



Polycyclic aromatic hydrocarbons (PAHs): sources, pathways and environmental data

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Executive summary

Polycyclic aromatic hydrocarbons (PAHs) are a group of structurally related hydrocarbons. This narrative focuses on 5 PAHs listed in Annex I of the Environmental Quality Standards Directive (EQSD; Directive <u>2008/105/EC</u> amended by Directive <u>2013/39/EU</u>): benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene.

These PAHs persist in the environment and accumulate in biota and food chains and have potential adverse effects on aquatic life and humans, including carcinogenic properties. They are classed as priority hazardous substances and ubiquitous persistent, bioaccumulative and toxic (uPBT) compounds under the Water Framework Directive (WFD) in the related EQSD (2008/105/EC amended by 2013/39/EU). Four of these, (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene) are listed in Annex III of the Persistent Organic Pollutants (POPs) Regulation (EC 850/2004). In June 2016, January 2019, and June 2018, benzo(a)pyrene, benzo(k)fluoranthene, respectively, were listed as substances of very high concern (SVHCs) under the REACH Regulation (EC/1907/2006).

Most PAHs are not deliberately produced and there are very few remaining intentional uses of substances that contain them. They occur naturally in fossil fuels, such as coal and oil and in other hydrocarbon-based materials like bitumen, used for the construction of roads. Substances containing PAHs include coal tar pitch and creosote, and PAHs are present in some of the raw materials used in industrial processes, such as those to make plastic and rubber. There are restrictions under REACH relating to the marketing and use of these substances.

Atmospheric emissions of PAHs are significantly greater than those to water. PAHs are mainly released to the atmosphere from combustion sources. Combustion of wood as a domestic fuel is a major diffuse source of PAHs to the atmosphere. Domestic combustion represents approximately 84% of the total atmospheric load. PAHs released to the atmosphere can then find their way into the water environment following atmospheric deposition to surfaces and subsequent run-off following rainfall. Road transport is estimated to contribute approximately 3% and is the second largest diffuse source; comparable with the main point source contributions from regulated industry.

Much of the PAH contamination in the environment can be considered as 'background' from natural sources and past industrial activity, giving rise to a legacy of contaminants already present in the soil and sediment. Models suggests that this historical contamination contributes a significant PAH load to surface waters.

As some PAHs can accumulate through food chains, we monitor for them in biota – crayfish and blue mussels when assessing risks from long-term exposure. We don't monitor in fish because fish are able to metabolise and break down PAHs.

Concentrations of PAHs in biota are below the biota environmental quality standard (EQS) set in 2013 (2013/39/EU) at almost all of our monitoring sites. Benzo(a)pyrene is used as a marker for the other PAHs and its biota EQS is based on a food standard for PAHs. The value is intended to cover risks to or via the water environment from these substances.

Our biota monitoring programme is limited by a number of practical and ethical constraints including animal welfare concerns and the availability of suitable animals. Although we can analyse benzo(a)pyrene in water at relevant concentrations we have not been able to establish a relationship between the levels observed and those in biota. We cannot

therefore use compliance with the annual average water column EQS to infer compliance or non-compliance with the biota standard.

However, water monitoring can still be useful to check that exposure to contaminant levels in water does not present a risk to the organisms themselves. Comparison of environmental concentrations of PAHs against maximum allowable concentration (MAC) EQSs set in 2013 for surface waters (2013/39/EU) indicate greater short-term risks to the aquatic environment at saline sites than in freshwaters.

There are no apparent national trends in concentrations of PAHs in either fresh or saline waters or biota over time. Some localised reductions of certain PAHs have been observed in shellfish and sediment in coastal waters.

There are a number of controls already in place on the release of PAHs which have brought about significant reductions in some sources of PAHS to the environment. For example, the Industrial Emissions Directive (2010/75/EU); implemented in England by The Environmental Permitting (England and Wales) (Amendment) Regulations 2013 (SI 2016/1154) has brought about significant reductions in atmospheric PAH emissions from industrial sources since the 1990s through the requirement for the use of abatement technologies. However, contributions from domestic combustion have changed little over this time and now represent the most significant contribution to the overall total load of PAH from diffuse atmospheric sources.

This should change moving forwards, with the implementation of the Government's recently published Clean Air Strategy. This strategy outlines a number of actions that will be taken to tackle emissions from domestic burning which will have an impact on PAH emissions.

Increasing use of sustainable urban drainage systems (SUDS) has the potential to manage and mitigate risks from the PAH load in urban run-off to watercourses. However, we still need to understand more about the breakdown of PAHs and other hydrocarbons within these systems and understand any impacts through connected systems such as groundwater.

Continued engagement will be needed with stakeholders and policymakers, alongside analysis of the above data, to ensure the effectiveness of these controls. Where risks from urban sources of PAHs are identified, we will encourage and work with others who have responsibilities in order to influence the development and co-delivery of risk mitigation solutions. For example, water companies can help address such risks through the development and delivery of drainage and water management plans (DWMPs), working closely with other stakeholders such as the Highways Agency.

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1. Introduction

Polyaromatic hydrocarbons (PAHs) are a group of organic compounds with two or more fused aromatic rings. Most PAHs are not deliberately produced but are formed as byproducts of combustion. PAHs are released mainly to the atmosphere from natural processes, such as forest fires, incomplete combustion, industrial processes, and other human activities. The majority of anthropogenic sources are associated with combustion, particularly domestic combustion.

For those products containing PAHs, such as creosote or extender oils, restrictions have been put in place over the last couple of decades.

This narrative looks at a group of 5 PAHs covered under the Water Framework Directive (WFD) (Directive 2000/60/EC) to assess their likely sources and potential risk to the surface water environment. This group is listed in Annex I of the related Environmental Quality Standards Directive (EQSD) (2008/105/EC) amended by the Priority Substances Directive (2013/39/EU) and consists of benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. These compounds are higher molecular weight PAHs comprising 5- and 6-rings.

There are other, smaller, PAHs listed separately in Annex I of the EQSD (naphthalene, anthracene, fluoranthene), but these are not the subject of this narrative. The term PAHs as used in this narrative concerns the group of 5 listed above.

These PAHs tend to partition to particulate matter and are persistent in the environment with biodegradation rates in the order of months to years (<u>European Union, 2008, 2012</u>). They have been found to bioaccumulate within organisms and are toxic, with effect concentrations reported in the low μ g/l range (<u>European Union, 2008, 2012</u>).

With the exception of benzo(g,h,i) perylene, these compounds have been identified as carcinogenic, with benzo(a) pyrene being the most carcinogenic of the group (European Union, 2012).

Benzo(a)pyrene, benzo(k)fluoranthene and benzo(g,h,i)perylene have been listed as substances of very high concern (SVHCs) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Regulation (EC/1907/2006) (see Section 5). Benzo(a)pyrene is listed because of its carcinogenic, mutagenic and reprotoxic (CMR), persistent, bioaccumulative and toxic (PBT), and very persistent and very bioaccumulative (vPvB) properties, benzo(k)fluoranthene because of its carcinogenic, PBT and vPvB properties, and benzo(g,h,i)perylene because of its PBT and vPvB properties.

As these PAHs persist in the environment, accumulate in biota and food chains, and have potential adverse effects on aquatic life and humans, they are classed as priority hazardous substances and ubiquitous PBTs (uPBTs) under the EQSD (2008/105/EC amended by 2013/39/EU).

The Priority Substances Directive (2013/39/EU) introduced a biota standard of 5 microgram per kilogram (μ g/kg) wet weight for benzo(a)pyrene in crustaceans and molluscs. Benzo(a)pyrene is used as an environmental marker for the other the PAHs. The setting of a biota EQS reflects the PBT characteristics of this group of substances.

The biota EQS is driven by risks to human health. The standard is based on a limit set under Commission Regulation <u>1881/2006</u> for benzo(a)pyrene in crustaceans and cephalopods, such as squid, intended for human consumption.

The Directive (2013/39/EU) also specifies maximum allowable concentration EQSs (MAC EQSs) for the individual PAHs, except indeno(12,3-cd)pyrene. MAC EQSs are thresholds set to protect aquatic life from short-term toxic effects.

The requirements of the 2013 Priority Substances Directive (<u>2013/39/EU</u>) took effect in December 2015 through national legislation (<u>UK Government, 2015</u>).

The focus of this narrative is on contributing effects to and assessment of the condition of surface waters in relation to PAHs. However, the contribution that groundwater makes to the surface water status failures is also considered as part of the WFD and the Groundwater Directive (2006/118/EC as amended by 2014/80/EU). If groundwater contributes more than 50% of the PAH load in any surface water status failure then the groundwater body will also go to poor chemical status. We will be assessing this further as we develop water body classifications for the draft river basin plans.

2. Use pattern

PAHs are not deliberately manufactured and they do not perform any specific function within a product (<u>Commission Regulation (EU) No 1272/2013</u>). They occur naturally in fossil fuels, such as coal and oil, and in other hydrocarbon-based materials like bitumen, used for the construction of roads.

PAHs are also present in some of the raw materials used to make plastic and rubber such as extender oils (used to soften) and carbon black (used as a reinforcing agent). Consequently they can be present in finished goods, such as tyres, toys, shoes, and bicycle grips (Federal Institute for Risk Assessment, 2010). The PAH content is limited in these products as described in Section 5.1 (Commission Regulation (EU) No 1272/2013).

3. Sources, emissions and pathways

PAHs are typically released to the environment as by-products of both natural and anthropogenic processes. They are formed during the incomplete combustion of organic materials, such as coal and wood, or during forest and moorland fires. Atmospheric emissions of PAHs are significantly greater than direct releases to water.

3.1. Atmospheric emissions

The UK reports emissions information to meet various international and EU commitments. Such data help provide a picture of important sources and trends over time. Further information on the purpose of the emissions inventories mentioned in this section, as well as the methodologies used to build them, can be found within the corresponding references.

For 2017, the UK Pollutant Release and Transfer Register (UK PRTR) (<u>Defra, 2018</u>) identifies the manufacture of paper, board and other primary wood products (617kg) and iron and steel manufacturing (251kg) at individual facilities in Northumberland and North Lincolnshire, respectively, as the largest reported atmospheric point source emitters of the 5 PAHs discussed in this narrative. The Environment Agency's Pollution Inventory (PI) – which reports on regulated emissions in England at lower thresholds – also describes atmospheric point source emissions of PAHs from power generation (22kg), energy from waste facilities (20kg), surface metal treatment (10kg), and refinery and fuel plants (1kg) for 2017 (<u>Environment Agency, 2019</u>).

Whilst power stations consume large quantities of coal, the high operating temperatures and advanced abatement systems mean that emissions per tonne of fuel are low compared to domestic solid fuel use (Hill & Whiting, 2015).

The UK's National Atmospheric Emissions Inventory (NAEI) reports emissions data that includes estimates for diffuse sources of 16 PAHs. In 2016, an estimated total of 28,385kg of the 5 PAHs under discussion were released to the atmosphere (NAEI, 2018).

Domestic combustion is identified as the main source of all PAH emissions to the atmosphere. The NAEI reports estimated total atmospheric emissions of 23,976kg in 2016 for all 5 PAHs, representing approximately 84% of the total load to the atmosphere. In contrast, the second largest source which is road transport – including all vehicle emissions, tyres and brake wear and road abrasion – contributes 665kg (approximately 3%) of estimated UK emissions to the atmosphere for the 5 PAHs (<u>NAEI, 2018</u>).

As shown in Figure 1, emissions from domestic combustion for benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene declined in the 1990s because of a significant decrease in the use of coal as a domestic fuel. However in more recent years there has been an increase in emissions of the 5 PAHs back to 1990 levels. This increase has been attributed to a significant increase in the use of wood as a domestic fuel in wood burning stoves (NAEI, 2018). The NAEI reported benzo(a)pyrene emissions from coal as 4,706kg in 1990, declining to 561kg in 2016. Conversely, 872kg of benzo(a)pyrene emitted to the atmosphere were attributed to the use of wood in domestic combustion in 1990, compared with 5,917kg in 2016 (NAEI, 2018).

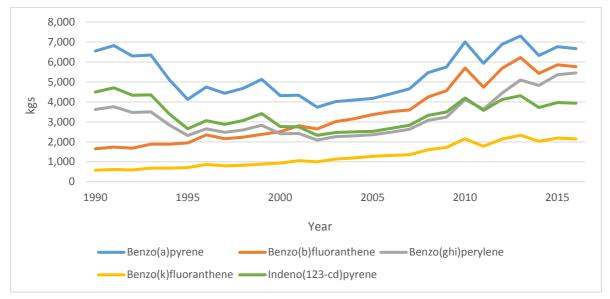


Figure 1. Atmospheric emissions of the 5 Water Framework Directive polycyclic aromatic hydrocarbons from domestic combustion from 1990 to 2016 (NAEI, 2018)

There has been a decrease in atmospheric emissions of PAHs from road transport since the 1990s (<u>NAEI, 2018</u>). Over a 10-year period between 2006 and 2016, for example, total emissions for the 5 PAHs were reported to be 1,224kg in 2006 compared with 665kg in 2016.

<u>Keyte et al. (2016)</u> also reported a decrease in the emissions of PAHs from road transport sources. The authors observed a decline of 86% in mean total (particulate and vapour) concentrations of 16 PAHs – including the WFD 5 PAHs – in the Queensway Road Tunnel in Birmingham between 1992 and 2012. The higher molecular weight PAHs showed declines of up to 96%. The reductions were mainly attributed to the introduction of catalytic converters and progressively stringent EU legislation on vehicle emissions.

There are many other sources emitting the 5 PAHs as by-products of combustion processes at lower levels than road transport. These include industrial off-road mobile machinery, coke production, agricultural mobile machinery, accidental fires, power stations and sinter production. A peak in emissions of PAHs from bonfires on and around 5th November each year in the UK (bonfire night) is also significant enough to be noted as a source in the <u>NAEI (2018)</u>.

The NASA Earth Observatory (2019) has detected more wildfires across the UK since 2017 compared with previous years, linking them to warm, dry weather. Such events would be expected to increase concentrations of PAHs in the atmosphere, although corresponding information is scarce. This is mainly due to the practical difficulties in obtaining such data.

The higher molecular weight PAHs, such as benzo(a)pyrene and other PAHs under discussion here, tend to be associated with atmospheric particulate matter (<u>Li et al., 2007;</u> <u>Živković et al., 2015</u>). The sorption of PAH to particles increases their chemical stability and resistance to degradation (Teinemaa and Kirso, 1999). As a consequence of their stability, they can be transported long distances (<u>Mastral et al., 2003</u>).

Annual mean ambient levels of benzo(a)pyrene in the UK appear to have decreased by nearly half from 2008 to 2009 and then been steady to 2014, followed by a slight drop until 2016 (<u>Defra, 2017</u>). This is considered to be a reflection of dramatic drops in emissions of benzo(a)pyrene of around an order in magnitude from the 1990s as a result of banning

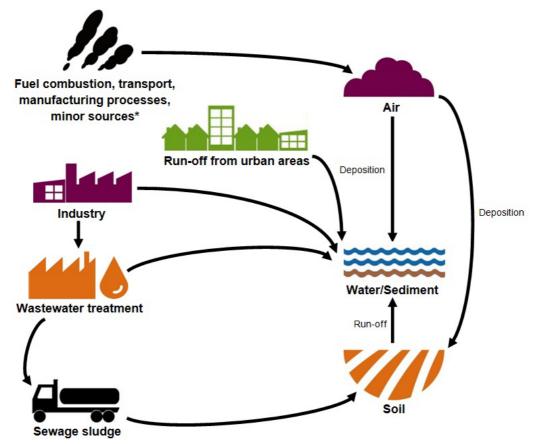
agricultural stubble burning in 1993 and reductions in emissions from industry. However, as noted above, domestic combustion has changed little over this time.

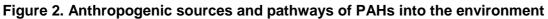
For benzo(a)pyrene, ambient annual mean concentrations in most UK urban areas are below the EU target value of 1ng/m³. In 2016, only one area in England – Yorkshire and Humberside – was above this value and this was attributed to emissions from industrial sources (Defra, 2017).

3.2. Emissions to water

PAHs released to the atmosphere subsequently reach the ground via dry and wet deposition (<u>Environment Agency, 2007</u>). Once deposited on soil, PAHs tend to accumulate for a long period of time and are subject to various partitioning, degradation and transport processes (<u>Bozlaker et al., 2008</u>). PAHs can either enter directly into water bodies via deposition from the air or surface run-off following rainfall, particularly from urban areas where high levels of PAHs may be present (<u>Neff and Burns, 1996</u>; <u>Neff et al., 2005</u>; <u>Pies et al., 2008</u>).

The main anthropogenic sources and pathways of PAHs into surface waters are illustrated in Figure 2.





*Such as accidental fires, bonfires and tobacco smoke, etc.

Data reported to the PI (Environment Agency, 2019) for 2017 show the largest point source releases of PAHs to water in England are from urban waste water treatment works (WwTWs) (335kg), followed by refinery and fuel plants (68kg), and iron and steel works (40kg).

The inventory of emissions, discharges and losses of priority and priority hazardous substances is a formal requirement of the WFD under the EQSD 2008 (2008/105/EC). The inventory for England can be found under the Emissions Inventory and Chemical Trends information for the cycle 2 River Basin Management Plans. It provides estimates of emissions, discharges and losses of the 5 PAHs from both point and diffuse sources, by river basin district, for the baseline year of reporting (2010).

Estimates have been determined using SAGIS (Source Apportionment Geographic Information System, v2010), a GIS-based source apportionment tool and surface water model (<u>Comber et al., 2012</u>), for benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3cd)pyrene. Loads were calculated using Chemical Investigations Programme (CIP) data available at the time and flow information for benzo(b)fluoranthene and benzo(k)fluoranthene. These have been combined with estimates of releases to sea from long sewer outfalls reported to the Pollution Inventory.

We estimate that approximately 656kg of PAHs were released to surface waters in England in 2010; 111kg were from point sources and 545kg from diffuse sources. Overall estimates are similar for benzo(g,h,i)perylene (196kg) and indeno(1,2,3-cd)pyrene (200kg), but higher for benzo(a)pyrene (250kg).

Emissions of benzo(b)fluoranthene (5kg) and benzo(k)fluoranthene (5kg) are relatively small. Total emissions, discharges and losses of PAHs to water per river basin district are shown in Figure 3 (results for Solway Tweed are reported by the Scottish Environmental Protection Agency and the Dee by Natural Resources Wales).

Estimates of emissions of PAHs vary across river basin districts, with emissions ranging from 23kg/year (Northumbria) to just over 150kg/year (Humber).

Point source and diffuse emissions show different patterns across each river basin district. Point source emissions range from approximately 2kg/year in Northumbria to 32kg/year in Humber. Diffuse inputs range from 20kg/year (Northumbria) to 125kg/year (Severn).

With only one year of data in the inventory we cannot yet describe any temporal trends in emissions. The next update of the inventory will be published as part of the 3rd cycle river basin management plans in 2021.

We have reviewed interim inventory results based on PI data only. For 2017, the data suggest increased emissions of the 5 PAHs in the South East and the Thames river basin districts and potentially a decrease in the Severn one. Loads released to surface waters in England for the different substances range from 50kg for benzo(k)fluoranthene to 138kg for indeno(1,2,3-cd)pyrene, suggesting a greater contribution from benzo(b)fluoranthene and benzo(k)fluoranthene than previously estimated.

The interim results also show an overall rise in estimated releases from 2012 to 2017 of 362 to 443kg for the sum of the 5 PAHs. This is particularly influenced by increased emissions of benzo(a)pyrene and indeno(1,2,3-cd)pyrene from 2014.

Given the interim data are generated in a different manner to the baseline inventory and focus solely on point sources, it is not possible to draw any further conclusions.

Figure 3. Baseline year (2010) total emissions, discharges and losses to water for PAHs (as listed in Annex I EQSD 2013/39/EU) for each river basin district

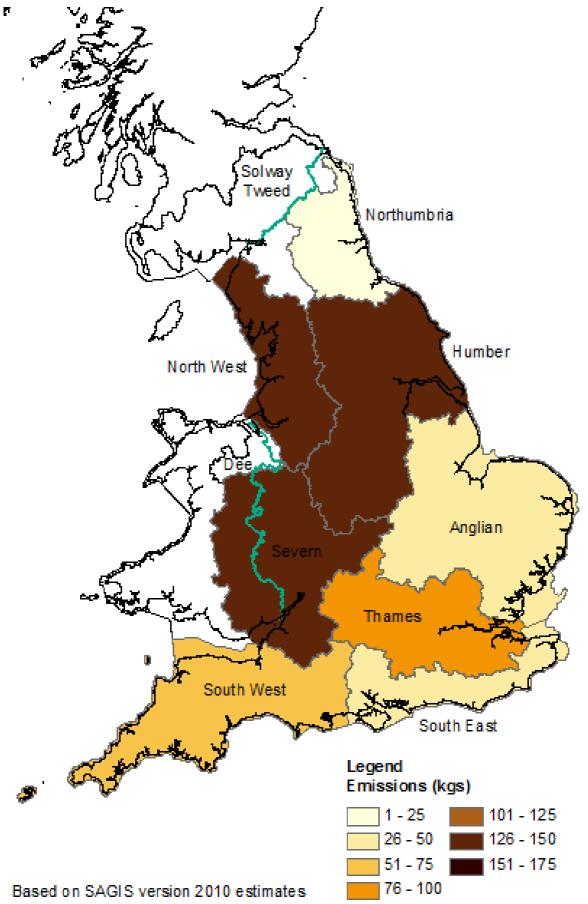
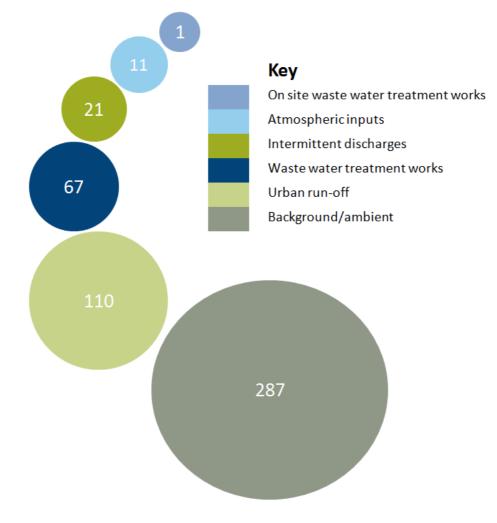


Figure 4 shows emissions of benzo(a)pyrene to water, split by source, using the modelled outputs from SAGIS (v2010). Data for benzo(a)pyrene has been presented as a surrogate for all 5 compounds. Estimates of emissions for benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, also determined using SAGIS, follow the same pattern. We do not have source apportionment data for benzo(b)fluoranthene and benzo(k)fluoranthene.

SAGIS uses measured PAH concentrations reported by the soil and herbage survey (Environment Agency, 2007) as input values for modelling background/ambient emissions of PAHs at the water body scale. These data are extremely variable between and within sites, reflecting the high degree of spatial variability in PAH concentrations across the UK. Concentrations of PAHs in urban and industrial soils are 5 to 8 times those in rural areas and similarly, concentrations of PAH in urban herbage are 2 to 5 times those in rural herbage (Environment Agency, 2007). A study by Vane et al. (2014) of 16 PAHs also showed greater concentrations in soils in more-urbanised areas.

At the river basin district level or a more local scale there is likely to be variability in the relative significance of different sources, depending on the degree of urbanisation and type of industry present as well as the degree of historical contamination. A study of 18 PAHs, including the 5 discussed in this narrative, in upland areas subject to moorland burning showed increased levels in local soils, sediments, moorland vegetation, upland peat, and stream water (<u>Vane et al., 2013</u>). Therefore, although modelling may provide a broad indication of national risk it is likely to be much more uncertain at the individual water body level or wider local scale.

Figure 4. Sectorial analysis of emissions (kg/yr) to water for benzo(a)pyrene as modelled by SAGIS v2010



Background/ambient discharges contribute the largest proportion of the total PAH load to water, based on our modelled source apportionment (Figure 4). Natural processes, incomplete combustion, industrial processes, and other human activities have led to a general build-up of PAHs in the environment over time.

Urban run-off is a significant contributor to the PAH load to water, particularly near to industrialised and densely populated urban areas where PAHs are typically at their highest environmental concentrations (<u>Neff and Burns, 1996</u>; <u>Neff et al., 2005</u>; <u>Pies et al., 2008</u>; <u>Zgheib et al., 2012</u>).

PAHs are deposited on to road surfaces as a result of the combustion of fuel by vehicles. Residual PAHs from bitumen used in road surfacing materials, fuel spills and particulates from brake and tyre wear can also contribute to the accumulation of PAHs on road surfaces. Various studies report concentrations of PAHs near to road environments (Harrison, et al., 2003; Zhou et al., 2014; Rothwell et al., 2015; Keyte et al., 2016; Pant et al., 2017). Following a rainfall event, surface runoff from roads and other urban surfaces enters nearby water courses. Emission rates are highly variable and strongly linked to the prevailing weather conditions, with highest concentrations being linked to long dry periods followed by a storm event (Hill and Whiting, 2015).

Monitoring of WwTWs influent and final treated effluent as part of the CIP (<u>UKWIR</u>, 2014a, 2014b) has demonstrated that typically 90% of the PAH load is removed during waste water treatment, although removal rates differ between individual PAHs (<u>Gardner et al.</u>, 2013). Further investigations in the second phase of the Chemical Investigations Programme (CIP2) show that the ubiquitous presence of benzo(a)pyrene in surface waters is likely to be from sources other than WwTWs (<u>UKWIR</u>, 2019), which is in agreement with the data presented above on emissions.

Higher molecular weight, hydrophobic PAHs such as those under discussion here tend to sorb to particulate material during waste water treatment, especially during primary treatment. Removal of PAHs during waste water treatment results in their presence in sewage sludge which may subsequently be spread on agricultural land.

Land spreading of sewage sludge is regulated by the Sludge (Use in Agriculture) (Amendment) Regulations 1990 (<u>SI 1990/880</u>) which set limits for the amounts of certain trace metals; there are no statutory limits currently for PAHs.

Soil acts as an environmental sink for high molecular weight PAHs as they adsorb strongly onto soil particles. They do not penetrate deeply in soils, other than sandy soils, therefore leaching to groundwater and uptake by plants is low (<u>European Commission, 2002</u>).

Sediments also act as a sink for the higher molecular weight PAHs (<u>Environment Agency</u>, <u>2007</u>). The larger PAHs such as benzo(a)pyrene have a low water solubility and tend to associate with suspended particles in the water column; settling on bottom sediments where they may persist (<u>Prabhukumar and Pagilla</u>, <u>2010</u>). These PAHs are degraded slowly by microorganisms with reported half lives in soil and sediment for benzo(a)pyrene ranging from 229 to >1,400 days (<u>European Union</u>, <u>2008</u>).

Re-suspension of contaminated sediment could be a potential source for release of PAHs into the overlying water column, but there is often uncertainty of the ecological significance of re-suspended contaminated sediments (<u>Roberts, 2012</u>; <u>Nicolaus et al</u>., 2015).

4. Environmental monitoring data

We have recent monitoring data for PAHs in surface waters and biota – crayfish and blue mussels – for benzo(a)pyrene from both English freshwaters and estuarine and coastal waters. In addition, the CIP2 measures concentrations of PAHs in and around WwTWs across England (<u>UKWIR, 2019</u>); data collection and analysis are ongoing and the current results are summarised in Section 4.2. Marine monitoring programmes under the Oslo Paris Convention (OSPAR) have also included the analysis of levels of PAHs in biota and sediment in UK saline waters over time (Section 4.4). We use saline waters in this narrative to cover estuaries and coastal waters out to 12 nautical miles (territorial waters).

We can compare our data against EQSs to get an understanding of risk. The 2013 Priority Substances Directive (2013/39/EU) lists the 5 PAHs given in Section 1 of this narrative as WFD priority hazardous substances. It specifies a biota EQS of 5µg/kg wet weight for benzo(a)pyrene – as a marker for the other PAHs – for the first time. This EQS refers to the presence of this substance in crustaceans and molluscs. It is based on a food threshold for human health (concentration in crustaceans and cephalopods of 5µg/kg; Commission Regulation 1881/2006/EC, setting maximum levels of contaminants in foodstuffs).

It is theoretically possible to derive an equivalent water threshold that corresponds to a biota standard. The approach is described in detail in the <u>EC Technical Guidance for</u> <u>Deriving Environmental Quality Standards</u> (EC, 2011) and results in a value sometimes termed the 'back-calculated' threshold.

For benzo(a)pyrene, the Directive (2013/39/EU) gives a revised annual average (AA) EQS of 1.7 x 10⁻⁴µg/l for inland and other surface waters. This concentration in water is the lowest value obtained from the back calculation of 3 different foodstuff thresholds for fish, crustaceans and cephalopods, and molluscs ranging from 2 to 10µg/kg wet weight. It is a water value for the same protection goal – human health via consumption – as the biota EQS.

The new AA EQS for water is 300 times lower than the previous EQS (<u>2008/105/EC</u>) for benzo(a)pyrene in surface waters because it has a different protection goal, that is human health rather than direct long-term toxic effects to the aquatic environment.

The Directive also sets out maximum allowable concentration EQSs (MAC EQSs) for 4 of the 5 PAHs, the exception being indeno(1,2,3-cd)pyrene. The values are given in Section 4.2.2. These are thresholds intended to protect the aquatic environment from short-term toxic effects. The Directive requires these thresholds to be applied where the biota EQS is applied or where emissions or environmental concentrations indicate potential short-term risk.

The data used to derive these values are summarised in the EQS dossier (<u>European</u> <u>Commission, 2012</u>).

4.1. Biota monitoring

As part of the programme of work to assess risks from PBT substances in England, we have gathered data on benzo(a)pyrene residues in freshwater and saline biota from a limited number of locations around England.

Monitoring in molluscs or crustaceans is recommended for PAHs because these substances are readily metabolised by fish. Monitoring in fish would underestimate the risk from PAHs.

Our EQSD sampling began in 2014. We have sampled at 29 freshwater and 30 saline sites. The number of sites and their locations have varied year on year, although a subset of sites have been consistently sampled and have been reviewed for trends in concentrations over time (see Section 4.3).

A summary of the mean concentrations of benzo(a)pyrene measured in signal crayfish 'Pacifastacus leniusculus' in freshwaters and in blue mussels 'Mytilus edulis' in saline ones is presented below.

The mean measured concentration is based on the most recent 3 years of data, where available. Some sites have means generated from only 1 or 2 years' data. We compare these data against the biota EQS to assess potential risk. The mapped results are shown in Figure 5. It should be noted that the limit of quantification (LOQ) for benzo(a)pyrene in biota is $5\mu g/kg$ wet weight, the same value as the biota EQS. Concentrations below the LOQ are reported as half the LOQ.

In freshwater biota, mean measured concentrations of benzo(a)pyrene in crayfish range from 2.5 to 8.4μ g/kg wet weight. Ninety-three per cent of sites are below the EQS. Of those, 24 sites (83%) report concentrations below the LOQ – that is, all samples are reported as 2.5μ g/kg wet weight – and 3 sites (10%) have mean concentrations of benzo(a)pyrene between the reported LOQ and the EQS.

There are very few sites where the mean concentrations of benzo(a)pyrene in crayfish exceed the EQS – only 2 sites, located in the Midlands and in the North West. However, these latter results are both based on 1 out of 3 of the crayfish samples from these sites having high residues of benzo(a)pyrene; the remaining samples were below the LOQ. These samples with high concentrations may be outliers. We would need to get a better understanding of sample variability at the sites to understand if the high concentrations in some animals are anomalies or a true reflection of the ambient levels.

In saline waters, mean measured concentrations in mussels range from 2.5 to 6.6µg/kg wet weight. Again, benzo(a)pyrene concentrations are below the EQS at the majority of sites (97%).

The EQS is exceeded at only 1 site in the North West near Crosby. This site is located in the Mersey estuary, a highly industrial and urbanised area. Eight sites (27%) have mean concentrations of benzo(a)pyrene between the reported LOQ and the EQS, with the remaining 21 sites (70%) reporting only concentrations below the LOQ.

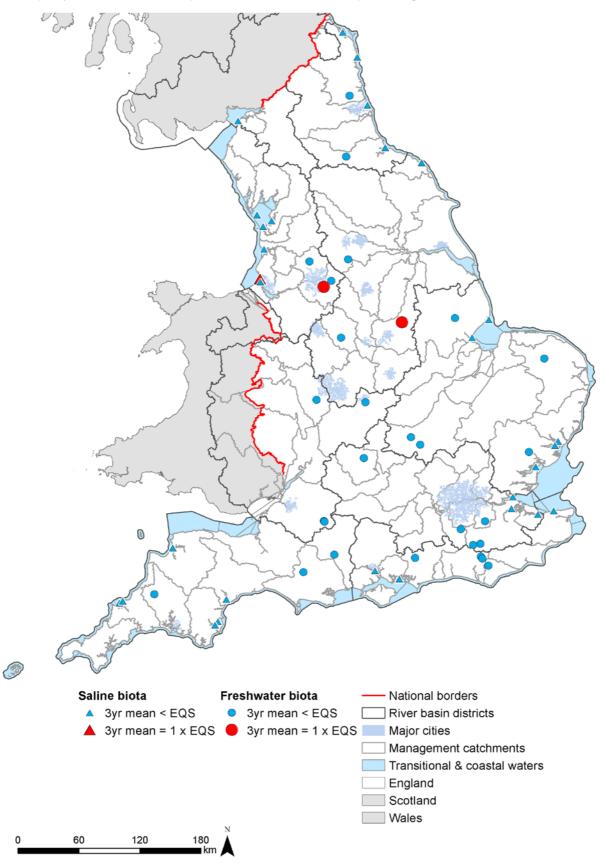
Annual mean concentrations of benzo(a)pyrene in crayfish are comparable with the 3-year mean range, suggesting little temporal variation over the time we have sampled. Ninety-four per cent of the yearly site results had annual averages below the EQS, with most sites reporting concentrations less than the LOQ. The highest annual average concentration was recorded on the Sowe River in the Midlands at 8.7µg/kg wet weight in 2016.

For saline sites, there was a notable result above the EQS in the Tees in 2014. An annual mean value of 202.3μ g/kg wet weight in blue mussels was recorded for this site – much higher than typically reported concentrations for other years. This high value is suspected to be due to sediment disturbance leading to the re-release of benzo(a)pyrene previously bound to sediment back into the water column. In subsequent years concentrations have been substantially lower at this site, decreasing from 12.1μ g/kg wet weight in 2015 to concentrations below the LOQ from 2017 (see also Section 4.3).

Ninety per cent of the yearly saline site results had annual averages below the EQS. Again there was little variation in the annual means from the 3-year mean range with the exception of the Tees site and annual averages of up to 10.8µg/kg wet weight were recorded for the Crosby site.

Our biota monitoring data suggest that the national risk to surface waters for benzo(a)pyrene is low. There is no obvious national pattern as to why there is higher risk at certain sites.

Figure 5. Three-year mean site results for concentrations of benzo(a)pyrene measured in biota (crayfish and mussels) from 2014 to 2018 compared against the biota EQS





4.2. Water monitoring

4.2.1. Investigative monitoring to assess long-term risks

The CIP2 investigations are ongoing and include monitoring of contaminants in rivers upstream and downstream of over 600 WwTWs, as well as in the sewage effluent from those works. The sites were selected because the receiving waters for their effluent are low dilution and so represent the greatest risk of noncompliance with the EQS downstream.

The findings from the CIP2 to date cover results for sites monitored for benzo(a)pyrene between 2015 and 2019 (<u>UKWIR, 2019</u>). Benzo(a)pyrene was found to be ubiquitous and showed high confidence failures in most cases when compared with the AA EQS. Overall mean results for samples taken at approximately 440 sites upstream and downstream of WwTWs' discharge locations were 0.025 and 0.017µg/l, respectively.

The presence of benzo(a)pyrene in those surface waters is not primarily derived from sewage effluents as the high concentrations in the upstream samples were generally not impacted further by WwTWs. There is no current information from the programme on likely sources, although the emissions information in Section 3 suggests that background/ambient levels and, to a lesser degree, urban run-off have a greater influence on loads to surface waters.

We took water samples at 20 of our freshwater biota sites (Section 4.1) between 2016 and 2018. Fourteen sites were monitored every year and 6 sites in 2018 only. Between 9 and 33 water samples were taken at the sites and the mean concentrations ranged from 9.7 x 10^{-4} to 0.0073µg/l. The concentrations of benzo(a)pyrene were above the AA EQS for surface waters at all sites. Conversely, the mean concentration results in biota at the same sites were all below the biota EQS.

The above water concentration results suggest current widespread pressure on the water column from benzo(a)pyrene. This pressure is not reflected in the biota results. This difference may be due to analytical reasons – the surface waters AA EQS is set as a total concentration and so this may include small particles with adsorbed PAHs that are not subsequently taken up by biota – and/or the assumptions used to back calculate the water threshold from the biota EQS on which it is based (see the beginning of Section 4). Differences between the biota results and the CIP2 monitoring may also be due to the biota not being in the most-polluted locations.

Measurement in biota allows a more relevant assessment of the risk given the goal to protect organisms further up the food chain from the effects of environmental exposure. Water data gives combined concentrations of benzo(a)pyrene on particulates and in the dissolved form; this may result in an overestimation of risk as PAHs adsorbed to suspended particulate matter may be less bioavailable. There is also a level of uncertainty around back-calculated water thresholds based on toxicological data. This is because they rely on bioaccumulation factors which are not always available or consistent.

4.2.2. Routine water monitoring to assess short-term risks

We have used our surface water monitoring data to examine the potential short-term risks from PAHs by comparing the results against the MAC EQSs. As mentioned at the beginning of Section 4, the MACs are thresholds designed to protect aquatic organisms from toxic effects associated with short-term exposure.

For the 4 PAHs with corresponding MAC EQSs, we have compared 90th percentile concentrations for each surface water site monitored between 2016 and 2018 with the standards and then examined the results to identify sites where we have high (95%)

confidence in any MAC exceedance. We look at 90th percentile site results to exclude any possible outliers. The sites assessed had from 4 to around 36 samples.

Tables 1 and 2 show the number of sites, as a percentage of total monitored, where we have high confidence that the water concentrations are above the corresponding MAC EQSs for PAHs. The remaining sites assessed have PAH concentrations in water that are either below the corresponding MAC EQSs or at levels that are above the EQS, but which would need further investigation to be more certain of the situation.

The MAC EQSs for each PAH alongside summary assessment information – type and number of sites and range of measured concentrations – are also shown in Tables 1 and 2 for fresh and saline waters, respectively.

Figure 6 shows the locations of those sites where we have high confidence that the concentrations in water are above the MAC EQSs. It gives an indication of those areas at risk based on the comparison against the MAC EQSs.

There are no high confidence exceedances of the MAC EQSs for benzo(a)pyrene and benzo(k)fluoranthene at freshwater sites (Table 1). There are slightly higher percentages of sites with high confidence exceedances for benzo(b)fluoranthene, followed by benzo(g,h,i)perylene in such waters.

For saline waters (Table 2), the percentages of sites with samples above the PAH MAC EQSs are greater than those for freshwater. The saline results show a similar pattern to the freshwater ones in terms of which substances appear to present the greatest potential risk: Benzo(k)fluoranthene and benzo(a)pyrene have the lowest percentages of high confidence MAC EQS exceedances in saline waters. An increase in the percentage of sites above the MAC EQS is seen for benzo(b)fluoranthene. Benzo(g,h,i)perylene has the greatest percentage of sites showing high confidence exceedances of the saline MAC EQS at 35 and 55% of coastal and estuarine sites, respectively.

The measured environmental concentrations of the different PAHs do not differ greatly within the different water types (Tables 1 and 2). Slightly higher concentrations of benzo(b)fluoranthene compared with those of benzo(k)fluoranthene might explain the increased exceedance of its MAC EQS in saline waters.

Benzo(g,h,i)perylene has a particularly low MAC EQS value and this drives the greater number of samples reported above the MAC EQS compared with the other PAHs, rather than different exposure patterns.

The map in Figure 6 shows widespread contamination from PAHs. This reflects the diffuse nature of the main sources of the PAHs. Higher risk is indicated for estuarine sites, particularly for benzo(g,h,i)perylene, in our major estuarine areas that would have industrial and urban inputs and historically contaminated sediment.

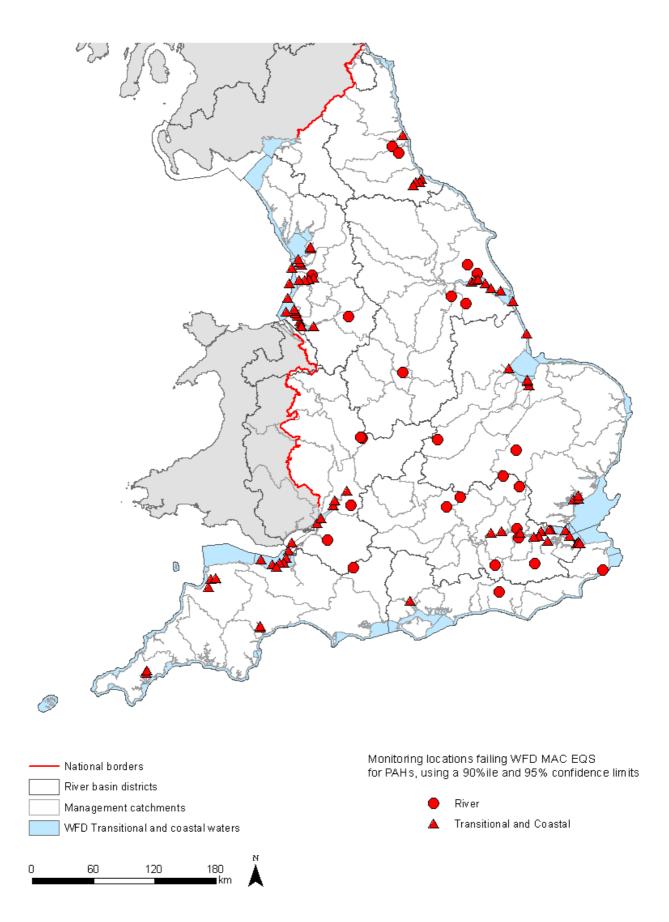
Table 1. Polycyclic aromatic hydrocarbons assessed for short-term risks to freshwaters,protection thresholds and summary of assessment for English sites monitored from 2016 to2018

| РАН | Fresh- water MAC EQS (µg/I) | Type of site | Number of sites assessed | Range of measurements (µg/I) | Sites (%) above the MAC EQS based on comparison against the 90th percentile (95% confidence) |
|----------------------|--------------------------------------|--------------------|--------------------------------|------------------------------------|---|
| Benzo(a)pyrene | 0.27 | Lake | 44 | 2.5x10 ⁻⁵ -0.0313 | 0 |
| | | River | 854 | 2.5x10 ⁻⁵ -2.49 | 0 |
| Benzo(b)fluoranthene | 0.017 | Lake | 44 | 2.5x10 ⁻⁵ -0.0256 | 0 |
| | | River | 817 | 2.5x10 ⁻⁵ –2.33 | 0.5 |
| Benzo(k)fluoranthene | 0.017 | Lake | 44 | 2.5x10 ⁻⁵ -0.0148 | 0 |
| | | River | 826 | 2.5x10 ⁻⁵ -1.30 | 0 |
| Benzo(g,h,i)perylene | 8.2 x 10 ⁻³ | Lake | 41 | 2.5x10 ⁻⁵ -0.037 | 0 |
| | | River | 820 | 2.5x10 ⁻⁵ –1.88 | 3.0 |

Table 2. Polycyclic aromatic hydrocarbons assessed for short-term risks to saline waters,protection thresholds and summary of assessment for English sites monitored from 2016 to2018

| PAH | Saline MAC EQS (µg/l) | Type of site | Number of sites assessed | Range of measurements (µg/l) | Sites (%) above the MAC EQS based on comparison against the 90th percentile (95% confidence) |
|----------------------|-----------------------------|-----------------|--------------------------------|------------------------------------|---|
| Benzo(a)pyrene | 0.027 | Estuaries | 101 | 2.5x10 ⁻⁵ -0.449 | 7.9 |
| | | Coastal | 63 | 2.5x10 ⁻⁵ -0.0773 | 1.6 |
| Benzo(b)fluoranthene | 0.017 | Estuaries | 102 | 2.5x10 ⁻⁵ -0.501 | 10.8 |
| | | Coastal | 63 | 2.5x10 ⁻⁵ -0.081 | 7.9 |
| Benzo(k)fluoranthene | 0.017 | Estuaries | 101 | 2.5x10 ⁻⁵ -0.391 | 5.9 |
| | | Coastal | 63 | 2.5x10 ⁻⁵ -0.050 | 1.6 |
| Benzo(g,h,i)perylene | 8.2 x 10 ⁻⁴ | Estuaries | 101 | 2.5x10 ⁻⁵ -0.548 | 55.4 |
| | | Coastal | 63 | 2.5x10 ⁻⁵ -0.109 | 34.9 |

Figure 6. Maps showing surface water samples that are above one or more of the polycyclic aromatic hydrocarbon MAC EQSs based on the 90th percentiles (95% confidence) at those sites



4.3. Trends

Our current biota monitoring uses an LOQ at the same level as the EQS based on best available techniques. Values below the LOQ are reported as 2.5µg/kg wet weight (half the LOQ). This limits the range of reported values and our ability to determine trends.

We have biota monitoring data for benzo(a)pyrene from 2014 to 2018 and have sampled at 7 freshwater sites for all 5 years. From a visual assessment, concentrations at 1 site appear to be declining and 4 sites show no obvious trend. This is based on a non-statistical analysis. The remaining sites have concentrations reported as half the LOQ.

Under OSPAR, the Clean Seas Environment Monitoring Programme (CSEMP) has collected data on concentrations of PAHs in sediment and mussels in UK marine waters since 1999. Data generated under this programme is collated for the International Council for the Exploration of the Sea (ICES) and can be viewed using the Database on Oceanography and Marine Ecosystems (DOME) web portal. Data are available for benzo(a)pyrene, as well as benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.

An overview of the trend monitoring data collected through the CSEMP for benzo(a)pyrene within English territorial waters, the saline area to which the Priority Substance Directive (2013/39/EU) applies, is given in Figure 7. Data are very variable with only a few sites exhibiting a statistically significant trend. The areas showing downward trends are those known to be historically contaminated by industry.

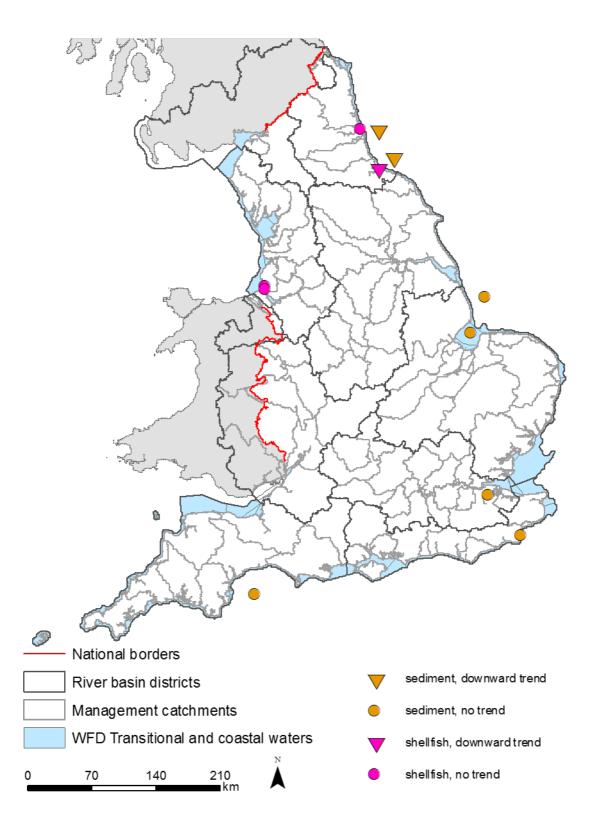
Under the CSEMP, mussels have been sampled from 28 sites for benzo(a)pyrene around England from 2002 to 2017. Four of these sites can be assessed for trends (Figure 7). Only one statistically significant trend has been reported for concentrations of this substance in mussel tissue: a downward trend at Teesmouth in the North East. This trend is also seen for benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene at this site.

The CSEMP have also monitored benzo(a)pyrene in sediments at 11 sites. Seven of these sites can be assessed for trends (Figure 7). The data show a couple of downward trends in the North East offshore from the Tyne and Tees areas. The data corresponding to the other two substances show no change. Sites in the Lower Medway and South West present sediment contaminated with benzo(a)pyrene at levels that could potentially cause adverse effects to marine life, based on comparisons with thresholds (ERLs) developed by the US Environmental Protection Agency (cited on DOME).

The OSPAR Intermediate Assessments for PAHs in shellfish and sediment report on data for the OSPAR maritime region collected between 1995 and 2015 under their Coordinated Environment Monitoring Programme (CEMP) (<u>OSPAR Commission, 2017a</u> and <u>2017b</u>, respectively); this includes the data under the CSEMP. The mean concentrations of PAHs, as a group, in shellfish and sediment show decreasing trends in 4 out of 8 and 2 out of 6 sub regions in the OSPAR region, respectively, assessed over time. The other sub regions showed no statistical change. Areas with decreasing trends included the English Channel for both media and the Southern North Sea for shellfish.

Mean concentrations in shellfish were above OSPAR background levels in all areas although not at concentrations likely to cause adverse effects (<u>OSPAR Commission</u>, <u>2017a</u>). Levels in sediment were also unlikely to cause adverse biological effects (<u>OSPAR Commission</u>, <u>2017b</u>).

Figure 7. Trends in concentrations of benzo(a)pyrene measured in biota and sediment in English coastal waters over the period from 1999 to 2017. Data accessed from the ICES DOME portal, extraction 15 February 2019; downloaded May 2019. Chemical data for the OSPAR Coordinated Environmental Monitoring Programme, reporting laboratories via the British Oceanographic Data Centre (UK). ICES, Copenhagen



The above assessment considers PAHs as a group and combines data for sites in a defined area which can hide the variation seen when looking at individual compounds and sites. Very limited data are reported in the scientific literature for the specific PAHs under discussion here.

A high spatial variability is reported, with concentrations influenced by adjacent land use. For example, sediment cores taken from 10 lakes across the UK showed a tarn in the Lake District to have the lowest levels of PAHs of those sites sampled, and a site in South Yorkshire, located close to an urban centre, to have the highest (Rippey et al., 2008).

Historical industrial contamination may also have a significant influence on local PAH concentrations. Rumney et al. (2015) examined data for PAHs in sediments at 12 saline sites around the coast of England, spanning the years 2008 to 2013, although not all sites had data for each year. Highest concentrations were seen in sediments from the Inner Tees in the north east in 2008 and the Tyne and Tees and this was attributed to high levels of PAHs from historical industrial activities persisting in sediments (CEFAS, 2012; Rumney et al., 2015).

The relationships, if any, between current emissions of PAHs, environmental concentrations and any trends are likely to be complex. For the studies summarised above, there appears to be little relationship between emissions of PAHs, as reported in the emissions inventory (Section 3) and measured environmental concentrations.

Total emissions to surface waters for the North West river basin district are predicted to be amongst the highest in England (see Section 3) so the low concentrations reported for the Lake District tarn illustrates the high degree of variability in emissions expected across a river basin district. In contrast, high concentrations of PAHs are reported in sediment in the Tees; however Northumbria is a river basin district reporting relatively low emissions of PAHs compared with other river basin districts. At these sites in the north east, historical contamination appears to be significant, although there are some indications of environmental improvement from the CSEMP data.

Contaminants such as PAHs contained in sediment may be mobilised by human activities, such as dredging, as well as natural events including tidal surges and extreme weather events (Eggleton and Thomas, 2002). Considering historical CSEMP data, <u>Nicolaus et al.</u> (2015) also concluded that re-suspension of sediment containing such contaminants may still cause a threat to the saline environment.

Where we see higher concentrations in our biota monitoring data (Section 4.1), these locations appear to be in river basin districts with higher predicted emissions to surface waters. However, again the biota data show variability across these river basin districts. Limitations owing to the relatively high LOQ we use means we cannot make further spatial comparisons.

5. Control measures

5.1. Restrictions

There are a number of measures that indirectly control emissions of PAHs. For industrial point source emissions this is the Industrial Emissions Directive (IED) (2010/75/EU); implemented in England by The Environmental Permitting (England and Wales) (Amendment) Regulations 2013 (SI 2016/1154). Under this legislation emissions from major industrial sources must be permitted. Abatement measures are used to reduce PAH emissions and to comply with permits. Target values are set for benzo(a)pyrene and other PAHs in ambient air under the Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC).

Any substance produced or marketed in the EU that contains PAHs above the relevant hazard classification threshold and is registered under REACH (EC 1907/2006) requires a Chemical Safety Report. This report states the conditions under which the substance can be safely used. This offers some level of control over the use of substances containing PAHs.

Other legislation under REACH restricts the marketing and use of PAHs and products containing them. Eight PAHs are classed as carcinogenic and entry 50 of Annex XVII of the REACH Regulation (EC 552/2009) – implemented in the UK by the REACH Enforcement Regulations 2008 (SI 2008/2852) – restricts several product types in relation to these PAHs. The listed PAHs in this restriction include benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene.

Since 2010, extender oils have been prohibited from being placed on the market or used in the production of tyres or parts of tyres that contain more than 0.0001% by weight of benzo(a)pyrene or more than 0.001% by weight of the sum of all listed PAHs.

From December 2015, further restrictions under REACH entry 50 (EC 1272/2013) came into force relating to the placing on the market and supply to the general public of articles containing rubber or plastic components that come into contact with the skin. Articles are restricted if they contain >0.0001% by weight of any of the listed PAHs and these articles include:

- sport equipment such as bicycles, golf clubs, racquets
- household utensils, trolleys, walking frames
- tools for domestic use
- clothing, footwear, gloves and sportswear
- watch-straps, wrist-bands, masks, head-bands

Toys and childcare articles that may come into direct contact with the skin or oral cavity are also restricted if they contain more than 0.00005% by weight of any of the listed PAHs.

Annex XVII entry 31 of REACH also places restrictions on creosote, coal tar, and other sources of PAHs for use by the general public. Since 2003, the marketing and use of these products is prohibited for the treatment of wood except in certain industrial facilities and for commercial purposes under certain conditions. Wood treated with these substances cannot be used for a variety of purposes such as in children's playgrounds and garden furniture.

In June 2016, January 2019 and June 2018, benzo(a)pyrene, benzo(k)fluoranthene and benzo(g,h,i)perylene, respectively, were listed as substances of very high concern (SVHCs) under the REACH Regulation (EC 1907/2006).

SVHCs are placed on the Candidate List. Whilst the use of substances on the Candidate List is not restricted, companies may have legal obligations regarding those substances. Controls on use of the substance may follow; for example, high-temperature coal tar pitch is now subject to authorisation because of its PAH content. Alternatively, substances could be proposed for restriction by a member state or by the European Chemicals Agency (ECHA). Further information is available on the <u>ECHA website</u>.

Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene are listed in Annex III of the Persistent Organic Pollutants (POPs) Regulation (\underline{EC} <u>850/2004</u>) – implemented in the UK by The Persistent Organic Pollutants Regulations 2007 (<u>SI 2007/3106</u>) – which requires that PAH emissions are recorded in an emissions inventory and an action plan produced to eliminate releases.

Legislation that places a maximum limit on the PAH content of diesel has been in existence for several years and in 2009 the upper limit for PAH content in diesel was reduced from 11 to 8% by weight (2009/30/EC; implemented in the UK by SI 2013/2620). However the PAH content of diesel in the UK is considerably lower than 8% (Department for Transport, 2010).

Maximum limits on the levels of certain PAHs in foodstuffs such as oils and fats, fish, meat, and infant formula are specified under the Contaminants in Food (England) Regulations (SI 2013/2196).

5.2. Managing risks from diffuse pollution

The government outlines actions to tackle pollutant emissions resulting from domestic burning in the Clean Air Strategy (<u>Defra, 2019</u>). These steps will contribute to addressing emissions of PAHs such as benzo(a)pyrene. The actions include:

- legislating to prohibit the sale of the most polluting fuels,
- changing existing smoke control legislation to make it easier to enforce,
- giving local authorities new power to tackle problem areas of pollution,
- ensuring by 2022 that only the cleanest stoves will be available for sale,
- improving awareness on the environmental impacts of domestic burners through a communications campaign,
- aligning government work on air quality, clean growth and fuel poverty in future policy design, and
- working with industry to establish standards for new fuels entering the market.

The strategy also highlights the difference between methods of heating and the relative cleanness of different fuels, e.g. the use of seasoned wood over wet wood, as well as advice on ways to cut down on domestic combustion. The government have run consultations on <u>cleaner domestic burning</u> which have informed the strategy and sought views on proposals to help households change to cleaner fuels for burning.

We still need a broader understanding of impacts of urban pollution on soil, water, sediment and wildlife but it is conventional drainage infrastructure allows pollutants accumulated on hard surfaces to be washed directly into water courses as urban run-off. Risks from urban run-off are increasingly being mitigated through the use of sustainable urban drainage systems (SuDS), a wide-ranging term covering a variety of solutions to intercept and remove sediment, metals and PAHs from urban run-off. There is still an evidence gap around the breakdown of hydrocarbons and PAHs within these systems; however, the higher molecular weight PAHs, such as those under discussion here, tend to be found in the sediment phase of run-off.

A study to investigate the effectiveness of various SuDS techniques in attenuating and degrading a range of diffuse source pollutants, including PAHs has been undertaken (SNIFFER, 2008). Further details can be found <u>here</u>. Pathway intervention measures such as grass filter strips, swales, and detention areas are advocated as priority features of sustainable urban drainage networks serving urbanised areas and highways where oil contamination may be significant

6. Discussion

PAHs are released to the environment as by-products of both natural and anthropogenic combustion processes; resulting in widespread contamination of the environment. There is a high degree of temporal and spatial variability in environmental concentrations of PAHs across the UK, with highest concentrations reported in urban areas (Environment Agency, 2007).

The UK's National Atmospheric Emissions Inventory (<u>NAEI, 2018</u>) identifies domestic combustion as the main source of PAHs to the atmosphere. The increasing use of wood as a domestic fuel has led to an increase in emissions from domestic combustion over approximately the past 15 years (<u>NAEI, 2018</u>).

Road transport, including vehicle emissions, tyre and brake wear and road abrasion also contributes to the total diffuse PAHs load to the atmosphere; although this has been steadily declining since the 1990s (NAEI, 2018). As the second largest diffuse source it is considerably less significant (approximately 3% of the total load) than domestic combustion and its contribution to atmospheric load is more comparable to those reported for regulated point sources (NAEI, 2018, Defra, 2018, Environment Agency, 2019). There are many other domestic and industrial sources emitting PAHs as by-products of combustion processes including industrial off-road mobile machinery, bonfire night, coke production, agricultural mobile machinery, accidental fires, power stations and sinter production (NAEI, 2018).

Atmospheric emissions of PAHs are significantly greater than those direct to water. PAHs released directly to the atmosphere are deposited on land and in water. The significance of atmospheric deposition and subsequent accumulation of PAHs on land over time is demonstrated through the large contribution that background/ambient sources make to our modelled PAH emissions to water (Figure 4). Urban run-off is also a significant source of PAHs to water.

Estimated emissions indicate that WwTWs are the next significant source of PAHs to water (Figure 4 and Environment Agency, 2019). However environmental monitoring near and at such works suggest the presence of benzo(a)pyrene in surface waters is not primarily derived from sewage effluent. The higher dilution arising from wastewater discharges from WwTWs often reduces PAH concentrations immediately below them.

At a local scale, the relative significance of different sources is likely to vary depending on the degree of urbanisation and local industry present.

Controlling environmental releases of PAHs is especially difficult because of the very high number of diffuse sources producing them.

There are a significant number of controls on the release of PAHs already in place under EU legislation (Section 5). The gradual replacement of older combustion processes with newer ones, which are generally more efficient and cleaner, will have helped reduce releases. Benzo(a)pyrene emissions have dropped by an order of magnitude since the 1990s. However, the contribution from domestic combustion has changed little over this time and annual mean ambient levels have been steady from 2009 to 2014, with a slight drop until 2016 (Defra, 2017). This diffuse source is being tackled through the Clean Air Strategy 2019 (Defra, 2019).

Our biota monitoring data in surface waters up to 2018 indicate very low risk from benzo(a)pyrene. Only a few sites exceed the biota EQS based on mean concentrations. However, mean water concentration data from the water industry CIP2 and from samples taken at some of our biota sites suggest the ubiquitous presence of benzo(a)pyrene at

levels exceeding the water AA EQS. Water results are taken as total concentrations and may include PAHs adsorbed to fine sediments which may not be subsequently accumulated by organisms and so may overestimate risk. However, our biota monitoring of crayfish is mostly in less populated areas because they prefer river substrates higher up river catchments and so may not reflect more-polluted urban waters.

Our surface water monitoring data suggest widespread short-term risks to the aquatic environment, particularly in some saline areas and for benzo(g,h,i)perylene. This is probably more because of the lower EQS for benzo(g,h,i)perylene than differences in exposure compared with the other PAHs. The saline areas are commonly large active estuaries likely to contain sediment historically contaminated with PAHs.

The available trend data are limited. Information relating to benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene in saline water – the most comprehensive example of available trend data – shows declines in concentrations in shellfish and sediment in some regions but, in the main, no trend. We would need improved analytical techniques to truly assess any trends for benzo(a)pyrene in biota below the EQS.

It will be difficult to reduce PAH exposure and we will need continued engagement with stakeholders and relevant policymakers to continue to reduce inputs and mitigate potential effects from historical environmental contamination. Where risks from urban sources of PAHs are identified, we will encourage and work with others who have responsibilities in order to influence the development and co-delivery of risk mitigation solutions. For example, water companies can help address such risks through the development and delivery of drainage and water management plans (DWMPs), working closely with other stakeholders such as the Highways Agency.

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8. List of abbreviations and acronyms

CEFAS

Centre for Environment, Fisheries and Aquaculture Science

CEMP

OSPAR Coordinated Environment Monitoring Programme

CIP

Chemical Investigations Programme

CIP2

Chemical Investigations Programme, phase 2

CSEMP

Clean Seas Environment Monitoring Programme

DOME

Database on Oceanography and Marine Ecosystems

EQS

Environmental quality standard

EQSD

Environmental Quality Standards Directive

ERL

Effects range low

ICES

International Council for the Exploration of the Sea

IED

Industrial Emissions Directive

LOQ

Limit of quantification

OSPAR Oslo Paris Convention

PAH Polyaromatic hydrocarbon

PBT

Persistent, bioaccumulative and toxic

POPs

Persistent organic pollutants

Second cycle river basin management plans

SAGIS

Source Apportionment Geographic Information Systems

SI

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Statutory Instrument

SVHC Substance of Very High Concern

uPBT Ubiquitous PBT

UK NAEI UK National Atmospheric Emissions Inventory

UK PRTR UK Pollutant Release and Transfer Register

WFD Water Framework Directive

WwTWs Waste water treatment works

9. Glossary

Adsorb

A sorption process in which one substance becomes attached to another via adhesion to the surface.

Atmospheric particulate matter

Also known as particulate matter (PM) or particulates. Microscopic solid or liquid matter suspended in the Earth's atmosphere.

Bioaccumulate

The accumulation of a substance, such as a toxic chemical, in various tissues of a living organism.

Biomagnify

The concentration of a substance in an organism exceeds the background concentration of the substance in its diet.

Effects range low

Thresholds developed by the US Environmental Protection Agency for assessing whether contaminants in sediment concentrations are of ecological significance. Concentrations below these thresholds rarely cause adverse effects in marine wildlife.

Isomers

Molecules that have the same molecular formula but have a different arrangement of the atoms in space.

Limit of quantification

The lowest concentration at which an analyte can be reliably detected with precision and accuracy meeting defined goals.

OSPAR

The mechanism by which 15 governments and the EU cooperate to protect the marine environment of the North-East Atlantic.

Passive samplers

Sampling device left in situ in the water column.

Pollution Inventory

The inventory collates data from large regulated industrial sites on emissions of specified substances to air and controlled waters and sewers, as well as quantities of waste transferred off site. The thresholds for reporting are generally lower than those under the UK PRTR.

SVHCs

Substances meeting one or more criteria defined in Article 57 of the REACH Regulation (EC 1907/2006) can be identified as SVHCs. SVHCs are included on the 'Candidate List' for consideration as a priority for authorisation.

UK PRTR

The register collates data from industrial and business facilities on emissions to air, water and soil, as well as data on quantities of waste transferred off site. Data from the PI that meet the required reporting thresholds form a subset of the UK PRTR, as well as data from Local Authorities.

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