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Relationship between the Concentrations of Dissolved Organic Matter and Polycyclic Aromatic Hydrocarbons in a Typical U.K. Upland Stream

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ⓈSupporting Information

ABSTRACT: Concentrations of total and freely dissolved polycyclic aromatic hydrocarbons (PAHs) and dissolved organic carbon (DOC) were measured in water collected during four sampling events at five sites from the River Wyre. The sites are typical of streams draining upland organically rich soils in northwest U.K. Freely dissolved PAHs were separated from those associated with DOC using a flocculation method. The sum of concentrations of the total and freely dissolved PAHs analyzed ranged from 2.71 to 18.9 ng/L and 2.61 to 16.8 ng/L, respectively. PAH concentrations and PAH fluxes derived from concentrations and water flow rates generally increased downstream, the trend in the latter being more pronounced. The concentration of individual PAHs containing five or more aromatic rings was found to be strongly correlated to the DOC concentration ($p < 0.0001$), suggesting common terrestrial sources and hydrological pathways. In contrast, no significant relationships were observed between concentrations of PAHs with four or fewer rings and DOC. Concentrations of PAHs with more than four rings showed similar seasonal variation as DOC concentration (peaking in the late summer), while variation in two or three ring PAHs was out of phase with DOC (peaking in the winter). As the PAH–DOC relationship appeared partly dependent on the molecular weight of the PAHs, a linear regression function that included an interaction between this variable and DOC concentration was used to model PAH concentrations over a 2 year period to estimate annual fluxes. The relationship identified between PAH concentrations and DOC should help to enhance interpretation of PAH monitoring data that are currently sparse both spatially and temporally and, thus, enable more robust assessments of the potential risks of these environmental pollutants to sensitive aquatic organisms and human water supplies.
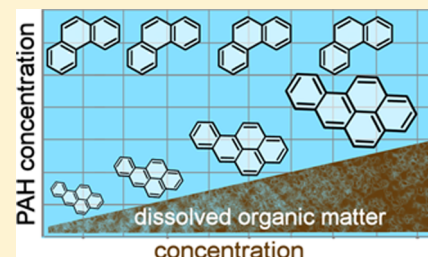
INTRODUCTION

In many regions, upland rivers play crucial roles as habitats for freshwater biodiversity and in the supply of potable water and the dilution of aquatic pollution from intensive agricultural, industrial, and highly populated areas further downstream.[1] Chemical water quality is central to these functions. Polycyclic aromatic hydrocarbons (PAHs) are a group of semivolatile, persistent, organic chemicals that are ubiquitous in the environment. They have been identified as "priority hazardous substances" under the Water Framework Directive as well as the Convention on Long-Range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UN ECE) because of their toxicity and suspected carcinogenicity and mutagenicity.[2,3] PAHs in the environment are mostly unintentional byproducts of domestic heating, traffic-related fuel combustion, electrical power generation, waste incineration, intentional and accidental biomass burning, etc.,[4] formed during incomplete combustion. Apart from these pyrogenic pathways, PAHs are also formed petrogenically, i.e., slowly, over long periods under moderate temperatures, and can be found in fossil fuels.[4] They are emitted into the atmosphere in exhaust gases or by volatilization and can be transported over long distances prior to their deposition to terrestrial and aquatic surfaces. They may be further transported within these systems or become fixed in soils or sediments that may act as the ultimate sinks for such compounds.[5] PAHs are able to enter aquatic and terrestrial organisms through the skin, gills, lungs, and digestive tract and tend to accumulate in fatty tissues due to their highly lipophilic and hydrophobic nature.[5,6] These characteristics also result in a high affinity of PAHs for organic matter, e.g., humic substances including humins and humic and fulvic acids, and particularly for their aromatic, and thus nonpolar, sites.

Our study area, within the catchment of the River Wyre in northwest England, is characterized by soils with high organic matter content that consequently have a large capacity to bind and store PAHs.[5] Recently, Rhind et al.[7] reported a strong link between PAH and organic carbon content in Scottish surface soils. In their study, peaty soils, similar to those found in the River Wyre catchment, showed comparably high PAH concentrations. However, organic matter has a tendency to dissolve in percolating rainwater or groundwater, forming dissolved organic matter that is commonly quantified through measurement of dissolved organic carbon (DOC). Hence soil-bound PAHs may become remobilized in association with

DOC as the latter is released into the water phase. For as long as these contaminants remain bound to the DOC they are far less readily available for uptake by organisms than when in a freely dissolved state.

Concentrations of DOC in streams draining organic upland soils are often considerable and have increased by a factor of 2 or more in several regions of northern Europe and North America over the last 2 decades or more in a direct response to reductions in acid deposition.[8−14] Recent field experiments indicate that this results from the increased solubility of organic matter as soil acidity has begun to decline.[15] To date, very little is known about the extent to which DOC acts as a conduit for PAHs and other atmospherically deposited contaminants through fluvial systems and whether the rise in DOC concentrations has had a concomitant influence on the contaminant export from these environments.[16]

The aim of this study was to determine the freely dissolved and DOC-associated concentrations of dissolved PAHs along a stream sampling transect from the upper reaches, draining upland areas, to lower reaches passing through agricultural/ semiurban areas, in order to gain a better understanding of their sources and determine the importance of DOC in their supply to the stream system. PAHs may be associated with DOC released from soils, and as a result, DOC may affect concentrations and fluxes of dissolved PAHs in the stream if soil-borne PAHs contribute significantly to the PAH burden in the water. Relationships between the two were therefore investigated, including the partitioning of PAHs between water and DOC. We discuss the applicability of the findings to other sites along the stream in order to inform the development of fate and transport models and the implications of temporal trends in DOC concentrations and chemical composition on loads of dissolved PAHs in this type of stream.

METHODS

Sampling Sites and Collection. Water samples were taken at five sites along the River Wyre, a typical river system in the northwest of England, draining upland and agricultural areas with soils rich in organic matter [see Figure SI-1, Supporting Information (SI); numbering starts at the upper-most site and continues downstream]. Clean amber glass bottles with Teflon-lined lids were used to collect 5 L water samples for the PAH analysis from each site during each of the four sampling events (August 19, 2010; December 6, 2010; March 6, 2011; and June 6, 2011). Additionally, 100 mL samples were collected for DOC analysis. Samples were kept at 4 °C and processed within 48 h of collection. Preliminary tests showed that concentrations of both freely and total dissolved PAHs remained stable over this period.

Analysis of DOC. Samples were passed through GF/F glass fiber filters (0.7 μm retention), and DOC concentrations were determined spectrometrically on the basis of UV absorbance at 270 and 350 nm using an algorithm described by Carter et al.[17]

Analysis of PAHs. Immediately prior to processing, each well-mixed GF/F-filtered 5 L sample was divided into two equal subsamples for the analysis of total dissolved and freely dissolved PAHs, respectively.

Concentrations of total dissolved (the sum of freely dissolved and DOC-associated) PAHs were determined in the first subsample. To isolate freely dissolved PAHs in the second subsample, the DOC and DOC-associated PAHs were precipitated by adding 0.4 g of $Al_2(SO_4)_3$ (dissolved in 5 mL of Milli-Q water) and adjusting the pH to 6, the optimal

flocculation pH for $Al_2(SO_4)_3$,[18] using NaOH or HCl. The flocculated DOC was then removed by passing the sample through a GF/F filter (0.7 μm retention) using a Millipore vacuum filtration unit. $Al_2(SO_4)_3$ was found to remove DOC efficiently, particularly those substances PAHs tend to partition to most strongly, and does not precipitate PAHs.[18]

The concentrations of PAHs associated with DOC were determined indirectly by subtracting the concentration of freely dissolved PAHs from the sum of freely dissolved and DOC-associated PAHs. Laboratory blanks were generated by treating Milli-Q water in exactly the same way as the samples.

Half of each filtered subsample was transferred to a 1.5 L separating funnel, spiked with a mixture of deuterated PAHs to monitor recovery of the extraction and cleanup method (see Table SI-1, SI), and liquid−liquid extracted with 80 mL of dichloromethane (DCM) three times. This procedure was repeated with the remainder of each subsample. The extracts of both portions were pooled, and anhydrous sodium sulfate (baked at 550 °C) was added to remove any remaining water. These were then reduced to 1 mL on a Buchi Syncore evaporation system and cleaned on a column packed with 0.8 g of alumina (activated at 550 °C) and a small amount of anhydrous sodium sulfate. The target compounds were eluted with 10 mL of DCM. After the subsamples and blanks were blown down under a gentle stream of nitrogen, they were transferred to small amber vials, further reduced to ca. 0.5 mL, spiked with a solution containing acenaphthene-d_{10} and benz(a)anthracene-d_{12} as internal standards, and analyzed for all compounds listed in Table SI-2 (SI) and the recovery compounds. Initially we also analyzed naphthalene. However, due to high and variable blank levels, this compound was excluded later and is not reported here. We refer to the sum of all 28 PAHs analyzed by GC−MS (excluding naphthalene) as $\sum$PAH from now on. Details on the GC−MS analysis are given in the SI.

QA/QC. Method detection limits for the extracts, derived from the lowest or lowest quantifiable calibration standard, ranged from 0.004 to 0.5 ng mL^{-1}, corresponding to ca. 0.001− 0.09 ng L^{-1} in the water samples, depending on the compound. Average recovery rates varied between 60% (naphthalene-d_8) and 107% (pyrene-d_{10}) (see Table SI-1, SI). All results were blank- and recovery-corrected.

RESULTS AND DISCUSSION

Concentrations of DOC and Dissolved PAHs. Concentrations of DOC ranged from 2.2 to 12.8 mg L^{-1}, with the highest values in samples collected in August and the lowest in December at all sites. The patterns of variation in concentrations over the year-long study are consistent with the annual cycle of DOC concentrations observed between February 2008 and March 2011 at the same sites (see Figure SI-2, SI) and typical of annual variation for streams more widely in this region.[19] In general, the lowest DOC concentrations were recorded at the uppermost site in the catchment (site 1) while sites 2−5 contained similar but higher concentrations.

Concentrations of total dissolved PAHs found in the Wyre water ranged from 2.7 to 20 ng L^{-1} ($\sum$PAHs) and are in the lower range reported for surface water systems internationally (Table SI-3, SI). They are higher than those measured in three European remote mountain lakes[20] but similar to those found at nonurban estuary sites in the eastern United States and western France[21,22] and lower than in samples taken from large rivers and estuary sites in or downstream of highly populated or
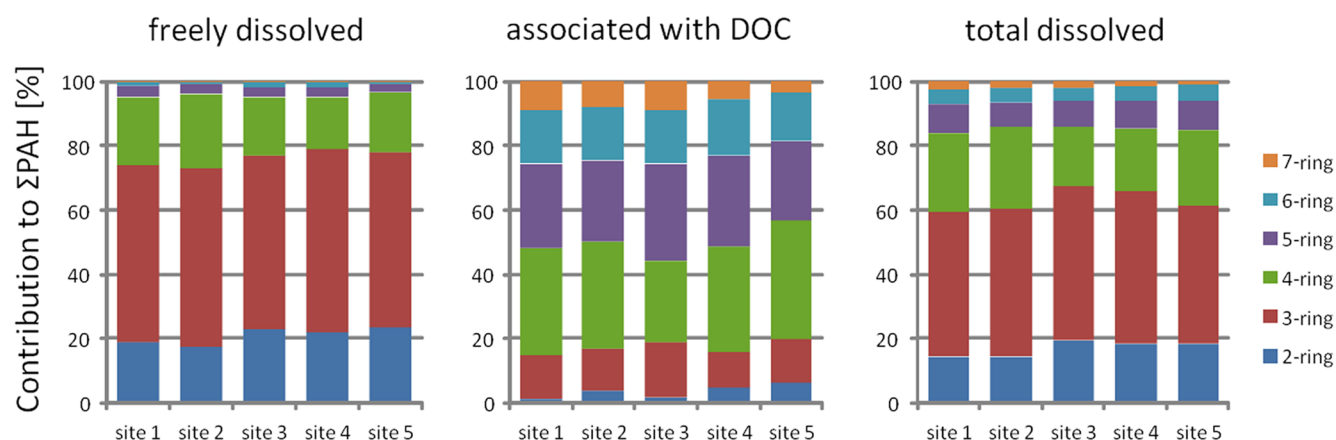
Figure 1. Contribution of two- to seven-ring PAHs to the sum of freely dissolved, DOC-associated, and total dissolved PAHs (average of all four sampling dates).
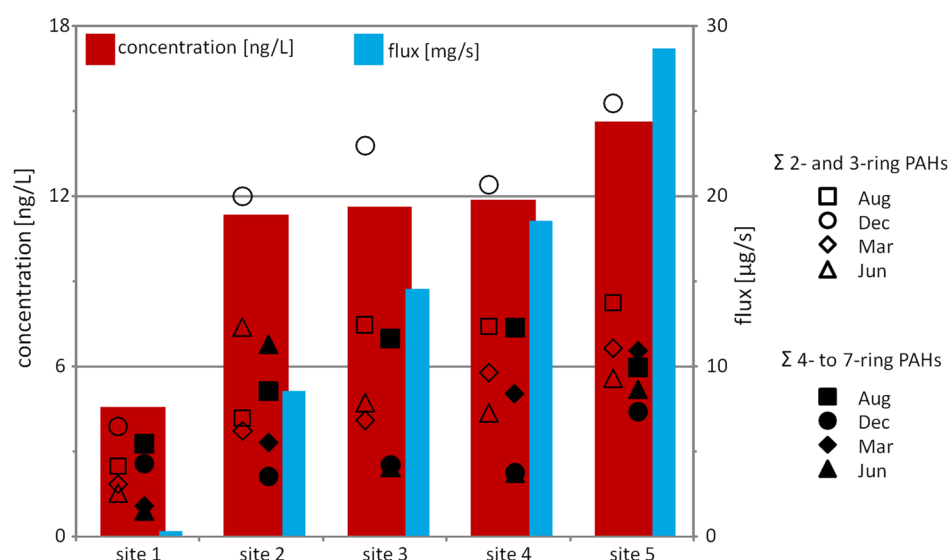

Figure 2. Total dissolved concentrations and fluxes of the sum of all PAHs measured in the water samples (bars represent averages for all four sampling events; symbols show concentrations of the sum of two- and three-ring PAHs and of four- to seven-ring PAHs during individual sampling events).

industrialized areas.[21,23−29] They are also much lower than concentrations measured in surface water samples taken in 1995 from Esthwaite Water, in the British Lake District, ca. 50 km north of the Wyre.[30] This apparent disparity could in part reflect the considerable reduction of atmospheric PAH concentrations in the intervening period[31] but may also be influenced by differences in surrounding land use.

Concentrations of freely dissolved PAHs in surface waters have been measured in a number of passive sampling studies (see Table SI-3, SI), some using field-derived uptake rates and others assuming fixed uptake rates, possible resulting in somewhat higher uncertainty. Even when taking this into account, concentrations of freely dissolved PAHs found in the Wyre samples (2.6−17 ng L^{-1} for $\sum$PAHs) are at the lower end of the range of those reported in other river systems (compare Table SI-3, SI). Few data are available for similar streams (i.e., rural to semiurban, remote from large local emission sources). However, given that concentrations of PAHs in the air in this area are not exceptional,[32] it seems reasonable to assume that the amounts found in the Wyre samples are representative of similar catchments in the wider region.

PAH Fingerprints and Fluxes. The contributions of PAHs by aromatic ring count to the sum of freely dissolved, DOC-associated, and total dissolved PAHs in the Wyre samples are shown in Figure 1. Overall, the more water-soluble two- to four-ring PAHs dominate over the virtually water-insoluble and strongly hydrophobic five- to seven-ring PAHs. This is typical for surface waters[20−23,29] and reflects the strong binding of highly hydrophobic substances to soil and sediment particles that skew their distribution toward aquatic particulate phases. Hydrophobic substances are also less likely to have leached from the soil into surface waters in the first place and may already be bound to airborne particles when deposited from the atmosphere to the water. However, it is clear from Figure 1 that PAHs with five or more rings are relatively more abundant in the DOC-associated fraction and contribute between 10 and 15% of the total dissolved PAH concentration across the five sites, thus implying a significant role of DOC in their transport. High molecular weight PAHs are much more toxic than those of low molecular weight[33] and therefore merit attention despite their relatively low concentrations.

Concentrations of total dissolved PAHs generally increased downstream (Figure 2) and ranged by up to 1 order of magnitude over the five sites. Most of this variation is accounted for by the relatively low concentrations at site 1. Differences between the remaining four sites were generally less marked, although the concentrations of some PAHs at site 2 were notably higher than at sites 3 and 4. Considering the sparse population, relatively high PAH concentrations observed at site 2 compared to the nearby site 1 may be linked to the presence of a reservoir ca. 100 m upstream of the sampling point, which may increase direct interception of atmospheric pollutants by the water.

In common with the observed temporal variations in DOC, concentrations of total dissolved PAHs with four or more rings were highest in the August samples and lowest in December and June, with a maximum/minimum ratio of 1.2−23 (mean of 4.2). In contrast, maximum concentrations for two- and three-ring PAHs occurred in December, when they were on average 2.9 times higher than the minimum values, mostly observed in the March or June samples (see Figure 2).

Fluxes of $\sum$PAHs were estimated (Figure 2) by combining concentration data with estimates of discharge (data provided by the UK Environment Agency[34] for site 4, with catchment area based estimates for the remaining sites). The downstream increase in flux was far more marked than the change in concentration, both reflecting the increase in flow and implying significant contributions from tributary streams throughout the catchment to the PAH burden of the Wyre. Similar patterns were observed for two- to six-ring PAHs in isolation.

Influence of DOC on Freely Dissolved PAHs. With respect to potential impacts on aquatic biota, concentrations and fluxes of freely dissolved PAHs are likely to be of greater direct importance than total dissolved levels because of their bioavailability.[35] Concentrations of freely dissolved PAHs depend not only on the total flux to the water column but also, given the high affinity of PAHs to DOC, on partitioning between DOC and the aqueous phase. The method we used to determine both fractions separately requires considerable resources and restricts the number of samples that can be analyzed. If the PAHs' DOC-water partition coefficients (K_{DOC}) can be predicted confidently from relationships available in the literature (see Table SI-4, SI), it should be possible to estimate the concentration of freely dissolved PAHs (c_{free} in ng L^{-1}) from the concentration measurements of total dissolved PAHs (c_{total} in ng L^{-1}) and DOC (DOC in mg L^{-1}) more widely. DOC−water partition coefficients (K_{DOC}) were calculated as follows:

$$K_{DOC} = \frac{10^6 \times (c_{total} - c_{free})}{DOC \times c_{free}} \quad (1)$$

We then regressed K_{DOC} values (on a logarithmic scale) against the compounds' octanol−water partition coefficient K_{OW}, which is more readily available from the literature for many chemicals.

Assuming an analytical uncertainty of 10%, log K_{DOC} values below ca. 4 could not be calculated reliably due to the relatively low DOC concentrations occurring in our study streams, because the difference between c_{free} and c_{total} was too small and the subtraction of c_{free} from c_{total} often resulted in negative values. We therefore excluded methylnaphthalenes, dimethyl-naphthalenes, trimethylnaphthalene, acenaphthene, and ace-naphthylene from these comparisons. Regression of log K_{DOC}

against literature K_{OW} (see Table SI-5 and SI-2, SI) for the remaining data set resulted in a slope of 0.81 and intercept of 0.55, both of which are within the range reported in the literature (see Table SI-4, SI). Differences between some of the literature values and our data may arise from variations in the chemical composition of DOC; e.g., some of the published data sets include much older groundwater-supplied DOC, DOC from lake sediments, and commercial humic acids that have been shown to be more hydrophobic than most natural DOC.[36] The range of compounds included in the regressions also varies between studies and limits comparability.

According to the regression parameters and corresponding standard errors in Table SI-5 (SI), no significant differences were observed between log K_{DOC}−log K_{OW} relationships determined for individual sampling dates and sites. This does not necessarily exclude some slight sampling date-dependent variations in the complexity/hydrophobicity of the DOC, but the K_{DOC} estimation may simply not be sufficiently precise to detect such subtle differences.

In order to further investigate the significance of DOC levels on PAH concentrations and fluxes in the Wyre water, it was then necessary to consider the likely origin of the dissolved PAHs and other parameters affecting PAH burdens in the water, as these may mask DOC-associated effects or interfere with them.

Origin of Dissolved PAHs. *Emission Sources.* Diagnostic concentration ratios of PAHs are sometimes used to infer possible sources,[4] but they were not very conclusive in the case of our data (see Table SI-6, SI). Some ratios were indicative of a dominance of petrogenic sources, whereas others pointed to pyrogenic sources, even within individual samples. Concentrations of nonalkylated phenanthrene and chrysene exceeded those of their monoalkylated counterparts in all samples by a factor of at least 1.1, and concentrations of alkylated naphthalenes decreased with increasing degree of alkylation. This suggests that pyrogenic sources dominated, but petrogenic sources may have made a minor contribution.[37] Variation in these ratios between sampling events is not consistent across sites. It would therefore appear that a variety of sources are implicated and that no single source dominates the overall signal. This is in agreement with the findings by Katsoyiannis et al.[4] and consistent with the absence of large petrogenic sources in the area. PAHs found in the Wyre system probably originate from a mixture of combustion processes associated with traffic, burning (of both fossil and renewable fuels), and also some small-scale petrogenic and possibly biogenic sources. Medium- to long-range atmospheric transport of PAHs emitted from distant sources is likely to have made a significant contribution, particularly at Marshaw Wyre (site 1), the most remote sampling site, whereas sites 4 and 5 would be expected to receive a greater proportion of their overall PAH load from local inputs, due to the closer proximity to roads and residential and small industrial areas.

Supply Pathways of PAHs to the Stream. Linear regression analysis was used to model the concentrations of dissolved PAHs in the water on the basis of their molecular weight (MW), DOC concentration (DOC) and an interaction term between those two

$$C_{PAH,norm-ind} = a + b\frac{DOC}{\overline{DOC}} + c \times MW + d\frac{DOC}{\overline{DOC}}MW \quad (2)$$

or

$$C_{\text{PAH,norm}-\text{all}} = a + b \times \text{DOC} + c \times \text{MW}$$
$$+ d \times \text{DOC} \times \text{MW} \qquad (3)$$

where $C_{\text{PAH,norm}-\text{ind}}$ and $C_{\text{PAH,norm}-\text{all}}$ are total dissolved PAH concentrations that have been normalized to the average concentration of the respective PAH during all sampling dates at either individual or all sites, respectively. As concentrations of PAHs in the environment vary greatly between different compounds as a result of their relative abundance in PAH-containing emissions, normalization was necessary in order to include all compounds in one model. Normalized data were then square-root-transformed to obtain a normally distributed data set. Modeled $C_{\text{PAH,norm}}$ were subsequently back-transformed by squaring and then multiplying by the normalization factors to estimate absolute concentrations. $\overline{\text{DOC}}$ represents the average DOC concentration during all sampling events at individual sites and was necessary to allow for estimation of $C_{\text{PAH,norm}-\text{ind}}$ across all sites within the one model. MW is the molecular weight of PAHs and a, b, c, and d are the regression coefficients. Equation 2 provides a tighter fitting model than eq 3 but requires sufficient site-specific supporting PAH data. Equation 3 is necessary for sites where such data are not available. Equation 2 therefore has the greater potential with respect to modeling temporal variation at sites of interest, but eq 3 could be used for coarser prediction of downstream spatial variation.

The molecular weight may not directly control PAH concentrations in the water. However, physicochemical properties such as the octanol−water partition coefficient, Henry's law coefficient, and aqueous solubility are strongly exponentially related to the molecular weight.[38,39] Given the uncertainties associated with these properties, as reported in the literature, molecular weight was applied here as an effective surrogate variable, and we found strong correlations between molecular weight and total dissolved PAHs using a linear model.

Figure 3 shows the regression surface obtained when all $C_{\text{PAH,norm}-\text{ind}}$ data are included. All coefficients are highly significant, as the p values presented in Table SI-7 (SI) show. Figure 4 illustrates the experimental data that Figure 3 is based on, separated according to the number of rings. These figures suggest that concentrations of low molecular weight (LMW) PAHs (two or three aromatic rings) decrease with increasing DOC concentration, medium molecular weight (MMW) PAHs (four aromatic rings) are not or are only slightly influenced by DOC, whereas concentrations of high molecular weight (HMW) PAHs (five and more rings) increase with increasing DOC concentration. Regression surfaces very similar to Figure 3 were obtained for individual sites (see Table SI-7 for regression coefficients and their p-values and Figure SI-3a−e, SI).

We were unable to explain the negative relationship between DOC and LMW-PAHs, so we repeated the analysis after removing data collected for two- and three-ring PAHs during the December sampling event, when relatively high concentrations of these compounds were observed. In the remaining data set, the DOC-dependence of LMW-PAHs is reduced considerably [see Figure 4a,b; also compare Figure SI-3f (SI) and Figure 3], suggesting that the relationship is coincidental rather than causal.

Normalizing PAH concentrations to the average measured at individual sites not only removes most of the variability resulting from differences in DOC concentrations between sites
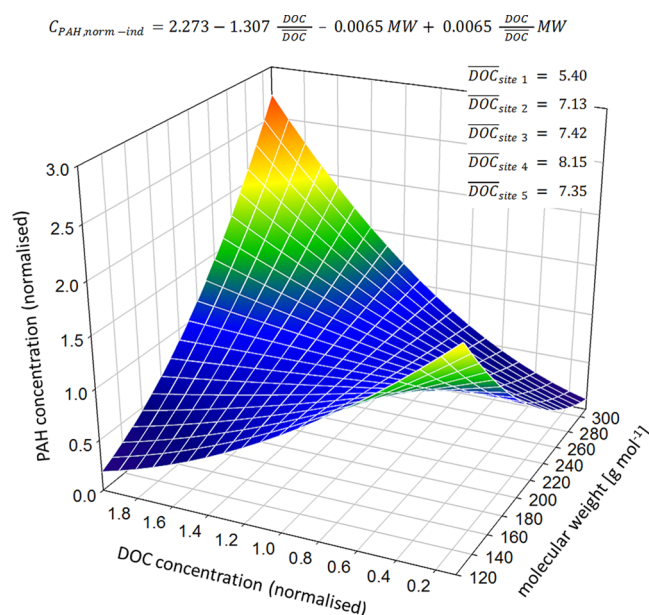
$$C_{\text{PAH,norm}-\text{ind}} = 2.273 - 1.307\frac{DOC}{\overline{DOC}} - 0.0065\,MW + 0.0065\frac{DOC}{\overline{DOC}}MW$$

$\overline{DOC}_{\text{site 1}}$	= 5.40
$\overline{DOC}_{\text{site 2}}$	= 7.13
$\overline{DOC}_{\text{site 3}}$	= 7.42
$\overline{DOC}_{\text{site 4}}$	= 8.15
$\overline{DOC}_{\text{site 5}}$	= 7.35

Figure 3. Surface illustrating the regression between normalized total dissolved PAH concentrations and both normalized DOC concentrations and the PAHs' molecular weight, including all sampling sites and dates.

but also controls for variability in PAH concentrations between sites that may result from the proximity of sampling sites to emission sources.

The regression analysis illustrated in Figure 3 was then repeated, but this time using PAH concentrations that had been normalized to the average during all sampling events and at all sites for each individual compound, retaining site-specific variations of PAH concentrations. In this case DOC concentrations were not normalized. As Figure SI-3g (SI) shows, this results in a very similarly shaped regression surface but a higher standard error compared to the model represented in Figure 3, indicating that site-specific differences not related to DOC concentrations also have an important influence on PAH concentrations in the streamwater.

Estimating PAH fluxes. By applying the relationship between concentrations of DOC and HMW-PAHs shown in Figure SI3-f (SI) we estimated average annual HMW-PAH fluxes at sites 1, 2, and 5. Fluxes of the sum of five-, six-, and seven-ring PAHs considered in this study were estimated at 24, 120, and 330 g year^{-1} at sites 1, 2 and 5, respectively (see SI for more details). Normalized by the catchment area feeding each site, this corresponds to 5.44, 2.46, and 2.92 g km^{-2} year^{-1} compared to catchment-area-normalized DOC fluxes of 68.3, 14.8, and 16.8 t km^{-2} year^{-1}. The relatively high DOC:HMW-PAH flux ratios at site 1 compared to sites 2 and 5 might reflect a lower HMW-PAH soil burden at this most remote site. As the system is used for drinking water abstraction, it may be important to consider such estimates, given that the chlorination often carried out in water treatment plants can generate chlorinated PAHs that have much higher toxicity than their parent compounds.[40]

Implications. The concentrations of dissolved PAHs found in the current study were relatively low compared to the range reported for other freshwater systems worldwide and are unlikely to be causing measurable adverse effects to aquatic biota.[33] However, in addition to the statistical model presented before, our findings lead to a number of implications that

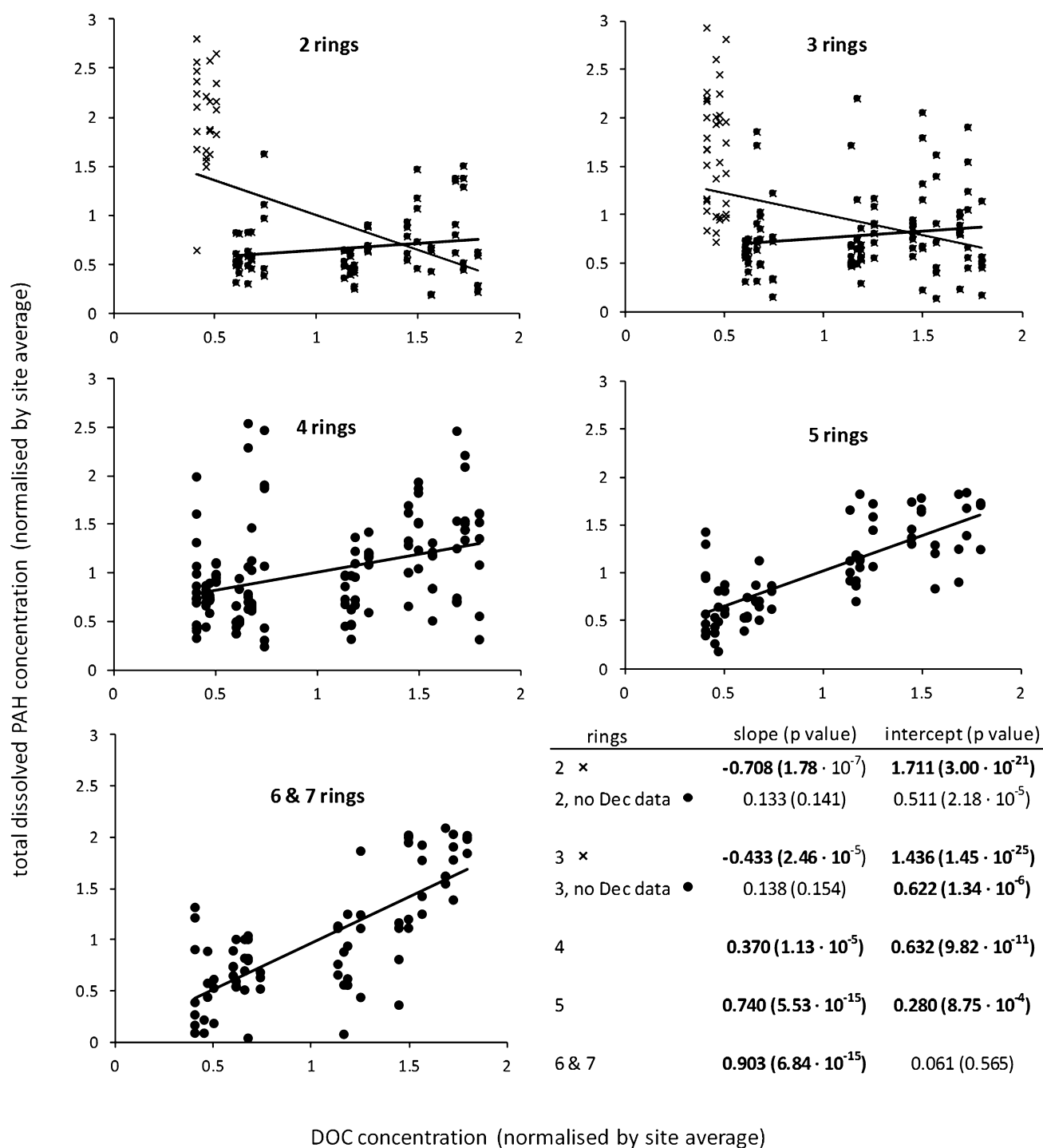| rings	slope (p value)	intercept (p value)
2 ×	-0.708 (1.78 · 10^{-7})	1.711 (3.00 · 10^{-21})
2, no Dec data ●	0.133 (0.141)	0.511 (2.18 · 10^{-5})
3 ×	-0.433 (2.46 · 10^{-5})	1.436 (1.45 · 10^{-25})
3, no Dec data ●	0.138 (0.154)	0.622 (1.34 · 10^{-6})
4	0.370 (1.13 · 10^{-5})	0.632 (9.82 · 10^{-11})
5	0.740 (5.53 · 10^{-15})	0.280 (8.75 · 10^{-4})
6 & 7	0.903 (6.84 · 10^{-15})	0.061 (0.565)

Figure 4. Correlation between concentrations of PAHs (total dissolved) and DOC (both normalized by site average).

should be considered when interpreting monitoring data on PAHs in upland streams with regard to the potential risks these environmental pollutants pose to sensitive aquatic organisms and human water supplies.

First, the input of light PAHs (two- and three-ring and most four-ring PAHs) to the water body does not seem to be linked to the input of DOC. Because of their relatively low affinity for DOC, these PAHs will partition into the streamwater once they leach out of the soil together with organic matter that becomes DOC at this time. Nevertheless, total dissolved PAHs were taken into account here and would be expected to correlate with DOC if both originated from the same pool and their

inputs to the water system were related. Therefore, DOC and light PAHs are either not delivered to the water from the same sources or, if they are, the parameters driving their release differ. Instead a major fraction of these PAHs would seem likely to enter the surface water via direct dry or wet deposition from the air to soils, vegetation, and water surfaces. This hypothesis seems most plausible for two- and three-ring PAHs, but also for some of the more volatile four-ring PAHs (e.g., fluoranthene and pyrene), whereas less volatile and water-soluble ones such as benz[a]anthracene and chrysene show a greater similarity with five-ring PAHs regarding their affinity for DOC. Our observations may illustrate the importance of direct or runoff-

mediated input of light PAHs from the air to drainage waters in this type of surface-water-dominated hydrological system.

Second, the regression analysis suggests that the molecular weight of PAHs, or closely related physicochemical parameters, is important in determining which route of supply to surface waters dominates, i.e., atmospheric deposition and direct runoff, or release from soils, either in association with DOC or simultaneously with DOC to re-establish the equilibrium of the PAH between particulate, DOC-bound, and freely dissolved phases. For medium-volatile PAHs (e.g., fluoranthene, pyrene, benz[*a*]anthracene and chrysene) both pathways are likely to play a significant role. While we acknowledge that a single year of sampling may not be representative of longer term behavior, the apparent "seasonality" in concentrations of dissolved LMW-PAHs is indicative of seasonal variation in the atmospheric bulk deposition due to variations in emissions or in the removal efficiency of the compounds from the air due to annual temperature and rainfall variations. Increased atmospheric bulk deposition of PAHs during winter months has been reported in the literature and was found to be strongest for LMW-PAHs.[41,42] Reduced degradation during the cold winter months may play a role too. Spatial differences are probably caused by the number and strength of emission sources in the vicinity of the sampling sites.

Third, input of HMW-PAHs can be linked to DOC inputs, and it would seem intuitive that they are released together or simultaneously from the soil into the water. Atmospheric bulk deposition of HMW-PAHs may undergo similar seasonal variations to those of LMW-PAHs.[41,42] However, variation in the concentrations of DOC that mediates the transfer of HMW-PAHs into the dissolved phase appears to dominate over seasonal variation in atmospheric deposition. Spatial differences in HMW-PAH concentrations are most likely related to sources in the vicinity of the sampling sites, emitting PAHs that are deposited to soils directly or indirectly via vegetated surfaces. The large surface area of plants and their waxy cuticles provide a large temporary storage capacity for hydrophobic compounds, and this pathway may dominate over direct deposition to soils.

Fourth, the strong correlation between concentrations of DOC and HMW-PAHs suggests that the molecular composition and, hence, the sources of DOC at individual sites were fairly similar during all four sampling events. Residual temporal variability, unexplained by DOC concentration, may have resulted from variations in the chemical composition of the DOC or a higher input of airborne, particle-bound HMW-PAHs during colder months, when the burning of coal and wood for domestic and industrial heating is highest. The average age of the DOC may also vary slightly between sampling dates. Generally, DOC in waters draining physically intact upland soils is mostly of recent origin[43,44] and is therefore derived largely from organic matter situated close to the soil surface. However, organic matter at greater depths within wet organic soil profiles may contribute more to total DOC export, following periods of drought if lower water tables stimulate its reoxidation. Such DOC is older and usually more recalcitrant than that formed from surficial organic matter.[44] Organic matter at intermediate depths may be expected to be most contaminated by PAHs, since it was formed during periods of higher deposition rates of HMW-PAHs. However, this fraction of the pollutant legacy is likely to be relatively stable in the absence of significant soil erosion and/or an increase in the occurrence of wet–dry cycles.

In recent decades, PAH emissions from electricity production, domestic heating, and transport have decreased substantially, resulting in a significant reduction in deposition.[45] Further comparable shifts in fuel use or emission control measures are not expected, and contemporary atmospheric fluxes of PAHs are therefore unlikely to change dramatically in the near future. However, as alternative noncombustion energy sources gradually replace fossil fuels, PAH fluxes to catchments such as the River Wyre should continue to decline over the next few years. Our results suggest that aqueous concentrations of LMW-PAHs should respond faster to changes in atmospheric concentrations than HMW-PAHs, since they appear to experience a more direct air–water transfer.

Given the link between widely observed rising concentrations of DOC over the past 2 decades and recovery from acidification,[13] an increasingly large proportion of organic matter fixed by net primary production is likely to be exported fluvially, relative to other carbon pathways (i.e., mineralization and loss as CO_2 or incorporation in the soil profile). The significant link our study shows between the release of heavy PAHs and DOC from soil may therefore be expected to have resulted in an overall slower reduction of concentrations and fluxes of total and freely dissolved PAH than the decrease in atmospheric inputs during the same period would suggest. It is even possible that the rise in DOC has increased the HMW-PAH aquatic flux in these systems in the short term. Regarding the freely dissolved fraction, this attenuated temporal reduction rate of PAH concentrations is expected to have weakened with increasing K_{DOC}. Clearer understanding of current trajectories and future threats of PAHs to upland water quality would only be achievable through the introduction of low-scale monitoring of representative systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Method details including a map of the sampling sites; GC–MS analysis; recovery statistics and PAH flux estimation; diagnostic PAH ratios and additional information on regression surfaces; and literature data on log K_{OW}, surface water PAH, and DOC concentrations and on log K_{DOC}–log K_{OW} relationships. The full data set of PAH and DOC concentration measured in this study can be found under http://doi.org/10.5285/24200DBA-D0F4-4BE4-AE6F-2C6EC1147FA4. This material is available free of charge via the Internet at http://pubs.acs.org

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