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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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Abstract

Concentrations of total and freely dissolved polycyclic aromatic hydrocarbons (PAHs) and dissolved organic carbon (DOC) were measured in water collected during 4 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 analysed 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 less rings and DOC. Concentrations of PAHs with 4+ rings showed similar seasonal variation to DOC concentration (peaking in the late Summer), while variation in 2-3 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 two 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 by-products 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 gasses or by volatilisation, and can be transported over long distances prior to their deposition on 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 to organic matter, e.g. humic substances including humins, humic and fulvic acids, and particularly to their aromatic, and thus non-polar, sites.

Our study area, within the catchment of the river Wyre in northwest England, is characterised 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 remobilised 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 two or more in several regions of northern Europe and North America over the last two 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/semi-urban 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, numbering starts at uppermost site and continues downstream). Clean amber glass bottles with Teflon-line lids were used to collect 5 L water samples for the PAH analysis from each site during each of the four sampling events (19th August 2010, 6th December 2010, 6th March 2011 and 6th June 2011). Additionally, 100 mL samples were collected for DOC analysis. Samples were kept at 4 °C and processed within 48 hours 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 fibre 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 developed by Carter et al.[17].

Analysis of PAHs

Immediately prior to processing, each well-mixed GFF-filtered 5 L sample was divided into two equal sub-samples 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 sub-sample. To isolate freely dissolved PAHs in the second sub-sample, 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 (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 strongest, 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 sub-sample, 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), and liquid-liquid extracted with 80 mL of dichloromethane (DCM) three times . This procedure was repeated with the remainder of each sub-sample. The extracts of both portions were pooled and anhydrous sodium sulphate (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 sulphate. The target compounds were eluted with 10 mL of DCM. After the sub-samples 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 d_{10}-acenaphthene and d_{12}-benz(a)anthracene as internal standards, and analysed for all compounds listed in Table SI-2 and the recovery compounds. Initially we also analysed 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 analysed by GC-MS (excluding naphthalene) as ∑PAH from now on. Details on the GC-MS analysis are given in the Supporting Information.

QA/QC

Method detection limits for the extracts, derived from the lowest or lowest quantifiable calibration standard, ranged from 0.004 – 0.5 ng mL^{-1}, corresponding to ca. 0.001 – 0.09 ngL^{-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). All results were blank- and recovery-corrected.

Results and Discussion

Concentrations of DOC and dissolved PAHs

Concentrations of DOC ranged from 2.2 - 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) 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} (ΣPAHs) and are in the lower range reported for surface water systems internationally (Table SI-3). They are higher than those measured in three European remote mountain lakes[20] but similar to those found at non-urban estuary sites in the eastern USA and western France[21, 22] and lower than in samples taken from large rivers and estuary sites in or downstream of highly populated or industrialised 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), 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 ΣPAHs) are at the lower end of the range of those reported in other river systems (compare Table SI-3). Few data are available for similar streams (i.e. rural to semi-urban, 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 contribution of PAHs by aromatic ring count to the sum of freely dissolved, DOC-associated, and total dissolved PAHs, in the Wyre samples is shown in Figure 1. Overall, the more water-soluble 2- to 4- ring PAHs dominate over the virtually water-insoluble and strongly hydrophobic 5- to 7-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 towards 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 10-15% 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 one order of magnitude over the five sites. Most of this variation is accounted for by the relatively low concentrations in 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, that 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 4 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 2- and 3-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 ∑PAHs were estimated (Figure 2) by combining concentration data with estimates of discharge (data provided by the UK Environment Agency[34] for site 4, 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 2-, 3-, 4-, 5- and 6-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 analysed. If the PAHs' DOC-water partition coefficients (K_{DOC}) can be predicted confidently from relationships available in the literature (see Table SI-4) 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:

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

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, Dimethylnaphthalenes, Trimethylnaphthalene, Acenaphthene and Acenaphthylene from these comparisons. Regression of log K_{DOC} against literature K_{OW} (see Table SI-5 and SI-2) for the remaining dataset 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). 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 datasets 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, 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 were not very conclusive in the case of our data (see Table SI-6). Some ratios were indicative of a dominance of petrogenic sources whereas others pointed to pyrogenic sources, even within individual samples. Concentrations of non-alkylated 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, 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:

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

or

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

where $C_{PAH,norm-ind}$ and $C_{PAH,norm-all}$ are total dissolved PAH concentrations that have been normalised 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, normalisation was necessary in order to include all compounds in one model. Normalised data were then square root transformed to obtain a normally distributed dataset. Modelled $C_{PAH,norm}$ were subsequently back-transformed by squaring and then multiplying by the normalisation factors to estimate absolute concentrations. $\overline{DOC}$ represents the average DOC concentration during all sampling events at individual sites and was necessary to allow for estimation of $C_{PAH,norm\text{-}ind}$ 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 equation 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 modelling temporal variation at sites of interest, but Equation 3 could be used for coarser prediction of down-stream 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 $C_{PAH,norm-ind}$ data are included. All coefficients are highly significant as the p values presented in Table SI-7 show. Figure 4 illustrates the experimental data Figure 3 is based on separated according to the number of rings. These figures suggest that concentrations of low molecular weight (LMW) PAHs (2 - 3 aromatic rings) decrease with increasing DOC concentration, medium molecular weight (MMW) PAHs (4 aromatic rings) are not, or only slightly influenced by DOC, whereas concentrations of high molecular weight (HMW) PAHs (5 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).

We were unable to explain the negative relationship between DOC and LMW PAHs, so repeated the analysis after removing data collected for 2- and 3-ring PAHs during the December sampling event when relatively high concentrations of these compounds were observed. In the remaining dataset, DOC-dependence of LMW PAHs is reduced considerably (see Figure 4a and b, also compare Figure SI-3f and Figure 3), suggesting that the relationship is coincidental rather than causal.

Normalising PAH concentrations to the average measured at individual sites not only removes most of the variability resulting from differences in DOC concentrations between sites 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 normalised 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 normalised. As Figure SI-3g 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 stream water.

Estimating PAH fluxes

By applying the relationship between concentrations of DOC and HMW-PAHs shown in Figure SI3-f we estimated average annual HMW-PAH fluxes at sites 1, 2 and 5. Fluxes of the sum of 5-, 6- and 7-ring PAHs considered in this study were estimated at 24, 120 and 330 g year^{-1} at sites 1, 2 and 5, respectively (see Supporting Information for more details). Normalised 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-normalised 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 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 (2- and 3-ring and most 4-ring PAHs) to the water body does not seem to be linked to the input of DOC. Because of their relatively low affinity to DOC, these PAHs will partition into the stream water 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 2- and 3-ring PAHs, but also for some of the more volatile 4-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 5-ring PAHs regarding their affinity to 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 behaviour, 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 non-combustion 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.

However, given the link between widely observed rising concentrations of DOC over the past two 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. mineralisation 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.

Supporting Information Available

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. This information is available free of charge via the Internet at http://pubs.acs.org

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Figures

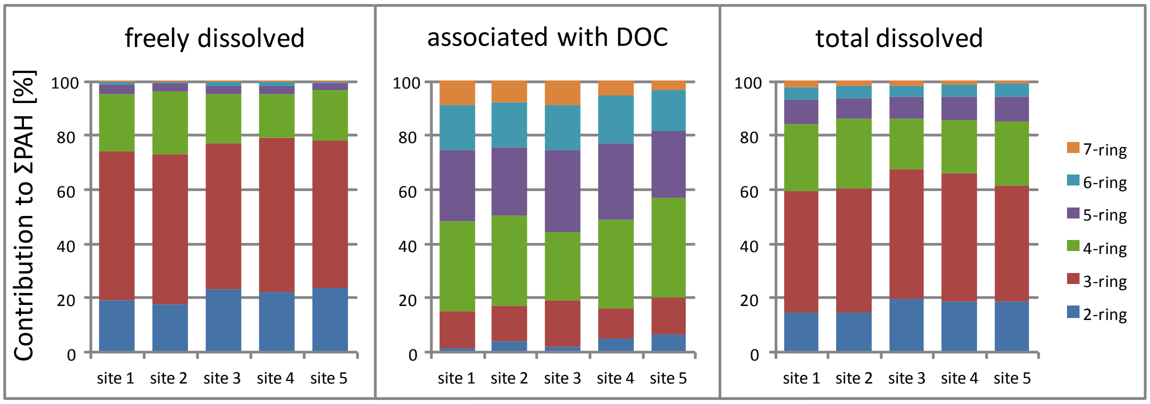


Fig. 1: Contribution of 2- to 7-ring PAHs to the sum of freely dissolved, DOC-associated and total dissolved PAHs (average of all four sampling dates)

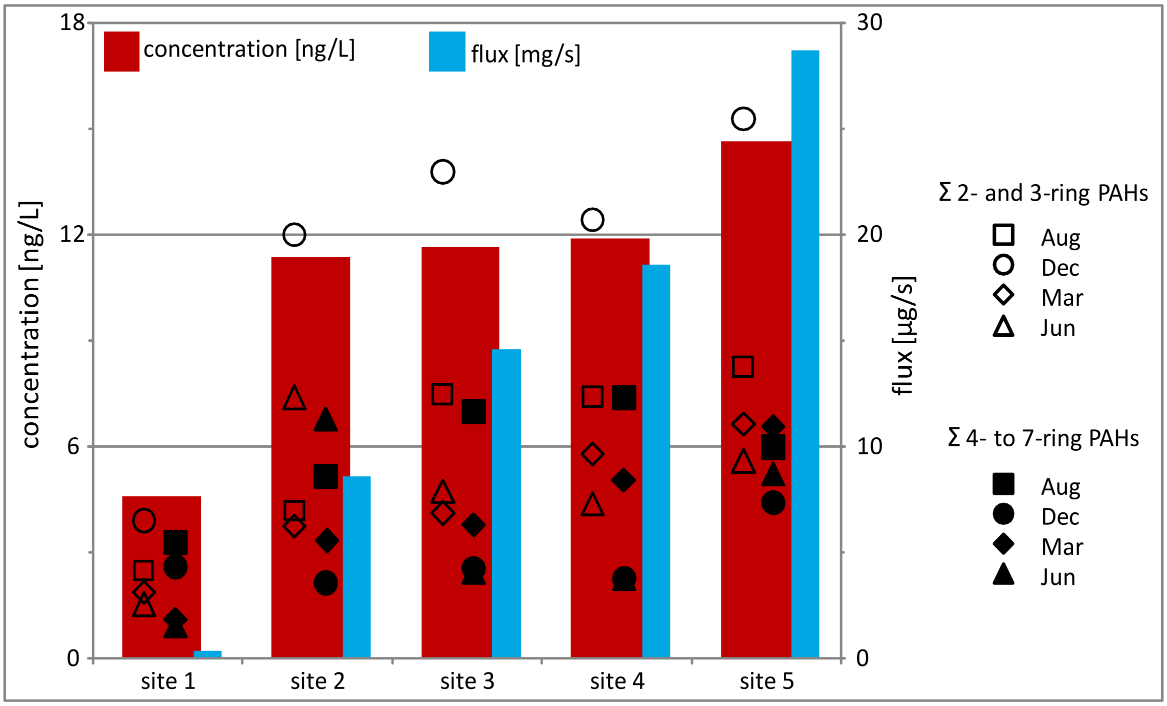


Figure 2: Total dissolved concentrations and fluxes of the sum of all PAHs measured in the water samples (bars represent averages for all four sampling events, symbols show concentrations of the sum of 2- and 3-ring PAHs and of 4- to 7-ring PAHs during individual sampling events).

$$C_{PAH,norm-ind} = 2.273 - 1.307\,\frac{DOC}{DOC} - 0.0065\,MW + 0.0065\,\frac{DOC}{DOC}\,MW$$

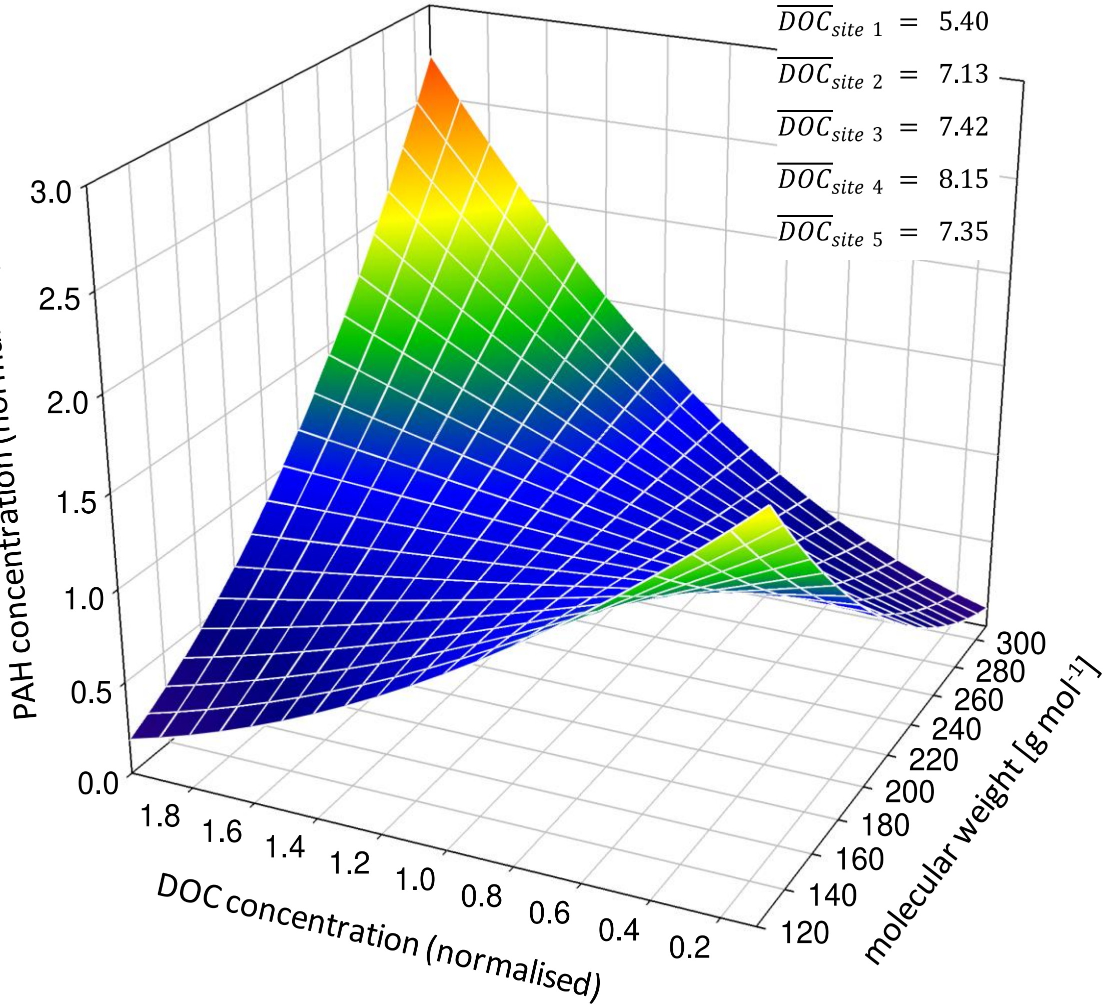
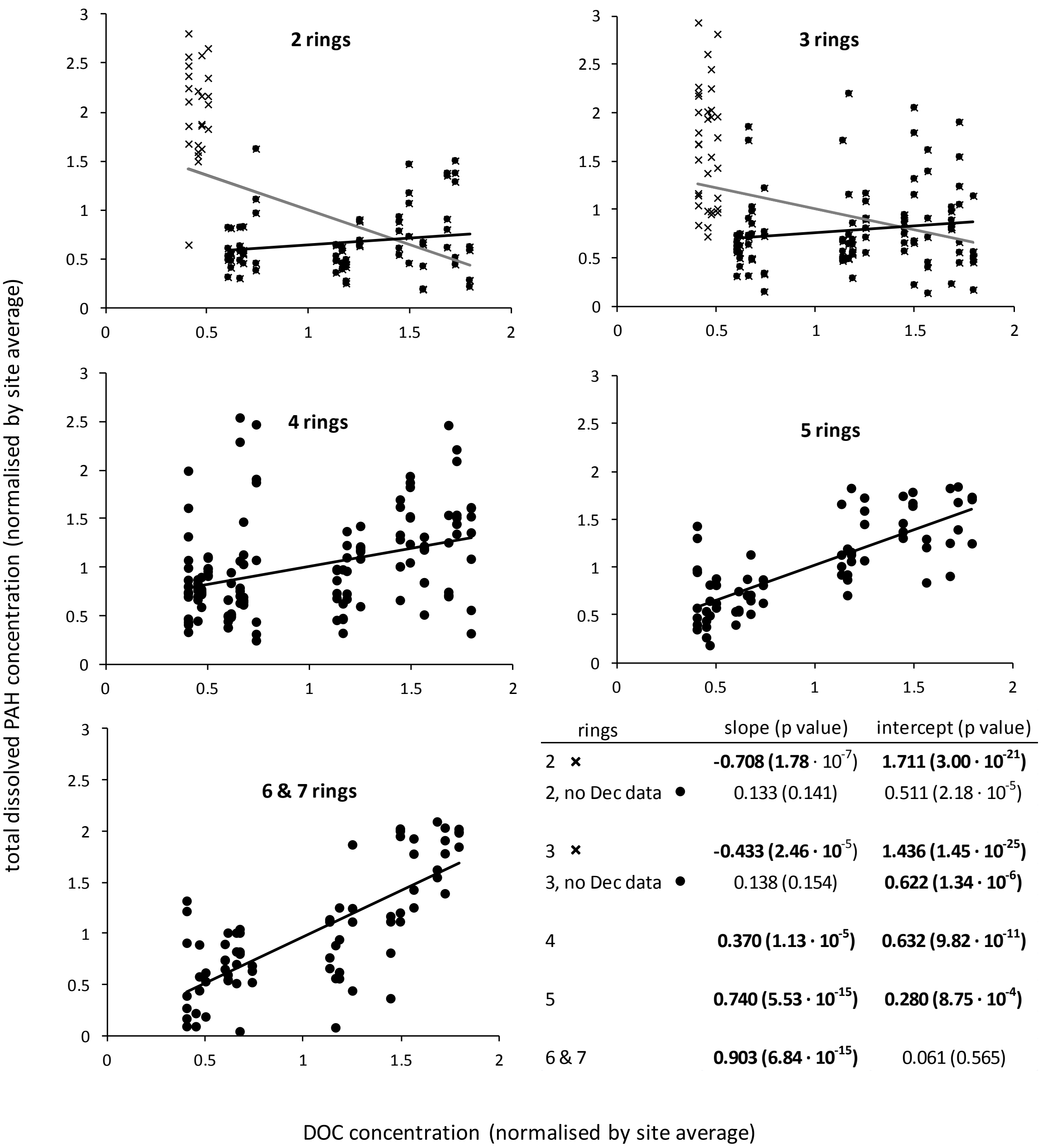


Figure 3: Surface illustrating the regression between normalised total dissolved PAH concentrations and both normalised DOC concentrations and the PAHs' molecular weight, including all sampling sites and dates.



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

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

Relationship between the concentrations of dissolved organic matter and polycyclic aromatic hydrocarbons in a typical U.K. upland stream

SUPPORTING INFORMATION

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Contents

GC-MS analysis

The analysis was carried out on an Agilent GC 6890N coupled to an Agilent MSD 5973N. 20 µL of the extracts were injected in solvent vent mode and separated on a HT8 column (SEG, 50 m, 0.22 mm I.D., 0.25 µm film thickness) with helium as the mobile phase at a constant flow of 2 mL min^{-1}. The programmable temperature vaporization (PTV) inlet was kept at 20 °C for 0.51 min, then heated to 350 °C at a rate of 700 °C min^{-1} and kept at 350 °C for 5 min. Then the temperature was reduced to 300 °C min^{-1} at a rate of 10 °C min^{-1}. The oven temperature programme was: isothermal at 50 °C for 2.5 min, 15 °C min^{-1} to 200 °C, 5 °C min^{-1} to 250 °C, 8 °C min^{-1} to 330 °C and was held at 330 °C for 25.5 min. The transfer line was heated to 350 °C. The MS detector was operated in EI-mode, using selected ion monitoring, the quadrupole temperature was set to 150 °C and the ion source temperature to 230 °C.

Estimation of monthly and annual PAH fluxes

Annual fluxes of HMW PAHs at the sampling sites studied were estimated using their relationship with DOC described in Table SI-6 (the regression including all sites and all data except for the concentrations of 2- and 3-ring PAHs during the second sampling event) and shown in Figure SI-3f as this seemed to be the most appropriate regression.

The estimation is based on a method that has previously been used to estimate DOC fluxes from water flow rates. It requires a set of known DOC concentrations and corresponding flow rates and after calculating DOC fluxes from these concentrations, a regression between the logarithm of DOC fluxes and the logarithm of the flow rate is performed. According to Scholefield (pers. comm.), from the intercept, slope and mean square residual of this regression DOC concentrations can be estimated for other times when only flow rate data is available, using the equation:

$$logF_{DOC} = (slope \cdot \log flow\,rate + intercept) \cdot e^{2.65 \cdot mean\ square\ residual} \qquad (1)$$

The same method was applied to PAH fluxes. First the known DOC concentrations (as shown in Figure SI-2) were used to estimate PAH concentrations using the regression mentioned above, then PAH fluxes were calculated from the concentrations and the corresponding water flow rates (UK Environment Agency, 2011), and a linear regression was calculated between the logarithmised fluxes and water flows. Finally, for times no measured PAH data was available for, the regression parameters obtained (see Table SI-8) were used to estimate PAH fluxes in the same way as shown for DOC fluxes in equation 1. As DOC concentration data was available only at sites 1, 2 and 5 (Scholefield et al. 2013) fluxes could be estimated only for these three sites. Detailed results for monthly and annual fluxes of 5-, 6- and 7-ring PAHs are shown in Table SI-9.

Table SI-1: Recovery statistics of water samples analysed in this study.

	average [%]	min [%]	max [%]	RSD [%]
Naphthalene-d_8	60	30	80	17
Acenaphthylene-d_8	77	47	111	16
Phenanthrene-d_{10}	77	52	101	13
Fluoranthene-d_{10}	107	85	125	10
Pyrene-d_{10}	107	84	127	11
Benzo(a)pyrene-d_{12}	98	82	111	9
Benzo(g,h,i)perylene-d_{12}	106	76	126	11

Table SI-2: Log K_{OW} used for regressions.

	log K_{OW}	reference
2-Methylnaphthalene	3.86	Mackay, 2006
1-Methylnaphthalene	3.87	Mackay, 2006
2,7-Dimethylnaphthalene	4.4	Luellen and Shea, 2002
1,2-Dimethylnaphthalene	4.31	Mackay, 2006
Acenaphthylene	4.00	Mackay, 2006
Acenaphthene	3.92	Mackay, 2006
Trimethylnaphthalene	4.9	Luellen and Shea, 2002
Fluorene	4.18	Mackay, 2006
Phenanthrene	4.57	Mackay, 2006
Anthracene	4.54	Mackay, 2006
2-Methylphenanthrene	5.24	Sangster, 1989
1-Methylphenanthrene	5.08	Sangster, 1989
Fluoranthene	5.22	Mackay, 2006
Pyrene	5.18	Mackay, 2006
Methylpyrene	5.72	Neff and Burns, 1996
Benz(a)anthracene	5.91	Mackay, 2006
Chrysene	5.60	Mackay, 2006
6-Methylchrysene	6.2	Luellen and Shea, 2002
1-Methylchrysene	6.2	Luellen and Shea, 2002
Benzo(b+k)fluoranthene	5.90	Mackay, 2006
Benzo(a)pyrene	6.04	Mackay, 2006
Perylene	6.25	Mackay, 2006
Dibenz(a,h)anthracene	6.50	Mackay, 2006
Indeno(1,2,3-c,d)pyrene	6.65	ACD/Labs, 2011
Benzo(g,h,i)perylene	6.50	Mackay, 2006
Anthanthrene	not available	
Dibenzo(a,e)pyrene	not available	
Coronene	6.75	Mackay, 2006

Table SI-3: Concentrations of freely and total dissolved PAHs (ng L^{-1}) in surface waters worldwide. All literature data on freely dissolved PAHs was determined using passive sampling devises.

	Fluorene	Phenanthrene	Fluoranthene	Pyrene	Chrysene	Benz(a)-anthracene	Indeno(1,2,3-c,d)-pyrene	Benzo(ghi)-perylene	Sum PAH^a	description of waterbody/sampling site	reference
freely dissolved	**0.77**	**1.88**	**0.77**	**0.79**	**0.14**	**0.07**	**0.05**	**0.12**	**6.30**	Wyre, U.K., rural - semiurban	this study
	0.40	0.81	2.80	6.10	0.42	0.26	0.02	0.03	11.90	Oslo Harbour, Norway	Cornelissen et al., 2008
	0.89	2.60	3.20	8.30	0.67	0.17	0.09	0.17	18.90	Oslo Alna River, Norway	Allan and Ranneklev, 2011
	2.21	7.06	5.26	5.66	4.98	0.70	1.05	1.75	33.80	Three Gorges Reservoir, China	Wang et al., 2009
	2.11	8.97	4.08	4.09	0.55	0.36	0.16	0.19	23.77	Seine (upstream of Paris), France	Tusseau-Vuillemin et al., 2007
		0.49	0.78	0.54	0.10	0.03	0.01	0.01		streams in the vicinity of highways, 200 km east of Melbourne, Australia	Schaefer et al., 2010
	6.83	5.51	4.36	6.36	0.99	0.14	0.12	0.08	29.89	Bilina River, Czech Republic, urban-semiurban	Blahova et al., 2011
	1.02	4.21	1.64	1.05	0.11				8.48	Reservoirs in Guangdong province, China	Bao et al., 2012
	0.53	1.43	1.64	1.21	2.82	0.03	0.02	0.02	9.23	Gulf of Mexico coastal water (concentrations slightly elevated due to the Deepwater Horizon oil spill)	Allan et al., 2012
		9.00		7.50						Boston Harbour, USA	Adams et al., 2007
total dissolved	**0.75**	**1.92**	**1.04**	**0.87**	**0.38**	**0.15**	**0.21**	**0.24**	**7.72**	Wyre, U.K., rural - semiurban	this study
	0.03	0.14	0.07	0.03	0.05	0.00	0.01	0.00		remote mountain lakes, Spain and Austria	Vilanova et al., 2001
		1.60	1.40	2.80	0.90	0.30	0.20	0.30		Seine estuary, France	Cailleaud et al., 2007
	2.57	3.90	0.28	0.23	0.04	0.01	0.01	0.01	8.20	Chesapeake Bay (Wolftrap, rural), USA	Gustafson and Dickhut, 1997
	1.16	2.22	0.86	0.53	0.12	0.01	0.00	0.01	7.00	Chesapeake Bay (York River, semiurban), USA	Gustafson and Dickhut, 1997
	1.54	2.88	11.27	5.41	0.84	0.05	0.02	0.02	26.60	Chesapeake Bay (Elizabeth River & Hampton, urban), USA	Gustafson and Dickhut, 1997
	3.83	6.58	2.60	1.09	0.68				18.20	Luan River and tributaries, China	Bai et al., 2008
	1.73	4.60	3.34	3.10	0.40	0.27	0.93	0.60	31.30	Seine (upstream of Paris), France	Tusseau-Vuillemin et al., 2007
	6.81	17.80	5.23	4.53	1.85	0.42	0.21	0.35	45.40	Pearl River Estuary, China	Luo et al., 2008
		8.83	3.08	5.20	1.28					Seine River and Estuary, France	Fernandes et al., 1997
	11.00	47.00	4.80	4.60	12.00	0.60		0.80	141.00	Esthwaite Water, U.K.	Gevao et al., 1998
	12.20	17.90	5.24	3.58	0.64	0.33		1.00	59.60	Xijiang River, China	Deng et al., 2006
			6.48			9.00	9.74	7.30		River Tiber (urban), Italy	Patrolecco et al., 2010
	10.98	28.03	1.96	12.88	7.39	12.81	0.41	1.76	98.78	Reservoirs in Guangdong province, China	Bao et al., 2012

[a] sum of Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenz(a,h)anthracene, Indeno(1,2,3-c,d)pyrene and Benzo(g,h,i)perylen

Table SI-4: Literature data: regression parameters describing the relationship between log K_{DOC} and log K_{OW}.

slope	intercept	notes	reference
0.27	3.83	commercial humic acid, 10 mg/L	King et al., 2004
1.18	-1.56	naturally occuring DOC	Burkhard, 2000
0.97	-1.27	surface water DOC, includes PAHs and other non-ionic substances	Burkhard, 2000
1.23	-0.91	commercial humic acid	ter Laak et al., 2005
0.58 - 1.12	-2.00 - 1.04	sediment pore water, freshwater harbour	Hawthorne et al., 2005
0.88 - 1.17	-0.06 - 1.18	sediment pore water	Haftka et al., 2010
1.16	0.60	river water DOC (includes only 3 PAHs)	Xia et al., 2013
0.77	0.71	commercial humic acid	Li and Lee, 2000
0.40 - 0.84	0.41 - 2.34	lake water DOC	Mei et al., 2009
0.77	1.07	commercial humic acid	Brown and Peake, 2003
0.19	2.89	stream water DOC	Brown and Peake, 2003
-0.86 - 0.49	4.47 - 9.65	reservoir water DOC	Bao et al., 2012
0.77 - 1.2	-1 - 1.39	commercial humic acids	Krop et al., 2001
0.34	2.9	humic acids from natural waters, includes PAHs and other non-ionic substances	Krop et al., 2001
-0.03	4.9	river water DOC, includes PAHs and other non-ionic substances	Krop et al., 2001
-0.08 - 0.13	5.26 - 6.61	river water DOC (Seine, upstream Paris), includes all PAHs measured	Tusseau-Vuillemin et al., 2007
0.22 - 0.45	3.17 - 4.33	river water DOC (Seine, upstream Paris), excluding PAHs with log $K_{\mathrm{OW}} < 4.5$	Tusseau-Vuillemin et al., 2007

Table SI-5: Parameters describing the regressions between experimental log K_{DOC} and literature log K_{OW}.

		Coefficient	Std. Error	p
all sites, all dates	A	0.55	0.33	0.093
	B	**0.81**	0.06	<0.0001
all sites, Aug	A	0.32	0.55	0.5606
	B	**0.82**	0.09	<0.0001
all sites, Dec	A	1.17	0.70	0.0991
	B	**0.68**	0.12	<0.0001
all sites, Mar	A	0.57	0.62	0.3627
	B	**0.83**	0.11	<0.0001
all sites, Jun	A	**1.49**	0.49	0.0031
	B	**0.67**	0.08	<0.0001
site 1, all dates	A	**2.67**	0.91	0.0052
	B	**0.47**	0.16	0.0044
site 2, all dates	A	0.41	0.69	0.5556
	B	**0.84**	0.12	<0.0001
site 3, all dates	A	0.22	0.66	0.7379
	B	**0.82**	0.11	<0.0001
site 4, all dates	A	0.40	0.52	0.4499
	B	**0.82**	0.09	<0.0001
site 5, all dates	A	0.66	0.51	0.1989
	B	**0.82**	0.09	<0.0001

Note: Methylnaphthalenes, Dimethylnaphthalenes, Trimethylnaphthalene, Acenaphthene and Acenaphthylene were excluded from these regressions (see main text for details).

Table SI-6: Diagnostic PAH ratios – literature values (Katsoyiannis et al., 2011) and values obtained for Wyre water samples.

		Ant/(Ant+Phe)	BaA/(BaA+Chr)	Flt/(Flt+Pyr)	Ind/(Ind+BghiP)	BaP/BghiP
petrogenic		<0.1	<0.2	<0.4	<0.2	
petro- and pyrogenic			***0.2 - 0.35***			
pyrogenic		**>0.1**	**>0.35**	**>0.4**	**>0.2**	
liquid fossil fuel				**0.4 - 0.5**		
coal/grass/wood				**>0.5** *		
non-traffic						<0.6
traffic						**>0.6**
site 1	Aug	0.05	*0.12*	0.32	**0.48**	0.26
	Dec	0.04	***0.30***	**0.66** *	**0.40**	0.49
	Mar	0.05	*0.15*	**0.58** *	**0.61**	**0.71**
	Jun		**0.41**	**0.55** *	**0.56**	**0.71**
site 2	Aug	0.06	*0.15*	**0.71** *	**0.53**	0.40
	Dec	0.04	***0.31***	**0.59** *	**0.67**	**7.14**
	Mar	0.04	*0.19*	**0.60** *	**0.52**	0.52
	Jun	0.01	0.20	**0.71** *	**0.48**	**0.67**
site 3	Aug	0.05	***0.20***	0.36	**0.43**	0.41
	Dec	0.05	***0.24***	**0.56** *	**0.39**	**0.81**
	Mar	0.02	*0.19*	**0.56** *	**0.53**	**0.65**
	Jun	0.03	***0.20***	**0.65** *	**0.44**	**0.72**
site 4	Aug	0.05	*0.17*	0.38	**0.47**	0.62
	Dec	0.03	***0.26***	**0.55** *	**0.25**	**1.79**
	Mar	0.05	***0.28***	**0.57** *	**0.46**	**0.84**
	Jun	0.05	***0.23***	**0.64** *	**0.45**	0.52
site 5	Aug	0.05	*0.19*	**0.59** *	**0.48**	0.43
	Dec	0.05	***0.29***	**0.55** *	**0.41**	**0.93**
	Mar	0.08	***0.29***	**0.56** *	**0.48**	**0.92**
	Jun	0.08	***0.25***	***0.46***	**0.39**	0.44

Table SI-7: Parameters of regression surfaces discussed.

Data included	**C_{PAH} normalised by**	**regression coefficients (p value)**				**standard error**
		a	**b**	**c**	**d**	
all data	average at individual sites	2.273 (2.7E-71)	-1.307 (3.0E-36)	-0.006 (2.6E-33)	0.006 (3.3E-40)	0.23
all data except for 2- and 3-ring PAHs during sampling event 2	average at individual sites	1.596 (4.0E-34)	-0.568 (1.5E-08)	-0.004 (1.1E-12)	0.004 (2.9E-15)	0.20
all data	average at all sites	2.083 (3.2E-48)	-0.162 (2.7E-22)	-0.006 (4.5E-22)	0.001 (8.7E-28)	0.29
all data from site 1	average at individual sites	1.710 (1.1E-07)	-0.735 (6.2E-03)	-0.003 (1.3E-02)	0.003 (6.1E-03)	0.28
all data from site 2	average at individual sites	2.777 (8.8E-24)	-1.854 (5.4E-17)	-0.008 (7.3E-14)	0.009 (6.2E-17)	0.22
all data from site 3	average at individual sites	2.058 (9.2E-15)	-1.110 (2.4E-07)	-0.006 (1.6E-07)	0.006 (4.2E-09)	0.23
all data from site 4	average at individual sites	2.182 (4.6E-16)	-1.112 (1.6E-07)	-0.007 (3.2E-09)	0.006 (5.2E-10)	0.21
all data from site 5	average at individual sites	2.669 (5.7E-22)	-1.730 (6.4E-14)	-0.008 (3.4E-12)	0.008 (5.4E-14)	0.20

Table SI-8: Parameters of the regression between log PAH flux [ng h^{-1}] and log water flow rate [L h^{-1}].

	Benzo(b+k)fluoranthene	Benzo(a)pyrene	Perylene	Dibenz(a,h)anthracene	Indeno(1,2,3-c,d)pyrene	Benzo(g,h,i)perylene	Anthanthrene	Dibenzo(a,e)pyrene	Coronene
site 1									
slope Feb-Jun	1.11	1.11	1.11	1.15	1.14	1.14	not available	1.18	1.18
intercept Feb-Jun	-1.20	-1.98	-2.01	-2.20	-1.85	-1.84	not available	-2.77	-2.03
MS residual Feb-Jun	0.00	0.00	0.00	0.00	0.00	0.00	not available	0.01	0.01
slope Jul-Jan	1.13	1.13	1.13	1.17	1.17	1.17	not available	1.20	1.20
intercept Jul-Jan	-1.26	-2.04	-2.07	-2.23	-1.89	-1.87	not available	-2.76	-2.03
MS residual Jul-Jan	0.01	0.01	0.01	0.01	0.01	0.01	not available	0.01	0.01
site 2									
slope Feb-Jun	1.07	1.07	1.07	1.09	1.09	1.09	1.09	1.11	1.11
intercept Feb-Jun	-0.69	-1.34	-1.52	-1.97	-1.26	-1.29	-2.11	-2.06	-1.31
MS residual Feb-Jun	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
slope Jul-Jan	1.07	1.07	1.07	1.09	1.09	1.09	1.09	1.11	1.11
intercept Jul-Jan	-0.62	-1.28	-1.46	-1.87	-1.16	-1.19	-2.01	-1.91	-1.16
MS residual Jul-Jan	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
site 5									
slope Jan-Jun	1.07	1.07	1.07	1.09	1.09	1.09	1.09	1.12	1.12
intercept Jan-Jun	-0.61	-1.19	-1.47	-1.50	-1.25	-1.16	-1.78	-2.17	-1.50
MS residual Jan-Jun	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
slope Jul-Dec	1.07	1.07	1.07	1.09	1.09	1.09	1.09	1.11	1.11
intercept Jul-Dec	-0.54	-1.12	-1.39	-1.39	-1.14	-1.05	-1.67	-2.01	-1.35
MS residual Jul-Dec	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table SI-9: Estimated monthly and annual fluxes [g month^{-1} and g year^{-1}] of HMW (5-, 6- and 7-ring) PAHs.

	Benzo(b+k)fluoranthene	**Benzo(a)pyrene**	**Perylene**	**Dibenz(a,h)anthracene**	**Indeno(1,2,3-c,d)pyrene**	**Benzo(g,h,i)perylene**	**Anthanthrene**	**Dibenzo(a,e)pyrene**	**Coronene**	**Sum HMW PAH**
site 1										
Jan	0.83	0.14	0.13	0.15	0.32	0.33	not available	0.07	0.38	2.36
Feb	0.08	0.01	0.01	0.01	0.03	0.03	not available	0.01	0.03	0.21
Mar	0.10	0.02	0.02	0.02	0.04	0.04	not available	0.01	0.04	0.27
Apr	0.05	0.01	0.01	0.01	0.02	0.02	not available	0.00	0.02	0.12
May	0.04	0.01	0.01	0.01	0.01	0.01	not available	0.00	0.02	0.11
Jun	0.03	0.00	0.00	0.00	0.01	0.01	not available	0.00	0.01	0.07
Jul	0.59	0.10	0.09	0.11	0.23	0.23	not available	0.05	0.27	1.66
Aug	0.98	0.16	0.15	0.18	0.38	0.40	not available	0.09	0.46	2.81
Sep	1.27	0.21	0.20	0.24	0.51	0.52	not available	0.12	0.62	3.69
Oct	1.53	0.26	0.24	0.29	0.61	0.63	not available	0.14	0.74	4.44
Nov	1.94	0.32	0.30	0.36	0.77	0.79	not available	0.18	0.93	5.60
Dec	0.97	0.16	0.15	0.18	0.37	0.38	not available	0.09	0.44	2.74
year	8.40	1.40	1.31	1.56	3.29	3.40	not available	0.77	3.94	24.07
site 2										
Jan	3.99	0.88	0.58	0.32	1.59	1.48	0.22	0.40	2.15	11.39
Feb	0.38	0.09	0.06	0.03	0.14	0.13	0.02	0.03	0.18	1.04
Mar	0.48	0.11	0.07	0.04	0.18	0.17	0.03	0.04	0.23	1.31
Apr	0.34	0.08	0.05	0.03	0.13	0.12	0.02	0.03	0.16	0.92
May	0.23	0.05	0.03	0.02	0.08	0.08	0.01	0.02	0.10	0.61
Jun	0.16	0.03	0.02	0.01	0.06	0.05	0.01	0.01	0.07	0.42
Jul	3.89	0.86	0.57	0.31	1.55	1.44	0.22	0.39	2.10	11.11
Aug	4.62	1.02	0.67	0.37	1.86	1.72	0.26	0.47	2.52	13.25
Sep	5.81	1.29	0.84	0.47	2.36	2.19	0.33	0.60	3.23	16.80
Oct	6.99	1.55	1.02	0.57	2.83	2.63	0.40	0.72	3.89	20.19
Nov	8.92	1.98	1.30	0.72	3.61	3.36	0.51	0.91	4.94	25.74
Dec	4.66	1.03	0.68	0.37	1.86	1.73	0.26	0.46	2.51	13.29
year	40.46	8.97	5.88	3.25	16.26	15.11	2.29	4.08	22.07	116.08
site 5										
Jan	2.47	0.65	0.35	0.48	0.83	1.02	0.24	0.15	0.68	6.63
Feb	1.19	0.31	0.17	0.23	0.39	0.48	0.11	0.07	0.32	3.16
Mar	1.49	0.39	0.21	0.28	0.49	0.61	0.14	0.09	0.40	3.97
Apr	1.06	0.28	0.15	0.20	0.35	0.43	0.10	0.06	0.28	2.79
May	0.70	0.18	0.10	0.13	0.23	0.28	0.07	0.04	0.18	1.85
Jun	0.48	0.13	0.07	0.09	0.16	0.19	0.05	0.03	0.13	1.28
Jul	11.82	3.11	1.66	2.39	4.15	5.11	1.21	0.81	3.57	32.62
Aug	14.04	3.69	1.98	2.86	4.96	6.10	1.45	0.97	4.29	38.87
Sep	17.68	4.65	2.49	3.63	6.31	7.75	1.84	1.24	5.51	49.26
Oct	21.26	5.59	2.99	4.37	7.58	9.32	2.21	1.50	6.62	59.23
Nov	27.13	7.13	3.82	5.56	9.66	11.88	2.82	1.90	8.41	75.50
Dec	14.15	3.72	1.99	2.86	4.97	6.10	1.45	0.96	4.26	39.01
year	113.47	29.81	15.97	23.07	40.08	49.27	11.69	7.83	34.66	314.16

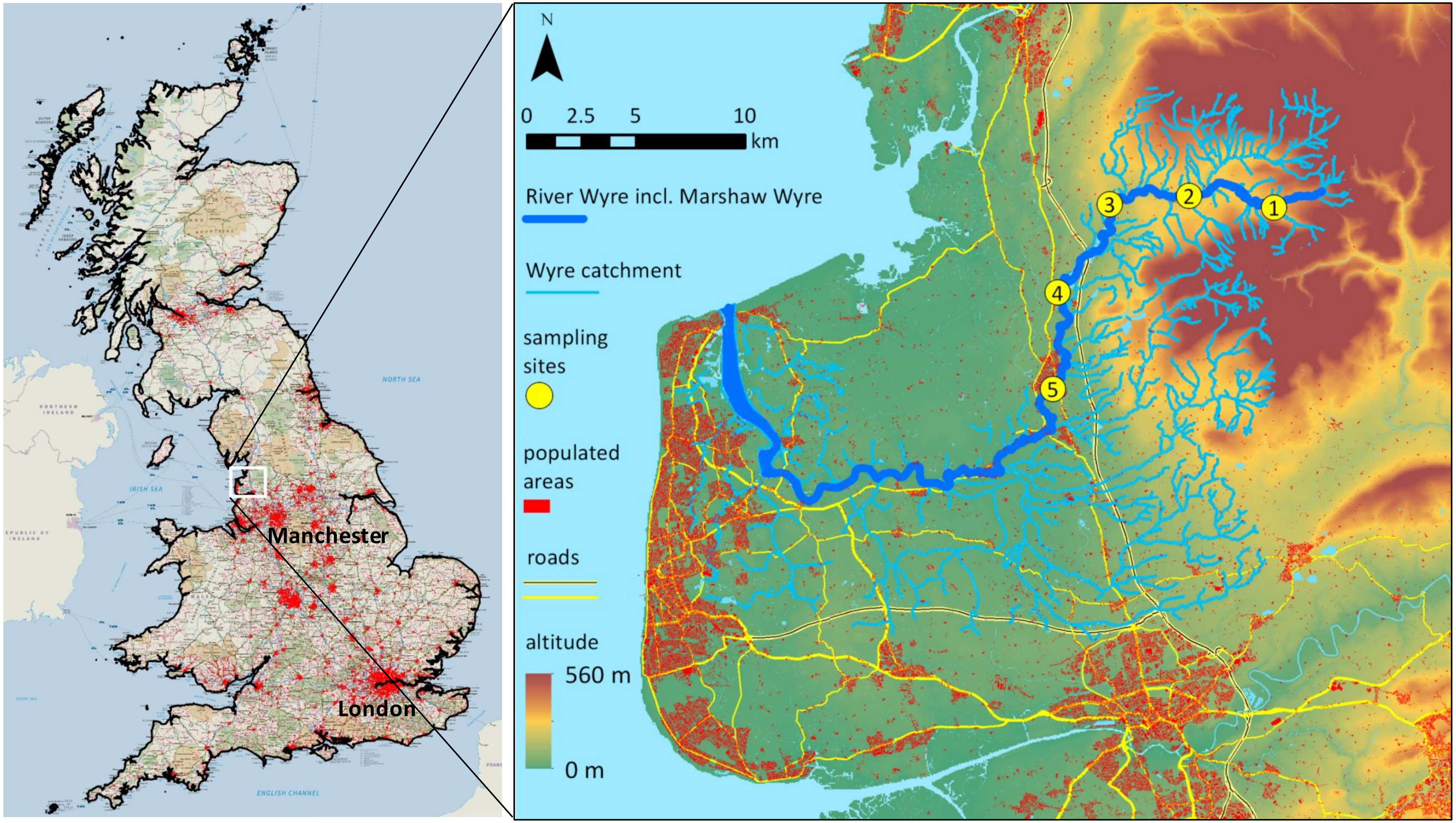


Figure SI-1: Map showing the sampling sites along the river Wyre.

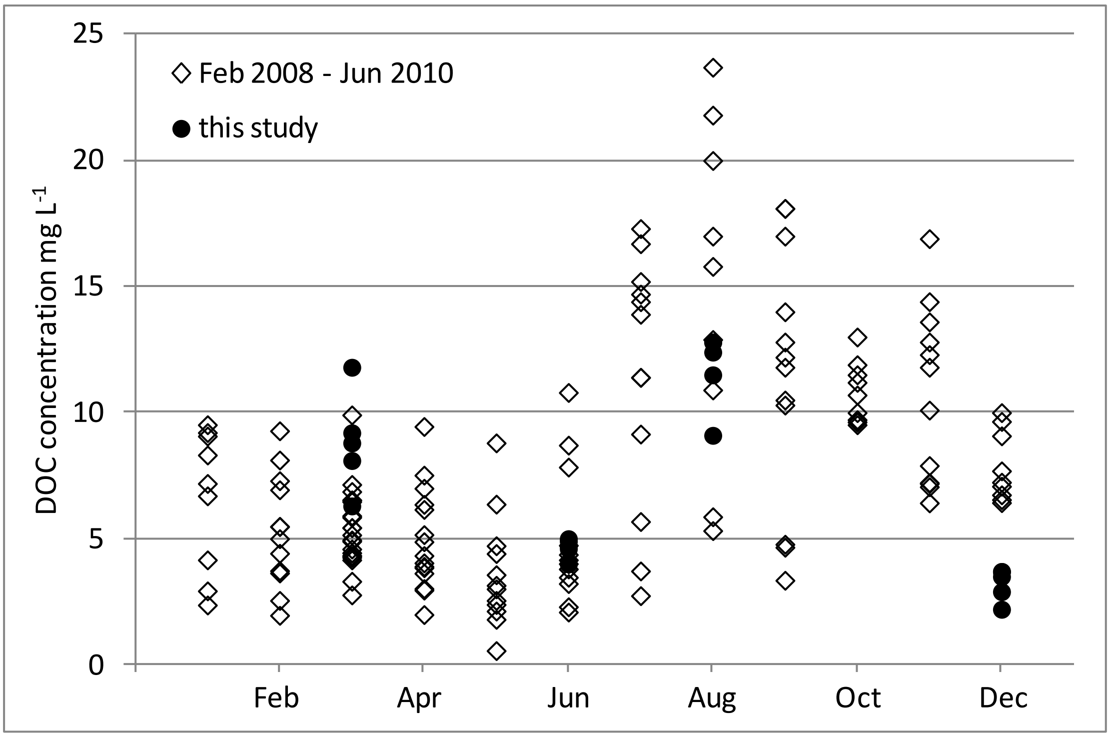


Figure SI-2: DOC concentrations in the samples of the current study and in Wyre water samples collected between February 2008 and June 2010 at the same locations (Scholefield et al., 2013).

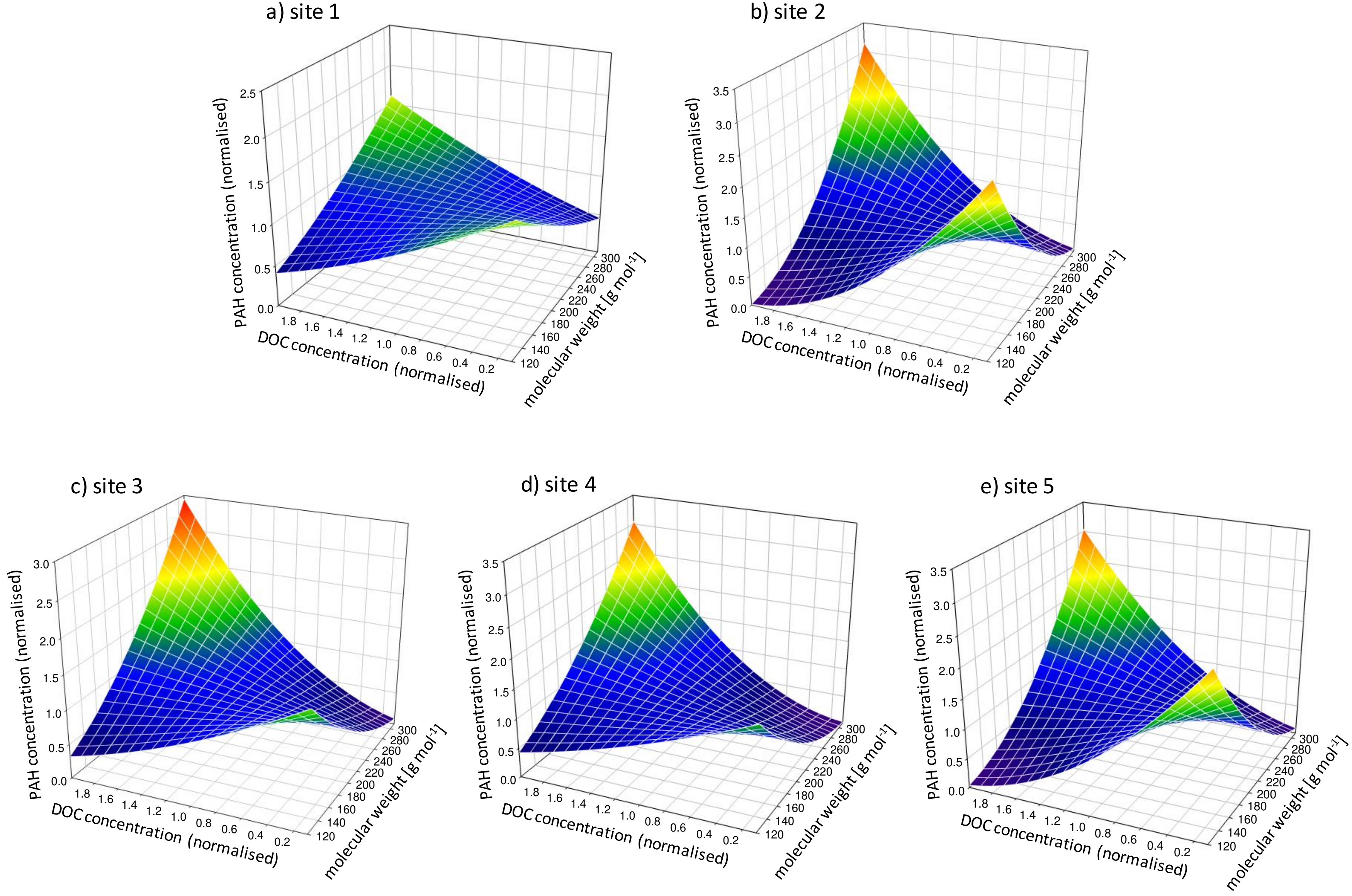
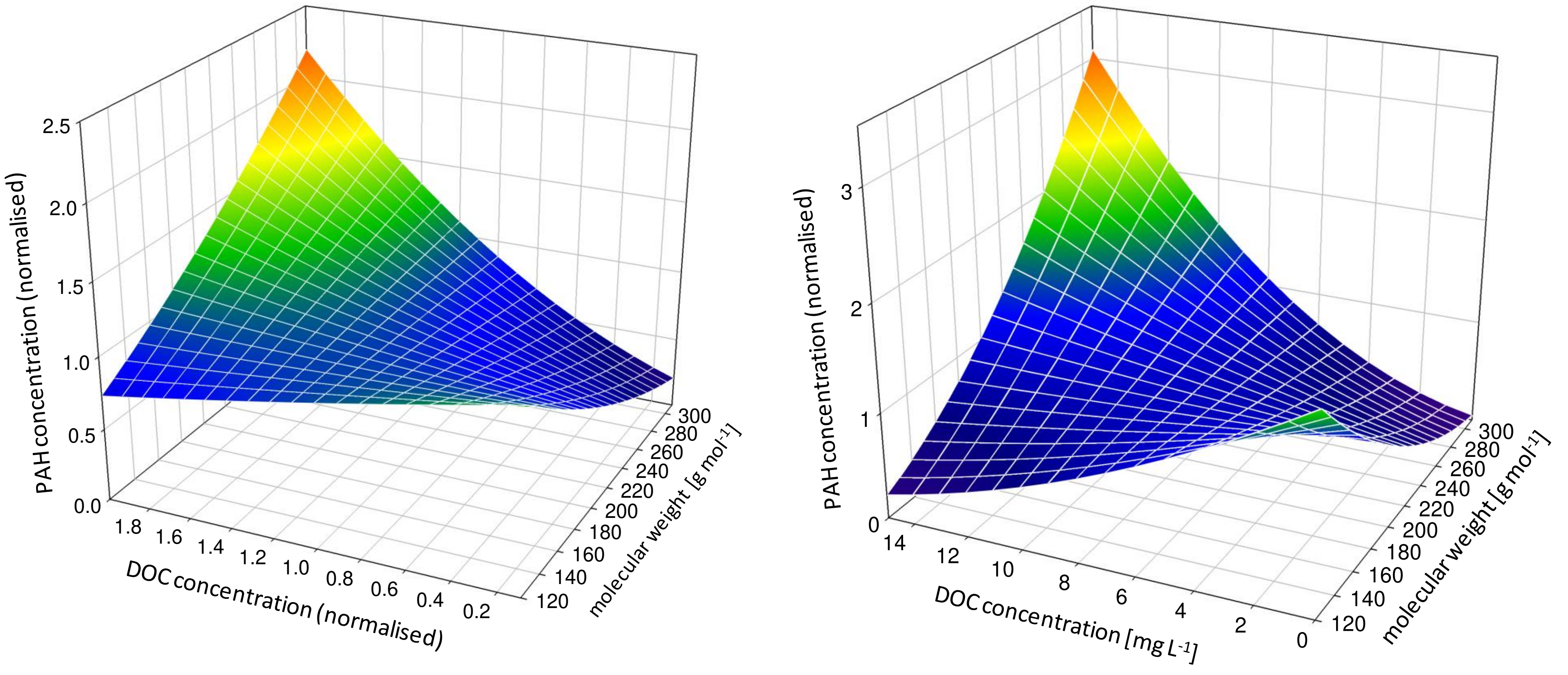


Figure SI-3: Surfaces illustrating the regressions between normalised total dissolved PAH concentrations and both normalised DOC concentrations (except for diagram g) where absolute concentrations were used) and the PAHs' molecular weight.

This figure presents selected subsets of the data, the regression surface for the whole dataset is shown in the main manuscript (Figure 3).



f) no 2- & 3- ring PAHs in December samples, normalised by average at individual sites

g) all data, PAHs normalised by average at all sites

Continued Figure SI-3: Surfaces illustrating the regressions between normalised total dissolved PAH concentrations and both normalised DOC concentrations (except for diagram g) where absolute concentrations were used) and the PAHs' molecular weight.

This figure presents selected subsets of the data, the regression surface for the whole dataset is shown in the main manuscript (Figure 3).

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