Combining Leaching and Passive Sampling To Measure the Mobility and Distribution between Porewater, DOC, and Colloids of Native Oxy-PAHs, N-PACs, and PAHs in Historically Contaminated Soil

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S *Supporting Information*

ABSTRACT: Different methods to quantify soil porewater concentrations of contaminants will provide different types of information. Passive sampling measurements give freely dissolved porewater concentrations ($C_{pw,free}$), while leaching tests provide information on the mobile concentration ($C_{pw,leach}$), including contaminants associated with dissolved organic carbon (DOC) and particles/colloids in the porewater. This study presents a novel combination of these two measurements, to study the sorption and mobility of polycyclic aromatic compounds (PACs) to DOC and particulate organic carbon (POC) in 10 historically contaminated soils. The PACs investigated were polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs, and nitrogen containing heterocyclic PACs. Observed $C_{pw,leach}$ was up to 5 orders of magnitude higher than $C_{pw,free}$; implying large biases when $C_{pw,leach}$ is used to assess bioavailability or soil partitioning. Sorption of PACs to DOC and POC was important for the mobility of compounds with log $K_{OW} > 4$. Average DOC/water-partitioning coefficients (K_{DOC}) correlated well with K_{OW} (log $K_{DOC} = 0.89 \times$ log $K_{OW} + 1.03$ ($r^2 = 0.89$)). This relationship is likely more accurate for historically contaminated soils than previously published data, which suffer from artifacts caused by problems in measuring $C_{pw,free}$ correctly or not using historically contaminated soils. POC/water-partitioning coefficients (K_{POC}) were orders of magnitude larger than corresponding K_{DOC}, suggesting sorption to mobile particles/colloids is the dominant mechanism for PAC mobility.
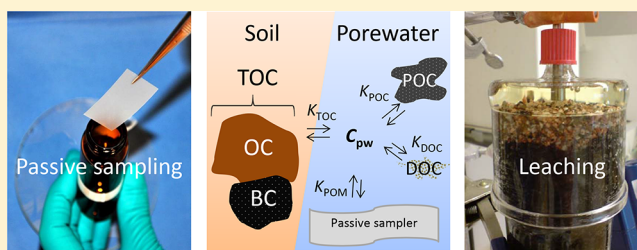
INTRODUCTION

Risk assessments of soil at sites contaminated with polycyclic aromatic compounds (PACs) are commonly based on the investigation of the 16 parent polycyclic aromatic hydrocarbons (PAHs) originally prioritized by the US Environmental Protection Agency (US EPA). However, recent studies have shown that semipolar PACs, such as oxygenated PAHs (oxy-PAHs) and nitrogen containing heterocyclic PACs (N-PACs), often are accompanying PAHs in contaminated soils.[1,2] Since several of these compounds are also toxic, mutagenic, and carcinogenic, they may contribute significantly to the overall risk.[3,4] The (bio)availability and mobility of PAHs at historically contaminated sites (e.g., former manufactured gas plant sites, wood impregnation facilities) are generally reported to be low. This is considered to be due to strong sorption of these compounds to black carbon, tars, and other carbonaceous materials, which co-occur at such sites (where the term "strong sorption" implies stronger sorption than observed for natural organic matter).[5,6] The occurrence of strong sorption also decreases the susceptibility of PAHs to undergo degradation by soil microorganisms,[7] making them less bioavailable but more persistent, thereby lowering environmental risks but extending their presence. The semipolar PACs have higher aqueous solubilities and lower octanol−water partition coefficients, K_{OW}, than PAHs of a similar ring size (Supporting Information (SI)-

Section S1, Table S1.1) and are therefore correspondingly less distributed to particles and organic matter. This potentially leads to a higher mobility in the environment and a higher availability for uptake in organisms. Along with similar or even higher toxicity of some semipolar PACs, e.g. N-PACs,[8,9] this implies a higher overall risk compared to the unsubstituted PAHs.[4,8,9] Current risk assessments of PAC-contaminated soils therefore underestimate risk in one way, by not accounting for all PACs, and overestimate risk in another way, by not sufficiently accounting for (bio)availability. Therefore, new approaches are needed for more realistic site assessments.

The importance of strong sorption of PACs and how to account for (bio)availability when performing risk assessment has been debated for two decades. Despite this, regulatory guidelines for PAC contaminated soil often still do not account for bioavailability in general and typically rely on screening values of total soil concentrations (C_{soil}).[10,11] Nevertheless, several different tools to assess bioavailability and mobility of these type of compounds have been developed, and their practice in site-specific risk assessment projects is evolving.[10,12]

One type of tool is equilibrium passive sampling. This tool is designed for the measurement of the *freely dissolved* concentrations in porewater, $C_{pw,free}$, i.e. the concentration of molecules completely solvated by water. This concentration is considered more closely associated with bioavailability[1,13] than the *total* porewater concentration, $C_{pw,total}$, which also includes compounds sorbed to dissolved organic matter carbon (DOM) and particulate/colloidal matter. After mixing the soil with water at a fixed liquid to solid (L/S) ratio and introducing a sampler device (made of a polymer) into the system, the system is allowed to reach equilibrium between all phases (water, soil/sediment, colloids, and polymer).[13−16] The mass of the polymer should be sufficient to enable adequate detection but not large enough to cause significant depletion.[15] The polymer is then removed and extracted to determine the concentration of the target chemical in the polymer, after which $C_{pw,free}$ is calculated using predetermined equilibrium polymer−water partition coefficients. The polymers most commonly used in this respect for hydrophobic organic compounds (HOCs) are poly-dimethylsiloxane (PDMS),[17−19] low density polyethylene (LDPE),[18−20] and polyoxymethylene (POM).[13,18,19,21,22] The latter polymer material was recently used in a parallel study to quantify $C_{pw,free}$ of several different PACs (PAHs, oxy-PAHs, and N-PACs) in 21 historical contaminated soils.[1] The main findings were that amounts extracted by passive samplers were representative for the uptake in earthworms, supporting previous findings of Gomez-Eyles et al.[13]

Another category of tools is leaching tests. These tests can be used for the assessment of leachable (mobile) concentrations, since they give estimates of the $C_{pw,total}$. At present standardized methods exist through a series launched by the international organization for standardization (ISO) and the European committee for standardization (CEN); ISO-CEN 21268 Parts 1−3. The standards for batch leaching (Parts 1−2) are designed as shake tests and are fast, relatively cheap, and easy to conduct. However, when applied for assessment of HOCs, like PAHs, these tests have proven to overestimate the leaching by orders of magnitude.[23−25] The main reason for this bias is caused by the vigorous mixing of the sample, which leads to release of small particles and colloids[26,27] accompanied by adsorbed contaminants.[28,29] Since filtration of leachates should be avoided when analyzing for HOCs due to risk of analyte losses by adsorption to filters,[30,31] the standard protocols for shake tests prescribe

centrifugation and decantation instead. This is, however, an imprecise method for separation since colloidal particles will be retained in the (supernatant) leachate. To avoid these problems, a chemical *E*quilibrium *R*ecirculation column test for HOCs (the ER-H-test) was designed by Gamst et al.[32] This test is equal to the batch test in the sense that it is conducted at a fixed low L/S-ratio and that it aims to simulate the system at chemical equilibrium. However, by placing the contaminated soil in a column and recirculating water through it, less colloids are released. Hence, the ER-H-test has been assumed to provide leachates with $C_{pw,total}$ more similar to realistic field conditions.[12,32]

At present, both passive sampling and leaching are being used for the assessment of soil-porewater distribution coefficients (K_d) and partitioning coefficients normalized to the total organic carbon content, K_{TOC} (L_{pw}/kg_{TOC}), through the following equation

$$K_{TOC} = \frac{K_d}{f_{TOC}} = \frac{C_{soil}/C_{pw,free}}{f_{TOC}} \tag{1}$$

where f_{TOC} is the fraction of total organic carbon (TOC) in the soil.

If leaching tests are used instead of passive sampling, $C_{pw,free}$ is replaced with $C_{pw,total}$ in eq 1. Hence, when using leaching tests (and especially shake tests), underestimations of K_{TOC} are to be expected if $C_{pw,total}$ is $\gg C_{pw,free}$. The magnitude of the bias is unclear, since no parallel studies on passive sampling and leaching have been performed up until now. Furthermore, if conducted in parallel they will provide valuable insight into the mechanisms controlling the mobility and the partitioning between dissolved and colloidal organic matter with the porewater phase. This study presents a novel combination of a passive sampling technique (POM) and a static leaching test (ER-H) to provide data on partitioning coefficients of PACs. By further investigating 10 out of the 21 soils studied by Arp et al.,[1] using the ER-H-test, we aimed to differentiate between the mobile and bioavailable concentrations and to assess the impact of DOC and POC on leaching of both nonpolar and semipolar PACs. To our knowledge, this is the first study presenting DOC/water partitioning coefficients (K_{DOC}) and POC/water partitioning coefficients (K_{POC}) for PACs, including oxy-PAHs and N-PACs, in historically contaminated soils.

■ MATERIALS AND METHODS

Chemicals. The PACs investigated in this study included 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz-[ah]anthracene, benzo[ghi]perylene), 11 oxy-PAHs (1-inda-none, 1-acenaphthenone, 9-fluorenone, anthracene-9,10-dione, 4H-cyclopenta[def]phenanthrenone, 2-methylanthracene-9,10-dione, benzo[a]fluorenone, 7H-benz[de]anthracen-7-one, benz-[a]anthracene-7,12-dione, naphthacene-5,12-dione, 6H-benzo-[cd]pyren-6-one), and 4 N-PACs (quinoline, benzo[h]-quinoline, acridine, carbazole). CAS numbers, molecular structures, and chemical properties are presented in the SI-Section 1 (Table S1.1), together with details of standards and chemicals used as extraction media.

Soil Analysis. The soil samples obtained from 2 contaminated sites in France (2 samples) and 3 sites in Sweden, Karlstad (3 samples), Riksten (4 samples), and Holmsund (1 sample),

Table 1. Concentrations of Sum PAH-16, Sum Oxy-PAH, Sum N-PAC, and Sum All Compounds in Soil (C_{soil}; mg/kg) and in Leachates ($C_{pw,leach}$; μg/L)[a]

	C_{soil} (mg/kg$_{dw}$)				$C_{pw,leach}$ (μg/L)			
	$\sum$PAH-16	$\sum$oxy-PAH-11	$\sum$N-PAC-4	$\sum$all cmpds	$\sum$PAH-16	$\sum$oxy-PAH-11	$\sum$N-PAC-4	$\sum$all cmpds
Karlstad 1a-1	56.3	9.74	0.540	66.5	2.78	0.529	0.0610	3.37
Karlstad 1a-2	56.3	9.74	0.540	66.5	1.56	0.359	0.0602	1.98
Karlstad 1a-3	56.3	9.74	0.540	66.5	0.801	0.183	0.0326	1.02
Karlstad 2	56.3	12.9	0.898	70.1	7.42	1.46	0.392	9.27
Karlstad 6	130	23.6	2.12	156	457	102	8.45	567
Riksten 1a	278	108	2.13	388	36.3	10.1	0.475	46.9
Riksten 2	40.8	14.1	0.548	55.4	461	84.4	1.89	547
Riksten 6a-1	48.5	9.57	0.266	58.4	5.45	1.51	0.0347	6.99
Riksten 11-1	50.1	12.2	0.325	62.7	1.87	0.316		2.19
France 2	1150	204	6.84	1360	52.1	9.09	0.174	61.3
France 4-1	1080	106	9.22	1200	23.8	30.6	3.12	57.6
France 4-2	1260	106	9.40	1380	120	57.3	6.54	184
France 4-3	1130	95.7	7.83	1230	155	68.4	7.11	230
Holmsund 1-1	2500	223	6.83	2730	1370	143	24.8	1540
Holmsund 1-2	2320	219	5.21	2540	1590	161	25.1	1780
Holmsund 1-3	2600	244	8.73	2850	1600	168	27.1	1800

[a]L/S = liquid to solid ratio and can be found in the SI-Table S3.1.

were characterized by the methods described in the study by Arp et al.[1] Data for particle size distribution, pH, CaCO$_3$-content, content of total organic carbon (TOC), black carbon (BC, as quantified by the chemical-thermal-oxidation at 375 °C (CTO-375) method,[33] which is more appropriate for soot than other methods[34]), and PACs can be found in the SI-Section 2.

Porewater Determination Using the ER-H Leaching Test. The ER-H-test (schematic figure in the SI-Section 3) has been thoroughly described and validated for PAHs[32] and for chlorinated HOCs.[29] The test is designed to provide leachate concentrations of HOCs that are in equilibrium with the solid material. An extended discussion on this matter is provided in the SI-Section 3. In our experiments, approximately 250 g of wet soil was packed into a glass column (6 cm i.d. × 16 cm length) under saturated conditions. To promote an even flow through the soil column and prevent movement of soil particles from the top of the column, a 1 cm layer of quartz sand was placed both above and below the soil. The tests were conducted at a fixed L/S-ratio (between 2.5 and 6.0 L/kg dry weight (dw) depending on the bulk density of the soil material tested, SI-Table S3.1), with a continuous vertical up-flow of liquid consisting of ultrapure water containing 0.001 M CaCl$_2$ and 0.015 M NaN$_3$ (biocide to prevent biodegradation[15,35,36]). The leachate was collected in a reservoir and recirculated through the soil column (using a piston pump) for 7 days, at a low flow rate of approximately 20 mL/h.

The concentration of PACs in the leachate ($C_{pw,leach}$) was determined by liquid–liquid extraction of a 250 mL-subsample of the total leachate using 4 × 30 mL of dichloromethane (DCM), after addition of internal standards. The first two extractions were performed at the leachate's original pH (5.1–7.9), and the following two at pH 10–11 by adding 10–20 droplets of 1 M KOH (to ensure a quantitative extraction of the slightly basic N-PACs). The four extracts were combined, evaporated, purified on a column (16 mm i.d.) consisting of 5 g of KOH-impregnated silica gel topped with 1 g of anhydrous sodium sulfate, and eluted with 30 mL of DCM. After another evaporation, solvent change to ~1 mL of toluene, and addition of recovery standard (enabling estimation of the internal standard loss during the extraction and cleanup), the sample was

transferred to a GC-vial and analyzed by GC/HRMS (see details in Josefsson et al.[37]). Recovery values for the internal standards varied between 50 and 100%, and analyte concentrations were corrected accordingly. Measurements of TOC in the leachate were performed (EN 1484) together with conductivity (EN 27888), pH (SS 028122), and turbidity (EN ISO 7027). Subsamples of the leachate were filtered (0.45 μm cellulose nitrate membrane filter) and analyzed for DOC (EN 1484), and UV absorbance at 254 nm was determined on a UV/Vis spectrophotometer (Amersham Pharmacia Biotech, Ultrospec 2100 pro) using a 1 cm quartz cuvette. The specific UV absorbance, SUVA, was determined as the ratio of absorbance per m of path length normalized to DOC in mg/L. POC was assumed to be the difference between TOC and DOC in the leachate; when this difference was significantly larger than 0 mg/L; otherwise, it was assumed POC = 0 mg/L.

Reproducibility of triplicate leaching tests (calculated as relative standard deviation (RSD) in %) varied for the soils and the PACs (from 5 to 96%, SI-Table S4.1), with a highly contaminated, homogenized soil showing a reproducibility within 51% for all compounds except one. This variation was just slightly more than found in the literature.[29,32] No clear correlation could be found between $C_{pw,leach}$ across the triplicates with the characterization parameters turbidity, POC or DOC (SI-Table S4.2), though it was observed that replicates having a higher $C_{pw,leach}$ had a higher SUVA. No difference in the variation could be found when using fresh wet soils vs dry homogenized soils. An extended discussion on reproducibility can be found in the SI-Section 4.

Porewater Determination Using the Passive Sampler POM. The POM method used for determining $C_{pw,free}$ was presented in Arp et al.[1] In brief, thin sheets of POM (76 μm thick) were equilibrated with approximately 10 g of wet soil (achieving a mass ratio of 100:1 soil:POM, which in a previous study resulted in 2–3% depletion[15]) and 35 mL of water containing 0.001 M CaCl$_2$ and 0.015 M NaN$_3$ by shaking for 28 days.[37] For more details see the SI-Section 3.

Determination of K_{DOC} and K_{POC}. The total concentration potentially available for transport through the soil profile

Table 2. Ratio between Concentrations Obtained by the Leaching Test and the Concentrations Obtained with the POM Passive Sampler ($C_{pw,leach}/C_{pw,free}$) of Selected PAHs (Acenaphthylene (ACEY), Pyrene (PYR) and Benzo(a)pyrene (BAP)), Oxy-PAHs (1-Acenaphthenone, (AceO), Benz(a)anthracene-7,12-dione (BaQ), and 6H-benzo(cd)pyren-6-one (BPO)), and N-PACs (Benzo(h)quinoline (BhQUIN), Acridine (ACR), and Carbazole (CBZ))[b]

$C_{pw,leach}/C_{pw,free}$	PAHs			oxy-PAHs			N-PACs		
	ACEY	PYR	BAP	AceO	BaQ	BPO	BhQUIN	ACR	CBZ
Karlstad 1a-1	1.8	1.4	160	0.045	28	25	NA	NA	0.84
Karlstad 1a-2	0.98	0.44	33	0.049	13	15	NA	NA	0.44
Karlstad 1a-3	0.53	0.40	20	NA	6.7	13	NA	NA	0.61
Karlstad 2	2.1	3.4	88	0.24	32	49	0.78	1.2	0.50
Karlstad 6[a]	**220**	**4400**	**570000**	**11**	NA	NA	NA	NA	**700**
Riksten 1a	16	79	2500	0.45	550	1200	NA	3.3	5.6
Riksten 2[a]	**97**	**2700**	**110000**	**3.3**	**8300**	**13000**	NA	NA	**56**
Riksten 6a-1	8.1	NA	780	1.1	120	230	NA	NA	NA
Riksten 11-1	5.7	NA	270	0.75	48	NA	NA	NA	NA
France 2	18	14	520	0.16	110	130	0.73	1.0	0.41
France 4-1	1.4	0.51	12	0.079	10	8.1	0.59	1.6	0.65
France 4-2	4.6	4.1	88	0.16	16	18	1.5	3.3	1.4
France 4-3	7.0	5.8	170	0.11	24	36	1.3	3.3	1.5
Holmsund 1-1	4.0	4.1	110	0.35	17	24	0.31	2.2	1.7
Holmsund 1-2	4.8	5.4	130	0.45	20	27	0.48	1.8	1.1
Holmsund 1-3	4.8	6.9	130	0.45	20	34	0.24	2.5	2.1

[a]Marked in bold are the samples with high turbidity and measurable amount of POC, which also gives the highest $C_{pw,leach}/C_{pw,free}$ ratios. [b]A $C_{pw,leach}/C_{pw,free}$ ratio of 1 indicates similarity, while values >1 indicate that DOC and POC sorbed compounds contribute to $C_{pw,leach}$. Ratios for all individual compounds studied can be found in the SI-Section 8. NA = not available due to values below limit of quantification.

(measured here with the ER-H-test as $C_{pw,leach}$) can theoretically be described with eq 2, using a three-phase partitioning model[38]

$$C_{pw,total} = C_{pw,leach} = C_{pw,free} + K_{DOC}*[DOC]*C_{pw,free}$$
$$+ K_{POC}*[POC]*C_{pw,free} \quad (2)$$

where K_{DOC} and K_{POC} (units L/kg of organic carbon) are the partitioning coefficients of the contaminant between DOC and POC, respectively, and the freely dissolved phase, on an organic carbon basis. For soil porewater systems with negligible concentrations of POC (i.e., POC ≈ 0 mg/L, or not significantly different from 0 based on measurement uncertainties), eq 2 can be rearranged into eq 3 in order to derive K_{DOC}:

$$K_{DOC} = (C_{pw,leach} - C_{pw,free})/([DOC]*C_{pw,free}) \quad (3)$$

As a criteria for using eq 3, both $C_{pw,leach}$ and $C_{pw,free}$ had to be > quantification limits, and $C_{pw,leach}$ had to be >1.5 × $C_{pw,free}$, to account for the RSD of the obtained measurements (presented above). The relative propagated error on K_{DOC} (based on triplicate tests of the soil samples France 4, Holmsund, and Karlstad 1a) ranged from 8 to 79% for the studied PACs (SI Section 4, Table S4.6).

For soils with a non-negligible POC content in the leachates, K_{POC} was determined using the average resulting K_{DOC} values from the other soils

$$K_{POC} = (C_{pw,leach} - C_{pw,free} - K_{DOC}*[DOC]*C_{pw,free})$$
$$/([POC]*C_{pw,free}) \quad (4)$$

■ RESULTS AND DISCUSSION

Soil Properties and PAC Concentrations in Soil. C_{soil} (mg/kg$_{dw}$) of PAC ranged over 4 orders of magnitude, with $\sum$PAH-16 from 41 to 2600, $\sum$oxy-PAH-11 from 9.7 to 240, and

$\sum$N-PAC-4 from 0.27 to 9.4 (Table 1). Concentrations of individual compounds are provided in the SI-Section 5.

Characteristics of the Leachates. The leachates of the soil samples collected at Riksten, a site with deciduous forest, had a lower pH (pH 5.1−5.7) compared to the leachates of the other tested soils (pH 6.3−7.9). The Riksten leachates also contained the highest concentrations of DOC, 131−269 mg/L, while concentrations found in the other leachates varied from 7 to 73 mg/L. Two leachates had high turbidity, Karlstad-6 (1000 FNU) and Riksten-2 (590 FNU), indicating higher concentrations of colloids and particulate matter. The POC concentrations in these leachates were 121 and 78 mg/L, respectively. The leachates from the eight remaining soils had negligible POC, and thus their porewater TOC was dominated by DOC (SI-Table S6.1). In follow-up experiments, POC should be independently quantified to confirm the mass balance assumption used here. The UV-absorbance of the filtered leachates exhibited a good linear correlation ($r^2 = 0.95$) with the concentration of DOC (SI-Figure S6.1). The highest SUVA, 53 L/(mg m), was found for Karlstad-6 (the leachate with extreme turbidity and high POC). SUVA of the other leachates ranged from 5.9 to 30 L/(mg m). This indicated a high to very high aromaticity of the DOM in all leachates compared to the SUVA found in soil solutions from uncontaminated arable soils, for which average values of 2.4 ($n = 30$; min/max = 0.84/4.6)[39] and 3.3 ($n = 189$; min/max = 0.6/7.5)[40] L/(mg m) have been reported. Full details of the leachates' characteristics are provided in the SI-Table S6.1.

PAC Concentrations in Leachates and Leached Fractions. The $C_{pw,leach}$ (μg/L) ranged from 0.80 to 1600 for $\sum$PAH-16, from 0.18 to 170 for $\sum$oxy-PAH-11, and from 0.033 to 27 for $\sum$N-PAC-4 (Table 1). Concentrations for individual PACs can be found in the SI-Tables S6.2 and S6.3 and expressed as leached fraction of C_{soil} in the SI-Tables S7.1 and S7.2. The leached fraction was generally higher for compounds with higher aqueous solubilities, i.e. lower log K_{OW}.

Comparing $C_{pw,leach}$ and $C_{pw,free}$. Ratios between $C_{pw,leach}$ and $C_{pw,free}$ are presented for representative PAHs, oxy-PAHs, and N-PACs in Table 2. Ratios for all compounds can be found in the SI-section 8 (Tables S8.1 and S8.2) together with the $C_{pw,free}$ used for the calculation (Tables S8.3−S8.5). With the exception of the two soils with high POC content (Karlstad-6 and Riksten-2) and the soils from Riksten and France-2, $C_{pw,leach}/C_{pw,free}$ ratios close to 1 (ranging from 0.1−10) were obtained for most of the oxy-PAHs and N-PACs and for low molecular weight (i.e., more hydrophilic) PAHs (from naphthalene to pyrene). $C_{pw,leach}/C_{pw,free}$ ratios < 0.1 were observed for 1-indanone, 1-acenaphthenone, and quinoline for some soils, perhaps due to transformation processes like abiotic oxidation[41] during the leaching test. Compounds with $C_{pw,leach}/C_{pw,free}$ generally greater than 10 were the 5- and 6-ring PAHs and large oxy-PAHs, such as benzo(a)fluorenone, benz(a)anthracene-7,12-dione, naphthacene-5,12-dione, and 6H-benzo(cd)pyren-6-one. The two leachate samples with high POC content (Karlstad-6 and Riksten-2) had, as expected, extremely high $C_{pw,leach}/C_{pw,free}$ ratios (up to >100 000), while the sample France-2 and the remaining Riksten samples displayed ratios >1000 for at least one compound. High ratios for the Riksten soils were expected due to the high DOC concentration in these leachates, while the results for France 2 were unexpected. Also for these samples it was generally observed that $C_{pw,leach}/C_{pw,free}$ increased with increasing K_{OW} (i.e., decreasing aqueous solubility). This will be discussed in further detail below.

Soil-Porewater Partitioning. In Figure 1, log K_{TOC} values based on $C_{pw,leach}$ are compared to log K_{TOC} values based on $C_{pw,free}$, as well as to log K_{OW} (raw data in the SI-Section 9). K_{TOC} is calculated using eq 1. As is evident in Figure 1a, the ER-H-test gives rise to average log K_{TOC} values ranging from 3.4 to 5.1, with most at 5, while the POM method gives average log K_{TOC} that range from 2.4 to 8.0. Between these two methods, there is a methodological bias in the partitioning coefficients, which increases with the hydrophobicity of the compounds. The leaching test will only produce K_{TOC} values in the same range as the POM method for compounds with approximately log K_{OW} < 4. As the hydrophobicity increases (Figure 1b) the correlation deteriorates. This is most likely explained by the prevalence of DOC and especially POC in the column leachates, which can act as carriers of hydrophobic PACs, leading to higher $C_{pw,leach}$ compared to $C_{pw,free}$, and erroneously low K_{TOC} values. Furthermore, the variability of the ER-H-derived K_{TOC}s (Figure 1b) is much larger than that of the POM-derived ones (Figure 1c). In addition, the study by Arp et al.[1] showed that K_{TOC} values derived from the POM method correlated well with theoretically derived values. An especially good correlation was found to K_{TOC} values predicted by the use of the Raoult's Law Coal Tar sorption model (see eq S1 and Figure S9.1 in the SI-Section 9) which has been proven to better describe sorption of HOCs to pyrogenic impacted sediments[6,42,43] and soils[1] than K_{TOC} values derived from proposed log K_{TOC} − log K_{OW} linear free energy relationships.[44]

The oxy-PAHs and the N-PACs tended to have larger K_{TOC} than the PAHs of corresponding hydrophobicity, i.e. the semipolar PACs were less available for leaching than expected from their K_{OW}; however, the difference was not statistically significant (Table S9.8). The trend is more pronounced in Figure 1c (log $K_{TOC,POM}$ versus log K_{OW}) than in Figure 1b due to the colloids and DOC that deteriorate the log $K_{TOC,Leach}$ − log K_{OW}-correlation. This trend could be interpreted as either a) oxy-PAH and N-PACs are capable of making more specific interactions
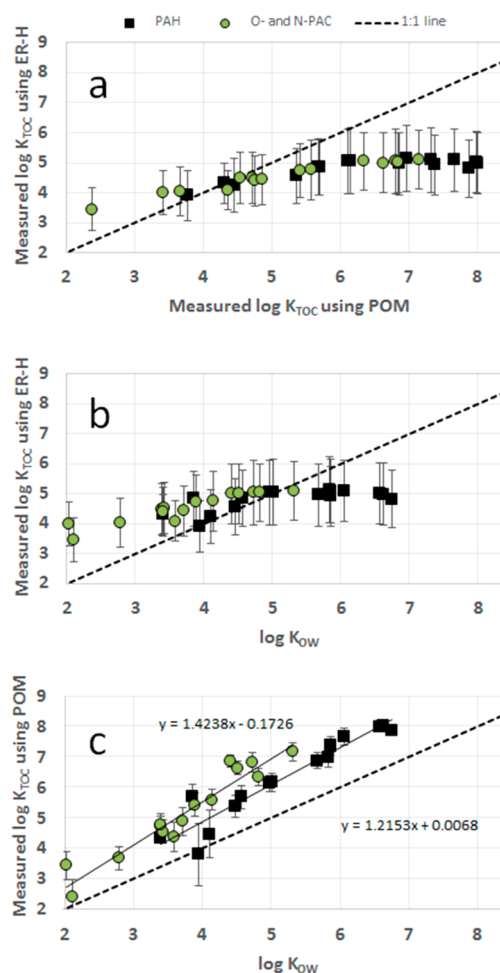
**Figure 1.** a) Calculated (using eq 1) log K_{TOC} values (L/kg$_{TOC}$) for the studied PACs using the ER-H-test versus values derived by the POM method, b) the log K_{TOC} values using ER-H-test versus log K_{OW} values, and c) the log K_{TOC} values using the POM method (reproduced from Arp et al. (2014)) versus log K_{OW} values. Error bars represent standard deviation determined from either the ER-H ($n = 16$) or POM experiments ($n = 16$).

with the soil TOC or the mineral surfaces in the soil than the nonpolar PAHs having a similar K_{OW} or b) there is a systematic bias in the predicted K_{OW} of oxy-PAHs in the way that they are lower than they should be. The latter is not unlikely since the K_{OW}'s used for the oxy-PAHs (and the N-PACs) were collected from the EPISuite database, which uses a molecular increment based approach to predict K_{OW} when experimental values are lacking, which was the case for 7 of the oxy-PAHs (Table S1.1 and Figure S9.3). Thus, if the molecular increment (e.g., an oxygen on a PAH) was not calibrated properly, this could cause a drift.

The relationship of BC-partition coefficients, K_{BC}, as based on $C_{pw,leach}$, was not determined here as in the previous study; using the same soils, log K_{BC} values based on $C_{pw,free}$ were found to be more broadly distributed than log K_{TOC} based on $C_{pw,free}$.[1] This implied that the BC fraction (measured using CTO-375) was not consistently the most dominating sorption phase and was inferior to TOC for describing sorption to these soils.

The Effect of DOC and POC on Leaching. K_{DOC} for the soil-porewater systems with negligible POC content ($n = 14$) calculated with eq 3 are presented in the SI-Section 10, and average log K_{DOC} are plotted versus log K_{OW} in Figure 2a.
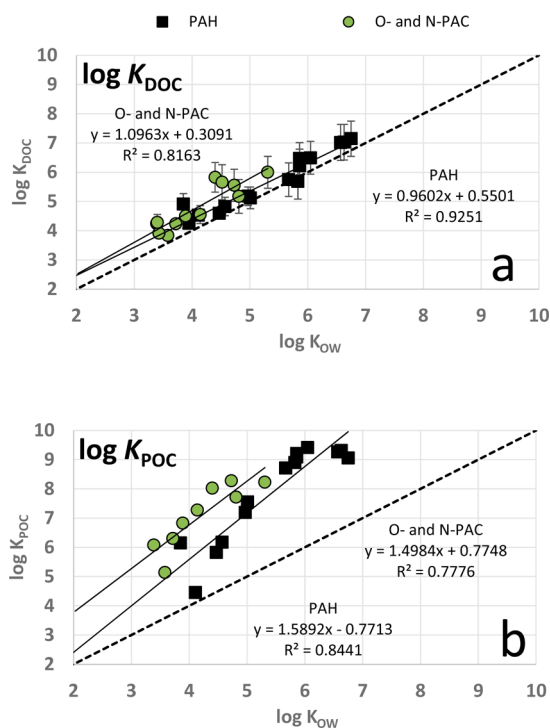
Figure 2. a) Average log K_{DOC} values (using eq 3 and $n = 14$ leachates with POC ≈ 0) for the studied PACs versus the compounds' log K_{OW} (error bars are standard deviation). b) Calculated average log K_{POC} values (using eq 4, average log K_{DOC} values and $n = 2$; i.e. Karlstad-6 and Riksten-2) for PACs versus the compounds' log K_{OW}. Error bars not included due to $n \leq 2$.

Linear relationships between average log K_{DOC} and log K_{OW}, with slopes of approximately 1, were observed for both PAHs and the semipolar PACs (Figure 2a). The K_{DOC} of semipolar PACs were in the same range as the K_{DOC} for PAHs of corresponding hydrophobicity; i.e. no noticeable trend of semipolar PACs capable of making fewer (or more) specific interactions with the DOC was evident (statistical information is given in the SI-section 10, Table S10.1). Individual and average log K_{DOC} can be found in Tables S10.2–S10.4.

The assessed K_{POC} values for Karlstad-6 and Riksten-2 (the two systems with POC above quantification limit) were orders of magnitude larger than the average K_{DOC} (comparison of Figures 2a and 2b). The stronger sorption is probably explained by higher contents of carbonaceous materials (e.g., BC or colloidal tars) in POC than in DOC. The K_{POC}'s of semipolar PACs were systematically higher than the K_{POC}'s of PAHs, but data was insufficient to justify this as statistically significant. In relation to the POM-derived K_{TOC} of these two soils, the K_{POC}'s were about 1 order of magnitude higher (Table S11.1), indicating in general stronger sorption affinity of the particles in the leachate compared to the leached material. This would imply that the POC could facilitate PAC transport to new areas, but at the same time a large fraction of the POC sorbed PAC would be unavailable.

Literature K_{DOC}'s of PAHs (Table 3 and SI-Figure S10.4) show high variability, up to several orders of magnitude for some PAHs,[38,45−48] and seem to increase with increasing log K_{OW}, while data on oxy-PAHs and N-PACs, to our knowledge, are not yet available. More recent studies using passive samplers have reported K_{DOC} values of PAHs comparable to ours (Table 3). For example, Haftka et al.[46] investigated partitioning of PAHs to natural DOM extracted from different types of freshwater sediments and observed log K_{DOC} values both below and above our average values (approximately ±0.4 log units). In addition, partitioning studies of PAHs to Aldrich humic acid using the passive sampler PDMS[47,49] have reported even higher values (log K_{DOC} up to +0.7 log units above ours). The calculated average log K_{DOC} values for the PAHs were approximately 0.5 to 2 log units higher compared to values reported in older compilations and reviews of K_{DOC} data that were not based on passive sampling[38,45] (SI-Figure S10.4). This discrepancy is most likely due to artifacts in the earlier methods used for the determination of K_{DOC}, which suffered from well-documented phase separation problems leading to overestimations of freely dissolved aqueous concentrations and, consequently, underestimations of K_{DOC}.[47,49]

The observed variability in log K_{DOC} values of porewater from different soils can be attributed to different origins of DOM,[38,46] but differences in pH, ionic strength, and temperature can also

Table 3. Results of Linear Regressions of Log K_{DOC} versus Log K_{OW} (i.e. Log K_{DOC} = A Log K_{OW} + B) for Experimental Data from This Study for PAHs, Oxy-PAH, and N-PACs and for All Compounds (All PACs) Together with Literature Data for PAHs[h]

this study	slope (A)	intercept (B)	R^2	PAH[f]	log K_{DOC}	(SD; n) n = no. of leachates	log K_{DOC} range	ref
						this study (POM+ER-H)	**lit. (passive sampling)**	
PAHs	0.96[a]	0.55[a]	0.93[a]	PHE	4.59	(±0.19; 7)	4.17−4.78	b, c
O- and N-PAC	1.10[a]	0.31[a]	0.82[a]	FLUA	5.18	(±0.32; 8)	4.75−5.50	b, c
all PACs	0.89[a]	1.03[a]	0.89[a]	PYR	5.12	(±0.37; 8)	4.76−5.55	b, c
				BBF	6.22	(±0.57; 14)	5.70−6.96	b, g
literature				BGP	7.03	(±0.61; 13)	5.90−7.43	b, g
PAH lit. 1	1.23[b]	−0.91[b]	0.99[b]					
PAH lit. 2	1.18[c]/1.31[c]	−0.61[c]/−1.86[c]	0.98[c]/0.97[c]					
PAH lit. 3	1.18[d]	−1.56[d]	0.76[d]					
PAH lit. 4	1.30[e]	−2.42[e]	0.87[e]					

[a]This study; derived with a combination of passive sampling (POM) and leaching (ER-H); historical contaminated soils ($n = 14$). [b]Sampling and dosing with SPME by ter Laak et al.;[47] Aldrich humic acid. [c]Sampling with PDMS by Haftka et al.;[46] natural DOM extracted from 2 freshwater sediments spiked with PAHs. [d]Various methods (literature review by Burkhard[38]) partitioning of PAHs to naturally occurring DOC; $n = 33$. [e]Aldrich humic acid; regression analysis made by Durjava et al.[49] of data from Krop et al.[45] [f]PAHs: phenanthrene (PHE); fluoranthene (FLUA); pyrene (PYR); benzo[b]fluoranthene BBF; benzo[g.h.i]perylene (BGP). [g]In situ mesurements of sediment porewater concentration with POM-55 and PDMS; study by Cornelissen et al.[48] [h]Average log K_{DOC} for some selected PAHs and range of log K_{DOC} values found in the literature for these compounds are also shown for comparison.

have some effect.[46,50] For example, a natural variation of 1.7 log units has been reported for PAH partitioning to DOM samples extracted from different freshwater sediments.[46] For some individual compounds of this study (PAHs with log K_{OW} > 5.7), ranges in log K_{DOC} exceeding 2 log units were observed (SI-Table S10.4). This large range can be due to the variability in structure and composition of the DOC released from the different historically contaminated soil samples. Systems containing large fractions of dissolved tars or other BC media could give rise to high K_{DOC}, due to the higher aromaticity of such DOC. However, no clear correlation was found between the derived log K_{DOC} and the BC content of the studied soils (BC content in leachates was not measured) (SI-Figure S10.5), nor the SUVA value of the filtered leachates (SI-Figure S10.6). Correlations with pH or conductivity of the studied leachates were also not found (Figures S10.7–S.10.8). It is plausible that some leachates contained small concentrations of POC, even though they were assigned as POC free (due to the uncertainties in the POC estimations). Considering the high K_{POC} values obtained in this study (Figure 2b), trace amounts of POC (below our detection limit) could cause positive biases in the calculated K_{DOC}.

Regarding the role of BC on leaching, there was no correlation between log K_{DOC} and BC content (as well as with log K_{DOC} and SUVA). There may be a correlation between BC and K_{POC}, but we cannot explore this, as only two soils with high enough POC content were investigated (though Karlstad 6 did have a higher content of f_{BC} than Riksten 2 (12.6% vs 0.2%, respectively) as well as higher K_{POC} (1.1–13.2 times higher compared to Riksten 2 (SI-Table S11.1)).

Environmental Implications and Relevance. This study confirms that passive sampling methods and leaching tests provide different, but complementary, information on risks related to PAC contamination. By measuring both $C_{pw,free}$ and $C_{pw,leach}$, risk assessments can account for both the bioavailability of PACs and the risk for contaminant transport to ground or surface waters, respectively. This risk can, for instance, be based on a comparison to a guideline value, such as an aquatic or porewater benchmark value in the case of $C_{pw,free}$, or based on a comparison to a maximum allowable emission concentration in the case of $C_{pw,leach}$.

Applying both methods in parallel on a large number of samples would probably not be possible in most site remediation projects due to limited budgets. The POM method is superior compared to the ER-H method when it comes to labor intensity and cost. It requires little more than a glass vial, POM strips, and a shaker and can be done in batches of dozens, requiring only about 2 work hours/sample, whereas the ER-H method requires custom built columns and equipment and about 7 work hours/ sample. Furthermore, besides the possibility to obtain a direct measure of $C_{pw,free}$, the POM method also offers the possibility to get an estimate of the $C_{pw,leach}$ in soils where particulate (POC) mediated transport of PACs can be ignored using

$$C_{pw,leach} = C_{pw,free} + K_{DOC}*[DOC]*C_{pw,free} \qquad (5)$$

Here, the empirical relationship log K_{DOC} = 0.89 × log K_{OW} + 1.03 (r^2 = 0.89; standard errors for slope = 0.064 and intercept = 0.312; derived for log K_{OW} values ranging from 3.4 of 6.8) can be used to estimate the contribution of DOC-bound PACs together with field realistic DOC concentrations. Since no significant difference between the regressions for PAHs and the semipolar PACs was found (SI-Table S10.1), this relationship represents a universal line for all PACs (Table 3), and it could be a useful tool

for estimations of K_{DOC}'s for PACs in the absence of measured $C_{pw,leach}$ values. The validity of this approach was also checked by selecting a subset of the data, representing 50% of the PACs for which a new regression was made. No significant differences were found between the two regressions (statistics and more information are given in the SI-Table S10.6). However, the large observed ranges in log K_{DOC} (over 2 log units for some PACs) must be kept in mind. Risk assessments based on this relationship will contain this level of uncertainty. It may be sufficient for initial screening purposes, but if more accuracy on $C_{pw,leach}$ is required, in situ measurements will have to be conducted, using for example lysimeter studies.

Anyhow, our K_{DOC} estimations are likely more accurate for historically contaminated soils than previous ones,[38,45] which suffered from artifacts caused by problems in measuring truly dissolved concentration correctly (SI-Figure S10.4) or not using historically contaminated soils. In addition, our study shows that the mobile concentration will be dominated by colloid facilitated transport if POC is present (log K_{POC} ≫ log K_{DOC}), which was found in two out of the 10 studied soils containing the highest turbidity levels (>500 FNU). Accordingly, in soils susceptible to colloidal transport it is recommended to perform the POM and the ER-H tests in parallel. However, the K_{POC} values presented here could also be of use (if field concentrations of POC are known) in order to generate a rough estimate of the mobile concentrations.

It should be noted that the *ex situ* lab methods used here to measure $C_{pw,free}$ and $C_{pw,leach}$ will most likely return concentrations that are either similar or larger than concentrations expected under true field conditions *in situ*. This is especially an issue when dealing with the unsaturated zone, where moisture content can vary with time, and by definition not reach the saturated conditions used in these tests. It also must be acknowledged that the soil structure is substantially altered within these tests, compared to their *in situ* state, as the tests expose more surface area for both equilibrium and leaching processes and introduce more energy. Therefore, an extension of understanding how to interpret these *ex situ* test results to *in situ* observations in the future would provide even more realistic risk assessments, as well as transport models. Some novel field setups for this work would be needed, such as the integration of passive samplers with lysimeters, to simultaneously assess real world, in situ $C_{pw,free}$ and $C_{pw,leach}$.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02774.

Tables S1.1, S2.1, S2.2, S3.1, S4.1–S4.6, S5.1, S5.2, S6.1–S6.3, S7.1, S7.2, S8.1–S8.5, S9.1–S9.8, S10.1–S10.6, and S11.1; Figures S1.2, S3.1–S3.3, S4.1, S6.1, S9.1–S9.3, and S10.1–S10.10; and references (PDF)

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Notes
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