotherms (example in Fig **3**) were plotted for the sediments and only plots that yielded significant linear relations ($p < 0.05$) were used to estimate the dissolved concentrations (C_w^0) in pore water and water extractable fractions by extrapolation to both axes.

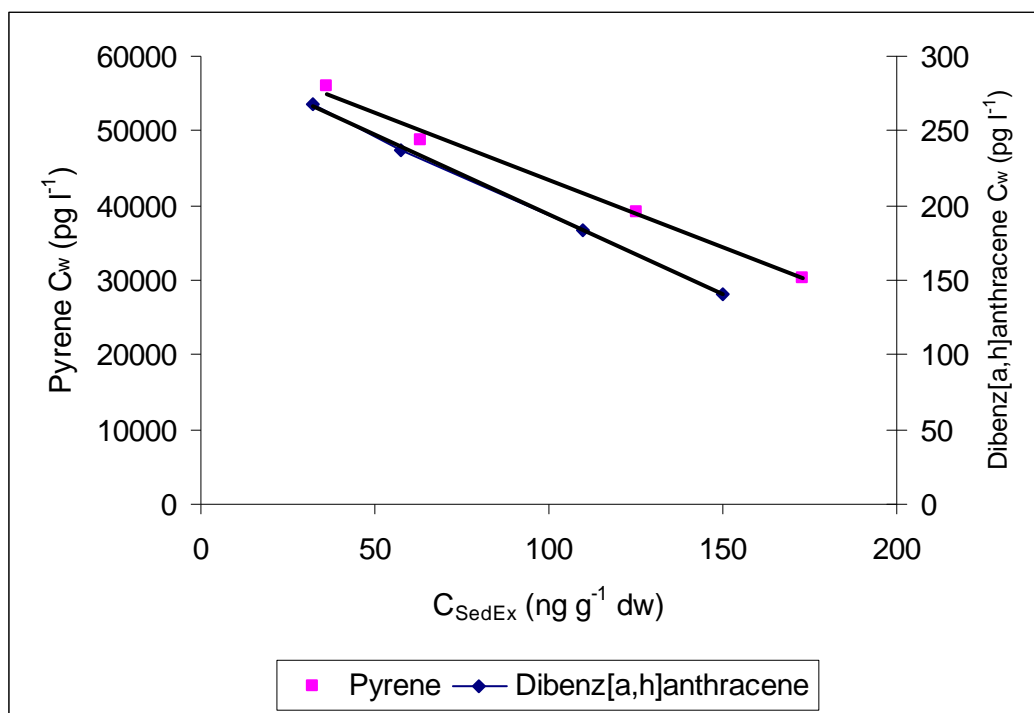Fig **3**: Sorption isotherm to determine pore water concentration of pyrene (squares) and dibenz[*a,h*]anthracene (diamonds) from station 8 in loch Leven.

The pore water concentrations obtained from the extrapolation are presented in Fig **4**. However for some PAHs (~ 10 %), the plots yielded poor correlations ($p > 0.05$), especially from station 5 (plots not shown).
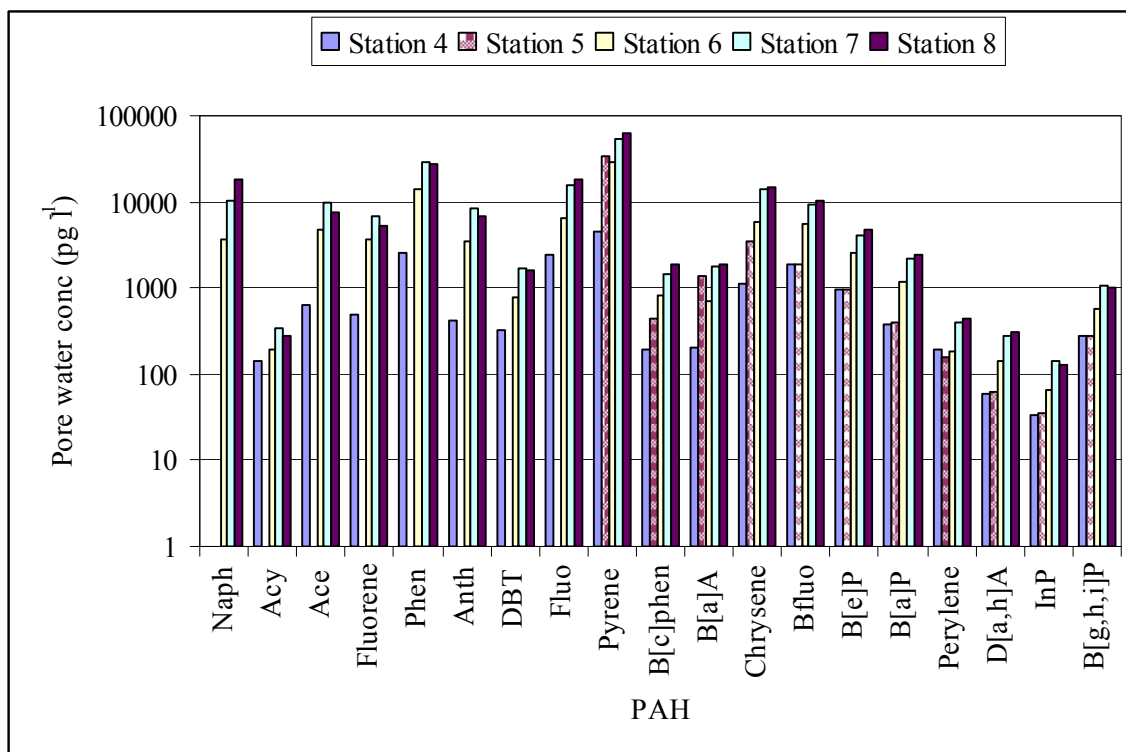
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Fig **4**: Pore water concentrations obtained from sorption isotherms similar to Fig 3 for the stations sampled and PAHs for which statistically significant regressions were obtained ($p < 0.05$). Naph-Naphthalene; Acy- Acenaphthylene; Ace-Acenaphthene; Phen-Phenanthrene; Anth-Anthracene; DBT-Dibenzothiophene; Fluo-Fluoranthene, B[*c*]phen-Benzo[*c*]phenanthrene; B[*a*]A-Benz[*a*]anthracene; Bfluo-Benzofluoranthenes; B[*a*]P-Benzo[*a*]pyrene; D[*a,h*]A-Dibenz[*a,h*]anthracene; InP-Indeno[1,2,3-*cd*]pyrene; B[*g,h,i*]P-Benzo[*ghi*]perylene.

The pore water concentrations were dominated by the 2- to 4- ring PAHs (like naphthalenes, phenanthrene, fluoranthene, pyrene and chrysene) with benzofluoranthenes and benzo[*e*]pyrene as exceptions from the higher ring PAHs. Generally though, the pore water concentrations tended to decrease in the order station 8> 7> 6> 5> 4 (e.g. chrysene in Fig **5**), i.e. generally decreases away from the smelter (see Fig **1**), with a decrease by factors ranging from 2 to 14 for individual PAHs. PAH concentration in the pore water also followed the general trend seen in the sediments
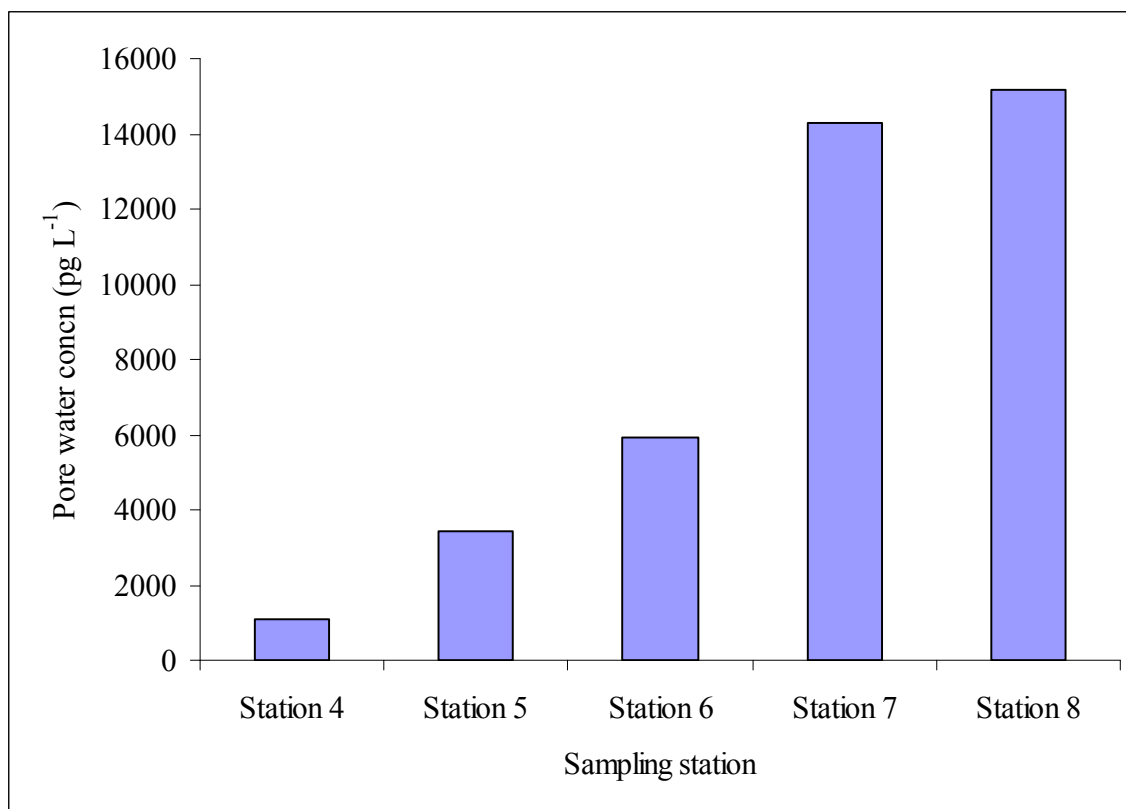
Fig **5**: Chrysene pore water concentrations profile along the sampling gradient.

The pore water concentrations estimated in this study were well below the draft European Union Water Framework Directive (EU-WFD) - proposed Maximum Allowable Concentration-Environmental Quality Standards (MAC-EQS) for PAHs (Table **3**) in surface waters (EU-WFD, 2007).

Table **3** Maximum allowable concentration – Environmental Quality Standards for PAHs in surface waters

PAH	MAC-EQS ng L^{-1}	Pore water concentration (ng L^{-1}) Station				
		4	5	6	7	8
Anthracene	400	0.42	ND*	3.48	8.31	6.93
Benzofluoranthene	30	1.92	1.92	5.60	9.13	10.34
Benzo[a]pyrene	100	0.38	0.40	1.16	2.21	2.47
Indeno[1,2,3-cd]pyrene	2	0.03	0.04	0.07	0.14	0.13
Benzo[ghi]perylene	2	0.28	0.28	0.58	1.07	1.00

*Not determined

4.2   Water extractable proportions

Water exchangeable concentrations were determined from extrapolation of the sorption isotherms to the sediment-extractable concentration axes of plots such as Fig **3**. These concentrations represent the fraction of the sediment PAH concentration that could potentially be mobilised into the pore water and consequently interact with biota, and are presented as a percentage of the total concentration of each PAH in the sediment (Fig **6**). The exchangeable proportions varied between station and compounds, generally between 5 and 40 % of the total concentration. The remaining percentage is tightly (irreversibly) bound to the sediment. Thus any risk assessment using the total concentration of PAHs in the sediment may overestimate the risks. The presence of a soot phase in sediments (Naes and Oug, 1998; Jonker and Koelmans, 2001) and ageing processes (Reid *et al.*, 2000) has also been shown to reduce availability of PAHs.
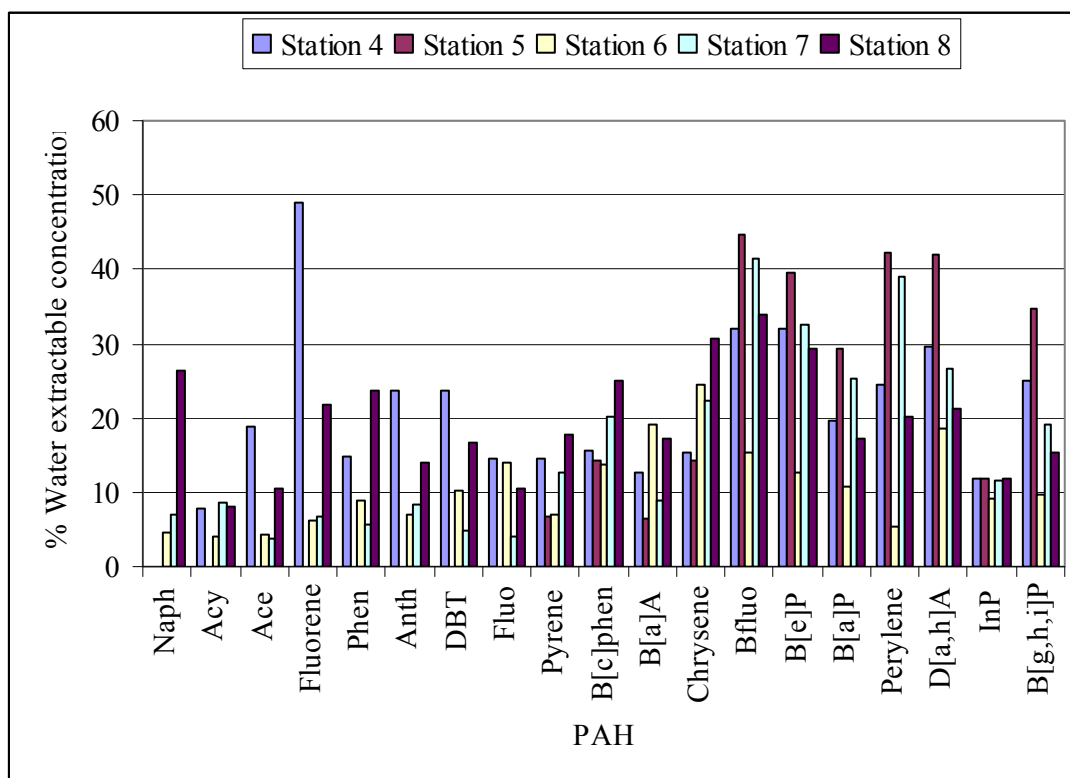

Fig **6**: Water extractable concentration as a percentage of sediment PAH concentration from the sampling stations. Data are not shown where the sorption isotherm plots (Fig 3) yielded poor correlations (*p* > 0.05). PAHs as defined in Fig 4.

A relatively high proportion of the 5- to 6- ring PAHs (up to 40 %) is more available for exchange into the water phase, with the exception of indeno[1,2,3-*cd*]pyrene (~12 %). There was no general observable trend across the stations of the water extractable proportions.

4.3 Sediment-water partition coefficients of PAHs

Sediment-water partition coefficients ($K_{sed,w}$) describe the partitioning of POPs between sediment and the water phase, and determine the activity (and hence availability and mobility) of contaminants in the environment (Booij *et al.*, 1997; Smedes, 1994) and are useful for risk assessments. Lack of adequate methodology for isolating and measuring the freely dissolved concentration has often hindered accurate determination of these partition coefficients. The importance of methodology in determining these coefficients was highlighted by Harkey *et al.* (1994); where they used four methods to determine the partition coefficients. Other methods have been used in determining these coefficients such as from the free-energy relationship of Karickhoff, *et al.* (1979), co-solvent method (Jonker and Smedes, 2000), the use of polyoxymethylene strips (Jonker and Koelmans, 2001), etc, with most of the methods dependent on attainment of equilibrium.

At equilibrium, the ratio of the concentration of a contaminant in the sediment to the concentration in the water phase gives the partition coefficients (equation **4**)

$$K_{sed,w} = \frac{C_{sed}}{C_w} \qquad\qquad\qquad \textbf{4}$$

The dependence of sorption of POPs to components of sediment with sorbent properties, such as organic material, has been shown (Karickhoff *et al.*, 1979; Borglin *et al.*, 1996 and Chen *et al.*, 2000) and mostly the partition coefficients are expressed relative to the organic carbon content as

$$K_{oc} = \frac{K_{sed,w}}{f_{oc}} = \frac{C_{sed}}{f_{oc} \cdot C_w} \equiv \frac{C_{oc}}{C_w} \qquad\qquad\qquad \textbf{5}$$

f_{oc} = Organic carbon fraction, C_{oc} = Organic carbon normalised sediment concentration, K_{oc} = partition coefficient normalised to organic carbon content.

In a similar way, having established equilibrium conditions in the exposure of sediments to silicone rubber in this study, $K_{sed,w}$ were calculated from the plots of C_w at versus $C_{res}(C_{Sed} - C_{SedEx})$ at each phase ratio (Fig 7). The slope of such a plot equals $\frac{1}{K_{sed,w}}$.
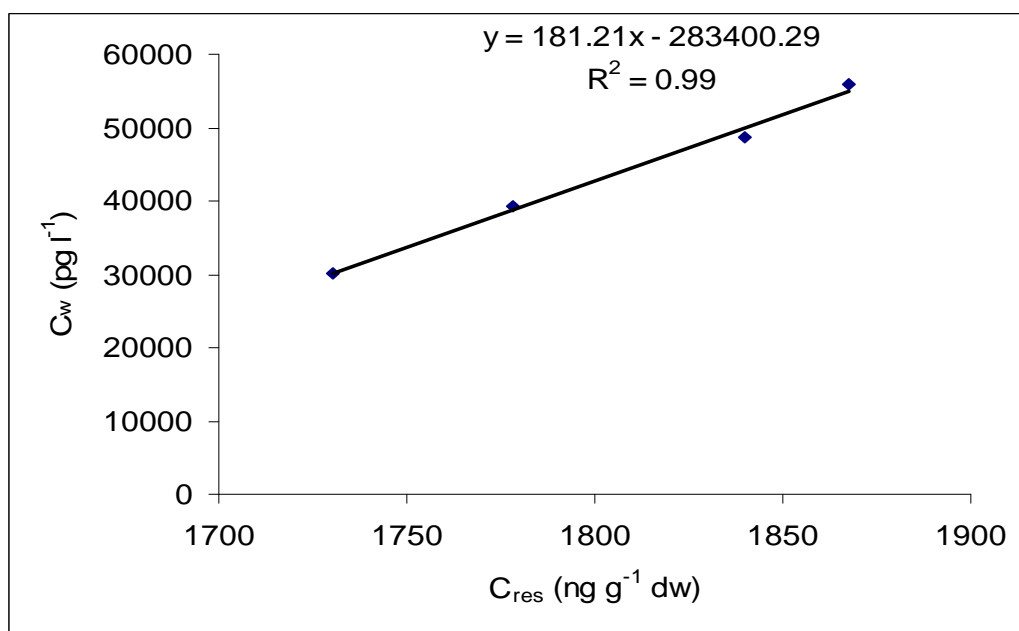

Fig **7**: Sorption isotherm of pyrene to determine sediment-water partition coefficient from the slope of the plot.

The calculated sediment-water partition coefficients were normalised to the total organic carbon for each sampling point and these are given in Table **4**. There was no observable trend in the $\log K_{oc}$ for individual PAHs along the contamination gradient, implying that changes in the pore water concentrations with distance from the smelter observed are probably due to differences in the concentrations of contaminants in the sediment as the K_{oc} is broadly similar across the locations. The $\log K_{oc}$ values were correlated to the $\log K_{ow}$ in Figure **8** and strong linear relationships were obtained which were similar (F-test, p> 0.001) across the stations with similar relationships with $\log K_{ow}$ having been reported (Table **5**).

Table **4** Log partition coefficients normalised to organic carbon content (Log K_{oc}) with values obtained from the Karickhoff relation shown as predicted log K_{oc} (Karickhoff *et al.*, 1979)

PAH	log K_{ow}[1]	Predicted Karickhoff, 1979	Log K_{oc} (l kg^{-1} oc)				
			Station				
			4	5	6	7	8
Naphthalene	3.35	3.14	nd	nd	3.97	3.68	4.06
Acenaphthylene	3.61	3.40	3.93	nd	3.93	3.99	4.06
Acenapthene	3.92	3.71	4.94	nd	4.23	3.85	4.49
Fluorene	4.18	3.97	5.47	nd	4.30	4.00	4.73
Phenanthrene	4.52	4.31	5.34	nd	5.12	4.56	5.28
Anthracene	4.50	4.29	5.62	nd	4.94	4.64	5.04
Dibenzothiophene	4.38	4.17	5.09	nd	5.02	4.34	4.98
Fluoranthene	5.20	4.99	5.58	nd	5.86	4.92	5.33
Pyrene	5.00	4.79	5.30	4.14	4.88	4.88	5.03
Benzo[c]phenanthrene	5.76	5.55	5.74	5.39	5.69	5.64	5.72
Benzo[a]anthracene	5.91	5.70	6.35	5.29	6.69	6.04	6.37
Chrysene	5.86	5.65	5.94	5.45	6.16	5.88	6.14
Benzofluoranthenes	6.11	5.90	6.91	7.04	6.65	7.01	6.95
Benzo[e]pyrene	6.44	6.23	6.82	6.90	6.50	6.83	6.82
Benzo[a]pyrene	6.35	6.14	6.89	7.04	6.74	6.96	6.82
Perylene	6.25	6.04	6.67	6.92	6.33	7.08	6.74
Dibenz[a,h]anthracene	6.75	6.54	7.55	7.62	7.32	7.43	7.26
Indeno[1,2,3-cd]pyrene	7.66	7.45	8.01	7.99	8.06	7.98	8.06
Benzo[ghi]perylene	6.90	6.69	7.47	7.61	7.17	7.38	7.31

nd- not determined due to poor regressions. [1] Obtained from Sangster, 2005.

Log K_{oc} values were in most cases higher than those predicted by the Karickhoff relation, on average by 0.78, 0.43, 0.56, 0.44 and 0.64 log units for stations 4, 5, 6, 7 and 8 respectively. Similar high partition coefficients have been reported for field sediments elsewhere (Jonker and Smedes, 2000; Hawthorne *et al.*, 2006) which suggests that the use of log K_{oc} in risk assessments to assess potential for transfer of contaminants from sediment to water or biota may over-estimate the true risk. Therefore experimental measurements of log K_{oc} in field sediments should improve the reliability of risk assessments.
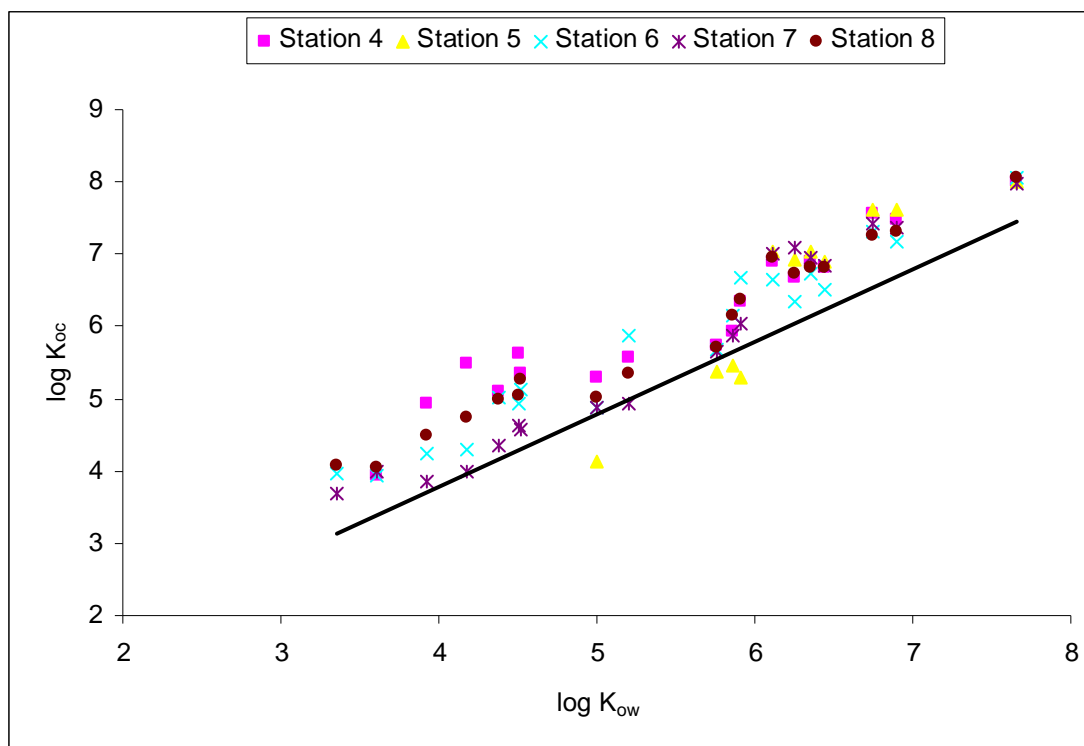
Fig **8**: Log K_{oc} as a function of log K_{ow} (Sangster, 2005) for sediments from Loch Leven. Drawn line is the Karickhoff relation $\log K_{oc} = \log K_{ow} - 0.21$ (Karickhoff *et al.*, 1979)

Estimates of log K_{oc} increased with increasing log K_{ow} values, indicating the partitioning of the PAHs is strongly determined by the hydrophobicity of the compounds and implies that the higher log K_{ow} PAHs are more strongly bound to the sediments than the low log K_{ow} PAHs. This is supported by the high concentrations of the low log K_{ow} PAHs in pore water. Booij *et al.* (1997) suggest that slopes equal to one in log K_{oc} versus log K_{ow} relations should be considered as exceptions rather than the rule due to possible differences in the effect of dissolved octanol on the activity coefficient in the water phase related to the hydrophobicity of the contaminants, and non-proportionality of the non-ideality of the solution of the contaminants in the organic matter to the non-ideality of the solution in octanol. Differences in the slope and intercept of these relationships could also be due to uncertainty in the measurements of K_{ow}. The close to one slopes with similar widths of 95 % confidence interval of the relationships obtained suggest the sorption is strongly determined by hydrophobicity.

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Table **5** Summary of linear regression analysis of $\log K_{oc}$ versus $\log K_{ow}$[a] with 95 % confidence interval of intercept and slope with regressions reported in literature for PAHs

Station/ Source	*Slope*	*Intercept*	r^2	s[b]	n[c]
4	0.88 ± 0.15	1.24 ± 0.84	0.91	0.33	18
5	1.13 ± 0.54	-0.40 ± 3.39	0.92	0.25	11
6	0.98 ± 0.11	0.50 ± 0.60	0.96	0.27	19
7	1.14 ± 0.13	-0.50 ± 0.71	0.95	0.32	19
8	0.96 ± 0.51	0.69 ± 0.51	0.97	0.23	19
Booij *et al.*, 2003 [d]	1.32	-0.39	0.95	0.26	39
Jonker and Koelmans, 2001[e]	1.07 ± 0.44	-0.77 ± 2.57	0.77	0.38	10
Jonker and Smedes, 2000[f]	1.14 ± 0.32	1.40 ± 1.89	0.86	0.38	12

[a] $\log K_{ow}$ values from Sangster, 2005; [b] standard deviation of the fit; [c] sample size; [d] determined from the ratio of concentrations in sediment to that in pore water measured using low density polyethylene (LDPE) samplers; [e] estimated from data provided; [f] Determined using the co-solvent method

5   Conclusions

Concentrations of PAHs in pore water in sediments from Loch Leven contaminated by waste from an aluminium smelter were dominated by acenaphthene, fluorene, fluoranthene, pyrene, chrysene, benzofluoranthenes and benzo[e]pyrene. The pore water concentrations decreased down the loch (Station 8> 7> 6> 5> 4), with higher concentrations being found close to the former smelter plant (Station 8). A similar spatial pattern was seen in the concentrations of PAHs in sediments. Concentrations in pore water were below the MAC-EQS for surface waters proposed under the Water Framework Directive. Water extractable concentrations of individual PAHs were below 50 % of their corresponding total concentrations in sediment. Log K_{oc} values were found to be significantly correlated with hydrophobicity expressed as $\log K_{ow}$ and can be useful in understanding the partitioning of PAHs in field sediments. This study has shown the use of silicone rubber membranes as an equilibrium sampler to measure pore water and water extractable concentrations as well as sediment-water partition coefficients of PAHs in sediments. These data are useful tools to assist in assessing the availability and consequently risks of these contaminants.

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