



Interim H4 indicator 2024: exposure and adverse effects of chemicals on wildlife in the environment

Supporting information and data

Date: May 2024

Version: 1.0

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Executive summary

Introduction

The H4 indicator 'Exposure and adverse effects of chemicals on wildlife in the environment' is one of a suite of indicators in the 25-Year Environment Plan's (25-YEP) Outcome Indicator Framework. The indicator contributes to measuring whether we are moving towards the goal of 'managing exposure to chemicals and pesticides' as given in the Environmental Improvement Plan 2023 ('the 2023 Plan'), the first revision of the 25-YEP. <u>Available updates to indicators under the framework</u> are reported annually on gov.uk alongside reports outlining environmental improvements made through the 25-YEP and the 2023 Plan.

This current report covers progress on the development of the H4 indicator and shows the 2024 update of our interim version, which uses a dashboard approach, and the corresponding data analysis behind it. The indicator is based on chemical concentrations found in water and in different organisms – sparrowhawk, common buzzard, red kite, red fox, freshwater fish, otter, blue mussel, estuarine and coastal fish, offshore fish (common dab), and harbour porpoise. It covers 3 environmental compartments: terrestrial, freshwater and marine (estuarine, coastal and offshore). The chemicals presented are representative of 3 groups requiring priority management as highlighted in the 25-YEP: (1) persistent, bioaccumulative – the accumulation of a substance over time in a living organism – and toxic (PBT) substances, (2) metals, and (3) pesticides and biocides. Mercury is considered within the PBT group because although it is a nonessential toxic heavy metal, its environmental behaviour is more akin to a PBT substance than to other metals

The dashboard illustrates statistically significant trends over time in environmental concentrations for the presented chemicals (see Figure at the end of this summary). Years for assessing trends vary for the data sources because of the different availability of relevant data. The earliest data are from 2001 for some data sets and we have considered data up to and including 2022 where possible, although some data sets represented in the dashboard stop at 2021 because no later data were available at the time of writing.

The indicator also considers potential risks to wildlife from chemicals by comparing national concentrations from the most-recent year (or 2 and 3 years in the case of offshore fish and water concentration data, respectively) against relevant environmental protection thresholds, if available. This assessment of risk provides a surrogate for effects reporting for this interim indicator and adds context to the reported trends in concentrations. It does not represent a compliance assessment but may be a trigger for further investigation. For PBT substances, the thresholds may differ from those used under other reporting regimes which are based on the protection of humans as the most-sensitive receptor.

The interim status of the indicator reflects that further development is necessary for the indicator to be complete, but that it is considered suitable and relevant for reporting now.

This reporting status of interim is a defined category under the 25-YEP Outcome Indicator Framework.

Since the previous reporting of the interim indicator in 2021:

- Monitoring has reduced for water samples taken from freshwater and estuarine and coastal waters, and for freshwater fish and mussels. Notable impacts of this are given in the description of the 2024 interim indicator below. Monitoring networks have also changed for water samples with the introduction of the River Surveillance Network (RSN) under the Natural Capital and Ecosystem Assessment Programme (NCEA) which considers the broadscale condition of the environment rather than likely impacted locations.
- Coverage of sparrowhawks has decreased with a move toward buzzard data. The transition between these 2 species is under development.
- Investigations are ongoing into sources of red foxes for assessments and how representative they are of the general fox population. Use of these data sources within the indicator is still under development.
- The introduction of per- and polyfluoroalkyl substances (PFAS) includes data sets within which the numbers of substances analysed have varied over time. Because archived samples are analysed in some cases, this does not necessarily mean an increase in PFAS over the years the samples represent. This is predominantly relevant for offshore fish and harbour porpoise data. The PFAS reporting is still under development.
- The freshwater assessment for pesticides is based on a threshold relating to the potential risk of long-term toxic effects. This is a change from the approach used in 2021, which looked at risks from acute exposure, and is now consistent with similar assessments within the indicator.

For some matrices – that is, the type of sample in which a chemical is being measured – additional data are available and are provided in this report, but they cannot be incorporated into the dashboard at present because there is not adequate information to allow for a trend or risk assessment. This largely relates to some PBT substances and metals in buzzards, red fox, and estuarine and coastal fish. It also includes PFAS in freshwater and in freshwater and offshore fish; perfluorooctanesulfonic acid (PFOS) data for offshore fish are also available.

Indicator dashboard summary

Many of our data sets are now showing statistically significant changes over time in chemical concentrations. For those that are not, this may be a consequence of some chemicals, such as PBT substances, being slow to respond to change or that some management actions may be in their early stages of implementation. It could also indicate that further investigation is needed as to why levels are stable. Limited data has also affected the interpretation of results in some cases.

Potential risk is seen for all 3 chemical groups, based on comparison of chemical concentrations at sites or within individual animals against thresholds chosen for the

purpose of this indicator. This is not unexpected given the choice of these substances as potential or known substances of concern.

For PBT substances, downward trends for polybrominated diphenyl ethers (PBDEs) and PFOS are observed in freshwater and marine wildlife, except for PFOS in otters which shows no trend. The downward trend for PBDEs in mussels has lower certainty. Downward trends are also seen for PFOS in freshwater. No trends are observed for polychlorinated biphenyls (PCBs) as a group; however, for the congener PCB 118, levels are decreasing in freshwater fish, but upward trends are seen in harbour porpoise. An upward trend is also seen for mercury in mussels, though this may be influenced by recent reductions in monitored sites. It should be noted that the results for PBTs in offshore fish and harbour porpoise in the interim indicator are generally based on well-established data sets covering long periods (greater than 10 sampling years). Within those data sets, PBDEs and PCBs in offshore fish and PBDEs and PFOS in harbour porpoise show levelling off or increasing concentrations in more-recent years.

The percentage of sites or samples exceeding thresholds is very high for mercury in the freshwater and marine environments, although this is either not observed or not known for top predators in all compartments. The result for mercury in offshore fish (common dab), however, is based on a threshold that could be considered over-precautionary for the tissue examined. Medium to very high potential risk is presented by PCBs; thresholds were only available for the marine environment for this assessment. Low potential risk is observed for PBDEs and PFOS in offshore fish and freshwater, respectively.

For metals, the trends over time are varied. Downward trends are observed for lead, cadmium, nickel, and zinc in freshwater, for lead in otters, and for lead and copper in mussels, though the result for copper in mussels has lower certainty. Lead also presents the majority of upward trends, which are seen in buzzards, freshwater fish, offshore fish (common dab), and harbour porpoise. Cadmium and zinc also have upward trends in offshore fish and mussels, respectively. Further investigation and increased monitoring may help provide a better understanding of the trends seen. The results for metals in offshore fish and harbour porpoise in the interim indicator are based on well-established data sets covering long periods (greater than 10 sampling years). Within those data sets, data for more-recent years for all metals in offshore fish, and for lead and nickel in harbour porpoise, suggest the need to review the situation over time as upward trends are observed.

The lack of thresholds relevant to many of the matrices covered in the indicator means it is often not possible to assess the potential risks that metals pose to wildlife. Recent levels of lead in buzzards and estuarine and coastal waters, and freshwater concentrations for lead, cadmium, nickel, and copper, show some but low potential risk. Zinc shows a medium to high percentage of sites exceeding thresholds in both water types. However, there has been more bias towards freshwater sampling sites affected by abandoned metal mines in recent years in the freshwater monitoring, and the number of sites assessed for metals in estuarine and coastal waters is substantially lower compared with previous reporting.

The freshwater sites from which water samples are taken can be split into 2 types: those located in waters polluted by metals from abandoned metal mines – as mentioned above – and those in other locations. Over the period from 2014 to 2022 for waters affected by abandoned metal mines, all metals show upward trends. For the same period in other waters not affected by abandoned metal mines, metal concentrations show overall downward trends. For waters affected by abandoned metal mines, their elevated levels of metals mean they comprise a high proportion of those sites which exceed available thresholds; very few 'other' sites are above the corresponding thresholds.

Pesticides in freshwater and the biocidal second-generation anticoagulant rodenticides (SGARs) in red kites show no statistically significant changes in concentrations over time. For SGARs in red foxes, a statistically significant upward trend is seen, although data for some years are few, increasing the uncertainty.

Percentage threshold exceedance suggests very high potential risk for pesticides in freshwater. However, there are some assumptions around the assessment, for example that additive toxicity occurs, to allow it to be based on exposure to multiple substances. Some of these substances may have environmental presence because of sources other than their use as plant protection products, for example imidacloprid is now primarily used as a veterinary medicine. Potential risk is indicated for less than a quarter of individuals considered for assessing SGARs in red kites. In this case only, the risk is assessed using an approach which includes looking at related SGAR effects observed in the birds, as opposed to solely assessing exceedances of threshold concentrations. Therefore, the trend in potential risk does not necessarily match that relating to concentration levels over time. Indeed, a statistically significant decrease in potential risk is observed in contrast to the steady levels of SGAR concentrations seen in these birds.

There is some variability across the different metrics in terms of years assessed, congeners or substances reviewed for PBDEs, PCBs and PFAS, treatment of limits of detection, and in the basis of the thresholds used. Our aim has been to make the assessment as comprehensive and consistent as possible using readily available data.

Further work

There remain data gaps for the terrestrial environment, and the baseline data for terrestrial species and estuarine and coastal fish are still being established. Representation of exposure at different trophic levels in the terrestrial environment needs improvement, although work such as that relating to honey monitoring and honeybees, for example, is starting to address this area. Exploration of the introduction of soil data remains a priority so that the entry point to exposure, at least to terrestrial wildlife, becomes known. This will also help contribute to the broader picture of the mobility of chemicals in the environment from source to receptor and their effects, in combination with other indicators under the Outcome Indicator Framework.

In addition, the specific monitoring activities that we depend on for these data have undergone challenges in recent years with the amount of available data decreasing. This is due to a range of issues, including pressures on the animals we monitor, the impact of the COVID-19 pandemic preventing collection, rising costs to deliver the same monitoring, and extreme weather events that have stopped us from being able to do some of the surveys we depend on. Further work is needed to establish the optimal way to collect data to reflect changes in chemical presence in the environment owing to action taken to manage these substances.

Research and development work is underway to improve the indicator in terms of harmonising our trend assessments, exploring how we assess risk further, understanding emerging risks and how to capture these, finding metrics to report on effects on wildlife, and strengthening our understanding of chemicals in the terrestrial compartment.

We will continue to explore options for all points raised through work on the indicator and its 2020 independent review. We are working to find ways to integrate our data into other areas of scientific investigation and policy development, where possible. In particular, we will explore opportunities to link our chemical information with that relating to biodiversity, to understand the influences of chemicals on ecosystem health and help inform the picture around biodiversity protection. Finally, we will take the indicator and its development back to expert national committees on chemicals for a second independent review before the next update.

Summary

- We have updated the H4 interim indicator and have included information on new species – buzzards and estuarine and coastal fish – and additional substances – PCB 118 and PFAS. Reporting for birds, foxes and PFAS is still under development.
- Statistically significant changes in concentrations over time are reported for representative chemicals in specific environmental matrices. The results are variable. Information on potential risk is given for context alongside points of note when considering the results.
- There are still some data gaps. The development of the terrestrial information within the indicator, in particular, is considered ongoing.
- Work is underway to improve our trend and risk assessments further, understand emerging risks and how to capture these, and find metrics to report on effects on wildlife.
- We continue to develop the indicator and integrate our data as widely as possible; we will seek independent review of the indicator before the next update.

The H4 indicator is a collaborative piece of work steered by representatives from Defra, the Environment Agency, Cefas, the Health and Safety Executive, the Joint Nature Conservation Committee, and Natural England. Contributors include these and the Cardiff University Otter Project, Fera Science Ltd. and the UK Centre for Hydrology and Ecology.

Figure Exposure of wildlife to chemicals in the environment – the interim H4 indicator dashboard

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1 Introduction

The UK Government's 25-Year Environment Plan (25-YEP) was published in 2018 (<u>UK</u> <u>Government, 2018</u>) and built upon through the first revision to the 25-YEP, the Environmental Improvement Plan 2023 ('the 2023 Plan'; <u>UK Government, 2023</u>).

One of the goals within the 2023 Plan is 'managing exposure to chemicals and pesticides'. This goal covers the safe use and management of chemicals and intends to ensure that levels of harmful chemicals entering the environment (including through agriculture) are significantly reduced. It is supported by a range of actions and specific targets relating to decreasing chemical and pesticide emissions (<u>UK Government, 2023</u>) and combines commitments within the 25-YEP for these substances under the one goal. To demonstrate any effect of those measures and progress towards the goal, it is important to consider other environmental information in relation to chemicals alongside emissions information.

To assist the monitoring of progress against commitments in the 25-YEP, the Department for Environment, Food and Rural Affairs (Defra) established a suite of indicators under an Outcome Indicator Framework (<u>Defra, 2023a</u>). Within that suite is the H4 indicator 'Exposure and adverse effects of chemicals on wildlife in the environment'.

The aim of the H4 indicator is:

- To show how exposure of wildlife on land or in water to harmful chemicals is changing, and
- To see whether wildlife is impacted by environmental exposure to such chemicals and compare this over time.

Other indicators under the Outcome Indicator Framework provide information complementary to H4 and support the measurement of progress towards the abovementioned goal. Directly related is the indicator H3 'Emissions of mercury and persistent organic pollutants to the environment'. Additionally, some of the water indicators such as B1 'Pollution loads entering water' help describe pressures on the environment relating to chemicals (<u>Defra, 2023a</u>). The Outcome Indicator Framework is updated yearly alongside the 25-YEP annual progress report (<u>Defra, 2023b</u>), which will be furthered with progress updates on the 2023 Plan from 2024.

Section 2 of this report describes progress on the development of the H4 indicator. Section 3 explains the approach taken for reporting and provides the 2024 interim indicator as a dashboard along with a summary. Section 4 describes the underlying data and its translation into the indicator. Tables and figures have been numbered based on their corresponding first-level subsection to ensure the text and data are easily associated. For example, the first table in Section 4.1 is numbered Table 4.1.1, the second Table 4.1.2, etc.

This interim version of the H4 indicator tracks changes over time in the exposure of wildlife to chemicals. It does this through looking at measured chemical concentrations in the environment in which wildlife lives and within such animals. It covers 3 environmental

compartments: terrestrial, freshwater, and marine (estuarine, coastal and offshore). Chemical groups considered are (1) persistent, bioaccumulative – the accumulation of a substance over time in a living organism – and toxic (PBT) substances, (2) metals, and (3) pesticides and biocides. The 3 groups reflect chemicals highlighted for management action in the 2023 Plan.

The indicator focusses on readily available data for these groups that are generated by repeat monitoring or have the potential to become regular sources of information. Much of the monitoring currently in place is undertaken for reporting commitments, such as:

- The Convention for the Protection of the Marine Environment of the North-East Atlantic (the 'OSPAR Convention') (<u>OSPAR Commission, 2023</u>)
- The UK Marine Strategy Regulations 2010 (<u>UK Government, 2010</u>) and the assessment of Good Environmental Status in Regional Seas
- The Water Environment (Water Framework Directive) Regulations 2017 (<u>UK</u> <u>Government, 2017</u>)
- The Water Framework Directive (Standards and Classification) Directions (England and Wales) 2015 (<u>UK Government, 2015</u>)

In addition, the indicator draws on data available from other monitoring campaigns and research activities.

The interim indicator also assesses potential risk to wildlife from chemicals by comparing the available monitoring data against relevant environmental protection thresholds, where possible. This helps add context to the levels of chemicals reported in the environment and acts as a surrogate for effects data while the reporting of that aspect of the indicator is still undergoing exploration.

Thresholds are generally derived from effects data, which are either generated in laboratories or based on field observations. Effects data can be categorised as sub-lethal or lethal. Some effects can be directly measured, such as changes in the morphology of an individual, altered reproductive success or death. Effects can also be measured indirectly, for example via changes in population levels or food resource over time.

As part of the H4 indicator development, we are running pieces of work to inform coverage on indirect and sublethal effects of chemicals. These are in early development (Section 2.4).

We are continuing to develop this indicator, guided by recommendations from the initial trial of the dashboard approach (<u>Shore, Walker and Chaplow, 2020</u>; <u>Shore and Walker</u>, <u>2020</u>), comments from the independent review of that work, and improvements identified through working with our partners (see also Section 2). We will also be steered by publications such as that resulting from the Natural England plant protection product monitoring review (<u>Natural England</u>, <u>2023</u>) and the planned UK Government Chemicals Strategy (<u>UK Government</u>, <u>2023</u>).

2 Development of the H4 indicator

2.1 Overview of the work since the 2021 update

The H4 indicator is multi-organisational work that is informed through technical and policy stakeholders on a steering group as well as individual experts on various related working groups (Figure 2.1.1).

The development of the H4 indicator up until the end of March 2021 is covered in the 2021 H4 indicator report (Environment Agency, 2021). Since we reported the 2021 indicator, a programme of research and development has been established to help strengthen our understanding of chemicals and their presence in and impact on the environment. The ultimate aim of the work is to hone the indicator and support policy partners to manage chemicals. The work is predominantly funded by Defra and is overseen through a project board (Figure 2.1.1); partner organisations lead on the delivery of that work.





As a result of our research and development to date, we have:

- refined our reporting to include additional substances and species, and increased our coverage of contaminants in existing species in the indicator (Sections 2.2.1 and 2.6)
- supported sample and data platforms, and analysed archived samples from these, to bring more robustness to our data sets (Sections 2.2.1 and 2.6)
- improved our reporting for some matrices in the indicator using better and/or more appropriate methods to assess them (Section 2.2.1)
- completed initial work exploring ways of assessing the reliability of the data 'power of the metrics' – to show change over time (Section 2.2.2)
- initiated work to increase our understanding of emerging risks, through targeted chemical screening, passive sampling, and nontarget and suspect screening (Section 2.2.2)
- completed initial desk-top study work to look for further suitable thresholds, and explored potential thresholds for future use through the Thresholds Task and Finish Group (Section 2.2.2)
- expanded our working groups to include an emerging risks and an effects working group, and addressed development feedback within these and the other working groups (Sections 2.3 and 2.4, respectively)
- initiated work to better understand chemical effects in different species (Section 2.4)
- investigated ways to improve on the coverage of the terrestrial environment as a critical entry point for chemicals to the environment (Section 2.5)
- maintained an awareness of or linked in with other related areas of work, such as the development of parallel indicators involving chemicals or ongoing exposure and effects research work (Sections 2.4 and 2.6)

To facilitate user involvement in the development of this indicator, we would welcome any feedback on this indicator, particularly on its usefulness and value, via email to: <u>25YEPindicators@defra.gov.uk</u>.

2.2 Chemical exposure development

2.2.1 Refinements to coverage within the current indicator

Since the previous round of reporting (<u>Environment Agency, 2021</u>), partners have worked to understand the availability of other data sources and have considered the possible inclusion of additional substances. The working groups have also contributed to the provision of the current H4 indicator data and its quality assurance.

Additional substances

We have introduced per- and polyfluoroalkyl substances (PFAS) and the polychlorinated biphenyl (PCB) congener 118 into the current indicator.

The selection of PFAS is discussed in detail in Section 2.3. The introduction of this group of substances is still under development, owing to the continuous improvement of analytical techniques to detect a wider range of PFAS and the need to explore further ways of reflecting that in the assessment of the data. Therefore, our assessments relating to PFAS are considered interim metrics. We have introduced PFAS under the PBT section of the H4 indicator as this group covers substances for which PBT is the primary (known) hazard. Those PFAS covered within the current indicator are given in Appendix A (see also Section 3.1.1).

The inclusion of PCB 118, as proposed in the previous indicator report (<u>Environment</u> <u>Agency, 2021</u>), was chosen to help improve our understanding and reporting of PCBs across different environmental compartments and trophic levels. There are more data sets available for this congener as it tends to be common across different reporting regimes. This is because it is a substance that is likely to be present in the environment, owing to its relatively high use in historical technical mixtures (Agency for Toxic Substance and Disease Registry, <u>ATSDR</u>, 2000) and its persistent and bioaccumulative properties. We have continued to report changes for PCBs – including PCB 118 – as a group, alongside reporting PCB 118 alone, to give a better idea of the magnitude of exposure to PCBs in general.

New species

For reasons discussed in Section 2.5, we are now building a baseline of PBT and metal contaminants in common buzzards, and these data are reported in the indicator for the first time. We will need to consider how best to transition from sparrowhawks to buzzards in our future reporting.

We have also introduced estuarine and coastal fish to our suite of matrices. This has the potential to allow us to improve our source to sea picture by having fish representative of freshwater, estuarine and coastal, and offshore areas. In addition, it helps improve our understanding and representation of chemicals in the estuarine and coastal environment; it may help to address potential gaps in knowledge that may occur in the future owing to mussel bed depletion (see Section 3.1.2). The baseline for these data is still being established.

Expansion of data using archived animal tissue

We have worked with partners from the Predatory Bird Monitoring Scheme (PBMS), Fera Science Ltd (Fera), the Cardiff University Otter Project (CUOP), and the Centre for Environment, Fisheries and Aquaculture Science (Cefas) to support and use existing wildlife sample and data platforms for birds, foxes, otters, and cetaceans, respectively.

The animal tissue from these platforms allows us to analyse chemicals in different top predators on a regular basis, improving our knowledge of contaminants moving up the food chain.

The work on birds and foxes aims to provide more insight on chemicals in the terrestrial compartment; further background on terrestrial development work since we last reported the indicator in 2021 (Environment Agency, 2021) is given in Section 2.5. As mentioned above, it has allowed us to report initial data on PBTs in birds; for foxes, we have been able to expand coverage of chemicals in these animals to some PBTs – mercury, PFOS and other PFAS – and metals.

Because the CUOP and the Cetaceans Strandings Investigation Programme (CSIP) hold archived samples, we have been able to create and/or expand on the timeline of PBT and metal contaminants in otters and harbour porpoise. Additionally, we have been able to strengthen the data for fish through the analysis of some archived samples.

Although we have extended our analyses to cover metals in top predators within the indicator, we are not reporting copper and zinc for these. This is because measured concentrations of these essential metals may be purely an indication of maintained physiological levels, and such species may not be good indicators of environmental change. Through the Thresholds Task and Finish (T&F) Group, we are conducting reviews of the literature to understand more about what concentration levels of these metals are considered typical within animals covered under the indicator and what thresholds may result in effects. Alongside the Metals Working Group, we will use any results and available monitoring data to determine whether we need to alter our approach to reporting for these metals.

Data assessment

We have used improved methodologies for the assessment of trends over time for freshwater and estuarine and coastal data compared with previous reporting (<u>Environment</u> <u>Agency</u>, 2021) to increase the robustness of our analysis.

For data sets that are well established and cover long periods (greater than 10 sampling years), we have provided commentary within the current report on more-recent trends to allow greater interpretation of the results for a single data set. This relates to the data for marine fish (common dab) and harbour porpoise.

The purpose of the Thresholds Task and Finish (T&F) Group is to review the appropriateness of the threshold values used to report potential risk in the H4 indicator. The group also considers suitable methods for assessment to ensure consistency within the indicator and with other reporting regimes, as far as reasonably possible.

The recommendations from the T&F group on the thresholds and their application have been incorporated into the data assessments in Section 4 and the thresholds used are summarised in Appendix B.

Compared with the last reporting of the indicator in 2021 (<u>Environment Agency, 2021</u>), we have introduced buzzards as a new environmental matrix alongside sparrowhawks for 2024 (see above). The thresholds used previously for metals in birds are considered as applicable to buzzards as for sparrowhawks. However, the concentrations of contaminants

measured in these birds have different units compared with the corresponding thresholds. A different conversion factor has been selected for buzzards compared with that for sparrowhawks as it is considered more appropriate for this species (Appendix B).

We have also moved to a chronic – rather than acute – risk assessment for pesticides in freshwater and consider their risk to a broader range of species and trophic levels, instead of solely the water flea *Daphnia magna*. This was recommended by independent review of the indicator in 2020 by the Hazardous Substances Advisory Committee (HSAC) and the Expert Committee on Pesticides (ECP) (<u>HSAC, 2020</u>; <u>ECP, 2020</u>) and is more in line with the approach used for other substances in freshwater.

An overview on the use of thresholds for generating the current H4 indicator can be found in Section 3.1.3.

2.2.2 Further research on exposure coverage and its assessment

Understanding data robustness

Reviewing the robustness of our data sets is particularly important. We need to understand the strength of our data in terms of its geographical coverage and whether it will reflect change over time owing to actions relating to chemicals management. The data sets must be the right magnitude to reflect any changes.

For any indicator, we need to work with available data. However, these data can be subject to different pressures or changes, such as:

- pressures on the animals we monitor, for example avian influenza or the depletion of mussel beds influencing our ability to have access to samples
- pandemics reducing or stopping sample collection
- rising costs to deliver the same monitoring
- moves to alternative monitoring networks
- extreme weather events preventing sample collection and/or potentially affecting the levels of contaminants in the environment

Some examples of how these pressures have influenced our approach and analysis are given in Section 3.1.2 and within the relevant subsections of Section 4.

Work has been undertaken to look at ways of understanding the ability of the current indicator data sets to show change over time (<u>Defra, 2024a</u>; <u>Environment Agency, 2024a</u>). This will be considered and the indicator data sets reviewed in future to allow further recommendations for improvement to our data collection and reporting. In addition, we are contributing, through our work and that of others, to improving the way we collect data on chemicals in the environment and their impacts through our research.

Improving the picture on exposure of chemicals to wildlife

As well as continuing to build on our existing indicator data sets, we are conducting research to understand how wildlife is exposed to a broader range of chemicals (see also Section 2.3).

We are exploring passive sampling in water as a technique to measure real-time exposure to chemicals. The intention is to link it to ongoing effects work (see Section 2.4) so we can understand impacts from environmental samples containing pesticides alongside a broader range of pollutants. We are using target screening to analyse water samples taken from areas where we expect to see exposure to a greater range of substances. And we are investing in nontarget screening techniques so we can conduct suspect screening on animals; we have started work in this area looking at archived otter tissue.

All these techniques have the potential to influence the future selection of substances under the indicator, contribute towards assessing the integrated impacts of diverse suites of pollutants (as recommended by HSAC and the ECP), improve our strategic monitoring, and broaden our understanding without using invasive monitoring techniques.

Soil data are currently absent from the indicator. We recognise the importance of this type of data for reflecting soil health and because soils can be an entrance point for the potential movement of chemicals both up the terrestrial food chain and to other environmental compartments. We plan to establish a soils group to consider the best way to represent this matrix and the chemicals within it.

To help address the evidence gap for lower trophic level terrestrial species, we have been supporting the measurement of pesticide residues in honey samples. These samples are collected directly from honey bee hives across England through the UK Centre for Ecology and Hydrology's (UKCEH) National Honey Monitoring Scheme. As well as developing our understanding of honey bee exposure to pesticides, this work is investigating how potential risk to bees may be considered using such data, and the intention is to link this work to effects measurements in the future. This work has been steered through the Pesticides and Biocides Working Group.

Finally, within our existing indicator, reporting of second-generation anticoagulant rodenticides (SGARs) is covered under the terrestrial component. Research (Kotthoff and others, 2018; Regnery and others, 2019) suggests that SGARs could be present in the freshwater compartment. As a result, we are investigating levels of these substances in otters in England to understand whether future coverage of SGARs under the freshwater component of the indicator is needed.

Improving our risk assessments

While contaminant data in soil are not yet available for reporting under the H4 indicator, the Thresholds T&F Group have decided any future soil risk assessments under the indicator will be conducted using soil screening values (<u>Environment Agency, 2022b</u>), where available.

Desktop studies have been completed (<u>Defra, 2024b</u>; <u>Environment Agency, 2024b</u>) to look for thresholds in the literature for certain contaminants and receptors of interest, for which gaps exist within our risk reporting. The T&F group will consider the outputs from these pieces of work, in combination with thinking both nationally and internationally under other reporting regimes, to identify potential thresholds that can be used in future reporting.

This includes considering the applicability of approaches to assess risk from unintentional chemical mixtures being developed under UK REACH (<u>Environment Agency, 2022a</u>) – regulation relating to the manufacture and use of industrial chemicals – and as part of the indicator work, using available monitoring data. The latter takes into account that pressures on the environment come from both legacy and emerging contaminants combined. For example, through the Pesticides and Biocides Working Group, we are now aware that some chemicals previously authorised as plant protection products are present in the environment because of alternative uses, such as in veterinary medicines.

Finally, we will need to determine a definition for when substances can be removed from the dashboard over time. This is considered low priority as the substances currently chosen are of national concern and show levels of potential risk.

2.3 Emerging risks

It was recognised that most chemicals within the H4 indicator might be considered legacy chemicals – that is, chemicals that have existing controls in place but are still found owing to their persistence. It is essential that the H4 indicator also reports on trends over time and risks to wildlife from emerging risks, so that it reflects current environmental exposure risks more holistically. In addition to using the indicator to help evaluate the impact of existing policy measures for legacy chemicals, by including coverage of emerging risks this may, in time, help inform future chemicals management actions so decisions, such as restrictions, can be made sooner.

In 2021, the Emerging Risks Working Group was formed to tackle this challenge and – as with the other H4 indicator working groups – comprises members from Cefas, CUOP, Defra, the Environment Agency, Fera, the Joint Nature Conservation Committee (JNCC), Natural England, and UKCEH.

Initially, the Emerging Risks Working Group's attention was focused on chemicals from the Environment Agency's Prioritisation and Early Warning System (PEWS) for chemicals of emerging concern (<u>Sims, 2022</u>) and the Environment Agency's programme of work on

PFAS. As of October 2023, PEWS had considered the potential risks to surface waters¹ (freshwater, estuarine and coastal), groundwater, soil, biota, and sediment from 281 individual chemicals. The results of this screening information are made externally available via a mailing list and through the sharing of heat maps, which give the Environment Agency's current view of the potential risk for each of those chemicals. The notable intentional omission within PEWS is PFAS, apart from trifluoroacetic acid, because of an extensive existing programme of work within the Environment Agency covering these substances.

The working group also recognised a need to keep a watching brief beyond individual chemicals, to cover broader emerging risk concerns. The working group is aware of other areas of ongoing discussion relating to emerging risks, such as chemicals that may have combined persistence and mobility and/or endocrine-disrupting properties. These encompass some subgroups of PFAS and plasticisers, some of which are being monitored through the PBT Working Group. In addition, the Emerging Risks Working Group watching brief covers antimicrobial resistance, microplastics, tyre wear particles, and advanced materials. As our understanding of these areas develops further, work is required to determine the potential for incorporating them into H4 indicator reporting or elsewhere.

The group has begun by looking at two groups of chemicals: PFAS and non-steroidal antiinflammatory drugs (NSAIDs).

2.3.1 Per- and polyfluoroalkyl substances

Per- and polyfluoroalkyl substances are a chemical family consisting of at least 5,000 individual substances. They are sometimes referred to as 'forever chemicals' because of their persistence in the environment and are of growing interest, as our understanding of them increases. As a result of their widespread use and persistence, PFAS are being found in many different environments. Data to determine exposure and hazard, and therefore understand risk, are not available for many PFAS.

As part of our previous reporting (Environment Agency, 2021), only perfluorooctanesulfonic acid (PFOS) was included within the H4 indicator as a representative PFAS of concern for which monitoring data were available, based on recommendations from the PBT Working Group. This was due to PFOS having much more extensive historical use prior to restrictions and existing drivers to assess its environmental presence (for example, <u>UK Government, 2017</u>). However, there is an increasing PFAS evidence base and increasing knowledge of the presence of a more

¹ It is noted that the lack of monitoring data in the terrestrial environment (globally and in England) may impact substances being prioritised because of a skew toward those identified within the freshwater and marine environments.

diverse number of individual chemicals that fall within the PFAS class. A more-robust approach to assessing exposure to PFAS within the indicator was considered necessary; in addition, looking to take a group approach is consistent with PFAS risk management elsewhere in Great Britain, such as in the PFAS Regulatory Management Option Analysis (<u>Health and Safety Executive (HSE), 2023</u>).

The Emerging Risks Working Group pulled together monitoring data that identified PFAS present in the environment, including in wildlife, in England. These data were used in the exposure section of the PFAS Regulatory Management Option Analysis (<u>HSE, 2023</u>) and the Life Apex project (<u>Environmental Institute, 2024</u>; <u>NORMAN Network, 2024</u>), which has further insights on PFAS in predatory birds and otters.

Following the review of the monitoring data, an additional 25 PFAS were identified and proposed as a minimum for inclusion in future monitoring for the indicator, where possible (Table 2.3.1). The substances presented in Table 2.3.1 were selected by considering PFAS that are (1) already regulated, or under consideration for regulation, (2) detected in UK monitoring either frequently or at very high concentrations, and/or (3) both detected in biota and considered novel replacements for other substances. The PFAS were generally only shortlisted if it was perceived that there would be analytical capabilities to incorporate them into monitoring, but it was noted that some further analytical development in some matrices may be required.

Through discussion within the PBT Working Group, it was considered appropriate to continue to report PFOS as a separate line in the H4 indicator for consistency with previous H4 reporting. As an interim approach, concentrations for any available additional PFAS have been summed together for each environmental matrix, and the results included in a separate line to PFOS. That is, PFOS is excluded from the PFAS line. This is considered appropriate as PFOS dominates the concentrations observed for PFAS in some environmental compartments when included in this group and may mask potentially important relationships being observed in other PFAS.

PFAS name	PFAS acronym	Chemical Abstracts Service number
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2

Table 2.3.1 Table of per- and polyfluoroalkyl substances (PFAS) for monitoring

PFAS name	PFAS acronym	Chemical Abstracts Service number
Perfluoroundecanoic acid	PFUnA; PFUdA	2058-94-8
Perfluorododecanoic acid	PFDoA; PFDoDA	307-55-1
Perfluorotridecanoic acid	PFTrDA; PFTriA	72629-94-8
Perfluorotetradecanoic acid	PFTeA; PFTreA; PFTeDA	376-06-7
Perfluorooctanesulfonamide	PFOSA	754-91-6
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2
Perfluorobutanesulfonamide	FBSA	30334-69-1
Perfluorohexanesulfonamide	FHxSA	41997-13-1
3-Perfluoroheptylpropanoic acid	7:3 FTCA	812-70-4
9-chlorohexadecafluoro-3- oxanonane-1-sulfonic acid	F-53B	756426-58-1
Perfluoropentanoic acid	PFPeA	2706-90-3

PFAS name	PFAS acronym	Chemical Abstracts Service number
Perfluoroheptanoic acid	PFHpA	375-85-9
1-Propanaminium, <i>N</i> - (carboxymethyl)- <i>N</i> , <i>N</i> -dimethyl-3- [[(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)sulfonyl]amino]-, hydroxide (Capstone B);	6:2 FTAB	34455-29-3
2-(Perfluorohexyl)ethanoic acid	6:2 FTCA	53826-12-3
Perfluoropropanoic acid	PFPrA	422-64-0
Trifluoroacetic acid	TFA	76-05-1

2.3.2 Nonsteroidal anti-inflammatory drugs

The Emerging Risks Working Group are reviewing the potential to include nonsteroidal anti-inflammatory drugs (NSAIDs) under the indicator. These are biologically active substances by design, with the potential to interact with biota, especially mammals.

From PEWS, ibuprofen stood out as a potential high risk because of having an established exposure pathway to the water environment, as well as requiring further consideration in soil, biota and sediment. Because of high levels of use by society, ibuprofen is continuously entering the environment, presenting a different challenge of pseudo-persistence owing to its frequency of use rather than its chemical properties.

Diclofenac also stood out as a substance of concern owing to risks presented to scavenging predatory birds. Like for ibuprofen (<u>Chopra and Kumar, 2020</u>), there is some (limited) evidence of possible effects in some aquatic species, including amphibians, fish and some invertebrates (<u>Joachim and others, 2021</u>).

Because both ibuprofen and diclofenac have similar functions, it was determined that the Emerging Risks Working Group would initially focus on these two substances. It will then consider how to represent NSAIDs as a group within the indicator, if possible.

2.4 Chemical effects development

One of the aims of the H4 indicator is to assess whether wildlife is impacted by exposure to chemicals and how this changes over time (see Section 1). The independent review by

HSAC and ECP (<u>HSAC, 2020</u>; <u>ECP, 2020</u>) highlighted the need for further consideration of the effects component of the indicator, as initial work had focussed on the assessment of exposure to chemicals. Work is underway to explore potential approaches to assess the impact of chemicals on wildlife that could be used for reporting under the H4 indicator. The work carried out to date is summarised below. This work is supported through the Effects Working Group, which was established in 2021 to help the translation of effects work into potential metrics for the indicator. Its membership is the same as that for other working groups (see Section 2.3).

Effects of chemicals on wildlife can involve consideration of changes observed in individual organisms through to those observed in populations and communities. The former could include, for example, the assessment of changes at the cellular and molecular levels – including changes in the expression of different genes – through to those relating to growth and reproduction measurements.

Several different approaches for considering effects from chemicals in terrestrial organisms, as well as those in freshwater and marine environments, are being considered through our research. The work varies from relatively small-scale scoping/review studies through to larger projects exploring more novel techniques and includes projects relating to:

1. Assessing existing data on concentrations of chemicals detected in organisms to determine whether they can be used to assess effects on organisms. This covers:

- comparison of concentrations of metals detected in sparrowhawks and buzzards under the PBMS with measurements relating their body, such as the organ weights of liver and kidney relative to body weight, to see if there is any relationship that could be used as a measure of effect
- assessment of whether data on concentrations of SGARs in the livers of red kites and common buzzards, collated through the PBMS and the Wildlife Incident Investigation Scheme (WIIS), can be used to indicate the likelihood of mortality in these species following exposure to these substances
- exploration of the use of PBMS data on levels of contaminants in peregrine eggs to determine whether there is a correlation between concentrations of contaminants and eggshell thinning that could be used as a potential indicator of effect
- consideration of whether information on insect populations collected for the Chick Food Index, which is used to predict the survival of farmland grain- and insectfeeding bird chicks – for example, grey partridge – and likely population change between years, could potentially be used to assess effects of pesticides on food resource – seed food and insect populations – and thereby indirect sublethal effects on bird populations
- assessment of the data collected through the CUOP to determine any links between concentrations detected in the otters assessed and indicators of otter health, such as population information, body condition, and organ and gland mass (<u>Hunt, Tilley and Chadwick, 2023</u>)

2. Considering currently available biological effects methods for assessing the impact of chemicals on wildlife. This covers:

- a review of potential approaches to assess effects in the freshwater environment, ranging from existing ecological approaches to assess changes in populations and communities through to more novel approaches including those based on changes at the genetic level in organisms
- review of available effects data to develop sensitivity assessments for mussel species, sea grass and oysters to chemical exposure

3. Conducting practical research creating or using novel approaches to assess effects and generate related data. This covers:

- consideration of the robustness of approaches based on genetic biomarkers for use in assessment of effects in soil (<u>Swart and others, 2022</u>)
- consideration of the use of a transcriptomic approach to assess effects of pesticides and mixtures of pesticides on aquatic life by looking at effects of chemicals on the expression of ribonucleic acid (RNA); the focus for this work is the invertebrate water flea *Daphnia pulex*
- use of a number of existing biological effects assessments in a survey of estuarine and marine environments across England; this work is building on a similar survey undertaken in 2010

The outputs from the above projects will be considered to identify their potential use in assessing effects of chemicals on wildlife for the H4 indicator. Some clear conclusions may be drawn during that process. For example, the study looking at heavy metals in sparrowhawks and the relationship with observed liver and kidney weights found that this is unlikely to be a sensitive and robust measure of effects for the H4 indicator. This is due to the likely sample numbers and conflicting factors that may influence the effect observed, for example the effects of starvation. However, other outputs may conclude the need for further research and consideration.

We will also need to take into consideration the outcomes of wider ongoing research on assessing the effects of chemicals in the environment. This includes work such as the Natural Environment Research Council (NERC) funded ChemPop project, which looked at the impact of chemicals on populations and ecosystems, and relevant work arising from the current UK Freshwater Quality Research Programme funded by NERC and Defra.

In addition, work undertaken by international organisations will need to be considered, such as the recently published OECD study on monitoring endocrine-disrupting effects in the freshwater environment (OECD, 2023). Historically, the use of effects-based methods to assess the environmental impacts of chemicals has focused mostly on the marine environment. The results from the above-mentioned estuarine and marine survey around England using established biological effects approaches, therefore, will be considered alongside data arising from existing schemes to see if, and how, they could be used within the H4 indicator. Examples of existing schemes include those undertaken through OSPAR and the Clean Safe Seas Environmental Monitoring Programme (CSEMP).

The assessment of the effects of chemicals on wildlife in the environment is complex and, as noted above, can potentially consider a range of endpoints, from effects at the gene

level to those on communities. While methods exist, the research community is very actively exploring more novel approaches. This, along with the work that has been undertaken for the H4 indicator, needs to be considered, as we work to identify potential approaches for reporting.

2.5 Terrestrial development

The availability of metrics for the terrestrial environmental compartment is less than for freshwater and marine. The underlying reason for this is the lack of regulatory frameworks, like the Water Environment (Water Framework Directive) Regulations 2017 (UK Government, 2017) or the Marine Strategy Regulations 2010 (UK Government, 2010). Data for the marine environment also come through reporting commitments under the OSPAR Convention (OSPAR Commission, 2023). These have been historically driven and supported by more-sustainably funded, long-term government monitoring programmes. For the terrestrial animals currently represented under the indicator, sample numbers reported on by year vary. This variation is largely not due to environmental factors, and can be explained by changes in funding, evidence needs and priorities, and capacity for sample collection and retrospective laboratory analysis. Therefore, our partners in Natural England have been developing the terrestrial evidence base and the framework required to support it.

Three disconnected, unstandardised sample and data platforms were identified and taken forward as part of a developmental chemicals and pesticides terrestrial monitoring programme for England. The platforms had a record of quality evidence, complementary funding sources and sampling methods, including the use of citizen science. The platforms were the PBMS, the WIIS for predatory birds and mammals – that is, red foxes – and the UKCEH National Honey Monitoring Scheme (see Section 2.2.2).

Alongside these, 2 additional platforms were included in 2021 because they were identified as necessary for the production of, and access to, metadata – including from post-mortems – and possible additional samples. The first was the Wildlife Disease Risk Analysis and Health Surveillance Programme at the Zoological Society of London in collaboration with Natural England, relevant for red kites and other potential species. The second was the *Echinococcus multilocularis* Surveillance Programme, relevant to foxes, undertaken by the Animal and Plant Health Agency (APHA) on behalf of Defra.

In the previous H4 indicator report (<u>Environment Agency, 2021</u>), it was possible to deliver reporting on some birds and mammals. The report, however, contained significant gaps in terms of the coverage of substances within these matrices owing to a lack of data or statistical power. In addition, there was no information across trophic levels, such as on soil communities and invertebrates.

Since 2021, the development of and reporting on the H4 indicator has been a driver and funding mechanism to deliver data through analysis of new and archived samples for chemicals. This has enabled us to build up backdated and ongoing baseline data on terrestrial wildlife exposure, with increased power of the data to detect changes over time

in concentrations of mercury, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), PFAS, metals, and SGARs (see Sections 3 and 4).

To deliver the data, our efforts have focused on three aspects: core capacity and capability building activities, targeted scientific investigations, and defining what 'fit-for-purpose terrestrial chemicals monitoring and indicators' means for the terrestrial environment.

Building monitoring capacity and capability was also important for the long-term delivery of data, with the intention of moving the key monitoring platforms from being developmental to operational. This involved improvements in sample handling procedures and investigations to understand what the supply versus tissue sample demand was.

The supply was mapped through re-cataloguing/digitising sample and data archives, including 8,350 samples from buzzards, sparrowhawks and red kites collected between 2015 and 2021. As such, the tracking of carcasses and samples through the PBMS systems and processes was enhanced. The analytical tissue sample demand was estimated through a review of sample mass requirements by contaminant, analytical method and tissue type for species of interest to the H4 indicator.

This information allowed us to assess whether adequate supply was available for the use of terrestrial species within the H4 indicator. There was no concern over supply in red foxes or red kites. The Eurasian sparrowhawk, however, with a low liver weight compared with that required for analysis, was identified as a possibly unviable H4 matrix. Common buzzards were a more-favourable and cost-effective alternative, having a greater liver weight.

Key technical questions were raised around the sampling design that required investigations and these were broken down by matrices and substances of interest. For all vertebrate matrices, investigations were initiated comparing contaminants in different target organs (kidney versus liver) to begin to enhance the sampling design and address the issue of limited sample supply, and to achieve a more cost-effective use of laboratory analysis. The data will need further interpretation before a shift is made to using kidney over liver tissue. We also need to consider how we can interpret such chemical concentrations and link them to acute or chronic endpoints.

To assess if a switch from sparrowhawks to buzzards as an indicator species was scientifically valid, a comparison of metal concentrations in livers from the 2 species was undertaken. The key findings were that buzzards presented comparable trends over time to sparrowhawks and overall had a better coverage of data (see Appendix C). Buzzards are more representative of terrestrial exposure pathways and food webs owing to their varied diet and prey items that are not commonly associated with freshwater habitats.

The use of buzzard data would allow for a more-consistent within-species measure of exposure, with more statistical power and less variability, and allow a larger analytical suite. Buzzards could, therefore, enable improved understanding of exposure to chemical mixtures. However, there were greater levels of mercury in sparrowhawks compared with those in buzzards (Appendix C). This was attributed to a potential aquatic pollution

exposure pathway. The risk of not being able to reflect this is considered manageable, as the otter metric would be able to depict aquatic exposure of top predators to mercury.

We undertook work to improve our understanding of SGAR exposure and effects across red kites and red foxes. This confirmed that red kites and red foxes were appropriate matrices for assessing exposure to SGARs. Additionally, improvements were made to the fox sampling design; the design was initially restricted to the use of WIIS, which had a limited sample size and potentially skewed data, owing to the link to suspected poisoning incidents (see Section 4.24). Therefore, we undertook additional analyses of SGARs – and other contaminants – in red fox livers gathered through the *Echinococcus multilocularis* Surveillance Programme.

Finally, because of our dependency on disconnected unstandardised sampling and data platforms, we have undertaken steps to understand how data from different platforms could be produced using comparable quality and ethical standards. Such harmonisation will enable transparent evidence-based decision making and reporting that meets regulatory needs and standards. We are addressing this through the application of systems thinking, workshops and the ongoing collaborative development of terrestrial chemicals monitoring sample and data protocols.

The development of the terrestrial information within the indicator is ongoing.

2.6 Future direction

The work described in Sections 2.2 to 2.5 reflects our response to recommendations from HSAC and the ECP (<u>HSAC</u>, 2020; <u>ECP</u>, 2020), as well as comments received from our partners during the indicator's development. We will continue to develop the indicator based on that advice and to find ways to integrate our data into other areas of scientific investigation and policy development, where possible. In particular, we will look for opportunities to link our chemical information with that relating to biodiversity, to understand the influences of chemicals on ecosystem health and help inform the picture around its protection.

Finally, we aim to take the indicator and its development back to independent review before the next update.

3 Indicator dashboard and reporting summary

3.1 Overview of the dashboard construction

The interim H4 indicator dashboard is shown in Figure 3.1.1.

The information in the interim indicator reflects our assessment of readily available data with which we have explored changes in chemical concentrations over time and assessed potential risk, as a surrogate for effects, using available thresholds. It is based on data up until at least the end of 2021 and to the end of 2022, where possible; the data sources differ in terms of what time periods are available (see Section 3.1.1).

In the dashboard, columns represent environmental compartments and available data for matrices within them. Rows are clustered by the 3 chemical groups considered under the indicator with representative priority chemicals shown. The 3 chemical groups are:

- PBT substances
- metals
- pesticides and biocides

Mercury is considered within the PBT group because although it is a nonessential toxic heavy metal, its environmental behaviour is more akin to a PBT substance than to other metals.

For some data sets, there is not yet enough information to describe trends in concentrations over time or to assess potential risk. Where entries are given as 'D', this reflects that we are still developing a baseline data set for these contaminants in those matrices, but that data are available and are reported here. This largely relates to some PBT substances and metals in buzzards, red fox, and estuarine and coastal fish. It also includes PFAS in freshwater and in freshwater and offshore fish; PFOS data for offshore fish are also available.

Some matrices may not have an entry for a particular contaminant; this is due in some cases to a particular matrix being less relevant as an exposure route. For example, most PBT substances are unlikely to be detected in water as they are highly insoluble and more likely to be found in organisms such as fish. In other instances, it is because there are no data yet for that data source.

There is some variability across the different data sets in terms of the substances reviewed under the groups polybrominated diphenyl ethers (PBDEs), PCBs and PFAS and in the treatment of results below detection limits (see Section 3.1.1).

Figure 3.1.1 Exposure of wildlife to chemicals in the environment – the interim H4 indicator dashboard



Monitoring networks, analytical methods and thresholds can change over time. Since reporting the indicator in 2021 (<u>Environment Agency, 2021</u>):

- Monitoring has reduced for water samples taken from fresh, estuarine and coastal waters, freshwater fish and mussels. Notable impacts of this are given in the description of the indicator. Monitoring networks have also changed for water samples with the introduction of the River Surveillance Network (RSN) under the Natural Capital and Ecosystem Assessment Programme (NCEA) which considers the broadscale condition of the environment rather than likely impacted locations. Monitoring for estuarine and coastal fish has been introduced into the indicator.
- Coverage of sparrowhawks has decreased with a move toward buzzard data. The transition between these 2 species is under development.
- Investigations are ongoing into sources of red foxes for assessments and how representative they are of the general fox population. Use of these data sources within the indicator is still under development.
- The introduction of PFAS includes data sets within which the numbers of substances analysed have varied over time. Because archived samples are analysed in some cases, this does not necessarily mean an increase in PFAS over the years the samples represent. This is relevant predominantly for offshore fish and harbour porpoise. The PFAS reporting is still under development.
- The freshwater assessment for pesticides is based on a threshold relating to the potential risk of long-term toxic effects. This is a change from the approach used in 2021, which looked at risks from acute exposure, and is now consistent with similar assessments within the indicator.

3.1.1 Summary of available data

The data sources considered within the dashboard are outlined in Table 3.1.1.

Compartment	Matrix	Species (common name)	Source organisation	Monitoring scheme
Terrestrial	Biota	Common buzzard	UKCEH	PBMS
Terrestrial	Biota	Eurasian sparrowhawk	UKCEH	PBMS
Terrestrial	Biota	Red kite	UKCEH/Fera Science	PBMS/WIIS
Terrestrial	Biota	Red fox	Fera Science	WIIS/APHA
Freshwater	Water	_	Environment Agency	WER/emerging substances surveillance sites/Watch List sites/CSF/RSN

Table 3.1.1 Data sources used for the H4 indicator¹

Compartment	Matrix	Species (common name)	Source organisation	Monitoring scheme
Freshwater	Biota	Brown trout, chub and roach	Environment Agency	WER
Freshwater	Biota	Eurasian otter	Cardiff University	CUOP
Marine (estuarine and coastal)	Water	_	Environment Agency	WER
Marine (estuarine and coastal)	Biota	Blue mussel	Environment Agency	OSPAR/WER
Marine (estuarine and coastal)	Biota	Predominantly dab, flounder and plaice	Environment Agency	WER
Marine (offshore)	Biota	Dab	Cefas	UK MSR–OSPAR
Marine (offshore)	Biota	Harbour porpoise	Cefas	CSIP, SMASS and Cefas GiA with Defra

¹UKCEH: UK Centre for Ecology and Hydrology; Cefas: Centre for Environment, Fisheries and Aquaculture Science; PBMS: Predatory Bird Monitoring Scheme; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency; WER: Water Environment Regulations 2017; CSF: Catchment Sensitive Farming; RSN: River Surveillance Network; CUOP: Cardiff University Otter Project; OSPAR: Oslo and Paris Convention; UK MSR: UK Marine Strategy Regulations; CSIP: UK Cetacean Strandings Investigation Programme; SMASS: Scottish Marine Animal Stranding Scheme; GiA: grant in aid.

The substances and time periods covered by the data are summarised in Table 3.1.2. The data are from over the last two decades and run to the end of 2022, where possible at the time of writing, or 2021 if not. The time periods for the different data sets vary. The year ranges are selected based on the availability of relevant chemical concentrations and to facilitate the assessment of trends over time.

Relevant data may be affected by changes in monitoring regimes over time, including analytical method changes, availability of samples in the case of animal collection, and events beyond the control of the organisations responsible for the monitoring. Any previous changes to sampling and analysis have been noted within the subsections of Section 4, as well as any influence that those changes have had on the year selection for that data set.

current report ¹						
Compartment	Species (common name) or media	Chemical group	Substance(s)	Time period		
Terrestrial	Common buzzard	PBTs Metals	Hg PBDEs, PCBs, PFOS and other PFAS Pb, Cd, Ni	2001, 2004–2006, ² 2010, 2013, 2016, 2018–2021 2018, 2019, 2021 2001, 2004–2006, ² 2010, 2013, 2016, 2018–2021		
Terrestrial	Eurasian sparrowhawk	PBTs Metals	Hg Pb, Cd, Ni	2000, 2005, 2006, 2011– 2013, 2020, 2021 ³ 2007–2014, 2020, 2021		

SGARs

Hg, PFOS and

other PFAS

PFOS, PFOA

Pb, Cd, Ni, Cu, Zn

active substances

Plant protection

PBDEs, PFOS

PBDEs, PCBs,

Pb, Cd, Ni

PFOS, other PFAS

Other PFAS

and their metabolites

Hg

PCBs

Pb, Cd

Hg

Pb, Cd, Ni

SGARs

2015-2021

2018-2021

2018-2021

2015-2022

2016-2022

2014-2022

2016-2022

2014-2019, 2022

2015–2019, 2022

2022

2014-2021

2015-2021

2014-2021

2015–2019, 2021, 2022

2016–2019, 2021, 2022

Pesticides

PBTs

Metals

PBTs

Metals

PBTs

Metals

PBTs

Metals

Pesticides

and biocides

Pesticides

and biocides

and biocides

Terrestrial

Terrestrial

Freshwater

Freshwater

Freshwater

Red kite

Red fox

Water

Brown trout,

Eurasian otter

chub and

roach

Table 3.1.2 Substances and time periods covered by the data in the H4 indicator and the

Compartment	Species (common name) or media	Chemical group	Substance(s)	Time period
Marine (estuarine and coastal)	Water	Metals	Pb, Cd, Ni, Cu, Zn	2014–2022
Marine (estuarine and coastal)	Blue mussel	PBTs Metals	Hg PBDEs PCBs Pb, Cd, Ni, Cu, Zn	2011–2019, 2021, 2022 2015–2022 2011–2022 2011–2022
Marine (estuarine and coastal)	Mainly dab, flounder and plaice	PBTs Metals	Hg, PCBs PBDEs, PFOS Pb, Cd, Ni, Cu, Zn	2018–2022 2017–2022 2018–2022
Marine (offshore)	Dab	PBTs Metals	Hg, PBDEs, PCBs PFOS and other PFAS Pb, Cd, Ni, Cu, Zn	2008–2022 2014–2022 2008–2022
Marine (offshore)	Harbour porpoise	PBTs Metals	Hg PBDEs PCBs PFOS Other PFAS Pb, Cd, Ni	2009, 2011–2021 2004–2008, 2010–2021 2004–2021 2001–2003, 2009, 2012– 2021 2009, 2012–2021 2009, 2011–2021

¹PBTs: persistent, bioaccumulative and toxic substances; Hg: mercury; Pb: lead; Cd: cadmium; SGARs: second-generation anticoagulant rodenticides; PFOS: perfluorooctanesulfonic acid; PFAS: per- and polyfluoroalkyl substances; PFOA: perfluorooctanoic acid; Ni: nickel; Cu: copper; Zn: zinc; PBDEs: polybrominated diphenyl ethers; PCBs: polychlorinated biphenyls.

²The trend assessments for mercury and cadmium were based on subsets of the data which did not include data from 2005 (see Sections 4.1 and 4.11, respectively).

³The trend assessment was based on a subset of the data which did not include data from 2021 (see Section 4.2).

The congeners included in the PBDE and PCB groups, and the individual PFAS summed for the PFAS group, differ between data sets. The specific substances included in each assessment are noted within the relevant subsections of Section 4. For PFAS, those included within each data set are also summarised in Appendix A. In some cases, the use of archived samples means that the analysis of the material was not performed in the same year as that in which it was collected. We have indicated in the relevant sections where historical samples have been analysed and included with the data set we previously reported. For new data sets established using archived material, such as for otters, analysis of the historical samples has been performed within the last few years.

For PFAS, it should be noted that the analytical suites for these substances are constantly expanding. In addition, some data sets comprise both results from the analysis of archived samples and from animals analysed in the same year in which they were collected. Together, these factors mean that the PFAS included can be very variable for a single matrix. Where this occurs, we have indicated the number of PFAS covered each year within the corresponding tables summarising the data in the relevant subsections in Section 4.

Another way that data sets may differ slightly is in their treatment of values below the limit of detection (LoD), so-called non-detects. For the indicator assessment, concentrations of individual congeners – for PBDEs and PCBs – or substances – for PFAS and SGARs – are summed to give a total value for each sample. To do this, generally, the congener or PFAS concentrations that are reported below the LoD have been given either a negligible or zero value. This approach is applied under reporting regimes for PCBs and PBDEs (for example, <u>European Commission (EC), 2009</u>), although may be implemented in slightly different ways, depending on the reporting requirements and calculation tools. It does mean that environmental concentrations may be assumed to be lower than they are. Conversely, it avoids falsely elevated concentrations that would be seen by summing non-detect results treated as half than or equal to the face value of the LoD. The handling of results below the LoD for each data set is explained in more detail in the subsections of Section 4.

3.1.2 Trend assessment

Statistically significant trends over time are indicated in the dashboard using arrows (Figure 3.1.1). A horizontal arrow indicates no change in concentrations over time, and upward and downward arrows denote increasing and decreasing trends in concentrations, respectively.

Our aim is to report exposure trends when there is a minimum of at least 5 full years of change within the data (6 independent sampling years). The results used in the dashboard are based on the full time periods of the data sets (Table 3.1.2).

A small number of matrices have well-established data sets covering long periods (greater than 10 sampling years). In these cases, it has been possible to assess trends for the full time period available and for more-recent years based on the minimum data requirements for trend assessment specified above. The former assessment is still used for the dashboard, but the latter is given as additional information in the text descriptions of the indicator (Sections 3.2 and 5) to provide further context to inform chemicals management.
Trends based on longer periods are potentially more meaningful, particularly for PBT substances for which policies are already in place to limit their input into the environment, but where the resulting changes are slow because of the persistent nature of the chemicals. It may be that as management action takes place over the lifetime of the UK Government environmental plans, such as on the remediation of water affected by abandoned metal mines to achieve targets set out in the 2023 Plan (<u>UK Government,</u> 2023), trends become visible in the short term for some substances.

The methods of trend assessment used vary for the different data sets depending on the data quantity and structure, and they are informed and/or conducted by partners who are familiar with those data. In addition, there may be small differences in the data given in tables showing summary statistics, their graphical visualisation and the graphs that illustrate the results of the trend analyses. There are generally two potential reasons for these differences:

- small differences in methods used for calculating medians and quantiles, especially for small data sets and those with an even number of observations
- means in tables are arithmetic means, whereas some trend assessments, particularly involving chemical concentrations in water, are undertaken on logtransformed data; in the latter case, this is equivalent to estimating the trend of the geometric mean of the data

We will work to further harmonise our methods for future trend assessment reporting.

In the case of top predators, measured concentrations of essential metals may be purely an indication of maintained physiological levels. For this reason, such species are not necessarily good indicators of environmental change and entries for copper and zinc in these animals in the dashboard are left blank. Essential metals are reported in lower trophic levels, where data are available, with the caution that changing levels of substances such as copper and zinc may be hard to interpret (see also Section 2.2.1).

It should be noted that the trends assessment may mask local changes in environmental concentrations of chemicals. We have endeavoured to comment on any observations relating to this where possible within specific data sections in Section 4 and have included any key findings in the dashboard summary (Section 3.2).

We have noted where our trend analysis is particularly influenced by reductions in monitoring in recent years. In particular, freshwater fish and blue mussel site numbers are low.

In relation to the blue mussel data, monitoring sites were first established to assess the trend in contaminants in biota over time in the UK Regional Seas and covered a range of geographical locations with varying background pressures. However, logistical challenges, including the disappearance of key blue mussel beds, has resulted in the alteration of the monitoring regime over time. We will need to consider the continued impact of such changes on the year-on-year balance of sites across geographical and pressure gradients when assessing overall concentrations and trends across English waters.

3.1.3 Threshold assessment

Exposure concentrations for the most-recent year(s) of data – see Table 3.1.2 for the latest year(s) – are assessed against available thresholds to give an indication of potential risk. In most cases, the assessment is based on monitored concentrations for one year; exceptions are those for concentrations of chemicals in dab, where 2 years of data are used, and for PFOS and metals in water, which is based on 3 years. These exceptions reflect the monitoring schemes in place because only partial coverage of the country – geographically or in terms of number of samples – is achieved in a single sampling year. This approach allows a more-complete assessment across England and its coastline.

The basis of the thresholds differs for each substance/matrix; further details can be found in the relevant subsections of Section 4 and the corresponding references. The thresholds used are summarised in Appendix B.

The results are graded according to how many sites or individual samples out of those examined are below or above the threshold. As the percentage above increases, the circles in the dashboard appear increasingly darker (Figure 3.1.1).

Where possible we have used statutory values for the threshold assessments, such as those under the Water Framework Directive (Standards and Classification) Directions (UK Government, 2015) which are used for water quality assessments, or values used as part of international assessments, for example OSPAR. Our focus is on wildlife and, therefore, the thresholds used in the indicator may not always be the same as those used under other reporting regimes where values for the protection of human health may be used instead. In the absence of a statutory or internationally used value for the protection of wildlife, we have used thresholds based on agreed guidance (EC, 2011a) and that have been subject to a review process by an independent committee.

Where threshold values are based on different tissues to those measured, we have highlighted any differences in the interpretation of the results.

Some of our data sets are for species for which nationally or internationally agreed threshold values for chemicals do not exist. In such cases, we have used values from primary literature or reviews of such information. It should be noted that their derivation will be slightly different to statutory values, where additional factors may have been applied to address uncertainty. Therefore, it is possible that concentrations reported as below a threshold for some data sources may reflect differences in the derivation of such values; this has not been assessed as part of this report.

In the assessment for SGARs in red kite, autopsy information was used, which represents a move towards looking at effects rather than potential risk (Section 4.23.4).

The available thresholds for PBDEs and PCBs are either for the whole chemical group or for several individual congeners, depending on the matrix being considered. For those matrices that have thresholds for individual congeners, each congener is assessed against

the corresponding threshold and the result indicating the greatest risk is used in the dashboard.

We have sought to apply thresholds in a way that is as consistent as possible across compartments and appropriate to the data being assessed. Our risk assessment is a general guide to determine where further investigation or action may be advised and is not a compliance assessment.

Future work is needed to consider negligible or background levels for the substances in different matrices in the indicator. This will help differentiate between those substances which report no change but still require management and those that are consistently at negligible levels. It will also provide a route to decide when to remove substances from the indicator.

3.2 Dashboard summary

We have been able to report the interim H4 indicator using data representing 12 different matrices (Figure 3.1.1).

The indicator represents data for England, except for some of the marine data for offshore fish (common dab) and cetaceans. The fish data include a Welsh site in the Bristol Channel, thus still following the England coastline, and the cetacean data cover Great Britain, reflecting the greater movement of these species. The approach for the cetacean data is consistent with that adopted for other marine indicators under the Outcome Indicator Framework.

We have addressed evidence gaps so that we are able to report more on contaminants in our indicator matrices than previously. We have also introduced the reporting of PCB 118 and PFAS. The former allows us to show changes across environmental compartments using a common PCB congener and is complementary to our PCB reporting. The latter reflects growing interest and research into PFAS and is complementary to our reporting on PFOS as a substance, which was originally selected as a representative PFAS of concern for which monitoring data were available. The assessment does not include PFOS, which we continue to report separately.

We are still building our baseline data in some cases, namely for PBTs and metals in terrestrial species and estuarine and coastal fish, and for PFAS in most media. These data sets do not contain enough adequate data to allow full reporting in the dashboard, but assessment of the data as far as possible is given in Section 4.

Data for the terrestrial compartment that are representative of the entry of chemicals into the environment – that is, soils data – and in species other than top predators are lacking. Future decisions will be required to determine which bird species to monitor over time and to set a sampling strategy for red foxes. The viability of using mussels in the long term will also require review. Data resulting from changes in monitoring networks and/or reductions in monitoring will need further consideration to ensure what we use within the indicator has

the potential to reflect changes over time as a result of actions taken to manage chemicals.

3.2.1 Persistent, bioaccumulative and toxic substances

This group covers mercury, PBDEs, PCBs, PCB 118, PFOS, and other PFAS. Data are available for PBT substances in all matrices – though not all bird species – except for PBDEs and PCBs in red foxes, PFOS and other PFAS in mussels and PFAS in estuarine and coastal fish. Water is not considered an appropriate matrix for PBT substances apart from PFOS and other PFAS.

For those matrices for which there are enough data to report trends over time, mercury levels appear to be steady in all environmental compartments (Figure 3.1.1). The exception to this is for mussels for which a statistically significant increasing trend is observed, though this may be influenced by recent reductions in monitored sites. For PBDEs, downward trends are observed in all matrices with adequate data for assessment; for mussels, this result has lower certainty. No trends are observed for PCBs as a group. However, trends are seen for PCB 118; these are a downward trend in freshwater fish and an upward one in harbour porpoise, with no changes in concentrations observed for otters, mussels and offshore fish. A downward trend is observed for PFOS in water, freshwater fish and harbour porpoise; levels in otters do not show any statistically significant trend. Trends in PFAS concentrations could only be analysed for otters and harbour porpoise, where they appear to be stable.

Some of the offshore fish and harbour porpoise data sets span more than a decade. While not shown in the dashboard, based on the most-recent 5 full years of change within the data (see Section 3.1.2), a levelling off of concentrations has been observed for PBDEs in offshore fish with fewer sites showing downward trends. Similarly, concentrations of PBDEs and PFOS in harbour porpoise appear to be levelling off. The corresponding information for PCBs indicates an upward trend in offshore fish. This suggests the need to continue to review the situation over time for these substances and understand the influences on these observations further.

Only limited data are available for terrestrial media, and more information is needed to establish a picture of trends in concentrations for this compartment.

Based on our consideration of potential risk owing to PBTs, mercury shows a very high percentage of results above available thresholds for all fish and mussels (Figure 3.1.1). For freshwater fish, there is a perceived increase in potential risk compared with 2021 reporting, although the results still fall within the same risk group; however, the current results are based on very low sample numbers. The result for mercury in dab is a tentative one as it is based on a threshold that could be considered over-precautionary for the tissue – muscle rather than whole fish – examined (see Section 4.9.4). No results are observed above the corresponding thresholds used for birds and otters for mercury.

Polychlorinated biphenyls are also found at levels above their corresponding thresholds in the marine environment in a medium to very high number of cases (Figure 3.1.1), and their

lack of decline suggests these substances continue to be a high priority for attention too. The congener PCB 118 has driven the risk assessment results for the PCBs group in the dashboard as individual congeners have been assessed. The results for mussels indicate a move to a lower risk category compared with 2021 reporting; however, the current results are based on a very limited number of sites. For offshore fish, there is a large increase in the percentage of results above the threshold, resulting in a move up 2 risk categories. While the results for harbour porpoise represent a decrease in risk category from the 2021 reporting, which used 2018 data, additional sample analysis since then for carcasses from 2018 means that the results for that year now show the same level of potential risk as the current results.

For PBDEs, only offshore fish have concentrations above the corresponding thresholds; less than a quarter of sampling locations indicated potential risk. A low level of risk is also observed for PFOS in freshwaters. The results for PFOS in freshwater fish indicate a perceived move to a lower risk category compared with 2021 reporting, with no results above the threshold; however, the current results are based on a very limited number of sites.

Levels of summed PFAS – without PFOS – were typically lower in each matrix compared with those of PFOS; they were most similar within freshwater fish.

3.2.2 Metals

This group covers the metals lead, cadmium, nickel, copper, and zinc. Copper and zinc are not reported in top predators because measured concentrations in these animals may be purely an indication of maintained physiological levels. Data are available for metals in all matrices, except for metals in red kite and nickel, copper and zinc in freshwater fish.

In most cases, trend assessment was possible. Only red foxes and estuarine and coastal fish did not have adequate data for this purpose; limitations around the data set for nickel in sparrowhawks also meant an assessment was not possible. The picture is varied for each metal across the different matrices (Figure 3.1.1).

Statistically significant upward trends are observed for lead in buzzards, freshwater fish, offshore fish, and harbour porpoise. Conversely downward trends are seen in freshwater, otters and mussels. No change in concentrations is observed in sparrowhawks and estuarine and coastal waters for lead.

For cadmium and zinc, the situation is less variable across the matrices: no changes in concentrations over time are observed except for decreasing concentrations in freshwaters for both metals and increasing ones in mussels for zinc and offshore fish for cadmium. Nickel and copper exhibit downward trends in freshwater and mussels, respectively, though the result for copper in mussels has lower certainty; no changes in concentrations over time are seen in the other matrices assessed.

Further investigation and increased monitoring may help provide a better understanding of why the picture for metals is varied. The data for buzzards, offshore fish and harbour

porpoise span more than a decade. While not shown in the dashboard, assessments have also been made based on the most-recent 5 full years of change within the data (see Section 3.1.2). The upward trend seen for lead concentrations in buzzards based on the full data set is not observed in more-recent years. However, for all metals in offshore fish and for lead and nickel in harbour porpoise, the assessments suggest the need to review the situation over time as upward trends are seen.

Like the other reported trends over time, those for metal concentrations in freshwater fish and mussels are statistically significant; however, they are based on limited data. The significance of the limited variation in the concentrations of copper and zinc in offshore fish, with a slight increase in values taken from the west coast in the last couple of sampling rounds, is not yet clear. These values may be a reflection of naturally regulated concentrations in fish as copper and zinc are essential metals.

Risk assessment shows lead concentrations are above the threshold for a very low percentage of buzzards, suggesting low potential risk for these birds (Figure 3.1.1). Low potential risk is also observed for lead, cadmium, nickel, and copper in freshwater and for lead in estuarine and coastal waters, as less than a quarter of the sites monitored are above the corresponding thresholds. The estuarine and coastal waters result for lead has moved up a risk category since the 2021 reporting; however, it should be noted that this change was influenced by a single site. Similarly, nickel is now showing no risk compared with 2021 reporting in this matrix owing to one site fewer exceeding the threshold.

For zinc, medium and high potential risk is observed in freshwater and estuarine and coastal waters; this is a perceived move up 1 and 2 potential risk categories, respectively, since 2021 reporting. For the former result, this is influenced by a decrease in monitoring at certain sites in recent years, resulting in bias towards waters affected by abandoned metal mines. In the latter case, the move up risk categories represents a change of 24 to 50% of sites being above the threshold, which is approximately the range of a single risk category.

In addition, the number of sites assessed for all metals in estuarine and coastal waters is substantially lower compared with previous reporting.

The freshwater data for metals show predominantly downwards trends from 2014 to 2022, except for copper where no statistically significant change in concentrations is reported. However, these results can be split into two types: those for waters affected by abandoned metal mines and those for sites in other locations. These data types are not distinguished between in the dashboard but are examined in Section 4.14.

All metals show upward trends for those waters affected by abandoned metal mines and all downward trends for the 'other' sites over the assessed time period. For waters affected by abandoned metal mines, their elevated levels of metals mean that they comprise a high proportion of those sites which exceed available thresholds; very few 'other' sites are above the corresponding thresholds.

3.2.3 Pesticides and biocides

This group covers pesticides and the biocidal SGARs.

The data set for pesticides in freshwater is based on targeted screening data from 2016 to 2022 which cover a broad range of substances, particularly compared with the number of those historically monitored using traditional quantitative methods. Contrary to previous reporting, the pesticide assessment looks at trends over time for the range of years available rather than grouping data for years to 2018 as a baseline. It focusses on plant protection products that have had national authorisation in the past or currently and their metabolites. No statistically significant change in concentrations over time is observed for pesticides in freshwaters.

The lack of change in concentrations over time is also observed for SGARs in red kites. For SGARs in red foxes, a statistically significant upward trend is seen. However, it is noted that the number of samples is very low for red foxes for many of the years, increasing the uncertainty.

The assessment of pesticides in freshwater against a threshold considers the potential risk of chronic effects from exposure, similar to other assessments used in the indicator. However, the assessment differs from others in that there are some assumptions around the assessment, for example that additive toxicity occurs, to allow it to be based on exposure to multiple substances. Threshold exceedance is indicated for the majority of freshwater sites assessed for pesticides. This suggests very high potential risk; however, it should be noted that some of these substances may have environmental presence because of sources other than their use as plant protection products and this requires further investigation.

Potential risk is indicated for less than a quarter of individuals considered for assessing SGARs in red kites. In this case only, the risk is assessed using an approach which includes looking at related SGAR effects observed in the birds, as opposed to solely assessing exceedances of threshold concentrations. Therefore, the trend in potential risk does not necessarily match that relating to concentration levels over time. Indeed, a statistically significant decrease in potential risk is observed in contrast to the steady levels of SGAR concentrations seen in these birds.

4 Underlying data considered in the dashboard

The underlying data considered for each of the entries in the dashboard are described in the following subsections. Each of these data reports is presented in a similar format covering the following:

- The source of the data for example, monitoring programme and sampling regime
- The structure of the data set considered for example, years considered, units of analysis, treatment of results below the LoD
- Presentation of the data and consideration of trends in chemical concentrations over time
- Proposed threshold for use and its comparison against the most-recent data

The translation of the results into the metrics in the dashboard is briefly explained in the relevant sections on trends and threshold comparison.

The running order for the data report subsections mirrors the dashboard. It begins with PBT substances. Each of Sections 4.1 to 4.10 covers the information for these chemicals relating to an individual matrix, progressing through the terrestrial, then freshwater and marine compartments. Similarly, metals are covered in Sections 4.11 to 4.21. Because the substances covered under the pesticides and biocides group within the indicator do not have common matrices, they are covered in the order that they appear in the dashboard: pesticides in freshwater appear in Section 4.22 and the biocidal SGARs in Sections 4.23 to 4.24.

Where modifications to the previous assessment data sets have been made for this report, this is indicated within the relevant subsections.

4.1 Persistent, bioaccumulative and toxic substances in common buzzard: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Mercury	\bigcirc
Polybrominated diphenyl ethers	
Polychlorinated biphenyls	
PCB 118	D
Perfluorooctanesulfonic acid	D
Per- and polyfluoroalkyl substances	D

4.1.1 Data source

Data on PBT substances in the livers of common buzzards (*Buteo buteo*) are provided by the Predatory Bird Monitoring Scheme (PBMS) (<u>UKCEH, 2023</u>).

Livers were collected from individual buzzards found dead throughout England. The majority of animals died as a result of collisions or starvation.

Mercury

Total mercury concentrations in livers are available for a number of years, but not all years, for common buzzards collected between 2001 and 2021. Sixty-one out of the 155 buzzards assessed were analysed as part of the EU project Life APEX (<u>Ozaki and others</u>, <u>2023a</u>); these relate to samples found between 2001 and 2019. Data from Life APEX is available via the <u>NORMAN Network (2024</u>). Chemical analysis of the other 94 samples collected since 2018 was supported by Natural England.

The data used for the analysis of trends over time for the dashboard represent a subsample of these birds, specifically non-starved, first-year female birds.

Birds assessed at post-mortem to be in a starved condition were excluded as starvation can mobilise mercury from other parts of the body into the liver and result in relatively elevated concentrations compared with those in non-starved birds (Wienburg and Shore, 2004). Moreover, variation in the nutritional condition of birds between years may obscure the detection of trends in exposure over time, supporting the decision to use non-starved, first-year birds.

Additionally, first-year birds – defined as individuals hatched in the current or previous year to that in which they were found dead – were used as they are likely to provide a more-sensitive measure of annual change in exposure than adults. This is because adults may be exposed to, and bioaccumulate, mercury in the liver over multiple years.

Female birds were chosen over males because although residues are typically higher in males than females, those in males also appear to be more variable <u>(Walker and others, 2016)</u>. Male birds were, therefore, considered to be less sensitive for detecting annual changes in concentrations.

For the assessment of threshold exceedance, all birds analysed were included irrespective of age, sex and whether they were in a starved state or not. This is because the assessment focusses on looking at potential risk owing to levels of contamination, therefore mercury concentrations in all birds are relevant.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Concentrations of PBDEs, PCBs and PFASs in liver are reported for common buzzards collected in 2018, 2019 and 2021. Samples selected for analysis were a subset of those received by the PBMS in each year. These subsets were selected, where possible, so that there was an even spread of samples throughout each year and a balance of the age (first-year or adult bird), sex (male or female) and nutritional status (starved or not) of birds were represented.

Chemical analysis of these samples was supported by Natural England.

4.1.2 Data structure

Mercury

The data consist of measurements of mercury concentrations in the livers of a variable number of individuals that died each year for the years 2001, 2004–2006, 2010, 2013, 2016, and 2018–2021. Concentrations are reported as mg/kg dry weight.

The LoDs for mercury ranged from 0.0311 to 0.101mg/kg dry weight. Only one result, which was for an adult bird, was below the corresponding LoD of 0.0426mg/kg dry weight; this was assigned a value that was half the LoD.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances

The data consist of measurements in the liver of 20 individuals that died each year for the years 2018, 2019 and 2021. Concentrations are reported as μ g/kg wet weight.

For PBDEs, data are available for 26 individual PBDE congeners – 17, 28, 30, 32, 35, 37, 47, 49, 51, 66, 71, 77, 85, 99, 100, 118, 119, 126, 128, 138, 153, 154, 183, 190, 196, and 197 – and the summed concentrations of these congeners (SUM PBDEs).

For PCBs, data are available for 35 individual PCB congeners – 8, 18, 28, 29, 31, 52, 77, 101, 105, 114, 118, 123, 126, 128, 138, 141, 149, 153, 156, 157, 163, 167, 169, 170, 171, 180, 183, 187, 189, 194, 199, 201, 205, 206, and 209 – and the summed concentrations of these congeners (SUM PCBs).

Data are available for PFOS and for a further 15 PFAS: PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, PFNA, PFDA, PFUdA, perfluorodecanesulfonic acid (PFDS), PFOSA, PFDoA, PFTrDA, and PFTeDA. Data for the summed concentrations of these additional 15 PFAS are given as SUM 15PFAS.

The summed values for PBDEs, PCBs and the 15 PFAS, alongside those for the individual substances PCB 118 and PFOS, are summarised in Section 4.1.3.

The LoDs for individual PBDE and PCB congeners varied within the data sets of 60 samples. No samples had non-detects for all congeners. Those substances that had results reported below the LoD had LoDs for the individual PBDE congeners ranging from 0.0271 to 0.105 μ g/kg wet weight; those for PCBs congeners ranged from 0.0573 to 0.115 μ g/kg wet weight. Congener concentrations below the LoD were assigned a zero value for the purposes of summing. None of the results for PCB 118 were reported below the LoD.

For PFOS, the LoD was 0.0192µg/kg wet weight and none of the results were reported below this. The other PFAS had the same LoD as PFOS except for PFBA and PFPeA, for which the LoD was 0.0769µg/kg wet weight, and PFUdA, which had an LoD of 0.0481µg/kg wet weight. Individual PFAS concentrations below the LoD were assigned a zero value for the purposes of summing.

4.1.3 Exploration of change in chemical concentrations over time

Mercury

The distribution of data by year for non-starved, first-year female buzzards is summarised in Table 4.1.1 and shown in Figure 4.1.1. Concentrations of mercury exceeded the LoD for all samples. There was no sample out of those available for 2005 meeting the criteria for the time trend analysis – that is, a non-starved, first-year female bird (see Section 4.1.1) – and, therefore, no data are shown for this year. Sample sizes were low (n between 1 and 5) in each year.

Table 4.1.1 Summary statistics for concentrations of mercury in the livers of non-starved, first-year female buzzards (mg/kg dry weight) from England¹

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2001	1	1.03	_	1.03	1.03	1.03	_	_
2004	2	0.198	0.195	0.198	0.0605	0.337	_	_
2006	3	0.348	0.254	0.242	0.164	0.638	-	-
2010	1	0.367	_	0.367	0.367	0.367	_	_
2013	1	0.316	_	0.316	0.316	0.316	_	_
2016	3	0.586	0.0814	0.622	0.493	0.644	_	_
2018	4	0.226	0.133	0.228	0.0812	0.368	0.133	0.321
2019	1	0.294	_	0.294	0.294	0.294	_	_
2020	2	0.365	0.125	0.365	0.277	0.453	_	_
2021	5	0.485	0.194	0.500	0.235	0.704	0.353	0.635

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.1.1 Scatterplot of mercury (Hg) concentrations in the livers of non-starved, firstyear female buzzards (mg/kg dry weight) from England from 2001 to 2021 (log10 y-axis scale). Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. The red line drawn across the plots for the different years represents a linear regression model applied to the data, with shading representing 95% confidence limits (diagram courtesy of UKCEH)



The analysis of trends over time for mercury concentrations in the livers of non-starved, first-year female buzzards was conducted after transforming the concentrations into natural logarithm values to correct the skewed distribution of the data. The assumptions of a linear model were met after this transformation.

The linear regression model used to analyse the change in mercury concentrations in the livers of the selected buzzards over time showed no statistically significant trend for the years from 2001 to 2021 (p = 0.65) (Figure 4.1.1).

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'no observed change in concentrations' is given.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

The distribution of data for SUM PBDEs, SUM PCBs, PCB 118, PFOS, and SUM 15PFAS by year is summarised in Tables 4.1.2 to 4.1.6, respectively, and shown in Figures 4.1.2 to 4.1.4.

Mean values of SUM PCBs and PCB 118 in 2019 were 421 and 101µg/kg wet weight, respectively, which were higher than for the two other years (Tables 4.1.3 and 4.1.4, respectively). The high mean values in 2019 are due to one sample in which concentrations of SUM PCBs and PCB 118 reached 6763 and 1835µg/kg wet weight, respectively.

Table 4.1.2 Summary statistics for concentrations of SUM PBDEs in the livers of buzzards (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	20	25.8	42.0	6.55	0.275	157	2.18	25.4
2019	20	13.4	18.5	6.89	0.804	65.2	3.07	13.7
2021	20	25.2	48.0	8.68	0.440	211	2.51	23.3

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.1.3 Summary statistics for concentrations of SUM PCBs in the livers of buzzards (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	20	131	187	21.4	2.02	594	8.32	186
2019	20	421	1497	43.5	1.23	6763	21.0	119
2021	20	167	316	45.8	3.25	1402	16.0	170

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.1.4 Summary statistics for concentrations of PCB 118 in the livers of buzzards
(μg/kg wet weight) from England ¹

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2018	20	15.7	26.3	3.52	0.432	87.5	1.19	17.6
2019	20	101	408	4.56	0.321	1835	2.08	12.3
2021	20	23.3	53.2	6.73	0.510	241	1.79	16.6

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.1.5 Summary statistics for concentrations of perfluorooctanesulfonic acid in the livers of buzzards (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2018	20	57.0	93.4	18.8	4.51	369	13.1	52.3
2019	20	47.3	61.6	28.2	4.47	280	15.6	65.0
2021	20	27.5	21.8	22.8	4.33	100	14.6	29.4

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.1.6 Summary statistics for concentrations of SUM 15PFAS¹ in the livers of buzzards (μ g/kg wet weight) from England²

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2018	20	19.1	24.3	11.2	1.26	106	6.92	17.4
2019	20	15.6	12.2	11.8	1.83	42.2	7.21	23.2
2021	20	19.1	20.7	12.1	2.02	84.0	7.33	19.2

¹Note that this excludes PFOS; see Section 4.1.2 for individual substances covered.

²n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.1.2 Scatterplots of SUM PBDE concentrations in the livers of buzzards (µg/kg wet weight) from England from 2018 to 2021 (log10 y-axis scale). Boxes represents median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year (diagram courtesy of UKCEH)



Figure 4.1.3 Scatterplots of SUM PCB and PCB 118 concentrations in the livers of buzzards (µg/kg wet weight) from England from 2018 to 2021 (log10 y-axis scale). Boxes represents median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year (diagrams courtesy of UKCEH)



Figure 4.1.4 Scatterplots of perfluorooctanesulfonic acid (PFOS) and SUM 15PFAS concentrations in the livers of buzzards (μ g/kg wet weight) from England from 2018 to 2021 (log10 y-axis scale). Boxes represents median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year (diagrams courtesy of UKCEH)



The medians of SUM PBDEs, SUM PCBs and PCB 118 slightly increased from 2018 to 2021; however, these changes were not significant by a non-parametric Kruskal–Wallis test (p > 0.05).

Because the data for SUM PBDEs, SUM PCBs, PCB 118, PFOS, and SUM 15PFAS do not meet the minimum requirements for trend reporting (see Section 3.1.2), formal trend

assessments have not been performed. The entry on the dashboard relating to trends is therefore blank.

4.1.4 Thresholds

Mercury

There is no established threshold or EQS value for mercury in the liver of buzzards. However, proposed a minimum indicative mercury concentration in liver of 2mg/kg wet weight, above which adverse effects on reproduction may occur in non-marine bird populations.

This value is based on the lowest species geometric mean for residues that have been associated with impaired reproduction including a range of effects, but predominantly decreased egg hatchability. The analysis is based on data for multiple species including ring-necked pheasants (*Phasianus colchicus*), mallards (*Anas platyrhynchos*), tree swallows (*Tachycineta bicolor*), and house wrens (*Troglodytes aedon*), with the lowest geometric mean observed in ring-necked pheasants (<u>Shore and others, 2011</u>). It is not indicative of a threshold for effects in individual birds but at population levels. Therefore, for the indicator, the threshold is compared against the average (geometric mean or median) results for all birds sampled in a year rather than values for individuals.

Using a mean wet weight to dry weight conversion factor for buzzards of 3.1 (<u>Scanlon</u>, <u>1982</u>; <u>Monclús</u>, <u>Shore and Krone</u>, <u>2020</u>), the indicative threshold concentration is equivalent to 6.2mg/kg dry weight.

The summary data for all birds for which mercury residues in their liver were assessed against the threshold are given in Table 4.1.7 (see also Section 4.1.1).

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2001	8	1.24	1.42	0.837	0.109	4.50	0.376	1.32
2004	5	0.326	0.166	0.337	0.0605	0.516	0.337	0.381
2005	2	0.391	0.164	0.391	0.275	0.507	_	_
2006	6	0.550	0.380	0.500	0.164	1.19	0.272	0.687
2010	8	1.31	1.29	0.877	0.357	3.90	0.368	1.50
2013	8	1.05	1.20	0.648	0.316	3.96	0.468	0.927

Table 4.1.7 Summary statistics for concentrations of mercury in the livers of all buzzards (mg/kg dry weight)¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2016	8	0.701	0.287	0.632	0.493	1.40	0.583	0.644
2018	29	0.921	1.18	0.550	0.0812	5.82	0.261	0.869
2019	27	0.471	0.384	0.382	0.0213	1.85	0.208	0.520
2020	16	0.746	0.698	0.437	0.182	2.55	0.264	0.885
2021	38	0.888	0.618	0.661	0.148	2.98	0.450	1.32

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

The median values for mercury in the livers of all buzzards ranged from 0.337 to 0.877mg/kg dry weight in the period from 2001 to 2021, which are below the proposed threshold.

The entry in the dashboard is based on the results for the most-recent year available, 2021. This year had a median value of 0.661mg/kg dry weight, an order of magnitude lower than the proposed threshold mercury concentration in liver of 6.2mg/kg dry weight. Therefore, the dashboard entry reads 'All sites/individuals or population average below threshold'.

As the threshold is based on reproduction effects, it may be appropriate to confine or compare this assessment to one that considers females. Based on data from 2021, the median value for mercury concentrations in the 13 female buzzards available was 0.635mg/kg dry weight. This result is comparable to that above for all birds for that year.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Because thresholds for PBDEs, PCBs, PFOS, and other PFAS in the liver of predatory birds have not yet been selected for use in the indicator, the entries reflect that there are no values for comparison.

4.2 Persistent, bioaccumulative and toxic substances in sparrowhawk: mercury

Mercury



4.2.1 Data source

Data on total mercury in the livers of Eurasian sparrowhawks (*Accipiter nisus*) are provided by the PBMS (<u>UKCEH, 2023</u>).

Livers were collected from individual sparrowhawks found dead throughout England. The majority of animals died as a result of collisions or starvation.

Mercury concentrations in liver are available for a number of years, but not all years, for sparrowhawks collected between 2000 and 2021. Chemical analysis for 2020 and 2021 was supported by Natural England.

The data used for the time-trend analysis for the dashboard represent a sub-sample of these birds, specifically non-starved, first-year female birds.

Birds assessed at post-mortem to be in a starved condition were excluded as starvation can mobilise mercury from other parts of the body into the liver and result in relatively elevated concentrations compared with those in non-starved birds (<u>Weinburg and Shore</u>, <u>2004</u>). Moreover, variation in the nutritional condition of birds between years may obscure the detection of trends in exposure over time, supporting the decision to use non-starved, first-year birds.

Additionally, first-year birds – defined as individuals hatched in the current or previous year to that in which they were found dead – were used as they are likely to provide a more-sensitive measure of annual change in exposure than adults. This is because adults may be exposed to, and bioaccumulate, mercury in the liver over multiple years.

Female birds were chosen over males because although residues are typically higher in males than females, those in males also appear to be more variable <u>(Walker and others, 2016)</u>. Male birds were, therefore, considered to be less sensitive for detecting annual changes in concentrations.

For the assessment of threshold exceedance, all birds analysed were included irrespective of age, sex and whether they were in a starved state or not. This is because the assessment focusses on looking at potential risk owing to levels of contamination, therefore mercury concentrations in all birds are relevant.

4.2.2 Data structure

The data consist of measurements of mercury in the livers of a variable number of individuals that died each year for the years 2000, 2005, 2006, 2011–2013, 2020, and 2021. Concentrations are reported as mg/kg dry weight.

The LoD for mercury was 0.0960mg/kg dry weight for the analyses of birds until 2013. The LoDs for the analyses in 2020 and 2021 varied and ranged from 0.0379 to 0.0526mg/kg dry weight. Only two results, which were for adult birds collected in 2011 and 2012, were below the LoD; these were assigned a value that was half the LoD.

4.2.3 Exploration of change in chemical concentrations over time

The distribution of data by year for non-starved, first-year female sparrowhawks is summarised in Table 4.2.1 and shown in Figure 4.2.1. Concentrations of mercury exceeded the LoD for all samples. Data are limited for more-recent years: There was no sample out of those available for 2021 meeting the criteria for the time trend analysis – that is, a non-starved, first-year female bird (see Section 4.2.1) – and, therefore, no data are shown for this year. Moreover, the sample size was low in 2020 (n = 2).

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2000	12	1.28	1.11	1.07	0.175	4.30	0.537	1.60
2005	6	0.452	0.162	0.472	0.164	0.631	0.422	0.543
2006	7	1.76	1.72	1.15	0.372	5.50	0.932	1.71
2011	8	1.02	0.504	1.19	0.393	1.58	0.511	1.43
2012	6	2.63	3.67	1.27	0.678	10.1	1.06	1.42
2013	6	0.696	0.280	0.684	0.349	1.07	0.494	0.891
2020	2	0.486	0.205	0.486	0.341	0.631	_	_

Table 4.2.1 Summary statistics for concentrations of mercury in the livers of non-starved,
first-year female sparrowhawks (mg/kg dry weight) from England ¹

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.2.1 Scatterplot of mercury (Hg) concentrations in the livers of non-starved, firstyear female sparrowhawks (mg/kg dry weight) from England from 2000 to 2020 (log10 y-axis scale). Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. The red line drawn across the plots for the different years represents a linear regression model applied to the data, with shading representing 95% confidence limits (diagram courtesy of UKCEH)



The analysis of trends over time for mercury concentrations in the livers of non-starved, first-year female sparrowhawks was conducted after transforming the concentrations into natural logarithm values to correct the skewed distribution of the data. The assumptions of a linear model were met after this transformation.

The linear regression model used to analyse the change in mercury concentrations in the livers of the selected sparrowhawks over time was showed no statistically significant trend for the years from 2000 to 2020 (p = 0.81) (Figure 4.2.1).

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'no observed change in concentrations' is given.

4.2.4 Thresholds

There is no established threshold or EQS value for mercury in the liver of sparrowhawks. However, <u>Shore and others (2011)</u> proposed a minimum indicative mercury concentration in liver of 2mg/kg wet weight, above which adverse effects on reproduction may occur in non-marine bird populations.

This value is based on the lowest species geometric mean for residues that have been associated with impaired reproduction including a range of effects, but predominantly decreased egg hatchability. The analysis is based on data for multiple species including ring-necked pheasants (*Phasianus colchicus*), mallards (*Anas platyrhynchos*), tree swallows (*Tachycineta bicolor*), and house wrens (*Troglodytes aedon*), with the lowest

geometric mean observed in ring-necked pheasants (<u>Shore and others, 2011</u>). It is not indicative of a threshold for effects in individual birds but at population levels. Therefore, for the indicator, the threshold is compared against the average (geometric mean or median) results for all birds sampled in a year rather than values for individuals.

Using a mean wet weight to dry weight conversion factor for sparrowhawks of $3.52 (\pm 0.02)$ (Shore, 2020), the indicative threshold concentration is equivalent to 7mg/kg dry weight.

The summary data for all birds for which mercury residues in their liver were assessed against the threshold are given in Table 4.2.2 (see also Section 4.2.1).

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2000	53	4.16	4.54	1.90	0.175	19.3	1.14	5.52
2005	27	2.31	2.13	1.50	0.164	8.44	0.810	3.29
2006	26	2.61	2.48	1.60	0.162	9.11	0.873	3.96
2011	24	1.10	0.563	1.24	0.0480	1.89	0.686	1.48
2012	23	1.90	2.42	1.14	0.0480	10.1	0.842	1.52
2013	22	1.56	1.31	1.03	0.123	4.66	0.690	1.87
2020	18	2.28	1.53	2.49	0.253	5.55	0.891	3.26
2021	9	5.54	4.68	3.58	0.661	13.9	2.14	6.73

Table 4.2.2 Summary statistics for concentrations of mercury in the livers of all sparrowhawks (mg/kg dry weight)¹

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

The median values for mercury in the livers of all sparrowhawks ranged from 1.03 to 3.58mg/kg dry weight in the period from 2000 to 2021, which are below the proposed threshold.

The entry in the dashboard is based on the results for the most-recent year available, 2021. This year had a median value of 3.58mg/kg dry weight, approximately half the value of the proposed threshold mercury concentration in liver of 7mg/kg dry weight. Therefore, the dashboard entry reads 'All sites/individuals or population average below threshold'.

As the threshold is based on reproduction effects, it may be appropriate to confine or compare this assessment to one that considers females. Based on data from 2021, the median value for mercury concentrations in the 4 female sparrowhawks available was 3.13mg/kg dry weight. This result is comparable to that above for all birds for that year.

4.3 Persistent, bioaccumulative and toxic substances in red fox: mercury, perfluorooctanesulfonic acid and perand polyfluoroalkyl substances

Mercury	
Perfluorooctanesulfonic acid	
Per- and polyfluoroalkyl substances	

4.3.1 Data source

Red fox livers from England were acquired by Fera Science Ltd via two sources: (1) WIIS and (2) APHA.

Under WIIS, red fox carcasses are submitted to the scheme as part of investigations into suspected poisoning incidents relating to pesticides and biocides. The samples are not necessarily the absolute total number of suspected poisoning cases per annum, as submissions are dependent on animals being found and subsequently reported. Foxes were found dead at various rural and urban locations.

The Animal and Plant Health Agency undertake surveillance of the disease *Echinococcus multilocularis* in red foxes on an annual basis. The agency uses a network of land managers, who cull foxes for pest control purposes, to supply the required carcasses. Shooting for this survey typically occurs between October and early March. A subset of these shot foxes was selected by APHA – providing a spread of geographic location, gender, weight, and overall condition of the fox – and their livers were used for the analysis of rodenticides (see Section 4.24).

Subsequent to the rodenticide analysis, any remaining liver tissue was used for the analysis of mercury, PFOS and other PFAS if sufficient material was available. Chemical analysis of these samples was supported by Natural England.

The use of these 2 existing opportunities, where red foxes are collected, to generate additional data for the indicator is in an exploratory phase to ascertain their suitability.

4.3.2 Data structure

The data consist of measurements of mercury, PFOS and other PFAS in the livers of a variable number of individuals for the years 2018–2021. Samples for 2018 and 2019 were

collected solely via WIIS and for 2021 via APHA. In 2020, samples were collected via both WIIS and APHA and these are reported as separate entities.

The WIIS samples were collected throughout the year, that is spanning several months, whereas APHA samples were collected during targeted campaigns over a single winter period, that is in December 2020 and January 2021. For some APHA locations, more than one sample was collected on a single occasion and/or within a year. For consistency, the data are assigned to the different years in which they were collected.

Mercury

Data on mercury concentrations in the livers of red foxes are reported as mg/kg wet weight.

All samples were above the LoDs, except 3 WIIS samples: one in 2019 that was below the corresponding LoD of 0.004mg/kg wet weight and 2 in 2020, which were below the LoD of 0.001mg/kg wet weight. Owing to the small number of non-detects, these values were set to zero.

Perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Data on PFOS and other PFAS concentrations in the livers of red foxes are reported as $\mu g/kg$ wet weight.

Data are available for PFOS and for a further 36 PFAS: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, perfluoropentanesulfonic acid (PFPeS), PFHxS, perfluoroheptanesulfonic acid (PFHpS), perfluorononanesulfonic acid (PFNS), perfluorodecanesulfonic acid (PFDS), 3:3 fluorotelomer carboxylic acid (3:3 FTCA), 5:3 fluorotelomer carboxylic acid (5:3 FTCA), 7:3 FtCA, FBSA, FHxSA, PFOSA, perfluoro-4-ethylcyclohexanesulfonic acid (PFECHS), 4:2 FTS, 6:2 FTS, 8:2 FTS, 2-(*N*-methylperfluorooctanesulfonamido)acetic acid (NMEFOSAA), 2-(*N*-ethylperfluorooctanesulfonamido)acetic acid (NEtFOSAA), hexafluoropropylene oxide dimer acid (HPFO-DA), dodecafluoro-3*H*-4,8-dioxanonanoic acid (ADONA), perfluoro{2-[(6-chlorohexyl)oxy]ethanesulfonic acid} (9CI-PF3ONS), perfluoro(11-chloro-3-oxaundecanesulfonic acid) (11CI-PF3OUdS), bis(perfluorohexyl)phosphinic acid (6:6 PFPi), perfluorooctyl)phosphinic acid (8:8 PFPi). Data for the summed concentrations of these additional 36 PFAS are given as SUM 36PFAS.

For PFOS, the branched and linear forms were used to generate a total PFOS value. The LoDs for the branched and linear forms were 0.005 and 0.018µg/kg wet weight, respectively; none of the results were reported below the LoDs. The remaining PFAS had LoDs which varied depending on the substance from 0.008 to 0.05µg/kg wet weight. Individual PFAS concentrations below the LoD were assigned a zero value for the purposes of summing.

4.3.3 Exploration of change in chemical concentrations over time

Mercury

The distribution of data for mercury by year are summarised in Table 4.3.1 and shown in Figure 4.3.1.

Table 4.3.1 Summary statistics for concentrations of mercury in the livers of red foxed	es
(mg/kg wet weight) from England ¹	

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
WIIS	2018	1	2	0.0134	0.00914	0.0134	0.00698	0.0199	_	_
WIIS	2019	13	15	0.0421	0.0282	0.0362	0	0.0997	0.0183	0.0648
WIIS	2020	9	9	0.0237	0.0146	0.0166	0	0.0411	0.00889	0.0382
APHA	2020	12	20	0.0392	0.0224	0.0311	0.00745	0.0970	0.0248	0.0518
APHA	2021	25	52	0.0631	0.143	0.0379	0.00362	1.05	0.0217	0.0556

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency.

Figure 4.3.1 Box plots of concentrations of mercury in the livers of red foxes from England from 2018 to 2021 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS) (log10 y-axis scale); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagram courtesy of Fera)



Using a Kruskal–Wallis test, there was no statistically significant difference (p = 0.13) in the median concentrations of mercury in fox livers between 5 groups of observations (for APHA 2020, APHA 2021, WIIS 2018, WIIS 2019, and WIIS 2020). Mercury concentrations in red fox livers were <0.1 mg/kg wet weight, except for 3 APHA 2021 samples, for which the mercury concentrations ranged from 0.109 to 0.174mg/kg wet weight, and one sample which was an order of magnitude higher at 1.05mg/kg wet weight.

There were too few years of data to allow for the analysis of the trend over time. Moreover, the APHA 2020 and 2021 data were taken in consecutive months (December 2020 and January 2021), severely limiting any ability to relate time to levels of mercury concentrations in red fox livers.

The entry in the dashboard reflects that data are available, but insufficient to report a trend assessment.

Perfluorooctanesulfonic acid and other per-and polyfluoroalkyl substances

The distribution of data for PFOS by year is summarised in Table 4.3.2 and presented in Figure 4.3.2. The PFOS concentrations were derived from data for the linear and branched forms. Data for the other PFAS as SUM 36PFAS are presented in Table 4.3.3 and Figure 4.3.3.

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
WIIS	2018	1	2	6.04	3.05	6.04	3.88	8.20	4.96	7.12
WIIS	2019	9	10	19.3	17.6	9.32	2.06	47.7	6.62	29.5
WIIS	2020	2	2	36.1	1.27	36.1	35.2	37.0	35.7	36.5
APHA	2020	12	20	37.0	28.9	26.0	11.9	129	18.7	47.4
АРНА	2021	25	52	31.7	23.1	24.5	2.59	95.9	13.3	42.4

Table 4.3.2 Summary statistics for concentrations of perfluorooctanesulfonic acid in the
livers of red foxes (μg/kg wet weight) from England ¹

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency. Figure 4.3.2 Box plots of concentrations of perfluorooctanesulfonic acid (PFOS) in the livers of red foxes from England from 2018 to 2021 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS) (log10 y-axis scale); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagram courtesy of Fera)



Table 4.3.3 Summary statistics of SUM 36PFAS¹ concentrations in the livers of red foxes (μ g/kg wet weight) from England²

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
WIIS	2018	1	2	1.15	0.370	1.15	0.886	1.41	1.02	1.28
WIIS	2019	9	10	5.10	6.00	1.97	0.977	17.8	1.22	7.89
WIIS	2020	2	2	8.72	2.38	8.72	7.04	10.4	7.89	9.58

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
APHA	2020	12	20	8.13	7.68	5.69	2.36	32.9	3.23	10.0
APHA	2021	25	52	6.92	7.06	4.80	0.893	37.0	3.40	7.98

¹Note that this excludes PFOS; see Section 4.3.2 for individual substances covered.

²n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency.

Figure 4.3.3 Box plots of concentrations of SUM 36PFAS in the livers of red foxes from England from 2018 to 2020 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS) (log10 y-axis scale); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points



For both PFOS and SUM 36PFAS, differences between concentrations found in APHA and WIIS samples cannot be determined at this stage owing to the limited data. Similarly, differences between years within data sources are difficult to determine because of the limited data for the WIIS samples in 2018 and 2020 and because, in practice, the APHA 2020 and 2021 data were taken in consecutive months. Further work is also needed to understand the representativeness of the data to the fox population.

There were too few years of data to allow for the analysis of trends over time. Nevertheless, the data clearly demonstrate that PFOS and other PFAS are observed in red foxes.

The corresponding entries in the dashboard reflect that data are available for PFOS and PFAS, but are insufficient to report trend assessments.

4.3.4 Thresholds

There are currently no thresholds for mercury, PFOS and other PFAS in red foxes against which to compare the exposure levels detected. This is reflected in the dashboard entries.

4.4 Persistent, bioaccumulative and toxic substances in freshwater: perfluorooctanesulfonic acid and other perand polyfluoroalkyl substances

Perfluorooctanesulfonic acid

Per- and polyfluoroalkyl substances



4.4.1 Data source

Data on PFOS and PFOA in freshwater have been provided by the Environment Agency from their freshwater statutory monitoring network. Information on other PFAS in freshwater is not available currently.

These are the only PBTs reported in this matrix because, unlike the other PBT substances under this indicator, PFOS and PFOA are water soluble and there is analytical capability to detect them in freshwater (Environment Agency, 2019).

Some sites have been sampled in multiple years, although there were fewer sites monitored and samples taken from 2019, particularly for 2020 owing to the COVID-19 pandemic. Between 2016 and 2018, monitoring was greater to support the establishment of an evidence base for risk assessment and classification based on the analysis of PFOS in water and fish. Freshwater sites were limited following that, though still include those at which fish monitoring is also undertaken (see Section 4.5).

The monitoring network has changed in recent years with the introduction of the RSN under the NCEA (<u>Defra, 2022</u>), and data from the RSN are included in the information presented here. Initial work has been done to understand the differences between levels of contaminants monitored at RSN sites, which represent broadscale condition, versus those from targeted sites; this is presented in Appendix D. However, the data are too limited currently across both types of monitoring sites for PFOS and PFOA to make any comparisons. Further consideration of any differences owing to the sites having different purposes is needed as more data come in over time.

4.4.2 Data structure

Data are available for the period 2016–2022 for PFOS and PFOA in freshwater samples taken across England. The data vary both in terms of the number of measurements taken within a year per site and the number of sites monitored per year.

A data summary is available for each year based on the total number of measurements made in a year – that is all data pooled from all sites (see Tables 4.4.1 and 4.4.2).

Summaries are also available for each site based on samples taken over the most-recent 3 years and for which there were at least 3 samples per year available for the purpose of the threshold assessment (see Section 4.4.4).

Concentration data are reported as μ g/L.

The LoDs for PFOS and PFOA varied within the data sets. Less than 1% of results were reported below the LoD for PFOS; for PFOA, 13% of the results were below the LoD. Where results were reported below the LoD, the LoDs ranged from 9 x 10^{-5} to 0.03 and from 3 x 10^{-4} to 0.01µg/L for PFOS and PFOA, respectively. Results recorded as below the LoD were assigned a value that was half the LoD.

4.4.3 Exploration of change in chemical concentrations over time

The distribution of data by year for PFOS and PFOA concentrations in freshwater is summarised in Tables 4.4.1 and 4.4.2, respectively. The corresponding modelled trend information for these substances is shown in Figure 4.4.1.

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2016	214	1701	0.00604	0.00955	0.00343	1.80 x 10 ⁻⁴	0.172	0.00171	0.00658
2017	337	1909	0.00623	0.0155	0.00292	1.20 x 10 ⁻⁴	0.428	0.00127	0.00644
2018	308	2305	0.00839	0.0663	0.00317	4.50 x 10⁻⁵	2.50	0.00139	0.00633
2019	161	790	0.00586	0.0266	0.00261	4.50 x 10⁻⁵	0.711	0.00112	0.00626
2020	49	92	0.00562	0.00914	0.00220	4.50 x 10⁻⁵	0.0620	8.58 x 10 ⁻⁴	0.00693
2021	154	1006	0.00384	0.00797	7.40 x 10 ⁻⁴	4.50 x 10⁻⁵	0.0630	2.00 x 10 ⁻⁴	0.00340
2022	107	1044	0.00256	0.00632	4.40 x 10 ⁻⁴	4.50 x 10 ⁻⁵	0.0720	1.50 x 10 ⁻⁴	0.00170

Table 4.4.1 Summary statistics for concentrations of perfluorooctanesulfonic acid	in
freshwater (μg/L) ¹	

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.4.2 Summary statistics for concentrations of perfluorooctanoic acid in freshwater $(\mu g/L)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2016	211	1469	0.00533	0.00992	0.00364	1.50 x 10 ⁻⁴	0.170	0.00210	0.00546
2017	337	1909	0.00453	0.00848	0.00282	1.50 x 10 ⁻⁴	0.174	0.00145	0.00502
2018	308	2305	0.00505	0.00970	0.00284	1.50 x 10 ⁻⁴	0.129	0.00141	0.00513
2019	161	790	0.00362	0.00443	0.00213	3.00 x 10⁻⁵	0.0380	0.00113	0.00418
2020	49	92	0.00450	0.00469	0.00225	3.00 x 10 ⁻⁴	0.0200	0.00130	0.00695
2021	155	1139	0.00385	0.00682	0.00155	3.00 x 10 ⁻⁴	0.0500	3.00 x 10 ⁻⁴	0.00370
2022	148	1449	0.00392	0.00610	0.00150	3.00 x 10 ⁻⁴	0.0500	3.00 x 10 ⁻⁴	0.00500

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.
Figure 4.4.1 Modelled trends for perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) concentrations in freshwater (log10 y-axis scale). The graphs show trends based on the predicted mean concentrations for all months together with shading representing 95% confidence intervals (left) and for individual months coloured by season (right)



To consider changes over time, a generalised additive mixed model was fitted to the log10-transformed concentration data on a substance-by-substance basis, with decimal date of sampling and calendar month number as the main predictors. This corresponds to modelling the geometric mean of concentration. The model-fitting process allowed the analysis of both the trends over time and trends in the seasonality within the data. The model also accounted for the data consisting of repeated observations at a set of monitoring sites, as observations over time from any particular site are more likely to be correlated with each other than with observations from other sites.

The resulting predicted mean concentrations for each month were back-transformed to the original concentration scale for between January 2016 and December 2022. The results are shown in Figure 4.4.1, based on all months (including 95% confidence intervals for the mean) and individual months coloured by season. Recent data are more uncertain owing to changes in monitoring programmes and the reduction in monitoring in 2020. Further work is needed to understand these issues, along with the influence of the substitution of values for observations below detection limits.

There is a clear annual cyclical pattern for both PFOS and PFOA (Figure 4.4.1). Both substances show a similar downward trend. There is a strong correlation between the concentrations of PFOS and PFOA on a sample-by-sample basis.

The result in the dashboard for PFOS represents the observed statistically significant trends. Therefore, the assignment of 'decreasing concentrations' is given for PFOS.

While there is an observed downward trend for PFOA, the data are limited to this single PFAS and may not reflect the situation for all PFAS. In addition, the results for PFOA are more uncertain, owing to the relatively large number of values below the detection limit. Therefore, the entry in the dashboard reflects that data are available, but insufficient to report a trend assessment.

4.4.4 Thresholds

To consider the risk to freshwater wildlife from PBT substances, secondary poisoning quality standards ($QS_{sec\ pois}$) have been used. These standards help protect wildlife from the effects of eating prey contaminated by PBT substances. A $QS_{sec\ pois}$ for PFOS of 33µg/kg wet weight (EC, 2011b) has been derived through the EU EQS derivation process, which considers different protection goals. The $QS_{sec\ pois}$ for PFOS does not have statutory status as an EQS because it is not the most critical (lowest) QS. The EQS has a different protection goal of human health; however, the $QS_{sec\ pois}$ is the most appropriate to use here.

An equivalent empirical water concentration value has been derived from the $QS_{sec pois}$ by the Environment Agency for PFOS based on the relationship seen between monitored concentrations of PFOS in water and in fish (see Appendix E). This value is $0.019\mu g/L$.

Typically, average site concentrations are used for comparison with the threshold for PFOS. These are based on available data for the most-recent 3 years for each site. Thus, the starting year may vary by site as well as the number of years of data available. Each site requires at least 3 samples taken over that period to be included in the assessment; the number of samples per site varied between 3 and 24.

Four out of 160 sites (3%) had mean concentrations of PFOS in freshwater above the threshold of 0.019μ g/L. The percentage result is used as the entry for the dashboard.

There is currently no threshold for PFOA in freshwater against which to compare the exposure levels detected. Additionally, this is a single PFAS and any threshold assessment relating to it may not reflect the situation for all PFAS. Therefore, the entry in the dashboard shows that it is not currently possible to assess potential risk.

4.5 Persistent, bioaccumulative and toxic substances in freshwater fish: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances



4.5.1 Data source

Data on mercury, PBDEs, PCBs, PFOS, and other PFAS in fish in England have been provided by the Environment Agency. Data on concentrations in whole fish (roach, chub and brown trout) have been collected by the Environment Agency as part of its biota monitoring, which began in anticipation of requirements under the Water Environment Regulations 2017 (<u>UK Government, 2017</u>), and as part of ongoing research on PFAS.

For all substances, individual sites are monitored once a year. Typically, 5 fish replicate samples are collected and analysed; however, the numbers in the past have varied from 2 to 10 samples.

Some sites have been sampled in multiple years and this varies for each contaminant. It should be noted that this data source is relatively new and a baseline data set relating to designated trend sites is still being established. We have considered all site data as part of this assessment. This includes wider monitoring that was undertaken in 2018. Fewer sites

have been monitored since 2020, partly owing to the COVID-19 pandemic. Monitoring for PFAS was first conducted in 2022.

A data summary is available for each year based on the total number of measurements made in a year – that is all data pooled from all sites (see Tables 4.5.1 to 4.5.6). Summaries are also available for each site per year for those sites that had more than 1 sample per year.

Since the previous round of reporting the H4 indicator (<u>Environment Agency, 2021</u>), additional fish samples from 2019 have been analysed for PBDEs. Therefore, data for 2019 are now reported for PBDEs which were not available previously. Data for earlier years for PCBs have also been updated to cover results based on measured data only; the previous report (<u>Environment Agency, 2021</u>) used default values for some data conversions.

4.5.2 Data structure

Relevant data are available for the period 2014–2019 and 2022 for total mercury, 2015–2019, 2021 and 2022 for PBDEs and PFOS, 2015–2019 and 2022 for PCBs, and 2022 for other PFAS. The data consist of a variable number of measurements of the substances in terms of the number of freshwater fish replicates sampled at a site and the number of sites monitored per year across England.

Concentration data are reported as μ g/L wet weight in whole fish, and those for PCBs have been converted into lipid weight values.

For PBDEs, concentration data are the summed concentrations of 6 PBDE congeners, specifically PBDEs 28, 47, 99, 100, 153, and 154 (SUM 6PBDEs).

For PCBs, the Environment Agency collect data on congeners that are known for having the same mode of toxic action as harmful polychlorinated dibenzo-*p*-dioxins and dibenzofurans. These 12 dioxin-like congeners are PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189. The PCB concentration data have been summed as their corresponding total TEQ (toxic equivalent) value for each sample for the purpose of assessing trends (Section 4.5.3). This total PCBs-TEQ value takes into account the relative toxicity of the different congeners so that their summed concentrations over time reflect those most likely to represent a risk to wildlife rather than looking at change in abundance alone.

For PFAS, the concentration data are the summed concentrations of 41 substances: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFNS, PFDS, 3:3 FTCA, 5:3 FTCA, 7:3 FtCA, FBSA, FHxSA, PFOSA, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS, 10:2 fluorotelomer sulfonic acid (10:2 FTS), NMeFOSAA, NEtFOSAA, HPFO-DA, ADONA, 9CI-PF3ONs, 11CI-PF3OUdS, 6:6 PFPi, 6:8 PFPi, 8:8 PFPi, perfluoro-8-chlorooctanesulfonic acid (CI-PFOS), 2-(perfluorodecyl)ethanoic acid (FDEA 10:2), perfluoro-2-ethoxyethanesulfonic acid (PFEESA), and perfluoro(2-ethoxy-2-fluoroethoxy)acetic acid ammonium salt (EEA-NH₄) These are given as SUM 41PFAS.

The summed values for PBDEs, PCBs and PFAS, alongside those for the individual substances mercury, PCB 118 and PFOS, are summarised in Section 4.5.3.

All reported mercury concentrations were above the LoD.

The LoDs for the individual PBDE congeners ranged from 0.006 to 0.2µg/kg wet weight for those results reported below the LoD. For PCB congeners, the LoDs varied across many orders of magnitude, but the majority ranged from 0.00001 to 0.61µg/kg wet weight. For both groups of substances, no samples had non-detects for all congeners. For PBDE and PCB congeners, values below the LoD were assigned a negligible value of 0.00000001µg/kg wet weight for each congener when calculating the summed values.

Nine of the results for PCB 118 (<2%) were reported below their LoDs, which ranged from 0.05 to $0.25\mu g/kg$ wet weight; these were assigned a value that was half the LoD.

Approximately 4% of the PFOS results were reported below the LOD. In those cases, the LoD was generally $1\mu g/kg$ wet weight, except for one sample with an LoD of $10\mu g/kg$ wet weight. Results below the LOD were assigned a value that was half the LoD.

For PFAS, the LoDs varied for the individual substances across samples. Those results reported below the LoD were assigned a zero value for the purposes of summing. No samples had non-detects for all substances.

4.5.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.5.1 to 4.5.6 for mercury, SUM 6PBDEs, total PCBs-TEQ, PCB 118, PFOS, and SUM 41PFAS, respectively. The corresponding modelled trend information is shown in Figure 4.5.1 for all substances except for SUM 41PFAS owing to the limited data.

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	26	143	32.6	25.9	24.5	6.18	156	17.8	35.5
2015	27	127	37.1	23.6	30.1	6.39	133	21.1	46.5

Table 4.5.1 Summary statistics for concentrations of mercury in whole freshwater fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2016	23	109	38.7	23.1	32.1	9.42	134	22.1	49.6
2017	21	99	33.2	20.6	25.9	7.78	97.4	19.1	39.4
2018	43	193	48.5	46.9	33.4	8.31	300	21.1	54.1
2019	29	137	39.3	39.6	28.1	10.7	326	19.9	46.4
2022	8	34	52.4	27.8	41.2	20.9	138	34.1	58.8

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.5.2 Summary statistics for concentrations of SUM 6PBDEs in whole freshwater fis	h
(µg/kg wet weight)¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	27	127	7.34	5.56	5.96	0.155	26.1	2.89	9.65
2016	14	65	4.91	3.37	4.51	0.263	14.5	2.22	6.61
2017	13	62	4.71	4.49	3.25	0.287	24.8	1.83	5.90
2018	12	57	5.24	6.19	3.36	0.245	41.0	1.71	7.15
2019	26	124	2.98	2.49	2.69	0.0240	12.0	0.978	4.10
2021	3	9	1.21	1.25	0.85	0.245	4.28	0.366	1.39
2022	8	34	2.01	1.73	1.30	0.282	6.65	0.835	3.23

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.5.3 Summary statistics for concentrations of total PCBs-TEQ in whole freshwater fish (TEQ based on ng/kg wet weight)¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2015	4	18	0.977	0.718	0.796	4.58 x 10 ^{−3}	2.69	0.541	1.50
2016	21	99	1.30	1.82	0.648	1.15 x 10 ^{−2}	14.8	0.346	1.71
2017	21	103	0.552	0.738	0.286	3.70 x 10 ^{−4}	6.00	0.135	0.789
2018	38	170	0.862	1.54	0.408	1.61 x 10 ⁻³	9.77	0.231	0.834
2019	27	128	1.68	1.56	1.18	2.60 x 10 ⁻⁴	6.50	0.457	2.48
2022	8	34	0.518	0.649	0.337	5.55 x 10 ⁻²	3.17	0.153	0.540

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.5.4 Summary statistics for concentrations of PCB 118 in whole freshwater fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2015	4	18	1.62	1.26	1.25	0.0875	3.71	0.563	2.90
2016	21	99	1.62	2.27	1.06	0.156	16.9	0.510	1.96
2017	21	103	1.20	1.34	0.590	0.0450	7.40	0.240	1.90
2018	38	170	1.28	2.53	0.610	0.0550	28.0	0.242	1.40
2019	27	128	3.51	7.56	1.49	0.0250	76.0	0.518	4.07
2022	8	34	0.639	0.533	0.480	0.0300	2.00	0.160	0.938

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.5.5 Summary statistics for concentrations of perfluorooctanesulfonic acid in whole freshwater fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2015	7	33	12.0	7.88	8.92	2.71	25.9	4.11	20.0
2016	22	104	14.0	11.2	99.9	0.500	47.5	4.97	20.1
2017	20	95	12.1	10.5	9.93	0.500	43.8	3.10	15.0
2018	43	195	11.4	12.3	6.17	0.500	57.4	3.51	13.9
2019	28	132	14.4	15.1	9.10	0.500	69.0	4.33	20.5
2021	1	4	0.500	0	0.500	0.500	0.500	0.500	0.500
2022	8	34	9.14	8.62	5.45	1.10	32.0	3.65	10.2

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Table 4.5.6 Summary statistics for concentrations of SUM 41PFAS¹ in whole freshwater fish $(\mu g/kg \text{ wet weight})^2$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2022	11	42	7.02	9.92	3.68	0.711	45.1	1.93	6.19

¹Note that this excludes PFOS; see Section 4.5.2 for individual substances covered.

²n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Figure 4.5.1 Modelled trends for mercury (Hg), SUM 6PBDEs, PCB 118, and perfluorooctanesulfonic acid (PFOS) in whole freshwater fish (A; units are µg/kg wet weight) and total PCBs-TEQ (B; TEQ calculated from wet weight values). Overall trends shown as solid lines with shading representing 95% confidence intervals



To describe changes over time, linear mixed-effects models were fitted to log10transformed concentrations for each substance or group of substances, with decimal date of sampling as the main predictor. This corresponds to modelling the geometric mean of concentration. This approach was chosen because of the relatively low number of sample sites and samples available. As replicate data were available, a random effects structure of replicate sample within site-visit was used to ensure statistical power was as good as possible. This accounted for the inherent correlations between observations over time from any particular site, and between replicate samples collected on the same visit to a site.

The fitted model was used to predict mean log10 concentrations for each year between 2014 and 2022 for mercury and 2015 to 2022 for the other substances. Fitted values and their confidence intervals were back-transformed to the original scale of the data, and the

significance of the linear trend term was then evaluated with reference to Satterthwaite's approximation for effective degrees of freedom (<u>Kuznetsova, Brockhoff and Christensen,</u> <u>2017</u>).

For mercury, an upward trend was observed, but this was not statistically significant owing to high uncertainty (wide confidence intervals). For PCBs, a downward trend was seen, but this was not statistically significant for the same reason. Statistically significant downward trends, however, were observed for PBDEs, PCB 118 and PFOS.

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'no observed change in concentrations' is given for mercury and PCBs and of 'decreasing concentrations' for PBDEs, PCB 118 and PFOS.

For PFAS, a trend cannot be assessed as there are only data for a single year. Therefore, the entry in the dashboard reflects that data are available, but insufficient to report a trend assessment. The summary statistics for SUM 41PFAS (Table 4.5.6) are generally of the same order of magnitude as those for PFOS in 2022.

4.5.4 Thresholds

To consider the risk to freshwater wildlife from PBT substances, secondary poisoning quality standards ($QS_{sec pois}$) have been used. These standards help protect wildlife from the effects of eating prey contaminated by PBT substances.

The EQS specified in the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>) for mercury is a QS_{sec pois} and is 20μ g/kg wet weight in fish.

For PBDEs and PFOS, $QS_{sec pois}$ values have been derived through the EU EQS derivation process, which considers different protection goals. The $QS_{sec pois}$ values for PBDEs and PFOS do not have statutory status as EQSs because they are not the most-critical (lowest) QSs. The EQSs have a different protection goal of human health; however, the $QS_{sec pois}$ values are the most appropriate to use here. The derived $QS_{sec pois}$ for PBDEs is $44\mu g/kg$ wet weight (EC, 2011c) and that for PFOS is $33\mu g/kg$ wet weight (EC, 2011b).

There are no standards available for solely dioxin-like PCBs or PFAS in freshwater fish.

Average concentrations for each substance or group of substances from sites assessed in 2022 were compared against the above values. Sites required more than 1 sample to be included in the assessment. The results are summarised in Table 4.5.7 and information on the percentage of sites above the corresponding thresholds was used for the dashboard.

Results for mercury suggest very high risk to wildlife. The potential risk category within the dashboard that this substance falls under has not changed since previous reporting (<u>Environment Agency, 2021</u>), but the percentage of sites above the threshold has increased. However, this is based on a very limited number of sites.

Both PBDEs and PFOS show no exceedances of the corresponding thresholds. For PFOS, the potential risk has improved to a lower category since previous reporting (<u>Environment Agency, 2021</u>), although again, this is based on a limited number of sites.

For PCBs, PCB 118 and PFAS, the entry in the dashboard reflects that there are no values available for comparison.

Substance	No. of sites	No. of sites above threshold	Percentage of sites above threshold (%)
Mercury	8	8	100
PBDEs	8	0	0
PFOS	7	0	0

 Table 4.5.7 Summary of threshold comparison information for freshwater fish for 2022

It should be noted that because of potential differences in protection goals and methods used for national assessments, the results reflected in the dashboard may differ slightly to those used for water quality classification reporting purposes.

4.6 Persistent, bioaccumulative and toxic substances in Eurasian otter: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluorinated substances

Mercury	\bigoplus
Polybrominated diphenyl ethers	\bigcirc
Polychlorinated biphenyls	\bigcirc
PCB 118	\bigcirc
Perfluorooctanesulfonic acid	\bigcirc
Per- and polyfluoroalkyl substances	\bigcirc

4.6.1 Data source

Data on PBT substances in otter livers have been provided by the CUOP (<u>Cardiff</u> <u>University</u>, 2023). Livers have been collected from individuals found dead each year. Most animals died as a result of traffic collisions, but some individuals died from other causes.

Individuals selected for chemical analysis were chosen to provide a balanced selection by sex and age class, and an even spatial distribution across England. All individuals were ≥900 mm in length, with 2 exceptions of 820 and 885mm length to ensure adequate sample size for analysis. Individuals excluded from selection included diseased, emaciated or decomposed otters, those with missing body length or weight data, and pregnant or lactating females (<u>Chadwick and Farrington, 2022</u>).

Chemical analysis of the samples was supported by the Environment Agency and has been conducted since the last round of reporting the indicator (<u>Environment Agency, 2021</u>) using archived tissue.

In the previous round of reporting, data for earlier years were used. However, these were selected using different criteria to that mentioned above; therefore, they are not directly comparable and have not been included here.

4.6.2 Data structure

The data consist of measurements of mercury concentrations in the livers from carcasses found each year from 2014 to 2021 in England. The corresponding data for PBDEs and PCBs, PFOS, and other PFAS cover 2015 to 2021.

Mercury

Data on mercury concentrations in the livers of otters are reported as mg/kg wet weight.

All samples were above the LoD.

Polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances

Data on PBDEs, PCBs, PFOS, and other PFAS concentrations in the livers of otters are reported as $\mu g/kg$ wet weight.

For PBDEs, data are available for 26 individual PBDE congeners – 17, 28, 30, 32, 35, 37, 47, 49, 51, 66, 71, 77, 85, 99, 100, 118, 119, 126, 128, 138, 153, 154, 183, 190, 196, and 197 – and the summed concentrations of these congeners (SUM PBDEs).

For PCBs, data are available for 35 individual PCBs congeners – 8, 18, 28, 29, 31, 52, 77, 101, 105, 114, 118, 123, 126, 128, 138, 141, 149, 153, 156, 157, 163, 167, 169, 170, 171, 180, 183, 187, 189, 194, 199, 201, 205, 206, and 209 – and the summed concentrations of these congeners (SUM PCBs).

Data are available for PFOS and for a further 40 PFAS: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFNS, PFDS, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA, FBSA, FHxSA, PFOSA, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS, 10:2 FTS, NMeFOSAA, NEtFOSAA, HPFO-DA, ADONA, 9CI-PF3ONS, 11CI-PF3OUdS, 6:6 PFPi, 6:8 PFPi, 8:8 PFPi, CI-PFOS, FDEA 10:2, and PFEESA. Data for the summed concentrations of these additional 40 PFAS are given as SUM 40PFAS.

The summed values for PBDEs, PCBs and the 40 PFAS, alongside those for the individual substances PCB 118 and PFOS, are summarised in Section 4.6.3.

The LoDs for individual PBDE and PCB congeners varied within the data sets. No samples had non-detects for all congeners. The LoDs for the individual PBDE congeners reported as non-detects ranged from 0.00474 to 0.972µg/kg wet weight; those for PCBs congeners ranged from 0.0273 to 0.256µg/kg wet weight. Congener concentrations below the LoD were assigned a value that was half the LoD for the purposes of summing. None of the results for PCB 118 were reported below the LoD.

For PFOS, none of the results were reported below the LoD. The remaining PFAS had variable LoDs. Just over a third of the results were reported below the LoD, where LoDs ranged from 0.008 to 0.1μ g/kg wet weight. Individual PFAS concentrations below the LoD were assigned a value that was half the LoD for the purposes of summing.

4.6.3 Exploration of change in chemical concentrations over time

Mercury

The distribution of data by year for otters is summarised in Table 4.6.1 and shown in Figure 4.6.1.

Table 4.6.1 Summary statistics for mercury concentrations in the livers of Eurasian otters	;
(mg/kg wet weight) from England ¹	

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	10	2.21	1.72	1.76	0.154	5.89	1.27	2.46
2015	34	1.57	0.889	1.58	0.400	3.92	0.862	2.10
2016	37	2.10	1.15	1.89	0.402	5.41	1.38	2.36
2017	35	2.06	1.67	1.57	0.449	8.68	1.06	2.74
2018	30	2.10	1.31	1.82	0.188	6.16	1.33	2.43
2019	29	1.43	0.813	1.29	0.237	3.89	0.900	1.88
2020	30	1.50	0.762	1.44	0.311	3.46	1.03	1.97
2021	15	1.35	0.656	1.30	0.270	2.88	0.924	1.69

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.6.1 Box plots of mercury concentrations in the livers of Eurasian otters (mg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)



The change in mercury concentrations in the livers of the selected otters over time was analysed using a linear regression model (Figure 4.6.1). This used concentration data

converted into natural logarithm (Ln) values with the year and otter sex information to assess changes over time and discern/control for any difference in concentration between sexes. Model fit was evaluated through visual examination of residual plots to check for normal distribution, homogeneity of variance and absence of leverage. The same analysis approach was adopted for the other PBTs in this section.

No statistically significant difference was seen in mercury concentrations between otter sexes (p = 0.349). From visual inspection, mercury concentrations in otter livers appear to decline (Figure 4.6.1); however, the change was not statistically significant (p = 0.071). Therefore, the assignment of 'no observed change in concentrations' is given in the dashboard.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

The distribution of data for SUM PBDEs, SUM PCBs, PCB 118, PFOS, and SUM 40PFAS by year is summarised in Tables 4.6.2 to 4.6.6 and shown in Figures 4.6.2 to 4.6.6, respectively.

For each substance or group of substances, the change in concentrations in the livers of the selected otters over time was analysed using the same method as described for mercury (see above). The modelled results are given in Figures 4.6.2 to 4.6.6 for SUM PBDEs, SUM PCBs, PCB 118, PFOS, and SUM 40PFAS, respectively.

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	34	53.8	59.1	32.6	3.41	294	17.5	74.8
2016	37	41.4	39.8	35.3	2.77	200	13.7	45.9
2017	35	31.5	27.9	19.6	3.20	116	14.2	32.6
2018	31	59.1	57.4	46.6	3.51	253	19.1	82.6
2019	28	32.5	30.7	24.3	2.67	117	11.2	40.4

Table 4.6.2 Summary statistics for concentrations of SUM PBDEs in the livers of Eurasian otters (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	30	25.5	23.8	15.1	2.30	84.6	7.21	37.7
2021	15	26.6	30.5	15.6	4.00	126	10.3	29.2

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.6.2 Box plots of SUM PBDE concentrations in the livers of Eurasian otters (µg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)





Table 4.6.3 Summary statistics for concentrations of SUM PCBs in the liver of Eurasian otters (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	34	377	545	198	34.9	3,040	117	399
2016	37	426	494	214	22.0	1,880	84.0	387
2017	36	429	937	238	28.6	5,780	142	375
2018	31	499	605	301	25.7	2,520	111	593
2019	28	322	418	184	15.9	2,010	128	293
2020	30	204	157	158	48.3	693	102	232
2021	15	444	780	128	38.7	2,860	81.7	268

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.6.4 Summary statistics for PCB 118 concentrations in the liver of Eurasian otters (μ g/kg wet weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	34	36.0	45.8	20.4	2.03	217	11.1	41.0
2016	37	38.6	40.9	24.6	1.14	141	8.65	44.3
2017	36	42.6	96.7	20.9	2.45	587	10.4	40.3
2018	31	41.6	40.5	31.8	4.34	157	9.93	52.9
2019	28	34.9	52.4	18.7	0.86	249	11.3	31.1
2020	30	27.7	42.1	15.2	4.41	234	11.4	27.2
2021	15	49.8	94.8	19.3	3.60	377	10.1	29.3

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.6.3 Box plots of SUM PCB concentrations in the livers of Eurasian otters (µg/kg wet weight) from England representing median and lower/upper interguartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles observations outside of this range are shown as points (with 5 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)





Year

Figure 4.6.4 Box plots of PCB 118 concentrations in the livers of Eurasian otters (µg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (with 5 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)



Table 4.6.5 Summary statistics for perfluorooctanesulfonic acid concentrations in the livers of Eurasian otters (μ g/kg wet weight) from England^{1,2}

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2015	30	2,580	5,450	1,260	260	30,500	692	2,020
2016	33	3,500	7,340	1,270	182	41,700	487	3,230
2017	30	1,780	1,630	1,200	108	6,680	590	2,320
2018	27	4,570	8,440	2,310	143	44,400	1,320	4,270
2019	26	2,340	2,730	1,290	280	12,300	817	2,630
2020	30	3,710	7,900	1,290	41.2	42,400	448	2,550
2021	15	2,450	2,630	1,320	205	9,910	696	3,040

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

²Based on detected total PFOS as a single determinand.

Table 4.6.6 Summary statistics for concent	rations of SUM 40PFAS	¹ in the livers of Eurasian
otters (µg/kg wet weight) from England ²		

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	30	540	380	437	98.9	1,900	312	713
2016	33	761	766	480	109	3,000	272	890
2017	30	607	578	470	53.4	3,030	321	695
2018	27	734	530	522	78.4	1,920	337	987
2019	26	643	508	484	143	2,250	342	733

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	30	638	641	450	31.0	3,250	272	782
2021	15	694	358	648	146	1,230	530	985

¹Note that this excludes PFOS; see Section 4.6.2 for individual substances covered.

²n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.6.5 Box plots of perfluorooctanesulfonic acid concentrations in the livers of Eurasian otters (μ g/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (with 4 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)





Figure 4.6.6 Box plots of SUM 40PFAS concentrations in the livers of Eurasian otters (μ g/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)





No statistically significant difference (p > 0.05) was seen in PFOS, SUM PBDE and SUM 40PFAS concentrations between otter sexes. For SUM PCBs (p = 0.0000171) and PCB 118 (p = 0.000092), statistically significant higher concentrations were observed in male compared with female otters.

For PBDEs, there was a statistically significant decline in concentrations over time (p = 0.003). Therefore, the assignment of 'decreasing concentrations' is given in the dashboard.

For PCBs, PCB 118, PFOS and other PFAS, no statistically significant changes in concentrations over time were observed (p > 0.05). Therefore, the assignment of 'no observed change in concentrations' is given in the dashboard.

4.6.4 Thresholds

There is no statutory threshold established for mercury concentrations in otter liver. However, <u>Shore and others (2011)</u> suggest average liver concentrations in sampled populations that are greater than 25mg/kg wet weight may be indicative of some lethality and impaired reproduction in that population. This value is an average for a sampled population and should be compared against an average (geometric mean or median value) rather than values for individuals.

The median value for mercury in the liver of otters that died in 2021 was 1.03mg/kg wet weight, which is considerably lower that the indicative threshold concentration of mercury in liver of 25mg/kg wet weight. The entry on the dashboard is therefore 'all sites/individuals or population average below threshold'.

There are no established thresholds for PBDEs, PCBs, PCB 118, PFOS, or other PFAS concentrations in otter livers and, therefore, no threshold values are proposed for the

corresponding assessment of potential risk. The entries in the dashboard reflect that there are no values available for comparison.

4.7 Persistent, bioaccumulative and toxic substances in blue mussel: mercury, polybrominated diphenyl ethers and polychlorinated biphenyls

Mercury	
Polybrominated diphenyl ethers	\bigcirc
Polychlorinated biphenyls	\longleftrightarrow
PCB 118	\leftarrow

4.7.1 Data source

Data on mercury, PBDEs and PCBs in blue mussels (*Mytilus edulis*) in England have been provided by the Environment Agency. Mussel data were originally collected as part of the UK-wide OSPAR Coordinated Environmental Monitoring Programme (CEMP), and analysis was later expanded in anticipation of monitoring requirements under the Water Environment Regulations 2017 (<u>UK Government, 2017</u>).

Data used in this assessment are also submitted, as part of the wider UK data set, to the DOME (marine environment) data portal for the International Council for the Exploration of the Sea (ICES) (<u>ICES, 2023</u>).

The monitoring methodology is described in the CEMP programme manual, the Green Book (British Oceanographic Data Centre (<u>BODC, 2020</u>). Where feasible, sites are monitored annually, with a target of three samples – consisting of pooled individuals – collected at each site on each sampling occasion. Samples are collected in the winter/early spring to avoid any seasonal influence from spawning.

For all substances, individual sites are sampled once a year. Fewer sites have been monitored since 2020, partly owing to the COVID-19 pandemic, and monitored sites have changed over time due to disappearing intertidal mussel beds in key locations. Change in in the balance of monitored catchments over time can influence the results of the trend and threshold assessments.

In comparison to the previous round of reporting the H4 indicator (Environment Agency, 2021), data for PCBs are now summarised in lipid weight to facilitate the threshold

assessment (Sections 4.7.3 and 4.7.4) and the threshold assessment for PBDEs is more stringent (Section 4.7.4).

4.7.2 Data structure

Data on total mercury and PCB concentrations in *Mytilus* flesh are available for the period 2000–2022, except for 2020 for mercury, but only data from 2011 onwards are included in this assessment to eliminate the impacts of historical changes in the monitoring programme. For PBDEs, relevant data are available from 2015 to 2022. The number and location of sites have varied over time.

For PBDEs, data are available for 6 individual PBDE congeners – 28, 47, 99, 100, 153, and 154 – and the summed concentration of these congeners (SUM 6PBDEs). For PCBs, data are available for the ICES-7 PCBs as individual congeners and as summed concentrations (SUM ICES-7). The ICES-7 PCBs are seven congeners commonly found in the environment and designated by the ICES as an indicator of the degree of PCB contamination. These congeners are PCBs 28, 52, 101, 118, 138, 153, and 180 and are monitored under the OSPAR CEMP.

Wet weight concentrations are available for all substances. Lipid weight concentrations are also available for the individual ICES-7 PCBs to allow threshold comparisons and are used in Sections 4.7.3 and 4.7.4 for SUM ICES-7 PCBs and PCB 118.

All reported mercury concentrations were above the LoD.

The LoDs for the individual PBDE and PCB congeners varied across samples and substances; they ranged from 0.006 to 0.2μ g/kg wet weight for PBDEs and from 0.1 to 2μ g/kg wet weight for PCBs. For PBDEs and PCBs, 34 and 59%, respectively, of the individual congener results were reported below the LoD. In these cases, values below the LoD were assigned a negligible value of 0.0000001μ g/kg wet weight for each congener when calculating the summed values. Those samples that had non-detects for all congeners comprised 3 and 21% of all samples for PBDEs and PCBs, respectively.

For PCB 118, 58% of the results were reported below their LoDs which ranged from 0.1 to $1\mu g/kg$ wet weight; these were assigned a value that was half the LoD.

The summed values for PBDEs and PCBs, alongside those for the individual substances mercury and PCB 118, are summarised in Section 4.7.3.

4.7.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.7.1 to 4.7.4 for mercury, SUM 6PBDEs, SUM ICES-7 PCBs, and PCB 118, respectively. The corresponding modelled trend information is shown in Figure 4.7.1.

Table 4.7.1 Summary statistics for concentrations	s of mercury in <i>Mytilus edulis</i> (μg/kg wet
weight) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2011	17	47	35.8	21.5	30.0	8.53	85.1	19.2	43.8
2012	17	33	34.8	16.1	32.6	10.3	76.1	23.8	39.8
2013	17	51	22.5	10.0	23.1	4.92	44.0	13.8	29.7
2014	20	61	37.4	21.7	31.7	5.00	122	24.5	45.8
2015	19	57	28.6	17.9	21.5	10.6	87.2	17.1	36.8
2016	16	48	33.9	14.0	33.9	12.9	60.2	21.7	45.3
2017	15	45	29.5	12.0	31.0	10.3	49.0	19.1	39.5
2018	13	37	32.3	12.7	34.0	12.0	51.9	20.9	43.3
2019	16	46	38.4	19.2	39.0	13.3	83.6	24.9	49.7
2021	6	18	41.8	17.9	42.9	16.9	69.0	24.4	58.0
2022	8	24	31.9	11.0	30.2	8.46	52.7	25.9	40.4

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.7.2 Summary statistics for concentrations of SUM 6PBDEs in Myti	lus edulis (µg/kg
wet weight) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	19	57	0.418	0.375	0.240	6.00 x 10 ⁻⁸	1.55	0.131	0.641
2016	16	48	0.378	0.460	0.359	6.00 x 10 ^{−8}	3.20	0.143	0.500
2017	15	45	0.534	0.433	0.434	0.0870	1.56	0.196	0.666

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	13	39	0.344	0.257	0.285	0.0330	0.905	0.107	0.506
2019	16	46	0.395	0.406	0.356	6.00 x 10 ^{−8}	2.25	0.127	0.533
2020	3	8	0.114	0.0684	0.0910	0.0380	0.214	0.0675	0.170
2021	6	18	0.115	0.0950	0.112	6.00 x 10 ^{−8}	0.314	0.0553	0.134
2022	8	24	0.136	0.101	0.0945	0.0500	0.410	0.0628	0.190

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.7.3 Summary statistics for concentrations of SUM ICES-7 PCBs in *Mytilus edulis* $(\mu g/kg \text{ lipid weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	79.2	124	5.56 x 10 ⁻⁶	3.61 x 10 ^{−6}	517	4.64 x 10 ^{−6}	110
2012	14	30	78.5	75.6	94.2	3.74 x 10 ^{−6}	291	6.70 x 10 ^{−6}	138
2013	17	51	50.8	74.0	6.03 x 10 ^{−6}	3.48 x 10 ^{−6}	280	4.12 x 10 ^{−6}	87.3
2014	20	61	72.0	96.7	51.4	3.15 x 10 ^{−6}	418	4.55 x 10 ^{−6}	103
2015	19	57	203	227	110	8.08	910	43.7	331
2016	16	48	242	236	99.1	7.87	883	66.6	451
2017	15	45	331	253	350	15.3	804	63.4	578
2018	13	39	218	261	98.4	35.3	963	55.7	196
2019	16	46	234	240	161	3.55 x 10 ^{−6}	769	53.4	356

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2020	3	9	126	135	84.4	1.00 x 10 ^{–5}	374	52.3	149
2021	8	24	113	182	45.7	8.43 x 10 ^{−6}	798	27.1	99.8
2022	8	24	157	118	104	21.4	451	69.3	208

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.7.4 Summary	statistics for concentration	ns of PCB 118 in	Mytilus edulis	(µg/kg lipid
weight) ¹				

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	36.3	10.6	34.0	24.0	89.2	31.2	37.5
2012	14	30	37.8	8.34	35.3	21.9	56.8	32.1	42.6
2013	17	51	31.9	9.61	29.1	13.5	56.2	25.7	38.2
2014	20	61	29.1	13.8	30.7	1.64	58.5	22.6	36.0
2015	19	57	27.0	30.5	13.8	2.28	128	5.92	40.8
2016	16	48	30.5	30.0	14.2	3.18	117	7.14	54.2
2017	15	45	69.0	109	45.5	3.03	514	11.1	71.1
2018	13	39	29.1	31.2	13.0	3.23	126	4.70	43.4
2019	16	46	33.7	27.3	28.3	3.68	97.7	12.7	44.6
2020	3	9	19.7	23.9	7.14	3.12	68.6	5.43	28.6
2021	7	21	18.5	16.8	7.14	5.95	70.5	7.14	28.0

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2022	8	24	19.8	18.3	10.4	6.02	74.3	7.14	27.2

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.7.1 Modelled trends for mercury (Hg), SUM 6PBDEs, SUM ICES-7 PCBs, and PCB 118 in *Mytilus edulis* (μ g/kg wet weight for Hg and PBDEs and μ g/kg lipid weight for PCBs) using 2 modelling approaches, shown as solid lines with shading representing 95% confidence intervals



Changes over time were assessed using the data for all individual samples analysed for mercury and PCB 118. For PCBs and PBDEs, the corresponding summed concentrations were used for the analysis.

To describe potential trends over time, 2 complementary approaches were used. In both cases, regression models were fitted to log10-transformed concentration data with decimal date of sampling as the main predictor. This corresponds to modelling the geometric mean of concentration. The approaches used were:

- Linear mixed-effects models (Ime green lines in the graphs). The model structure specified random intercepts for replicate sample nested within sampling site. This approach should give better statistical power if the underlying trends are genuinely linear.
- Generalised additive mixed models (gamm orange lines in the graphs). These allow the trend to follow the data in a curvilinear manner. This is a better option if the data length and quantity are sufficient, and if the true trend is non-linear. In this approach, a random intercept for sample site was specified; the replicate samples were averaged to give one value per site visit.

Use of random effects in the models accounts for the inherent correlations between observations over time from any particular site, and in the case of the linear mixed-effects model approach between replicate samples collected on the same visit to a site.

Fitted values and their confidence intervals were back-transformed to the original concentration scale of the data. For the linear trends, the significance of the linear trend term was then evaluated with reference to Satterthwaite's approximation for effective degrees of freedom (Kuznetsova, Brockhoff and Christensen, 2017).

The final assessment of trend was a combination of results from the linear and non-linear analyses. Where the results agreed this was flagged as 'higher certainty'; if there were some inconsistencies between the results, the result from the linear analysis was given precedence, but the result was flagged as 'lower certainty'.

Statistical confidence will also have been influenced by changes in the monitoring over time; there is a general downward trend in the number of sites that could be sampled, particularly in the last three years.

The results are illustrated in Figure 4.7.1 and summarised in Table 4.7.5.

Table 4.7.5 Summary of the assessment of trends over time for mercury, SUM 6PBDEs, SUM ICES-7 PCBs, and PCB 118 concentrations in *Mytilus edulis*

Substance	Trend	Certainty
Mercury	Increasing	Higher
SUM 6PBDEs	Decreasing	Lower
SUM ICES-7 PCBs	No change	Lower
PCB 118	No change	Lower

For mercury, there was close agreement between the trends from the two analytical approaches. For the other PBTs, there were greater differences between the two approaches so the results have been flagged as lower certainty.

Differences between the results from the 2 models for the PBT substances are caused by several factors:

- the reduction in samples available in recent years: no to few data were available for 2020, and only 6–8 sites were visited in 2021 and 8 in 2022
- for SUM ICES-7 PCBs, there was an apparent increase in concentrations in 2022, albeit based on a relatively small number of sites
- the within-sample variances, which are removed in the averaging undertaken to fit the gamm
- changes in limits of detection over time

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'increasing concentrations' is given for mercury, 'decreasing concentrations' for PBDEs, and 'no observed change in concentrations' for PCBs and PCB 118. The certainty of these results should also be taken into account.

The previous report (<u>Environment Agency, 2021</u>) noted that owing to significant change in the LoDs over time, a formal trend assessment was not performed for PCBs. For this report, a tentative trend assessment has been made, which suggests no change, however it has been flagged as low certainty.

4.7.4 Thresholds

There are no environmental assessment criteria (EAC) for mercury under OSPAR which cover the protection of wildlife. The EQS for mercury specified in the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>) is derived to protect top predators from secondary poisoning (QS_{sec pois}). However, it is based

on fish, which represent a different trophic level to *Mytilus* – that is, trophic level 4 rather than 2. To consider a level of trophic adjustment, it is proposed that an interim threshold value of 1.6µg/kg wet weight (<u>OSPAR Commission, 2016</u>) is used. However, the high uncertainty of converting an EQS in fish into an equivalent value in molluscs has to be recognised, as discussed in the OSPAR Commission report (<u>OSPAR Commission, 2016</u>).

There are no derived EACs for PBDE congeners under OSPAR. However, an approach adopted by the OSPAR Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) (<u>OSPAR Commission, 2020</u>) is to use the Canadian FEQGs for biota (<u>Environment and Climate Change Canada, 2013</u>) as EAC equivalents. These are threshold values for individual PBDEs (Table 4.7.6), which correspond to the 6 congeners monitored in mussels. The values specified are for fish. To allow for the lower lipid content in individual mussels, where these chemicals are likely to reside, the thresholds are adjusted based on the measured lipid content of the monitored mussels against that typical for fish (5%). This approach has been applied here and the resulting values are lower thresholds compared with previous reporting (<u>Environment Agency, 2021</u>). The QS_{sec pois} derived through the EU EQS derivation process for SUM 6PBDEs (<u>EC, 2011c</u>) was considered by the OSPAR MIME, but rejected in favour of the individual thresholds to allow more-stringent assessment of the more-toxic congeners.

In future, we may want to apply an approach for PBDEs in mussels that uses dry weight equivalent concentrations instead, as now applied by OSPAR (ICES, 2024), to remove any uncertainties associated with measuring low lipid content in mussel tissue. However, the lipid values we have used for the threshold conversions are generally lower than that suggested by OSPAR as typical for blue mussels and, therefore, conservative in comparison.

The EAC thresholds used in OSPAR assessments for the individual ICES-7 PCB congeners are used in this assessment. These are based on lipid weight (Table 4.7.6).

When performing the threshold assessment for each substance or group of substances, the most-recent site means – that is, those for 2022 – were assessed against the threshold. Only sites for which there was more than 1 sample were included; the assessment comprised all 8 sampling sites.

PBDE congener number	Canadian FEQG based values (µg/kg wet weight)¹	ICES-7 PCB congener number	OSPAR EAC (µg/kg lipid weight)
28	120	28	67
47	44	52	108

Table 4.7.6 Summary of thresholds used in the indicator for assessing polybrominated diphenyl ethers and polychlorinated biphenyls in *Mytilus edulis*

PBDE congener number	Canadian FEQG based values (µg/kg wet weight) ¹	ICES-7 PCB congener number	OSPAR EAC (µg/kg lipid weight)
99	1	101	121
100	1	118	25
153	4	138	317
154	4	153	1585
-	_	180	469

¹These individual FEQG values relating to fish are adjusted for bivalves by multiplying them by the ratio of the typical percentage lipid content of the shellfish / 5; the value of 5 corresponds to fish having a typical lipid content of 5%.

For mercury, all site mean concentrations (100%), and indeed all individual samples, for 2022 were above the threshold. The entry on the dashboard reflects this result.

For the PBDEs, all site mean concentrations for 2022 for all individual congeners were below the corresponding thresholds. The entry on the dashboard reflects this result.

The 2022 site mean concentrations for the individual PCBs 28, 52, 101, 138, 153, and 180 were below their respective thresholds. For PCB 118, mean concentrations at 3 sites were above the threshold. Information on the percentage of sites (38%) above the PCB 118 threshold is used for the dashboard for both PCBs and PCB 118.

The potential risk for PCBs has improved to a lower category since previous reporting (<u>Environment Agency, 2021</u>), although this assessment is based on a relatively limited number of sites.

It should be noted that because of potential differences in protection goals and methods used for national assessments, the results reflected in the dashboard may differ slightly to those used for water quality classification reporting purposes.
4.8 Persistent, bioaccumulative and toxic substances in estuarine and coastal fish: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid



4.8.1 Data source

Data on mercury, PBDEs, PCBs, and PFOS in estuarine and coastal fish in England have been provided by the Environment Agency. Data on concentrations in whole fish, primarily dab (*Limanda limanda*), but also flounder (*Platicthys flesus*) and plaice (*Pleuronectes platessa*), have been collected; other fish also have been monitored to a lesser degree. Data have been collected under the Water Environment Regulations 2017 (<u>UK</u> <u>Government, 2017</u>).

Data are collected once a year at multiple sites. On each sampling occasion, multiple replicate samples – generally 3 – are taken from each monitoring site. Each sample consists of one or more fish of the same species; where more than one fish is needed for the required quantity for analysis, this typically comprises 2 or 3 fish, occasionally 4.

Survey teams are guided to collect data preferentially from a ranked list of fish species, based on what was previously found at each site.

4.8.2 Data structure

Data are available from 2018 to 2022 for mercury and PCBs and from 2017 to 2022 for PBDEs and PFOS in estuarine and coastal fish.

Concentrations are reported as μ g/kg wet weight in whole fish; for PCBs, these have been converted into lipid weight values.

All the reported mercury concentrations were above the LoD.

For PBDEs, data are available for 6 individual PBDE congeners – 28, 47, 99, 100, 153, and 154 – and the summed concentration of these congeners (SUM 6PBDEs). For PCBs, data are available for the ICES-7 PCBs as individual congeners – 28, 52, 101, 118, 138, 153, and 180 – and as summed concentrations (SUM ICES-7).

The LoDs for the individual PBDE and PCB congeners varied across samples and substances; they ranged from 0.006 to 0.3μ g/kg wet weight for PBDEs and from 0.1 to 10μ g/kg wet weight for PCBs. For PBDEs and PCBs, 19 and 12%, respectively, of the individual congener results were reported below the LoD. In these cases, values below the LoD were assigned a negligible value of 0.0000001μ g/kg wet weight for each congener when calculating the summed values. For PCB 118, 4% of the results were reported below their LoDs, which ranged from 0.1 to 0.3μ g/kg wet weight; these were assigned a value equal half the LoD.

For PFOS, 48% of the results reported as below the LoD had an LoD of $1\mu g/kg$ wet weight. These results were assigned a value that was half the LoD.

4.8.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.8.1 to 4.8.5 for mercury, SUM 6PBDEs, SUM ICES-7 PCBs, PCB 118, and PFOS, respectively.

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	16	34	132	72.3	132	28.5	336	74.7	169
2019	25	73	97.8	52.0	91.2	19.8	250	59.9	125
2020	17	37	84.1	46.0	74.4	22.4	230	52.5	104

Table 4.8.1 Summary statistics for concentrations of mercury in estuarine and coastal	fish
(µg/kg wet weight) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2021	21	62	103	54.3	95.4	14.2	264	65.4	148
2022	16	46	92.0	72.1	88.4	2.86	312	32.2	130

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.8.2 Summary statistics for concentrations of SUM 6PBDEs in estuarine and coastal fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2017	1	9	0.856	0.651	0.880	0.219	2.26	0.353	1.01
2018	16	36	1.35	1.21	1.12	0.164	5.43	0.368	2.02
2019	26	76	1.08	1.28	0.652	0.0440	5.87	0.207	1.61
2020	24	67	1.01	1.42	0.449	0.0510	6.45	0.249	1.24
2021	21	63	1.05	0.926	0.665	6.00 x 10 ⁻⁸	3.75	0.373	1.43
2022	16	45	1.25	1.13	0.933	0.0650	4.37	0.375	1.56

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.8.3 Summary statistics for concentrations of SUM ICES-7 PCBs in estuar	rine and
coastal fish (μg/kg lipid weight) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2018	10	16	705	538	633	90.0	1820	294	1050
2019	26	76	416	514	278	7.86	3370	153	436

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	23	65	277	315	191	32.3	1700	104	301
2021	21	63	402	315	317	33.5	1320	147	529
2022	16	43	603	833	311	2.78 x 10 ⁻⁴	4120	202	557

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.8.4 Summary statistics for concentrations of PCB 118 in estuarine and coastal fish $(\mu g/kg \ lipid \ weight)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	9	15	82.8	59.2	80.6	10.5	198	40.7	115
2019	26	76	49.0	63.2	29.9	2.00	375	14.3	54.1
2020	22	55	32.6	35.4	22.8	2.88	200	12.1	37.5
2021	21	63	45.4	36.5	32.7	3.54	162	17.2	66.1
2022	16	43	67.2	79.4	38.8	2.30 x 10 ⁻⁵	400	23.4	58.6

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.8.5 Summary statistics for concentrations of PFOS in estuarine and coastal fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2017	1	9	2.21	1.51	1.99	0.500	5.95	1.48	2.21
2018	16	33	6.06	6.99	3.95	0.500	30.3	2.45	6.64

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2019	26	76	3.14	5.16	0.500	0.500	29.0	0.500	3.25
2020	23	64	2.23	4.80	1.00	0.500	34.0	0.500	2.02
2021	21	63	1.77	2.20	1.10	0.500	12.0	0.500	2.05
2022	14	36	0.992	0.828	0.500	0.500	4.00	0.500	1.40

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Unlike for freshwater fish (see Section 4.5), species data are available for each replicate sample. Data are available for 136–168 samples of dab (*Limanda limanda*), 63–76 of flounder (*Platicthys flesus*) and 40–45 of plaice (*Pleuronectes platessa*) across all substances; the ranges represent the fact that different numbers of results are available for different PBT substances. Data for a small number of un-named non-flatfish species (4 samples) and for sole (3 samples) were excluded from the trend analysis. The corresponding modelled trend information is shown in Figure 4.8.1. The overall trend is based on the result for all species together.

To describe changes over time, linear mixed-effects models were fitted to log10transformed concentrations for each chemical substance or group of substances, with decimal date as the main predictor. This corresponds to modelling the geometric mean of concentration. This approach was chosen because of the relatively low number of sample sites and years of data available. Species identity was used as a covariate in the trend analysis, and trends were identified for the main 3 species individually and together. The model accounted for the inherent correlation between observations over time from any particular site. These are more likely to be correlated with each other than with observations from other sites. The same principle applies to replicate samples collected on the same visit. This was achieved through specifying random intercepts for replicate sample nested within sampling site.

The fitted model was used to predict mean log10 concentrations for each year with the available data. Fitted values for each species and averaged across species were predicted for each year. Fitted values and their confidence intervals were back-transformed to the original scale of the data. The significance of the linear trend term was then evaluated with reference to Satterthwaite's approximation for effective degrees of freedom (Kuznetsova, Brockhoff and Christensen, 2017). Where there was a differing trend among species, this may reflect the geographical distribution and exposure of the species; further work is required try to separate these factors.

The results of the trend analyses are shown in Figure 4.8.1 and Table 4.8.6. All conclusions are conditional on the short length of the available records.

Figure 4.8.1 Modelled trends for A: mercury (Hg), SUM 6PBDEs and perfluorooctanesulfonic acid (PFOS) (μ g/kg wet weight) and B: SUM ICES-7 PCBs and PCB 118 (μ g/kg lipid weight) in estuarine and coastal fish. Trends shown for all 3 species combined (solid green line) and for dab, flounder and plaice separately (dashed lines), with shading representing 95% confidence intervals; the highest values for the upper confidence intervals for PFOS, PCB-ICES and PCB-118 have been truncated



Table 4.8.6 Summary of the trends over time based on the limited data available for mercury, SUM 6PBDEs, SUM ICES-7 PCBs, PCB 118, and PFOS in estuarine and coastal fish tissue, showing trend information for all species together and whether mean concentrations and trends differ among species

Substance	Trend all species	Difference in mean concentration among species	Difference in trend among species	
Mercury	Decreasing	Yes	Yes	
SUM 6PBDEs	No trend	No	No	
SUM ICES 7 PCBs	No trend	No	No	
PCB 118	No trend	No	No	
PFOS	Decreasing	Yes	Yes	

The minimum requirements for reporting a trend are not met (see Section 3.1.2), except for PBDEs and PFOS; however, they have the minimum required data because a year is included for which there are only data for a single site. Therefore, the entry in the dashboard reflects that data are available, but insufficient to report a trend assessment.

4.8.4 Thresholds

To consider the risk to estuarine and coastal wildlife from PBT substances, secondary poisoning quality standards ($QS_{sec pois}$) have been used. These standards help protect wildlife from the effects of eating prey contaminated by PBT substances.

The EQS specified in the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>) for mercury is a QS_{sec pois} and is 20μ g/kg wet weight in fish.

There are no derived EACs for PBDE congeners under OSPAR. However, an approach adopted by the OSPAR MIME (<u>OSPAR Commission</u>, 2020) is to use the Canadian FEQGs for biota (<u>Environment and Climate Change Canada</u>, 2013) as EAC equivalents. These are threshold values for individual PBDEs (Table 4.8.7), which correspond to the 6 congeners monitored in estuarine and coastal fish. The QS_{sec pois} derived through the EU EQS derivation process for SUM 6PBDEs (<u>EC</u>, 2011c) was considered by the OSPAR MIME, but rejected in favour of the individual thresholds to allow more-stringent assessment of the more-toxic congeners.

For PCBs, EAC thresholds used in OSPAR assessments for the individual ICES-7 PCB congeners are used in this assessment. These are based on lipid weight (Table 4.8.7).

For PFOS, a QS_{sec pois} value has been derived through the EU EQS derivation process, which considers different protection goals. The QS_{sec pois} value for PFOS does not have statutory status as an EQS because it is not the most-critical (lowest) QSs. The EQS has a different protection goal of human health; however, the QS_{sec pois} value is the most appropriate to use here. The derived QS_{sec pois} for PFOS is $33\mu g/kg$ wet weight (EC, 2011b).

Average concentrations for each substance or group of substances from sites assessed in 2022 were compared against the above values. Sites required more than 1 sample to be included in the assessment.

Table 4.8.7 Summary of thresholds used in the indicator for assessing polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyl (PCBs) in estuarine and coastal fish for 2022

PBDE congener number	Canadian FEQG based values (µg/kg wet weight)	ICES-7 PCB congener number	OSPAR EAC (µg/kg lipid weight)
28	120	28	67
47	44	52	108
99	1	101	121
100	1	118	25
153	4	138	317
154	4	153	1585
-	_	180	469

For mercury, 13 sites (93%) had mean concentrations above the threshold. The entry on the dashboard reflects this result.

For PBDEs and PFOS, all site mean concentrations were below the corresponding thresholds. The entry on the dashboard reflects this result.

The 2022 site mean concentrations for the individual PCBs 153 and 180 were below their respective thresholds. For PCBs 28, 52, 101, and 138, one site (7%) was above the corresponding threshold in each case; for the first 3 congeners this was the same site in the Thames, and for PCB 138 this was at a site in the north-west. For PCB 118, mean concentrations at 12 sites were above the threshold. Information on the percentage of

sites (86%) above the PCB 118 threshold is used for the dashboard for both PCBs and PCB 118.

Results for mercury and PCB 118 suggest very high risk to wildlife.

It should be noted that because of potential differences in protection goals and methods used for national assessments, the results reflected in the dashboard may differ slightly to those used for water quality classification reporting purposes.

4.9 Persistent, bioaccumulative and toxic substances in offshore fish: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances



4.9.1 Data source

Data on concentrations of mercury in fish muscle tissue, and of PBDEs, PCBs, PFOS and other PFAS in fish livers, are available for dab (*Limanda limanda*). These data for offshore marine fish are collected as part of UK Marine Strategy Regulations–OSPAR monitoring for assessing good environmental status. The data are collected and held by Cefas and are submitted to the national MERMAN database.

Data used in this assessment are also submitted, as part of the wider UK data set, to the DOME (marine environment) data portal for the ICES (<u>ICES, 2023</u>).

Stations – around which sampling is conducted – are selected on the basis that they reliably support dab populations that can be sampled for analysis and that there are no direct impacts from local point sources so that they are representative of the overall sub-region. There are a minimum of 3 stations required within each OSPAR hydrogeographical sub-region (<u>OSPAR Commission, 2023</u>).

Between 2008 and 2010, sampling around the country was done annually. From then onwards, fish were collected on alternate sides of the country each year with sampling around east coast stations occurring in odd years and west coast ones in even years. For mercury, a couple of west coast sites were also included in the 2011 monitoring. Up to 17 stations can be monitored in odd years and up to 10 in even ones.

All data relate to designated English waters, except for those from a Welsh station in the Bristol Channel as this is a shared water body in which fish are likely to move freely across territorial water.

Typically, 5 or fewer pools of fish were sampled around each station. Each pool comprised 5 fish.

Sampling is typically carried out in mid-summer, but monitoring deviated to winter for 2020 and 2022, and to spring for 2021. Reasons for this include the COVID-19 pandemic and vessel problems.

Since the previous round of reporting the H4 indicator (Environment Agency, 2021), fish samples from 2016 and 2017 have been analysed retrospectively in 2021 and 2022 for PFAS using archived tissue, as opposed to year-on-year analysis. Therefore, data for 2016 and 2017 are now reported for PFOS which were not available previously. Data for PFOS have also been updated to cover results for both the linear and branched forms, where available, as a total value; the previous report (Environment Agency, 2021) used linear PFOS results only.

4.9.2 Data structure

The data consist of measurements of mercury, PCB and PBDE concentrations in dab for 2008–2022. The corresponding data for PFOS and other PFAS cover 2014–2022.

The data summaries that were provided comprise results from individual pool samples taken around the stations. These individual samples were used in the trend and threshold assessments (Sections 4.9.3 and 4.9.4, respectively) rather than station means for the purposes of the dashboard indicator. This is because the pooled samples are already representative of a mean of 5 fish and this approach allows assessment of trends across the stations and nationally.

Mercury

Data are for total mercury² in muscle. All mercury concentrations are reported as mg/kg

² All mercury species transformed to elemental mercury and the concentration is then determined.

wet weight. The LoDs varied across the data set of 984 samples. Only 6 samples were reported below LoDs of 0.01 and 0.02mg/kg wet weight in 2009 and 2008, respectively, and these were assigned a value that was half the LoD.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Data are available for 11 individual PBDE congeners – 17, 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183 – and the summed concentrations of these congeners (SUM 11PBDE). All concentration data are reported in mg/kg wet weight and those for key congeners and the SUM 11PBDE value are also reported as their converted lipid weight values. The summed lipid weight values are summarised in Section 4.9.3 and results for individual PBDEs have been used for the threshold assessment (Section 4.9.4).

For PCBs, data are available for 25 individual PCB congeners. These include the ICES-7 PCB congeners: 28, 52, 101, 118, 138, 153, and 180. The remaining 18 PCB congeners for which there are data are 18, 31, 44, 47, 49, 66, 105, 110, 128, 141, 149, 151, 156, 158, 170, 183, 187, and 194. Data are also available for the summed concentrations of the ICES-7 PCBs (SUM ICES-7 PCBs) and for the 25 congeners in total (SUM 25PCB). All concentration data are reported in mg/kg wet weight. The individual ICES-7 PCBs and both summed values are also reported as their converted lipid weight concentrations. The summed lipid weight values are summarised in Section 4.9.3. Results for the individual ICES-7 PCBs have been used for the threshold assessment (Section 4.9.4).

Data are available for PFOS and other PFAS. However, the different forms of PFOS analysed – linear only and branched and linear combined – have varied; these are summed where possible to give a total value. Similarly, the number of other PFAS analysed over time has varied over the years from 13 to 40. At the time of analysing samples in 2022, these were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFNS, PFDS, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA, FBSA, FHxSA, PFOSA, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS, NMeFOSAA, NEtFOSAA, HPFO-DA, ADONA, 9CI-PF3ONS, 11CI-PF3OUdS, 6:6 PFPi, 6:8 PFPi, 8:8 PFPi, CI-PFOS, FDEA 10:2, PFEESA, and 10:2 FTS. Data for the summed concentrations of other PFAS – without PFOS – are given as SUM PFAS. All concentration data are reported in μ g/kg wet weight.

The summed values for PBDEs, PCBs and PFAS, alongside those for the individual substances PCB 118 and PFOS, are summarised in Section 4.9.3.

All 479 samples analysed had PFOS concentrations that were above the LoD. For other PFAS, the LoDs varied for the individual substances and across samples and years. Only one sample from 2016 had non-detects for all PFAS.

4.9.3 Exploration of change in chemical concentrations over time

Mercury

Summary data for mercury concentrations in dab muscle analysed across the period are given in Table 4.9.1.

The measured concentrations were converted into Ln values for the purpose of assessing trends. A plot of the overall change over time in Ln values of mercury concentrations in dab muscle from 2008 to 2022 is shown in Figure 4.9.1. The pattern for alternate years from 2011 broadly reflects the biennial sampling of alternate sides of the country.

Table 4.9.1 Summary statistics for samples of mercury concentrations in the muscle of	dab
(mg/kg wet weight) ¹	

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2008	23	111	0.108	0.0787	0.0800	0.0100	0.370	0.0500	0.150
2009	23	114	0.156	0.127	0.130	0.00500	1.10	0.0700	0.210
2010	16	78	0.127	0.101	0.0850	0.0100	0.550	0.0575	0.190
2011	16	79	0.0766	0.0329	0.0700	0.0300	0.170	0.0600	0.0900
2012	8	40	0.155	0.104	0.145	0.0300	0.430	0.0500	0.235
2013	15	73	0.0993	0.0430	0.0900	0.0400	0.260	0.0700	0.110
2014	9	45	0.155	0.106	0.140	0.0300	0.440	0.0600	0.240
2015	14	66	0.0958	0.0422	0.0900	0.0400	0.230	0.0600	0.123
2016	8	37	0.161	0.105	0.150	0.0200	0.480	0.0700	0.225
2017	15	75	0.106	0.0471	0.100	0.0300	0.260	0.0700	0.120
2018	9	45	0.131	0.0943	0.108	0.0294	0.363	0.0464	0.193

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2019	15	71	0.0953	0.0386	0.0944	0.0362	0.238	0.0693	0.111
2020	9	42	0.115	0.0788	0.103	0.0159	0.318	0.0391	0.180
2021	15	74	0.140	0.0591	0.129	0.0535	0.321	0.100	0.167
2022	9	39	0.141	0.0829	0.164	0.0141	0.270	0.0491	0.212

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.9.1 Scatterplot of mercury concentrations (mg/kg wet weight, log10 y-axis scale) in the muscle of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Mercury in Fish

The minimum data requirements for trend assessment are met (see Section 3.1.2), though the monitoring regime has altered over time (see Section 4.9.1). A generalised additive model (GAM) (<u>Wood, 2017</u>) was used to estimate trend using the individual Ln-

transformed sample data and time in years as the explanatory variable. The smoothing parameter for the trend was set so it did not respond to minor deviations between years.

When interpreting the GAM plots, two criteria were used: (1) the overall trend needed to be statistically significant at the 5% level and (2) the difference between the predicted values at the start and the end of the time series needed to be statistically significant at the 5% level. The second criterion was a basic way of determining overall trend direction when this could be variable over the years.

Whilst the trend line shown in Figure 4.9.1, based on all samples from all stations, is statistically significant (p = 0.03) owing to the large number of observations and was supported by the second criteria as an increase, it appears to be very level.

The overall trend for the dashboard was based on the changes in concentrations over time at individual stations. This was assessed by fitting a GAM to the data for each station and tabulating the results. Scatterplots of results for samples taken at these stations can be found in Appendix F, Figure F.4.9.1.

To produce an overall national trend, a statistic D was then calculated as follows: The number of stations showing downward trends was deducted from those showing upward ones. This value was reported as a percentage of the total number of stations examined. Where $D \ge 20\%$, an overall upward trend is assigned; where $D \le -20\%$, a downward trend is reported.³ Between these two values, a level result of no observed change is recorded.

Three stations appear to show a downward trend and 4 show an upward trend out of the 24 sites that had time series data (see Appendix F, Figure F.4.9.1 and Table F.1). The 4 stations showing an upward trend are in the east; one station in this area showed a decreasing trend. The resulting D value (D 4%) supports the assignment of 'no observed change in concentrations' and this is used within the dashboard.

Polybrominated diphenyl ethers and polychlorinated biphenyls

Summary data for SUM 11PBDE concentrations in dab livers across the analysed period are given in Table 4.9.2. The corresponding values for SUM 25PCB, SUM ICES-7 and PCB 118 are given in Tables 4.9.3 to 4.9.5, respectively.

The measured concentrations were converted into Ln values for the purpose of assessing trends. Plots of the overall change over time in Ln values of the SUM 11PBDE, SUM

³ The use of the D statistic is a pragmatic approach for reflecting the national trend from statistically significant trends at stations. The thresholds of 20% are proposed because they give a balance between reporting trends when there is very little difference and not seeing any trends at all.

25PCB and PCB 118 concentrations in dab livers are shown in Figures 4.9.2 to 4.9.4, respectively.

Table 4.9.2 Summary statistics for samples of SUM 11PBDE concentrations in the livers of	
dab (mg/kg lipid weight) ¹	

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2008	20	94	0.0690	0.0609	0.0439	0.00195	0.220	0.0196	0.102
2009	19	94	0.0277	0.0215	0.0231	0.00136	0.142	0.0119	0.0367
2010	16	79	0.0503	0.0551	0.0328	0.00121	0.352	0.0217	0.0666
2011	12	60	0.0395	0.0366	0.0339	0.00283	0.158	0.0124	0.0516
2012	8	40	0.0362	0.0284	0.0315	0.00327	0.100	0.00883	0.0566
2013	15	73	0.0428	0.0422	0.0317	0.00193	0.185	0.0146	0.0525
2014	9	44	0.0254	0.0251	0.0198	0.00185	0.117	0.00616	0.0366
2015	14	66	0.0329	0.0452	0.0188	3.66 x 10 ^{−4}	0.222	0.00690	0.0315
2016	8	37	0.0157	0.0117	0.0122	0	0.0444	0.00845	0.0227
2017	15	72	0.0235	0.0257	0.0158	0.00139	0.142	0.00766	0.0281
2018	9	45	0.0104	0.00694	0.00755	0.00143	0.0263	0.00482	0.0179
2019	15	71	0.0227	0.0277	0.0128	0.00117	0.135	0.00775	0.0246
2020	9	42	0.0117	0.00857	0.00907	0.00207	0.0331	0.00370	0.0182
2021	15	57	0.0404	0.0394	0.0268	0.00183	0.194	0.0184	0.0456
2022	9	39	0.0247	0.0195	0.0255	0.00131	0.0701	0.00613	0.0388

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.9.2 Scatterplot of SUM PBDE concentrations (in units of mg/kg lipid weight, log10 y-axis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



PBDE in Fish

Table 4.9.3 Summary statistics for samples of SUM 25PCB concentrations in the livers of dab (mg/kg lipid weight)¹

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2008	20	94	0.815	0.755	0.555	0.170	3.87	0.299	1.06
2009	19	94	0.487	0.406	0.362	0.0487	1.87	0.177	0.684
2010	16	79	0.655	0.637	0.445	0.0996	3.49	0.260	0.765
2011	12	60	0.387	0.217	0.310	0.140	1.14	0.242	0.459
2012	8	40	0.883	0.646	0.734	0.149	2.62	0.406	1.15
2013	15	73	0.430	0.234	0.366	0.133	1.36	0.273	0.526
2014	9	44	0.754	0.675	0.558	0.105	3.17	0.262	1.07

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	14	66	0.381	0.312	0.261	0	1.56	0.209	0.420
2016	8	37	0.499	0.351	0.400	0.119	1.79	0.270	0.671
2017	15	72	0.318	0.185	0.272	0.131	1.09	0.205	0.343
2018	9	45	0.393	0.229	0.304	0.125	0.937	0.201	0.562
2019	15	71	0.285	0.166	0.235	0.0699	0.777	0.176	0.361
2020	9	42	0.373	0.263	0.303	0.0678	1.08	0.140	0.575
2021	15	57	0.733	0.587	0.567	0.120	3.05	0.375	0.868
2022	9	39	0.750	0.501	0.689	0.107	1.92	0.371	1.13

¹n: number of samples analysed; SUM: summed values; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.9.4 Summary statistics for samples of SUM ICES-7 concentrations in the livers	of
dab (mg/kg lipid weight) ¹	

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2008	20	94	0.514	0.457	0.351	0.116	2.42	0.209	0.665
2009	19	94	0.313	0.243	0.236	0.0487	1.10	0.134	0.390
2010	16	79	0.432	0.427	0.293	0.0667	2.61	0.184	0.538
2011	12	60	0.259	0.149	0.210	0.0919	0.772	0.168	0.291
2012	8	40	0.530	0.401	0.437	0.0900	1.67	0.230	0.701
2013	15	73	0.295	0.177	0.231	0.105	0.975	0.178	0.377

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	9	44	0.454	0.413	0.324	0.0623	1.86	0.150	0.653
2015	14	66	0.257	0.213	0.180	0	1.07	0.139	0.268
2016	8	37	0.292	0.207	0.235	0.0691	1.06	0.152	0.382
2017	15	72	0.221	0.131	0.188	0.0896	0.792	0.147	0.243
2018	9	45	0.234	0.137	0.176	0.0798	0.570	0.121	0.319
2019	15	71	0.198	0.114	0.161	0.0422	0.533	0.125	0.246
2020	9	42	0.218	0.153	0.183	0.0461	0.648	0.0830	0.321
2021	15	57	0.529	0.438	0.399	0.120	2.36	0.254	0.598
2022	9	39	0.431	0.284	0.394	0.0738	1.13	0.206	0.634

¹n: number of samples analysed; SUM: summed values; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.9.5 Summary statistics for samples	s of PCB 118 concentrations in dab liver (r	ng/kg
lipid weight) ¹		

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2008	20	94	0.0606	0.0527	0.0449	0.0166	0.302	0.0277	0.0692
2009	19	94	0.0389	0.0295	0.0309	0.00509	0.151	0.0199	0.0458
2010	16	71	0.0623	0.0680	0.0396	0.00949	0.409	0.0269	0.0688
2011	12	60	0.0335	0.0165	0.0286	0.0121	0.0887	0.0231	0.0383
2012	8	40	0.0567	0.0428	0.0450	0.0125	0.188	0.0223	0.0762

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2013	15	73	0.0331	0.0156	0.0283	0.0108	0.0914	0.0228	0.0416
2014	9	44	0.0497	0.0452	0.0370	0.00836	0.193	0.0154	0.0714
2015	14	66	0.0296	0.0207	0.0211	0.00106	0.0968	0.0174	0.0359
2016	8	37	0.0307	0.0203	0.0239	0.00878	0.103	0.0173	0.0429
2017	15	72	0.0258	0.0121	0.0234	0.0107	0.0710	0.0188	0.0286
2018	9	45	0.0261	0.0147	0.0194	0.00920	0.0695	0.0159	0.0350
2019	15	71	0.0233	0.0111	0.0205	0.00123	0.0559	0.0159	0.0281
2020	9	42	0.0237	0.0159	0.0186	0.00605	0.0726	0.0109	0.0328
2021	15	57	0.0564	0.0373	0.0459	0.0129	0.196	0.0339	0.0710
2022	9	39	0.0452	0.0288	0.0366	0.0122	0.123	0.0214	0.0633

¹n: number of samples analysed; SUM: summed values; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.9.3 Scatterplot of SUM 25PCB concentrations (in units of mg/kg lipid weight, log10 y-axis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



PCB in Fish

Figure 4.9.4 Scatterplot of PCB 118 concentrations (in units of mg/kg lipid weight, log10 yaxis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



CB118 in Fish

The minimum data requirements for trend assessment are met (see Section 3.1.2), though the monitoring regime has altered over time for PBDEs and PCBs (see Section 4.9.1). The same GAM (<u>Wood, 2017</u>) approach and criteria as described for mercury in dab (see above) was used to estimate trends.

The trend lines shown in Figures 4.9.2 to 4.9.4 for SUM 11PBDEs, SUM 25PCBs and PCB 118, respectively, based on all samples from all stations, are all statistically significant (p <0.001) owing to the large number of observations. However, only a decrease for SUM 11PBDEs and increase for SUM 25PCBs were supported using the criteria. It is noticeable for all three substance(s) that the modelled trend lines appear to show an increase from around 2018.

To determine the overall trends for these substances for the dashboard, changes in concentrations over time at individual stations were assessed using the same GAM method.

Scatterplots of results for SUM 11PBDEs, SUM 25PCBs and PCB 118 in samples taken at these stations can be found in Appendix F, Figures F.4.9.2 to F.4.9.4, respectively. The statistic D for SUM 11PBDEs, SUM 25PCBs and PCB 118 was then calculated from the station results, as also described above for mercury.

For SUM 11PBDEs, 7 east coast and 8 west coast stations show statistically significant downward trends out of the 24 sites (see Appendix F, Figure F.4.9.2 and Table F.1). No stations exhibited any upward trends. The resulting D value (–63%) strongly supported the assignment of 'decreasing concentrations' and this is used within the dashboard. However, the rise in concentrations in more-recent years noted above was observed at most individual stations.

The individual stations around which SUM 25PCBs in dab livers were measured appear to show geographical differences. There are 6 downward trends observed in the west and only 1 in the east. Increasing concentrations over time are seen at 7 stations in the east only (see Appendix F, Figure F.4.9.3 and Table F.1). The resulting D value of 0% supports the assignment of 'no observed change in concentrations' and this is used within the dashboard. This reflects the levelling of concentrations over time for some sites as well as the effect of increasing concentrations at others in more-recent years.

The example of PCB 118 supports the above conclusions for SUM 25PCBs on the west coast with 6 sites showing downward trends. For the east coast, the picture is slightly improved compared with that for SUM 25PCBs: 5 sites exhibit upward trends and 3 downward ones (See Appendix F, Figure F.4.9.4 and Table F.1). The resulting D value of -17% supports the assignment of 'no observed change in concentrations' and this is used within the dashboard.

For further context, national trends were determined for PCBs and PBDEs based on data relating to individual stations from 2011 to 2022 – that is, the minimum data required for a trend assessment (see Section 3.1.2) rather than using the full data set. The results

suggest the need to continue to review the situation over time as an upward trend is observed for PCBs and a lower percentage of stations show downward trends for PBDEs.

Perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

Summary data for PFOS and SUM PFAS concentrations in dab livers across the analysed period are given in Tables 4.9.6 and 4.9.7, respectively.

The measured concentrations were converted into Ln values for the purpose of assessing trends. Plots of the overall change over time in Ln values of the PFOS and SUM PFAS concentrations in dab livers are shown in Figures 4.9.5 and 4.9.6, respectively. Because the dates of fish collection were provided, these were used to look more closely at trends over time and they are reflected in the plots.

Table 4.9.6 Summary statistics for samples of perfluorooctanesulfonic acid concentrations in the livers of dab (μ g/kg wet weight)^{1,2}

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	9	34	6.80	3.84	6.61	1.28	17.6	3.65	8.54
2015	14	64	4.12	2.73	3.64	0.507	12.5	2.17	5.66
2016	8	38	6.73	5.52	4.94	0.793	19.3	2.23	10.4
2017	15	71	4.42	2.57	4.35	0.631	13.4	2.34	5.97
2018	9	45	7.86	4.50	7.80	1.35	18.3	4.10	9.99
2019	15	71	3.14	2.09	2.68	0.652	12.7	1.45	4.18
2020	9	42	9.06	10.5	4.16	0.956	38.6	2.70	12.3
2021	15	75	3.10	1.67	2.81	0.617	7.98	1.70	4.21
2022	9	39	5.96	4.41	4.95	1.18	23.2	3.47	7.53

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

²The analysed linear and branched forms of PFOS were summed to give a total PFOS value. For the years 2014, 2015 and 2018, only the linear forms were analysed; this was

also the case for 15 samples in 2019. In the last round of reporting (<u>Environment Agency</u>, <u>2021</u>), only data for the linear form was reported.

Year	No. of PFAS	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	13	9	34	3.49	2.78	2.71	0.845	13.6	1.79	3.99
2015	13	14	64	2.46	1.33	2.29	0.390	6.54	1.39	3.38
2016	30	8	38	1.16	1.21	0.857	0	5.07	0.226	1.89
2017	35–39 ³	15	71	1.94	1.46	1.65	0.130	7.10	0.829	2.83
2018	13	9	45	3.03	1.97	2.71	0.470	11.5	1.72	4.28
2019	15–30 ⁴	15	71	2.16	1.70	1.71	0.110	7.73	0.914	2.75
2020	30	9	42	2.57	2.09	1.91	0.0723	8.31	1.03	3.59
2021	30	15	75	1.89	1.09	1.61	0.444	6.20	1.21	2.18
2022	40	9	39	1.95	1.14	1.75	0.596	5.09	0.963	2.29

Table 4.9.7 Summary statistics for samples	of SUM PFAS ¹	concentrations in	n dab livers
(µg/kg wet weight) ²			

¹Note that this excludes PFOS; see Section 4.9.2 for individual substances covered.

²n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

³The majority of samples were analysed for 35 PFAS; 6 samples were analysed for 36 PFAS and 2 samples were analysed for all PFAS.

⁴The majority of samples were analysed for 30 PFAS; 15 samples were analysed for 15 PFAS.

Figure 4.9.5 Scatterplot of perfluorooctanesulfonic acid concentrations (in units of μ g/kg wet weight, log10 y-axis scale) in the livers of dab from marine waters around England between 2014 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Figure 4.9.6 Scatterplot of SUM PFAS concentrations (in units of μ g/kg wet weight, log10 yaxis scale) in the livers of dab from marine waters around England between 2014 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)





For PFOS and SUM PFAS, there are limited data with only 3 to 4 cycles of monitoring available for the east and west coast, respectively.

The same GAM (Wood, 2017) approach and criteria as described for mercury in dab (see above) was used to estimate trends based on all samples from all stations. The results for PFOS and SUM PFAS (Figures 4.9.5 and 4.9.6, respectively) are all statistically significant (p < 0.001) owing to the number of observations. However, only a decrease for PFAS was supported using the criteria. For PFOS, from visual observation of Figure 4.9.5 and the data in Table 4.9.6, slightly higher concentrations are seen at the west coast stations compared with those from the east coast.

For the analysis at the station level, owing to the few data, a standard t-test was used to compare the mean Ln levels for both PFOS and SUM PFAS across the corresponding first and last years for each side of the country. This was used because the data were reasonably symmetric and the variation within years was similar for each station. The t-test also assumes that the data are independent within stations, reflecting that each sample comes from different fish. A two-sided t-test was used as there was no theoretical information as to whether the trend was up or down.

For PFOS, 5 of the east coast stations show statistically significant downward trends; for the west coast, 2 upward and 3 downward trends were observed. The corresponding D value is -25% indicating decreasing concentrations.

For SUM PFAS, 2 of the east coast stations show statistically significant downward trends. For the west coast, 4 stations show statistically significant differences: 2 upward trends and 2 downward trends. The resulting D value was –8% indicating decreasing concentrations.

For both PFOS and SUM PFAS, while statistically significant differences are seen, the minimum data requirements (see Section 3.1.2) are not met for reporting trends for these substances in dab livers. In addition, further data over time is needed to understand the influence of the change in the number of PFAS analysed in both cases.

The corresponding entries in the dashboard reflect that data are available for PFOS and PFAS, but are insufficient to report trend assessments.

4.9.4 Thresholds

Mercury

There are currently no agreed criteria for assessing the ecological significance of mercury concentrations under OSPAR. However, under the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>), a biota EQS of 20µg/kg wet weight is available. This value is intended to protect predators from the effects of secondary poisoning and, therefore, is relevant to whole fish. Because the tissue measured in dab is muscle, the application of this EQS as a threshold for the indicator can be considered an interim approach and over-precautionary.

Data for 2021 and 2022 were compared against the EQS of 20µg/kg wet weight to assess the most recent results for all sites around the country. Only one sample was below this value, equating to 99% above the threshold, and this result is used in the dashboard.

Polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances

There are no EACs derived for PBDE congeners under OSPAR. However, an approach adopted by the OSPAR MIME (<u>OSPAR Commission, 2020</u>) is to use the Canadian FEQGs for biota (<u>Environment and Climate Change Canada, 2013</u>). This approach results in threshold values for 6 of the 11 individual PBDEs (Table 4.9.8).

The FEQGs for biota either relate to fish health (concentrations that should not cause adverse effects on fish) or mammalian wildlife health (concentrations in fish that should not cause adverse effects on mammalian predators). As such, they might be less protective than an EAC (the concentration that should not cause adverse effects on the most sensitive marine organisms). Conversely, the FEQGs are for whole fish concentrations which will be lower values than for the liver concentrations to which they are generally compared. To make the data directly comparable in the latter case, we have compared the lipid weight values of PBDEs in fish liver against the corresponding lipid weight thresholds so that they are assessed on the same basis.

The EAC thresholds used in OSPAR assessments for the individual ICES-7 PCB congeners, including PCB 118, are used here (Table 4.9.8).

The number of individual samples that had concentrations above these proposed values was calculated for the most recent pair of years, that is 2021 and 2022, to allow assessment of results taken from across the whole country.

PBDE congener number	Canadian FEQG based values (µg/kg lipid weight) ¹	Canadian FEQG based values (µg/kg wet weight)	PCB congener number	OSPAR EAC (µg/kg lipid weight)
28	2400	120	28	67
47	880	44	52	108
99	20	1	101	121
100	20	1	118	25

Table 4.9.8 Suggested thresholds for polybrominated diphenyl ethers and polychlorinated
biphenyls

PBDE congener number	Canadian FEQG based values (µg/kg lipid weight) ¹	Canadian FEQG based values (µg/kg wet weight)	PCB congener number	OSPAR EAC (µg/kg lipid weight)
153	80	4	138	317
154	80	4	153	1585
-	_	_	180	469

¹Converted from wet weight threshold using a conversion factor of 20 (for a standard whole fish with a lipid content of 5% (EC, 2014)).

For PBDEs, only 4 out of 96 samples (4%) of dab liver were above the FEQG for the congener PBDE100. The 4 samples were from 2 stations on the east coast in 2021. There were no exceedances for the other PBDE congeners for which Canadian FEQGs are available.

For PCBs, 48 samples from the east coast in 2021 and 26 from the west in 2022 out of 96 in total (77%) had mean PCB 118 concentrations in dab liver that were above the EAC. For PCB 101, one sample from the east coast in 2021 was above the threshold, and for PCB 138, 6 samples from 4 stations on the east coast in 2021 were above the EAC. There were no exceedances for the other ICES-7 PCB congeners for which OSPAR EACs are available. This represents a large increase in the percentage of samples showing potential risk for PCBs compared with previous reporting when 34% of samples were above the PCB 118 threshold (Environment Agency, 2021).

An EAC is not available for PFOS or PFAS, but a $QS_{sec pois}$ has been derived for PFOS through the EU EQS derivation process, which considers different protection goals. The $QS_{sec pois}$ does not have statutory status as an EQS because it is not the most critical (lowest) QS. The EQS has a different protection goal of human health; however, the QS_{sec} pois is the most appropriate to use here.

The derived $QS_{sec pois}$ for PFOS is 33µg/kg wet weight (<u>EC, 2011b</u>). However, it should be noted that the threshold is based on whole fish concentrations whereas the available data for marine fish are for concentrations of PFOS in liver, which are typically 3 times higher than for whole fish⁴. Caution is therefore needed in interpreting this threshold assessment

⁴ Based on an unpublished assessment of internal data by Cefas.

in terms of potential risk to predators as the result is likely to be over-precautionary. None of the 114 samples exceeded this value.

The values used for the dashboard indicator are the percentage of samples that exceeded the above-mentioned thresholds for 2021 and 2022 combined. In the case of PCBs and PBDEs, the congeners that had the highest percentage of results above their corresponding thresholds are used for this purpose.

For PFAS, the entry in the dashboard reflects that there are no thresholds currently available for comparison.

4.10 Persistent, bioaccumulative and toxic substances in harbour porpoise: mercury, polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances



4.10.1 Data source

Data on concentrations of mercury, PFOS and other PFAS in liver tissue and of PBDEs, and PCBs in blubber are available for harbour porpoise (*Phocoena phocoena*). These data are collected as part of the UK CSIP and the Scottish Marine Animal Stranding Scheme (SMASS) funded by Defra and the Devolved Administrations, as well as through Cefas, the NERC ChemPop project and other ad hoc funding obtained by the CSIP and the SMASS. The first samples were analysed in 1991 and a minimum of 20 UK samples are analysed each year.

Tissue samples are taken opportunistically from marine mammal stranding and bycatch incidents. A subset is chosen for analysis that contains an even split of trauma vs infectious disease as causes of death, adult vs juvenile and male vs female, with samples covering England, Wales and Scotland that are broadly in proportion with the number of individuals found.

The contaminant data are collected and held by Cefas.

Data are for Great Britain and not restricted to the England level, as for most of the other metrics within this indicator. This is because the wider geographical data set maintains an even split between animal types in the data set – not biasing a certain type that may be more (or less) susceptible to accumulating contaminants, such as adult males or those dying from infectious disease or starvation. It also reflects that these species are likely to move more widely along the British coast and enables more robust trend determination because of the increased number of samples per year. This approach is consistent with other marine indicators within the 25-YEP Outcome Indicator Framework.

Since the previous round of reporting the H4 indicator (<u>Environment Agency, 2021</u>), additional harbour porpoise samples from 2017 and 2018 have been analysed for PBDEs and PCBs, and from 2009, 2012–2015, 2017, and 2018 for PFOS, using archived tissue as opposed to year-on-year analysis. Therefore, data for earlier years are now reported that were not available previously. Data for PFOS have also been updated to cover results for both the linear and branched forms, where available, as a total value; the previous report (<u>Environment Agency, 2021</u>) used linear PFOS results only.

4.10.2 Data structure

Each sample is from a single individual.

Mercury

Data for individual animals were provided for the years 2009–2021, excluding 2010.

All mercury data are reported in mg/kg wet weight in liver. All 241 samples analysed had mercury concentrations that were above the LoD.

Polybrominated diphenyl ethers, polychlorinated biphenyls, and perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

For PBDEs and PCBs, data are available for individuals for the years 2004–2021, excluding 2009 for PBDEs. For PFOS, the data cover 2001–2003, 2009 and 2012–2021; for other PFAS, the data are for 2009 and 2012–2021.

The PBDE and PCB congeners were the same as those described in Section 4.9.2, that is PBDEs 17, 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183, and PCBs 18, 28, 31, 44, 47, 49, 52, 66, 101, 105, 110, 118, 128, 138, 141, 149, 151, 153, 156, 158, 170, 180, 183, 187, and 194.

SUM 11PBDE and SUM 25PCB data are reported in mg/kg wet weight in blubber and have been converted into lipid weight to enable comparison with potential threshold concentrations.

Data are available for PFOS and other PFAS. However, similar to the situation described in Section 4.9.2, the different forms of PFOS analysed – branched and linear – have varied; these are summed where possible to give a total value. Similarly, the number of other PFAS analysed over time has varied over the years from 13 to 40. At the time of

analysing samples in 2021, these were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFPeS, PFHxS, PFHpS, PFNS, PFDS, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA, FBSA, FHxSA, PFOSA, PFECHS, 4:2 FTS, 6:2 FTS, 8:2 FTS, NMeFOSAA, NEtFOSAA, HPFO-DA, ADONA, 9CI-PF3ONS, 11CI-PF3OUdS, 6:6 PFPi, 6:8 PFPi, 8:8 PFPi, CI-PFOS, FDEA 10:2, PFEESA, and 10:2 FTS. Data for the summed concentrations of other PFAS – without PFOS – are given as SUM PFAS. All concentration data are reported in μ g/kg wet weight in liver.

The summed values for PBDEs, PCBs and PFAS, alongside those for the individual substances PCB 118 and PFOS, are summarised in Section 4.10.3.

The LoDs for individual PBDE and PCB congeners varied within the data sets of 489 and 481 samples, respectively. Those congeners that had results reported below the LoD had LoDs ranging from 0.0001 to 0.0032mg/kg wet weight for individual PBDEs and from 0.0043 to 0.016mg/kg wet weight for individual PCBs. However, no samples had non-detects for all congeners. Only one sample in 2004 for PCB 118 was reported below its LoD of 0.0100mg/kg wet weight and this was assigned a value that was half the LoD.

None of the 324 samples analysed for PFOS had concentrations below the LoD, except for 2 taken in 2002 which had LoDs of $32\mu g/kg$ wet weight; the detection limits have lowered since that date. These two samples were assigned a value that was half the LoD, that is $16\mu g/kg$ wet weight, for statistical analysis. No samples had non-detects for all PFAS.

4.10.3 Exploration of change in chemical concentrations over time

The distribution of data by year is summarised in Table 4.10.1 for mercury concentrations in harbour porpoise livers. The measured concentrations were converted into Ln values for the purpose of assessing trends, and then back-transformed to the original concentration scale. A plot of the overall change over time for mercury concentrations in harbour porpoise livers from 2009 to 2021 is shown in Figure 4.10.1.

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2009	23	19.3	24.2	7.40	0.280	89.0	2.30	26.0
2011	3	80.8	65.5	74.8	18.5	149	18.5	149
2012	3	15.0	12.3	16.2	2.22	26.7	2.22	26.7
2013	4	34.1	38.3	31.46	0.931	72.4	1.03	69.7

Table 4.10.1 Summary statistics for samples of mercury concentrations in harbour porpoise livers (mg/kg wet weight)¹

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	17	21.1	25.6	8.44	0.928	76.7	2.94	26.2
2015	23	26.6	42.0	3.85	0.867	160	1.99	42.5
2016	20	28.8	38.2	16.4	0.874	137	3.47	30.3
2017	29	26.2	37.1	11.2	0.863	166	3.44	28.8
2018	29	25.7	28.2	20.1	0.989	127	3.10	39.1
2019	30	27.6	40.8	14.9	1.03	192	3.57	33.0
2020	30	26.0	32.3	12.0	0.901	136	2.38	39.9
2021	30	32.4	35.2	22.3	1.54	143	4.26	46.1

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.10.1 Scatterplot of mercury concentrations in the livers of harbour porpoise from marine waters around the UK between 2009 and 2021 (in units of mg/kg wet weight, shown on a log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence intervals (diagram courtesy of Cefas)



Year

A GAM (<u>Wood, 2017</u>) was used to estimate trend using the individual Ln-transformed sample data and time in years as the explanatory variable. The degrees of freedom for the trend were set so they did not respond to minor deviations between years.

When interpreting the GAM plots, two criteria were used: (1) the overall trend needed to be statistically significant at the 5% level and (2) the difference between the predicted values at the start and the end of the time series needed to be statistically significant at the 5% level. The second criterion was a basic way of determining overall trend direction when this could be variable over the years.

For mercury, while the GAM line shown in Figure 4.10.1 suggests a slight upward trend for the full time series, it is not statistically significant (p = 0.09), although the data did meet the second criterion of the assessment approach in terms of significance (p = 0.04). No significant time trend was observed for the most-recent years, from the end of 2015 to the end of 2021 (p = 0.09, p = 0.14).

The results in the dashboard represent the observed trends from the full data set. Therefore, the assignment of 'no observed change in concentrations' is given.

Polybrominated diphenyl ethers and polychlorinated biphenyls

The distribution of data by year is summarised in Tables 4.10.2 to 4.10.4 for SUM 11PBDE, SUM 25PCB and PCB 118 concentrations, respectively, in harbour porpoise blubber. The lipid concentrations were converted into Ln values for the purpose of assessing trends, and then back-transformed to the original concentration scale. Plots of the overall change over time for SUM 11PBDE, SUM 25PCB and PCB 118 concentrations are shown in Figures 4.10.2 to 4.10.4, respectively.

Table 4.10.2 Summary statistics for samples of SUM 11PBDE concentrations in harbour
porpoise blubber (mg/kg lipid weight) ¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2004	35	1.11	1.14	0.828	0.276	5.99	0.390	1.31
2005	55	0.636	0.643	0.517	0.0314	4.01	0.221	0.800
2006	41	0.656	0.634	0.456	0.0983	3.15	0.224	0.832
2007	39	0.461	0.460	0.311	0.0953	2.81	0.195	0.602
2008	30	0.385	0.370	0.240	0.0569	1.40	0.143	0.469
2010	20	0.361	0.273	0.317	0.0581	1.21	0.143	0.493

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	20	0.401	0.284	0.303	0.0880	1.19	0.196	0.603
2012	20	0.316	0.303	0.186	0.0576	1.34	0.136	0.397
2013	20	0.272	0.187	0.241	0.0297	0.602	0.130	0.416
2014	18	0.159	0.165	0.129	0.0143	0.738	0.0535	0.220
2015	20	0.223	0.218	0.133	0.0360	0.775	0.0814	0.292
2016	21	0.278	0.303	0.163	0.0630	1.43	0.111	0.380
2017	30	0.377	0.609	0.201	0.0119	3.19	0.105	0.331
2018	31	0.285	0.271	0.172	0.0293	1.12	0.117	0.355
2019	30	0.243	0.214	0.168	0.0593	1.04	0.0960	0.337
2020	30	0.329	0.244	0.250	0.0401	0.942	0.130	0.549
2021	29	0.222	0.169	0.185	0.0568	0.733	0.0917	0.265

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.10.2 Scatterplot of SUM 11PBDE concentrations in the blubber of harbour porpoise from marine waters around the UK between 2004 and 2021 (in units of mg/kg lipid weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence intervals (diagram courtesy of Cefas)



Table 4.10.3 Summary statistics for samples of SUM 25PCB concentrations in harbour porpoise blubber (mg/kg lipid weight)¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2004	31	14.3	11.7	12.6	1.62	53.8	5.54	17.5
2005	49	15.0	13.4	11.1	1.03	60.2	5.18	20.9
2006	26	20.7	30.9	9.85	3.19	139	5.18	19.3
2007	28	11.8	11.5	7.87	1.75	44.8	3.45	15.8
2008	25	10.7	8.62	8.45	1.67	38.7	5.15	13.6
2009	23	18.1	23.8	7.79	0.662	81.2	3.29	18.3
2010	20	11.5	11.1	7.33	0.693	36.6	3.07	16.7
2011	21	14.0	11.9	10.9	1.13	40.9	4.75	21.2
Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
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2012	22	16.0	23.5	8.47	1.13	108	3.54	18.2
2013	22	11.6	9.04	9.54	0.800	30.9	3.39	17.1
2014	23	18.7	21.8	10.7	1.35	103	5.29	23.6
2015	20	7.52	8.18	5.05	1.45	39.0	3.24	9.08
2016	21	20.1	39.6	6.68	1.23	181	3.09	19.1
2017	30	17.4	24.5	7.60	0.374	101	2.55	22.1
2018	31	15.6	18.2	7.30	1.04	67.0	3.03	23.6
2019	30	17.3	24.6	9.54	1.52	133	4.37	19.9
2020	30	27.0	34.1	18.7	0.756	158	5.80	28.3
2021	29	17.4	17.1	8.61	1.75	53.3	4.51	28.7

Figure 4.10.3 Scatterplot of SUM 25PCB concentrations in the blubber of harbour porpoise from marine waters around the UK between 2004 and 2021 (in units of mg/kg lipid weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines denote its 95% confidence interval (diagram courtesy of Cefas)



Table 4.10.4 Summary statistics for sample	es of PCB 118	8 concentrations in	n harbour _l	porpoise
blubber (mg/kg lipid weight) ¹				

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2004	31	0.415	0.278	0.319	0.00658	1.22	0.231	0.576
2005	49	0.455	0.398	0.355	0.0531	2.45	0.203	0.645
2006	26	0.520	0.523	0.376	0.0994	2.21	0.243	0.525
2007	28	0.335	0.225	0.271	0.0655	0.841	0.186	0.421
2008	25	0.439	0.496	0.289	0.0638	2.66	0.246	0.480
2009	23	0.344	0.302	0.302	0.0403	1.50	0.168	0.443
2010	20	0.420	0.421	0.238	0.0339	1.52	0.124	0.634
2011	21	0.438	0.316	0.283	0.0856	1.24	0.209	0.598

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2012	22	0.502	0.410	0.371	0.111	1.69	0.200	0.716
2013	22	0.477	0.379	0.376	0.0605	1.36	0.252	0.591
2014	23	0.526	0.426	0.391	0.0974	1.76	0.240	0.772
2015	20	0.363	0.270	0.310	0.0731	1.16	0.162	0.479
2016	21	0.584	0.880	0.349	0.0680	4.22	0.212	0.523
2017	30	0.536	0.495	0.400	0.0346	2.04	0.141	0.742
2018	31	0.542	0.614	0.320	0.0660	2.43	0.161	0.565
2019	30	0.664	0.786	0.366	0.0872	3.87	0.233	0.770
2020	30	1.01	2.23	0.471	0.0860	12.6	0.224	0.946
2021	29	0.461	0.264	0.387	0.0844	1.29	0.327	0.555

Figure 4.10.4 Scatterplot of PCB 118 concentrations in the blubber of harbour porpoise from marine waters around the UK between 2004 and 2021 (in units of mg/kg lipid weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence intervals (diagram courtesy of Cefas)



The same GAM (<u>Wood, 2017</u>) approach and criteria as described for mercury in harbour porpoise (see above) was used to estimate trends.

For PBDEs, a statistically significant downward trend was observed for the complete time series (p < 0.01 for both criteria). While a significant time trend was observed based on the most-recent years, from the end of 2015 to the end of 2021, for the first criteria (p < 0.01), this was not confirmed for the second (p = 0.39). This agrees with the levelling off of concentrations for SUM 11PBDEs shown in Figure 4.10.2. The results in the dashboard represent the observed trends from the full data set. Therefore, the assignment of 'decreasing concentrations' is given.

For PCBs, no statistically significant change in concentrations was found based on the complete time series (p = 0.17, p = 0.59). The results based on the last 5 years suggest no recent change either (p = 0.17, p = 0.054). For PCB 118, a statistically significant upward trend was observed from the full data set (p = 0.026, p = 0.01); the short-term situation for PCB 118 did not show any conclusive trend (p = 0.026, p = 0.09).

The results in the dashboard represent the observed trends from the full data sets. Therefore, the assignment of 'no observed change in concentrations' is given for PCBs and 'increasing concentrations' for PCB 118.

Perfluorooctanesulfonic acid and other per- and polyfluoroalkyl substances

The distribution of data by year is summarised in Tables 4.10.5 and 4.10.6 for PFOS and SUM PFAS concentrations, respectively, in harbour porpoise livers. These concentrations were converted into Ln values for the purpose of modelling trends, and then back-transformed to the original concentration scale. Plots of the overall change over time in the corresponding Ln values of PFOS and SUM PFAS concentrations are shown in Figures 4.10.5 and 4.10.6, respectively.

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2001	10	873	629	952	138	1810	216	1490
2002	16	508	654	232	16.0	2420	119	771
2003	14	510	551	256	83.0	1820	140	784
2009	23	186	309	64.6	21.6	1458	43.4	213
2012	21	160	131	118	6.56	495	52.7	250
2013	23	188	152	138	26.3	533	77.9	257
2014	23	204	227	157	15.9	1144	73.2	234
2015	23	196	165	131	12.9	633	74.7	291
2016	21	89.1	73.4	71.9	7.34	263	30.7	143
2017	30	114	110	95.0	15.2	578	49.3	132
2018	30	200	139	115	4.08	507	66.4	261
2019	30	266	344	160	16.2	1763	46.0	384

Table 4.10.5 Summary statistics for samples of perfluorooctanesulfonic acid concentrations in harbour porpoise livers (μ g/kg wet weight)^{1,2}

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	30	134	164	89.2	7.63	820	39.9	161
2021	30	152	129	117	13.1	563	60.3	244

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

²The analysed linear and branched forms of PFOS were summed to give a total PFOS value. For the years 2001–2003 and 2016, only the linear forms were analysed; this was also the case for samples in 2012–2014 and 2017 except for 2, 10, 2, and 10 samples, respectively, for which both forms were analysed.

Figure 4.10.5 Scatterplot of perfluorooctanesulfonic acid (PFOS) concentrations in the livers of harbour porpoise from marine waters around the UK between 2001 and 2021 (in units of μ g/kg wet weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence intervals (diagram courtesy of Cefas)



Year

Table 4.10.6 Summary statistics for samples of SUM PFAS¹ concentrations in harbour porpoise livers $(\mu g/kg \text{ wet weight})^2$

Year	No. of PFAS (n) ³	n	Mean	SD	Median	Min	Max	Q1	Q3
2009	30 (23)	23	57.4	53.1	39.9	6.02	244	25.2	69.7
2012	13 (19), 30 (2)	21	58.4	35.9	47.0	12.9	137	33.1	80.2
2013	13 (13), 28 (7), 30 (3)	23	61.3	37.1	53.0	12.1	178	39.2	73.4
2014	13 (21), 30 (2)	23	65.0	56.6	52.8	12.6	279	30.6	72.9
2015	28 (17), 30 (3), 38 (3)	23	86.4	57.3	69.6	15.3	262	50.5	124
2016	13 (21)	21	40.5	28.8	25.6	3.86	119	19.4	57.9
2017	13 (20), 28 (1), 40 (9)	30	66.1	50.5	47.9	10.6	217	33.7	85.4
2018	28 (18), 30 (12)	30	66.3	29.6	62.4	9.25	120	29.7	86.1
2019	36 (10), 40 (20)	30	164	165	105	31.4	813	67.3	203
2020	36 (20), 40 (10)	30	87.5	63.2	72.1	13.2	241	40.3	151
2021	40 (30)	30	65.6	30.6	57.1	9.00	144	45.8	86.3

¹Note that this excludes PFOS; see Section 4.10.2 for individual substances covered.

²n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

³The number of PFAS covered by the analytical method varies across samples for some years because tissue samples are not necessarily analysed in the same year they are collected and the number of PFAS within the method has increased over time. Many of the samples here have been retrospectively analysed. Therefore, the number of PFAS analysed are given with the corresponding number of samples analysed for those PFAS in brackets.

Figure 4.10.6 Scatterplot of SUM PFAS concentrations in the livers of harbour porpoise from marine waters around the UK between 2009 and 2021 (in units of μ g/kg wet weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time, the thinner red lines show the 95% confidence intervals (diagram courtesy of Cefas)



The same GAM (<u>Wood, 2017</u>) approach and criteria as described for mercury in harbour porpoise (see above) was used to estimate trends.

For PFOS, a statistically significant downward trend was observed for the complete time series (p <0.01 for both criteria). While a significant time trend was observed based on the most-recent years, from the end of 2015 to the end of 2021, for the first criteria (p <0.01), this was not confirmed for the second (p = 0.83). This agrees with the levelling off of concentrations for PFOS shown in Figure 4.10.5.

For PFAS, no statistically significant change in concentrations was found based on the complete time series because while the first criterion was met (p < 0.01), the second was not (p = 0.94). The results based on the last 5 years suggest no recent change either (p < 0.01, p = 0.61). Further data over time is needed to understand the influence of the change in the number of PFAS analysed.

The results in the dashboard represent the observed trends from the full data sets. Therefore, the assignment of 'decreasing concentrations' is given for PFOS and 'no observed change in concentrations' for PFAS.

4.10.4 Thresholds

Mercury

There are currently no thresholds for mercury in harbour porpoise livers against which to compare the exposure levels detected. This is reflected in the dashboard entry.

Polybrominated diphenyl ethers, polychlorinated biphenyls, perfluorooctanesulfonic acid, and other per- and polyfluoroalkyl substances

There are no established statutory or international thresholds for SUM 11PBDE, SUM 25PCB concentrations in blubber.

A potential threshold of 1.5mg/kg lipid weight has been proposed for SUM 11PBDEs in blubber (<u>Hall, Kalantzi and Thomas, 2003</u>) based on thyroid disruption in juvenile grey seals (*Halichoerus grypus*). None of the 29 individuals analysed in 2021 had blubber SUM 11PBDE concentrations were above this proposed value. The proportion of harbour porpoises with blubber SUM 11PBDE concentrations >1.5mg/kg lipid weight in 2021 (0%) is used as the dashboard entry.

For SUM 25PCBs, two potential thresholds have been proposed: 9mg/kg lipid weight for immunological effects in aquatic mammals (Kannan and others, 2000) and 41mg/kg lipid weight for reproductive effects, based on studies on seals (Helle, Olsson and Jensen, 1976). Thirteen individuals were above the lower threshold and 4 of these the upper value out of 29 samples from 2021. The dashboard entry is based on the proportion of harbour porpoises analysed in 2021 with blubber SUM 25PCB concentrations above the proposed threshold for immunological effects (45%).

While this represents a decrease in risk since the previous indicator report, which was based on samples collected in 2018 (Environment Agency, 2021), additional sample analysis since then for carcasses from 2018 means the overall result for that year (45%) is now the same as for 2021.

There is no threshold established for PCB 118 in harbour porpoise blubber; this is reflected in the dashboard entry.

There is no threshold established for PFOS concentrations in marine mammal liver tissue but Lam and others (2016) suggested a tentative critical concentration in cetacean (dolphin) liver of 775µg/kg wet weight for PFOS. This was based on toxicological information – a no observed adverse effects level – for mammalian species (rat) with an assessment factor added to account for cross-species extrapolation. This value has been converted into a threshold of 1075µg/kg wet weight for harbour porpoise liver taking into account the mass of these animals. There were no exceedances of this value out of 30 samples analysed in 2021. The dashboard entry indicates the proportion of harbour porpoise that had liver concentrations that exceeded this tentative critical concentration in 2021 (0%).

There is no threshold established for other PFAS in harbour porpoise liver; this is reflected in the dashboard entry.

4.11 Metals in buzzard: lead, cadmium and nickel



4.11.1 Data source

Data on lead, cadmium and nickel in the livers of common buzzards (*Buteo buteo*) are provided by the PBMS (<u>UKCEH, 2023</u>).

Livers were collected from individual buzzards found dead throughout England. The majority of animals died as a result of collisions or starvation.

Concentrations of the metals in livers are available for a number of years, but not all years, for buzzards collected between 2001 to 2021. Sixty-one out of the 155 buzzards assessed were analysed as part of the EU project Life APEX (<u>Ozaki and others, 2023a</u>); these relate to samples found between 2001 and 2019. Data from Life APEX are available via the NORMAN Network (2024). Chemical analysis of the other 94 samples collected since 2018 was supported by Natural England.

The data used for the dashboard are drawn from all birds collected and analysed for lead and nickel, except for 3 outliers for lead in the trend assessment (see Section 4.11.3).

For cadmium, data restricted to first-year birds were used for the time trend analysis. Firstyear birds – defined as individuals hatched in the current or previous year to that in which they were found dead – were used because they are likely to provide a more-sensitive measure of annual change in exposure than adults, which may bioaccumulate cadmium over multiple years (Wayland and Scheuhammer, 2011). This was not done for lead because half-lives for lead in liver are relatively short (1–3 months) (Krone, 2018). Halflives for nickel are also short (several days), and its concentrations are regulated in a homeostatic manner, as nickel is considered essential to animals (Eisler, 1998). Therefore, there should not be any age-related bioaccumulation of these 2 metals.

For the cadmium assessment of threshold exceedance, all birds were used irrespective of age.

4.11.2 Data structure

The data consist of measurements of lead, cadmium and nickel concentrations in the livers of a variable number of individuals that died each year for the years 2001, 2004–2006, 2010, 2013, 2016, and 2018–2021. Concentrations are reported as mg/kg dry weight for all 3 metals.

The LoDs ranged from 0.000622 to 0.00978mg/kg dry weight for lead and from 0.000622 to 0.00202mg/kg dry weight for cadmium and nickel. However, none of the results for lead and cadmium were below the LoD. Twenty-eight per cent of the results for nickel were below the corresponding LoDs; these were assigned values that were half the LoD.

4.11.3 Exploration of change in chemical concentrations over time

The distribution of data for lead, cadmium and nickel by year is summarised in Tables 4.11.1, 4.11.3 and 4.11.4, respectively, and shown in Figure 4.11.1.

For lead, there was one sample in 2019 and 2 samples in 2021 with extremely high lead concentrations in the liver (>100 mg/kg dry weight). The distribution of data for lead excluding these 3 samples is in Table 4.11.2, and the 3 samples were not included in the trend assessment as they were considered outliers.

Within the available data, there was no sample meeting the criteria for the time trend analysis – that is, a first-year bird (see Section 4.11.1) – for cadmium in 2005 (Table 4.11.3 and Figure 4.11.1).

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2001	8	0.327	0.232	0.310	0.0579	0.774	0.185	0.376
2004	5	0.446	0.449	0.391	0.0318	1.19	0.174	0.440
2005	2	0.391	0.409	0.391	0.101	0.680	_	_
2006	6	1.59	2.21	0.810	0.116	6.00	0.416	1.33
2010	8	0.750	0.681	0.481	0.223	2.25	0.305	0.949
2013	8	0.691	1.01	0.315	0.0720	3.14	0.205	0.631
2016	8	0.850	0.602	0.709	0.179	2.10	0.480	1.11

Table 4.11.1 Summary statistics for concentrations of lead in the livers of buzzards (mg/kg dry weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	29	1.03	1.17	0.430	0.0703	3.89	0.288	1.70
2019	27	9.95	45.5	0.500	0.0531	238	0.230	1.77
2020	16	1.05	2.53	0.251	0.0232	10.0	0.194	0.330
2021	38	9.24	30.4	1.44	0.0760	147	0.538	2.78

Table 4.11.2 Summary statistics for concentrations of lead in the livers of buzzards (mg	/kg
dry weight) from England excluding outliers ¹	

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2001	8	0.327	0.232	0.310	0.0579	0.774	0.185	0.376
2004	5	0.446	0.449	0.391	0.0318	1.19	0.174	0.440
2005	2	0.391	0.409	0.391	0.101	0.680	_	_
2006	6	1.59	2.21	0.810	0.116	6.00	0.416	1.33
2010	8	0.750	0.681	0.481	0.223	2.25	0.305	0.949
2013	8	0.691	1.01	0.315	0.0720	3.14	0.205	0.631
2016	8	0.850	0.602	0.709	0.179	2.10	0.480	1.11
2018	29	1.03	1.17	0.430	0.0703	3.89	0.288	1.70
2019	26	1.20	1.52	0.499	0.0531	5.74	0.229	1.27

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	16	1.05	2.53	0.251	0.0232	10.0	0.194	0.330
2021	36	2.23	3.16	1.32	0.0760	16.1	0.494	2.55

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.11.3 Summary statistics for concentrations of cadmium in the livers of first-year buzzards (mg/kg dry weight) from England¹

Year	n	Mean	SD	Median	Median Min M		Q1	Q3
2001	7	0.655	0.540	0.487	0.0317 1.33		0.237	1.13
2004	4	1.56	2.59	0.397 0.0193 5.41		0.0612	1.89	
2006	5	0.844	0.927	['] 0.382 0.229 2.42		2.42	0.245	0.948
2010	3	0.808	0.308	0.951 0.455 1.02		_	_	
2013	4	0.258	0.176	0.260	60 0.0413 0.471		0.191	0.326
2016	4	0.854	0.554	0.951	0.107	1.41	0.640	1.17
2018	19	1.37	2.25	0.769	0.0254	9.97	0.252	1.43
2019	15	1.99	3.86	0.579	0.127	15.1	0.367	1.35
2020	11	0.246	0.214	0.153	0.0243	0.609	0.0867	0.399
2021	27	1.57	1.33	1.37	0.102	6.10	0.732	2.02

Table 4.11.4 Summary statistics for concentrations of nickel in the livers of buzzards (mg/kg dry weight) from England¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2001	8	0.0203	0.0210	0.0162	3.88 x 10 ^{−4}	0.0646	0.00748	0.0239
2004	5	0.0262	0.0457	4.45 x 10 ^{−4}	3.86 x 10 ^{−4}	0.106	4.41 x 10 ⁻⁴	0.0238
2005	2	0.0669	0.0552	0.0669	0.0278	0.106	-	_
2006	6	0.0423	0.0434	0.0302	0.00711	0.118	0.00968	0.0567
2010	8	0.0400	0.0345	0.0409	3.94 x 10 ⁻⁴	0.0956	0.0103	0.0592
2013	8	0.0421	0.0475	0.0244	4.04 x 10 ⁻⁴	0.122	0.00718	0.0594
2016	8	0.0289	0.0321	0.0146	4.04 x 10 ⁻⁴	0.0845	0.00353	0.0532
2018	29	0.0252	0.0478	0.00261	3.71 x 10 ⁻⁴	0.231	4.28 x 10 ⁻⁴	0.0296
2019	27	0.0287	0.0265	0.0257	3.97 x 10 ^{−4}	0.0929	0.00980	0.0477
2020	16	0.0183	0.0311	0.00719	3.86 x 10 ^{−4}	0.106	0.00159	0.0164
2021	38	0.165	0.423	0.0386	3.56 x 10 ⁻⁴	2.51	0.00414	0.161

Figure 4.11.1 Scatterplots of concentrations of lead (Pb), cadmium (Cd) and nickel (Ni) in the livers of buzzards (mg/kg dry weight, log10 y-axis scale) from England from 2001 to 2021; cadmium values are for first-year birds. Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. The red dashed line for lead represents a threshold value (see Section 4.11.4) and the red dots show outliers; the solid red lines drawn across the plots for the different years for lead and cadmium represent a linear regression model applied to the data, with shading representing 95% confidence limits; (diagrams courtesy of UKCEH)



For the data on lead, the 3 samples with extremely high lead concentration values were removed from the time trend analysis (see Table 4.11.2).

The change in metal concentrations in the livers of buzzards over time was analysed with a linear model. The assumptions of linear regression, such as homogeneity of variance and normal distribution of model residuals, were met after applying logarithmic transformations to both the lead and cadmium data.

For lead, the result showed a statistically significant increasing trend for the complete time series from 2001 to 2021 (p <0.01) (Figure 4.11.1). The concentrations of lead in the livers of buzzards did not significantly increase over the most-recent years, from 2013 to 2021 (p = 0.052).

For the change in cadmium concentrations in the livers of first-year buzzards over time, the model showed no statistically significant trend over the years from 2001 to 2021 (p = 0.14) (Figure 4.11.1) or over the most-recent years (from 2013 to 2021) (p = 0.06).

For the data on nickel, the assumptions of a linear model, particularly the normality of residuals, were not met even after the logarithmic transformation owing to the high proportion of results below the LoD. Furthermore, the normality of residuals was not respected even for a GAM. Therefore, change in concentrations of nickel in the livers of buzzards over time was analysed by non-parametric Spearman's rank correlation. The result showed no statistically significant time trend over the years from 2001 to 2021 (p = 0.18).

In contrast, concentrations of nickel in the livers of the birds significantly increased in the most-recent years, from 2013 to 2021 (p = 0.03). The significance of this trend is not clear because we cannot determine currently whether the levels observed are within those naturally regulated by avian species, as nickel has essential uses within the body, or whether they are likely to cause harm.

The results in the dashboard represent the observed trends from the full data sets. Therefore, the assignment of 'increasing concentrations' for lead and that of 'no observed change in concentrations' for cadmium and nickel is given in the dashboard.

4.11.4 Thresholds

Thresholds are available in the literature for lead and cadmium in birds though these are based on limited data sets.

Concentrations of lead in liver of >6mg/kg wet weight are associated with clinical poisoning in individuals from the order Falconiformes (<u>Fransome and Pain, 2011</u>). Using a mean wet weight to dry weight conversion factor for buzzards of 3.1 (<u>Scanlon, 1982</u>; <u>Monclús, Shore and Krone, 2020</u>), a concentration of 6mg/kg wet weight is the equivalent of a dry weight concentration of 18.6mg/kg. This is the threshold proposed for use in the dashboard assessment.

A cadmium residue of 45–70mg/kg wet weight in liver has been suggested for adult birds. The exceedance of this may be associated with adverse physiological effects, such as alterations to energy metabolism or structural/functional damage to kidneys, testes, liver, gut, or salt glands in eiders, mallards, Leach's storm petrels, and starlings (Wayland and Scheuhammer, 2011). The threshold residue for young birds has not been defined but may be lower. Applying the wet weight to dry weight conversion factor of 3.1, as above, 45–70mg/kg wet weight is equivalent approximately to 139.5–217mg/kg dry weight. The lower value of this range (139.5mg/kg dry weight) is the suggested threshold for the dashboard.

No threshold values for nickel are available.

Data for all birds used for the threshold assessment of cadmium concentrations in buzzard livers are given in Table 4.11.5 (see also Section 4.11.1).

Table 4.11.5 Summary statistics for concentrations of cadmium in the livers of all buzzards (mg/kg dry weight)¹

Year	n	Mean	SD	Median	Min Max		Q1	Q3
2001	8	0.788	0.627	0.752	0.0312	1.72	0.318	1.26
2004	5	1.29	2.32	0.202	0.0193	5.41	0.0751	0.718
2005	2	0.876	0.233	0.876	0.711	1.04	_	_
2006	6	3.95	7.64	0.665	0.229	19.5	0.279	2.05
2010	8	1.08	0.613	0.985	0.455	2.50	0.777	1.08
2013	8	1.18	1.67	0.609	0.0413	5.16	0.269	1.24
2016	8	1.35	0.683	1.39	0.107	2.20	1.02	1.85
2018	29	1.26	2.02	0.728	0.0254	9.97	0.257	1.08
2019	27	2.34	4.11	0.825	0.127	16.3	0.389	1.74

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	16	0.575	0.694	0.360	0.0243	2.66	0.109	0.640
2021	38	1.74	1.49	1.44	0.102	6.10	0.745	2.12

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

For lead, one and 2 buzzards in 2019 and 2021, respectively, had residues in the liver exceeding the threshold for lead of 18.6mg/kg dry weight (Figure 4.11.1). For 2021, these were 2 birds out of 38 individuals, and this proportion (5%) is used for the dashboard entry which is based on the most-recent year available.

None of the buzzards for which data are available exceeded the threshold for cadmium in the liver. The entry in the dashboard is based on the results for the most-recent year available, 2021. Therefore, the dashboard entry reads 'all sites/individuals or population average below threshold'.

The entry in the dashboard for nickel reflects that there is no threshold value available for comparison.

4.12 Metals in sparrowhawk: lead, cadmium and nickel



4.12.1 Data source

Data on lead, cadmium and nickel in the liver of Eurasian sparrowhawks (*Accipter nisus*) are provided by the PBMS (<u>UKCEH, 2023</u>).

Livers were collected from individual sparrowhawks found dead throughout England. The majority of animals died as a result of collisions or starvation.

Metal concentrations in liver are available for a number of years, but not all years, for sparrowhawks collected between 2007 and 2021. The chemical data relating to 175 samples collected in the period between 2007 and 2013 were provided by the PBMS and reported in the previous H4 report (<u>Environment Agency, 2021</u>). Chemical analysis of a further 27 samples for 2020 and 2021 was supported by Natural England. The data used for the dashboard are drawn from all birds collected and analysed for lead and nickel.

For cadmium, data restricted to first-year birds were used for the time trend analysis. Firstyear birds – defined as individuals hatched in the current or previous year to that in which they were found dead – were used because they are likely to provide a more-sensitive measure of annual change in exposure than adults, which may bioaccumulate cadmium over multiple years (Wayland and Scheuhammer, 2011). This was not done for lead because half-lives for lead in liver are relatively short (1–3 months) (Krone, 2018). Halflives for nickel are also short (several days), and its concentrations are regulated in a homeostatic manner, as nickel is considered essential to animals (Eisler, 1998). Therefore, there shouldn't be any age-related bioaccumulation of these 2 metals.

For the cadmium assessment of threshold exceedance, all birds were used irrespective of age.

4.12.2 Data structure

The data consist of measurements of lead, cadmium and nickel concentrations in the livers of a variable number of individuals that died each year for the years 2007–2014, 2020 and 2021. Concentrations are reported as mg/kg dry weight for all 3 metals.

For the data relating to birds collected until 2014, the LoDs were 0.07, 0.01 and 0.22mg/kg dry weight for lead, cadmium and nickel, respectively. The LoDs for the metals analysed in birds collected in more-recent years were more variable and ranged from 0.000758 to 0.00105mg/kg dry weight for each metal.

Thirteen per cent of the results for lead, 0.5% for cadmium and 78% for nickel were below the corresponding LoDs. These results were mainly associated with data relating to the years up to 2014 which were obtained with the higher LoDs; the exception was for nickel, for which 11 out of the 27 samples for 2020 and 2021 were also below the corresponding LoDs. The result below the LoD for cadmium was for adult bird in 2009. All results below the LoD were assigned values that were half the LoD.

4.12.3 Exploration of change in chemical concentrations over time

The distribution of data for lead, cadmium and nickel by year is summarised in Tables 4.12.1 to 4.12.3, respectively, and shown in Figure 4.12.1.

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2007	18	0.475	0.938	0.108	0.0350	3.15	0.0718	0.271
2008	26	0.400	0.554	0.210	0.0350	2.66	0.0883	0.474
2009	19	1.80	3.82	0.363	0.0350	16.8	0.157	1.53
2010	26	0.872	2.44	0.221	0.0350	12.6	0.109	0.591
2011	22	0.257	0.232	0.188	0.0350	0.782	0.0988	0.278
2012	22	0.961	1.28	0.331	0.0350	4.40	0.125	1.64
2013	22	0.308	0.384	0.163	0.0350	1.43	0.105	0.349
2014	20	0.300	0.259	0.204	0.0350	0.924	0.126	0.416
2020	18	1.16	3.93	0.135	0.0112	16.9	0.0682	0.353
2021	9	0.397	0.337	0.241	0.125	1.22	0.197	0.445

Table 4.12.1 Summary statistics for concentrations of lead in the livers of sparrowha	wks
(mg/kg dry weight) from England ¹	

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2007	8	0.454	0.363	0.443	0.0650	1.09	0.130	0.640
2008	20	0.460	0.406	0.390	0.0420	1.29	0.129	0.600
2009	8	0.449	0.247	0.471	0.0620	0.823	0.347	0.580
2010	20	0.380	0.344	0.235	0.0360	1.16	0.116	0.573
2011	17	0.334	0.242	0.275	0.0470	0.942	0.176	0.418
2012	13	1.06	2.04	0.485	0.0870	7.71	0.167	0.617
2013	11	0.232	0.151	0.196	0.0490	0.519	0.121	0.300
2014	11	0.374	0.327	0.301	0.0750	1.01	0.153	0.389
2020	13	0.327	0.212	0.312	0.0352	0.800	0.164	0.410
2021	4	0.965	0.776	0.738	0.298	2.09	0.627	1.08

Table 4.12.2 Summary statistics for concentrations of cadmium in the livers of first-year sparrowhawks (mg/kg dry weight) from England¹

Table 4.12.3 Summary statistics for concentrations of nickel in the livers of sparrowhawk	S
(mg/kg dry weight) from England ¹	

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2007	18	0.0273	0.0250	0.0110	0.0110	0.0940	0.0110	0.0350
2008	26	0.0119	0.00471	0.0110	0.0110	0.0350	0.0110	0.0110
2009	19	0.0291	0.0320	0.0110	0.0110	0.106	0.0110	0.0350

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2010	26	0.0209	0.0506	0.0110	0.0110	0.269	0.0110	0.0110
2011	22	0.0169	0.0146	0.0110	0.0110	0.0650	0.0110	0.0110
2012	22	0.129	0.316	0.0110	0.0110	1.39	0.0110	0.0423
2013	22	0.0200	0.0422	0.0110	0.0110	0.209	0.0110	0.0110
2014	20	0.0110	0	0.0110	0.0110	0.0110	0.0110	0.0110
2020	18	0.0224	0.0367	0.00631	3.95 x 10 ⁻⁴	0.127	4.66 x 10 ⁻⁴	0.0193
2021	9	0.0209	0.0251	0.0158	4.70 x 10 ⁻⁴	0.0689	4.80 x 10 ⁻⁴	0.0293

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; median: min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.12.1 Scatterplots of concentrations of lead (Pb), cadmium (Cd) and nickel (Ni) in the livers of sparrowhawks (mg/kg dry weight, log10 y-axis scale) from England from 2007 to 2021; cadmium values are for first-year birds. Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. The red dashed line for lead represents a threshold value (see Section 4.12.4); the solid red line drawn across the plots for the different years for cadmium represents a linear regression model applied to the data, with shading representing 95% confidence limits (diagrams courtesy of UKCEH)





The analysis of trends over time for metal concentrations in the livers of sparrowhawks was conducted after applying a logarithmic transformation to correct the skewed distribution of the data.

For the data on lead, the assumptions of a linear regression model, particularly the normality of residuals, were not met even after the logarithmic transformation owing to the high proportion of samples below the LoD. Furthermore, the normality of residuals was not respected even for a GAM. Therefore, significant change in concentrations of lead in the livers of sparrowhawks over time was analysed by non-parametric Spearman's rank correlation. The result showed no statistically significant time trend for the complete time series from 2007 to 2021 (p >0.99) or over the most-recent years (from 2011 to 2021) (p = 0.86).

For the data on cadmium, the assumptions of a linear regression model were met after applying the logarithmic transformation. Change in its concentrations in the livers of sparrowhawks over time was analysed with a linear regression model. The model showed no statistically significant time trend over the years from 2007 to 2021 (p = 0.65) (Figure 4.12.1) or over the most-recent years (from 2011 to 2021) (p = 0.55).

For the data on nickel, the assumptions of a linear regression model, particularly the normality of residuals, were not met owing to the high proportion of results under the LoD. Therefore, change in its concentrations in the livers of sparrowhawks over time was analysed by a non-parametric Spearman's rank correlation test. The result showed a significant decrease in concentrations from 2007 to 2021 (p = 0.01) and over the most-recent years (2011 to 2021) (p = 0.02).

However, this decreasing trend for nickel could be due to the difference in the LoDs between years. The step change in the analytical results achieved with the more-sensitive LoDs for the 2020 and 2021 samples is evident from Table 4.12.3 and Figure 4.12.1. Additionally, as nickel is an essential metal in avian species and it will be regulated in the body, the significance of any trends is not yet clear.

The results in the dashboard represent the observed trends from the full data sets. Therefore, the assignment of 'no observed change in concentrations' for lead and cadmium is given in the dashboard. For nickel, the entry reflects the uncertainties around the assessment and that there are insufficient data to report a trend.

4.12.4 Thresholds

Thresholds are available in the literature for lead and cadmium in birds though these are based on limited data sets.

Concentrations of lead in liver of >6mg/kg wet weight are associated with clinical poisoning in individuals from the order Falconiformes (<u>Fransome and Pain, 2011</u>). Using a mean wet weight to dry weight conversion factor for sparrowhawks of $3.52 (\pm 0.02)$ (<u>Shore, 2020</u>), a concentration of 6mg/kg wet weight is the equivalent of a dry weight concentration of 21mg/kg. This is the threshold proposed for use in the dashboard assessment.

A cadmium residue of 45–70mg/kg wet weight in liver has been suggested for adult birds. The exceedance of this may be associated with adverse physiological effects, such as alterations to energy metabolism or structural/functional damage to kidneys, testes, liver, gut, or salt glands in eiders, mallards, Leach's storm petrels, and starlings (<u>Wayland and Scheuhammer, 2011</u>). The threshold residue for young birds has not been defined but may be lower. Applying the wet weight to dry weight conversion factor of 3.52, as above, 45–70mg/kg wet weight is equivalent approximately to 160–250mg/kg dry weight. The lower value of this range (160mg/kg dry weight) is the suggested threshold for the dashboard.

No threshold values for nickel are available.

Data for all birds used for the threshold assessment of cadmium concentrations in sparrowhawk livers are given in Table 4.12.4 (see also Section 4.12.1).

Table 4.12.4 Summary statistics for concentrations of cadmium in the livers of all sparrowhawks (mg/kg dry weight)¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2007	18	0.375	0.358	0.277	0.0210	1.20	0.103	0.565
2008	26	0.515	0.403	0.444	0.0420	1.43	0.176	0.616
2009	19	0.354	0.399	0.164	0.00500	1.69	0.102	0.473
2010	26	0.477	0.416	0.393	0.0360	1.65	0.161	0.683
2011	22	0.357	0.235	0.285	0.0470	0.942	0.216	0.528
2012	22	1.87	2.97	0.571	0.0450	11.3	0.200	1.48
2013	22	0.585	0.720	0.312	0.0490	2.71	0.210	0.502
2014	20	0.569	0.445	0.412	0.0750	1.80	0.278	0.861
2020	18	0.391	0.275	0.350	0.0352	0.994	0.190	0.493
2021	9	0.851	0.634	0.580	0.298	2.09	0.554	0.739

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

None of the sparrowhawks for which data are available exceeded the thresholds for lead or cadmium in liver. The entry in the dashboard is based on the results for the most-recent year available, 2021. Therefore, the dashboard entry reads 'all sites/individuals or population average below threshold'.

The entry in the dashboard for nickel reflects that there is no threshold value available for comparison.

4.13 Metals in red fox: lead, cadmium, and nickel



4.13.1 Data source

Red fox livers from England were acquired by Fera via two sources: (1) WIIS and (2) APHA.

Under WIIS, red fox carcasses are submitted to the scheme as part of investigations into suspected poisoning incidents relating to pesticides and biocides. The samples are not necessarily the absolute total number of suspected poisoning cases per annum, as submissions are dependent on animals being found and subsequently reported. Foxes were found dead at various rural and urban locations.

The Animal and Plant Health Agency undertake surveillance of the disease *Echinococcus multilocularis* in red foxes on an annual basis. The agency uses a network of land managers, who cull foxes for pest control purposes, to supply the required carcasses. Shooting for this survey typically occurs between October and early March. A subset of these shot foxes was selected by APHA – providing a spread of geographic location, gender, weight and overall condition of the fox – and their livers were used for the analysis of rodenticides (see Section 4.24).

Subsequent to the rodenticide analysis, any remaining liver tissue was used for the analysis of the metals if sufficient material was available. Chemical analysis of these samples was supported by Natural England.

The use of these 2 existing opportunities, for collecting red foxes, to generate additional data to support the indicator is in an exploratory phase to ascertain their suitability.

4.13.2 Data structure

The data consist of measurements of lead, cadmium and nickel concentrations in the livers of a variable number of individuals for the years 2018–2021. Samples for 2018 and 2019 were collected solely via WIIS and for 2021 via APHA. In 2020, samples were collected via both WIIS and APHA and these are reported as separate entities.

The WIIS samples were collected throughout the year, that is spanning several months, whereas APHA samples were collected during targeted campaigns over a single winter period, that is in December 2020 and January 2021. For some APHA locations, more than one sample was collected on a single occasion and/or within a year. For consistency, the data are assigned to the different years in which they were collected.

Data on lead, cadmium and nickel concentrations are reported as mg/kg wet weight.

The LoDs ranged from 0.00053 to 0.0072mg/kg wet weight for lead, 0.0015 to 0.020mg/kg wet weight for cadmium and 0.00074 to 0.010mg/kg wet weight for nickel. All samples were above the LoD except one APHA sample from 2021 which was below the LoD of 0.001mg/kg wet weight for nickel alone. Owing to the small number of non-detects, this value was set to zero.

4.13.3 Exploration of change in chemical concentrations over time

The distribution of data for lead, cadmium and nickel are summarised in Tables 4.13.1 to 4.13.3 and shown in Figures 4.13.1 to 4.13.3, respectively.

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
WIIS	2018	1	2	0.187	0.0311	0.187	0.165	0.209	_	_
WIIS	2019	13	15	1.02	1.45	0.265	0.0548	4.91	0.111	2.25
WIIS	2020	9	9	0.647	0.947	0.421	0.0250	3.03	0.0690	0.767
АРНА	2020	12	20	2.74	9.13	0.138	0.0340	40.9	0.0700	0.670
АРНА	2021	25	52	10.2	40.4	0.262	0.0340	274	0.110	1.18

Table 4.13.1 Summary statistics for concentrations of lead in the livers of red foxes (mg/kg wet weight) from England¹

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency.

Figure 4.13.1 Box plots of concentrations of lead in the livers of red foxes (mg/kg wet weight, log10 y-axis scale) from England from 2018 to 2021 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagram courtesy of Fera)



Concentrations of lead in fox livers were broadly similar for both data sources (WIIS and APHA) and across years. Using a Kruskal–Wallis test, there was no statistically significant difference (p = 0.562) found between the groups of data for APHA 2020, APHA 2021, WIIS 2018, WIIS 2019, and WIIS 2020. The lack of significant difference is unsurprising given the large variance in the data which had 4 orders of magnitude difference. The highest lead concentrations were associated with the shot foxes with approximately 10% of the samples from 2021 having a concentration of >10 mg/kg wet weight, but the proportion of foxes with lead concentrations of >1 mg/kg wet weight (27%) was the same for WIIS 2019 and APHA 2021. Except for one sample, lead concentrations from WIIS samples fell within the range of those of the APHA samples. Foxes were chosen by APHA such that the liver was intact and had not been affected by the ammunition. The fact that APHA samples were shot should not, therefore, impact on the lead concentrations in the liver.

Table 4.13.2 Summary statistics for concentrations of cadmium in the livers of red foxes (mg/kg wet weight)¹

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
WIIS	2018	1	2	0.175	0.236	0.175	0.00830	0.342	_	_
WIIS	2019	13	15	0.386	0.250	0.355	0.00818	0.898	0.208	0.646
WIIS	2020	9	9	0.783	1.59	0.209	0.00500	4.95	0.0160	0.635
APHA	2020	12	20	0.419	0.240	0.361	0.0751	0.968	0.247	0.540
АРНА	2021	25	52	0.315	0.274	0.233	0.0271	1.45	0.104	0.367

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency.

Figure 4.13.2 Box plots of concentrations of cadmium in the livers of red foxes (mg/kg wet weight, log10 y-axis scale) from England from 2018 to 2021 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagram courtesy of Fera)



Cadmium concentrations were broadly similar for both data sources (WIIS and APHA) and across the years. Using a Kruskal–Wallis test, there was no statistically significant difference (p = 0.215) found between the groups of data for APHA 2020, APHA 2021, WIIS 2018, WIIS 2019, and WIIS 2020.

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
WIIS	2018	1	2	0.0244	0.0208	0.0244	0.00969	0.0391	_	_
WIIS	2019	13	15	0.0269	0.0379	0.0118	0.00281	0.153	0.0100	0.0233
WIIS	2020	9	9	0.0270	0.0159	0.0240	0.00694	0.0508	0.0128	0.0412
АРНА	2020	12	20	0.0210	0.0175	0.0186	0.00248	0.0766	0.00809	0.0261
АРНА	2021	25	52	0.0300	0.0272	0.0220	0	0.134	0.0147	0.0371

Table 4.13.3 Summary statistics for concentrations of nickel in the livers of red foxes (mg/kg wet weight)¹

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value; WIIS: Wildlife Incident Investigation Scheme; APHA: Animal and Plant Health Agency.

Figure 4.13.3 Box plots of concentrations of nickel in the livers of red foxes (mg/kg wet weight, log10 y-axis scale) from England from 2018 to 2021 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS); the boxes represent the median and first and third quartiles of observations; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagrams courtesy of Fera)



Nickel concentrations in fox livers were broadly similar for both data sources (WIIS and APHA) and across years. Using a Kruskal–Wallis test, there was no statistically significant difference (p = 0.346) found between the groups of data for APHA 2020, APHA 2021, WIIS 2018, WIIS 2019, and WIIS 2020.

There were too few years of data to allow for analysis of trends over time for all the metals. Moreover, the APHA 2020 and 2021 data were taken in consecutive months (December 2020 and January 2021), severely limiting any ability to relate time to levels of metal concentrations in red fox livers.

The corresponding entries in the dashboard reflect that data are available for lead, cadmium and nickel, but are insufficient to report trend assessments.

4.13.4 Threshold

There are currently no thresholds for lead, cadmium or nickel in red foxes against which to compare the exposure levels detected. This is reflected in the dashboard entries.

4.14 Metals in freshwater: lead, cadmium, nickel, copper, and zinc



4.14.1 Data source

Data on bioavailable lead, nickel, copper, and zinc and dissolved cadmium concentrations have been provided by the Environment Agency from their freshwater statutory monitoring network.

Bioavailable metal concentrations are calculated values based on the corresponding dissolved metal concentrations and pH, calcium and/or dissolved organic carbon (DOC) content at a site (<u>UKTAG, 2014</u>). Where those physico-chemical parameters have not been derived from the same sample as the analysed dissolved metal concentration, site means are used for the bioavailability calculation. Most results have analysed values from 2014. The bioavailable metal concentrations are calculated using the Metals Bioavailability Assessment Tool (M-BAT) (<u>UKTAG, 2014</u>).

In the case of zinc, ambient background concentrations (ABCs) have been removed from dissolved zinc measurements before using the M-BAT to allow for any species acclimatisation to such levels. The corresponding threshold for zinc allows for this 'added risk' approach; that is, it is a threshold relating to the concentration over and above the ABC (UKTAG, 2014).

Fewer sites were monitored and samples taken in recent years, particularly for 2020 owing to the COVID-19 pandemic.

The monitoring network has changed in recent years with the introduction of the RSN under the NCEA (<u>Defra, 2022</u>), and data from the RSN are included in the information

presented here. Initial work has been done to understand the differences between levels of contaminants monitored at RSN sites, which represent broadscale condition, versus those from targeted sites; this is presented in Appendix D. The inclusion or exclusion of RSN data does affect the shape of the trends, especially for zinc, but not the overall results for the metals trend assessment (see Section 4.14.3 and Appendix D). Further consideration of any differences owing to the RSN and other sites having different purposes is needed as more data come in over time.

The national data sets for bioavailable lead, nickel, copper, and zinc and dissolved cadmium contain a subset of data for rivers which are polluted by abandoned metal mines. Cleaning up pollution from such sites – 'WAMM' sites identified by the Water and Abandoned Metal Mines Programme – has been highlighted as beneficial to the environment in the 25-YEP. For this reason, we have included analysis of data from WAMM waterbodies and for those from non-WAMM ones alongside our national overview of all data. The national overview is used for the indicator dashboard, but results for WAMM and non-WAMM waterbodies are also used in the indicator description. The locations of the WAMM sites are shown in Appendix G.

There is slight variation in the number of sites and samples reported previously (<u>Environment Agency, 2021</u>) compared with this assessment; this is due to minor differences in the use of supporting parameters required for assessing metal concentrations in water.

4.14.2 Data structure

Relevant data are available for the period 2014–2022 for bioavailable lead, nickel, copper, and zinc and dissolved cadmium in freshwaters across England. The data vary both in terms of the number of measurements taken within a year per site and the number of sites monitored per year. Most sites have been sampled in multiple years.

A data summary is available for each year based on the total number of measurements made in a year – that is all data pooled from all sites (see Tables 4.14.1 and 4.14.5). Summaries are also available for each site based on samples taken over the most-recent 3 years and for which there were at least 3 samples per year available for the purpose of the threshold assessment (see Section 4.14.4).

Concentration data are reported as µg/L.

Bioavailable metal concentrations are calculated values and so there is no corresponding LoD, but dissolved metal results which were used in those calculations that were below the LoD were taken at half their face value. The LoDs for dissolved lead, nickel, copper, and zinc are 0.1, 0.5, 1, and 0.5μ g/L, respectively. The LoDs for dissolved cadmium are variable; those results reported below the LoD (33%) had LoDs predominantly ranging from 0.01 to 0.1μ g/L with a nominal amount of samples reported up to a value of 10μ g/L. Results recorded as below the LoD were assigned a value that was half the LoD.

Analytical methods with lower LoDs have been introduced over time, in particular from 2014, and monitoring sites have been continuously reviewed – removing sites that do not show contamination issues and including new ones where a potential source of contamination has been newly identified. For these reasons we have selected the period 2014–2022 for reporting here to maintain the integrity of the time series, although data are available prior to that.

It should also be noted that while analytical methods have been improved, older methods may have been used for a limited number of more-recent datapoints for cadmium. Compared with other metals, Cadmium data show the largest proportion of samples with concentrations below the detection limit, and also the largest proportion of sites where no value was above the detection limit.

4.14.3 Exploration of change in chemical concentrations over time

The distribution of data by year is summarised in Tables 4.14.1 to 4.14.5 for bioavailable lead, dissolved cadmium, and bioavailable nickel, copper and zinc, respectively.

The approach for depicting trends is described below (see also Figure 4.14.1). Modelled trend information is shown in Figure 4.14.2 for bioavailable lead and dissolved cadmium and in Figure 4.14.3 for bioavailable nickel, copper and zinc.

Table 4.14.1 Summary statistics for concentrations of bioavailable lead in samples at al
freshwater monitoring sites (μg/L) ¹

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Year
2014	1064	9587	0.290	1.00	0.0815	0.00289	28.0	0.0303	0.230
2015	1303	10033	0.262	1.04	0.0477	0.00250	33.5	0.0227	0.153
2016	1232	8332	0.314	1.44	0.0437	0.00250	30.7	0.0219	0.111
2017	929	6711	0.335	1.42	0.0460	0.00250	28.3	0.0235	0.118
2018	767	5826	0.343	1.54	0.0420	0.00250	40.7	0.0219	0.116
2019	775	5325	0.294	1.27	0.0444	0.00263	34.3	0.0218	0.125
2020	590	1094	0.374	2.30	0.0479	0.00250	62.9	0.0221	0.144

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Year
2021	468	3323	1.55	15.4	0.0514	0.00250	338	0.0252	0.330
2022	497	3162	1.80	12.9	0.0800	0.00313	314	0.0273	0.692

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.14.2 Summary statistics for concentrations of dissolved cadmium in samples at all freshwater monitoring sites $(\mu g/L)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	1170	10177	0.0898	0.338	0.0486	0.00500	8.60	0.0127	0.0500
2015	1328	10183	0.0839	0.278	0.0248	0.00500	6.85	0.0105	0.0500
2016	1260	8495	0.107	0.434	0.0237	0.00500	19.0	0.0104	0.0536
2017	957	6982	0.121	0.513	0.0227	0.00500	20.5	0.0104	0.0594
2018	798	6025	0.125	0.390	0.0238	0.00500	7.51	0.0103	0.0636
2019	795	5505	0.104	0.399	0.0220	0.00500	16.0	0.00500	0.0527
2020	622	1138	0.121	0.337	0.0260	0.00450	4.70	0.0110	0.0650
2021	481	3445	0.230	1.24	0.0230	0.00500	45.0	0.00500	0.0650
2022	504	3258	0.314	1.20	0.0320	0.00500	30.0	0.0100	0.150
Table 4.14.3 Summary statistics for concentrations of bioavailable nickel in freshwater	S								
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[μg/L) ¹									

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	931	7702	1.39	4.55	0.678	0.0400	214	0.440	1.12
2015	1246	8445	1.30	2.74	0.670	0.0300	59.2	0.380	1.14
2016	1194	7181	1.38	4.01	0.725	0.0300	276	0.420	1.30
2017	892	5592	1.53	3.78	0.745	0.0300	173	0.420	1.34
2018	729	4872	1.44	2.78	0.704	0.0400	55.8	0.390	1.34
2019	762	4510	1.22	2.91	0.720	0.0500	127	0.430	1.19
2020	531	829	1.18	1.87	0.690	0.0400	22.5	0.440	1.08
2021	341	2129	1.29	2.98	0.565	0.0400	51.0	0.310	1.08
2022	373	2510	1.52	2.99	0.606	0.0300	28.3	0.370	1.12

Table 4.14.4 Summary statistics for concentrations of bioavailable copper in freshwate	ers
[μg/L) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	977	7416	0.959	13.4	0.166	0.00150	543	0.106	0.269
2015	1328	8239	0.784	8.70	0.167	0.00600	337	0.107	0.272
2016	1259	7114	1.19	15.0	0.157	0.00115	482	0.101	0.267
2017	959	5458	0.880	7.69	0.147	0.00331	244	0.0897	0262
2018	803	4722	2.21	22.6	0.148	0.00373	415	0.0943	0.261

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2019	836	4323	1.12	15.2	0.135	0.00399	444	0.0844	0.230
2020	584	824	3.49	30.8	0.126	0.00821	569	0.0856	0.206
2021	342	2135	4.23	34.3	0.124	0.00429	550	0.0716	0.246
2022	375	2500	3.93	31.5	0.115	0.00718	710	0.0635	0.244

Table 4.14.5 Summary statistics for concentrations of bioavailable zinc in freshwa	aters
(μg/L) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	978	7312	18.0	94.1	1.88	0	2140	0.483	5.57
2015	1315	8157	17.0	80.6	2.12	0	1340	0.482	6.44
2016	1252	6986	21.0	93.3	2.55	0	2300	0.676	7.92
2017	946	5508	27.2	104	2.91	0	1420	0.732	10.2
2018	789	4733	34.0	136	2.84	0	1870	0.657	11.7
2019	817	4277	18.1	83.3	1.89	0	1610	0.440	6.47
2020	578	825	27.5	117	2.18	0	1870	0.630	8.29
2021	340	2129	88.8	690	2.58	0	22000	0.549	17.1
2022	381	2566	77.4	220	3.90	0	2480	0.665	28.4

For the trend assessment, the concentration data were log10 transformed on a substanceby-substance basis prior to analysis. This corresponds to modelling the geometric mean of concentration. Because of the large amount of data, individual samples were aggregated as a mean on a substance-by-substance basis to the spatial scale of Environment Agency waterbodies – of which there are just over 4000 in England – and by month of sampling. This aggregation was performed separately – and separate models fitted – firstly for all national sample data and secondly using an indicator variable to discriminate (and produce separate predictions) between WAMM/non-WAMM waterbodies (see Section 4.14.1).

For each data set (combined and WAMM/non-WAMM), a generalised additive mixed model was fitted to the data on a substance-by-substance basis with date – expressed as a decimal – and month of sampling as the main covariates. The model-fitting process allowed identification of any seasonality in the data, any trend in the data and also any trend in the seasonality itself. The model also accounted for the fact that the data are naturally clustered and aggregated observations over time for each waterbody are likely to be correlated with each other. This was achieved through specifying a random intercept for site identity. To reflect that different numbers of samples – between 1 and 14 – were aggregated for each month/waterbody, each mean log10 concentration value in the model was weighted by the square root of the number of samples used to calculate it.

The fitted models were used to predict mean log10 concentrations for each month from January 2014 to December 2022. Fitted values and their confidence intervals were back-transformed to the original scale of the data. As noted in Section 3.1.2, there may be differences between the estimated trends based on fitting models to the log-transformed data, and trends in the face-value annual means from the summary statistics data. This is particularly notable for zinc.

The graphical presentation for the trend assessment is illustrated in Figure 4.14.1, while Figure 4.14.2 shows the results for bioavailable lead and dissolved cadmium and Figure 4.14.3 shows the results for bioavailable nickel, copper and zinc.

Figure 4.14.1 Explanation of the trend graphs for metals in freshwater (example data)



Mean concentration separated by colour for all waterbodies (combined), and separately for WAMM and non-WAMM waterbodies. This includes both the annual and seasonal trend. The y-axis scale is logarithmic (log10).

Mean concentration showing the annual trend separated by colour for season. Where only one line per season is shown, this corresponds to the middle month (Winter-January; Spring-April; Summer-July; Autumn-October). Subsets show in the separate panels: for all waterbodies (combined), and separately for WAMM and non-WAMM waterbodies. The data points are the same as in the top graph, only the colouring and connection of the points is different. The y-axis scale is logarithmic (log10). Figure 4.14.2 Modelled trends for dissolved cadmium and bioavailable lead concentrations (μ g/L, log10 y-axis scale) in freshwater for all samples and for those from WAMM and non-WAMM waterbodies, shown as solid lines with shading representing 95% confidence intervals (top), and by season (bottom)



Figure 4.14.3 Modelled trends for bioavailable nickel, copper and zinc (μ g/L, log10 y-axis scale) in freshwater for all samples and for those from WAMM and non-WAMM waterbodies, shown as solid lines with shading representing 95% confidence intervals (top), and by season (bottom)



Simple visual inspection of the data for the WAMM versus the non-WAMM waterbodies for all metals indicates that they clearly differ both in terms of their corresponding levels in the environment and observed trends (Figures 4.14.2 and 4.14.3). Concentrations at WAMM

sites are higher. The results of the national trend assessment for the metals, alongside those of the WAMM- and non-WAMM-affected waters, is summarised in Table 4.14.6.

National trends in all metal concentrations are shown to be downwards; however, the effect for copper is marginal. For bioavailable copper, increasing concentrations in spring and summer are finely balanced with decreasing concentrations in autumn and winter. For all metals, the overall trends are driven by the balance of sites in the WAMM and non-WAMM categories: of the approximately 54,000 samples available, around 17% are for the WAMM programme. The ratio of WAMM to non-WAMM sites has altered over time with a decrease in available samples for non-WAMM sites in more-recent years (see Appendix G). In the combined data set, WAMM sites are effectively over-represented. Aggregation of data to the waterbody scale reduces, but does not eliminate the disproportional influence of the WAMM sites in the combined data set.

For lead and cadmium there was little seasonal difference between the trends, regardless of the data set. For nickel, copper and zinc there were seasonal differences: the combined data clearly illustrate the combined effects of merging WAMM and non-WAMM trends which were generally different. For copper and nickel in WAMM waterbodies and for the combined data, there were decreasing or level concentrations in autumn and winter, but no change or sometimes increasing concentrations in spring and summer. For zinc, there were even greater seasonal differences.

	Bioavailable lead	Cadmium	Bioavailable Nickel	Bioavailable Copper	Bioavailable Zinc
Overall nationally	Down	Down	Down	Down (marginal)	Down
WAMM affected areas	Up	Up	Up	Up	Up
Non-WAMM affected areas	Down	Down	Down	Down	Down

 Table 4.14.6 Summary of the time trend assessment of the geometric means of bioavailable

 lead, nickel, copper, and zinc and dissolved cadmium concentrations in freshwaters

The results in the dashboard represent the observed statistically significant trends based on the overall national assessment. Therefore, the assignment of 'decreasing concentrations is given for lead, cadmium, nickel, and zinc, and 'no observed change in concentrations for copper.

4.14.4 Thresholds

Annual average EQS values of 1.2 and $4\mu g/L$ for bioavailable lead and nickel, respectively, in inland surface waters are given in the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>).

For dissolved cadmium, the annual average EQS values vary between ≤ 0.08 and 0.25μ g/L depending on the hardness of the water (<u>UK Government, 2015</u>) and are shown in Table 4.14.7.

For bioavailable copper and zinc, the EQSs are 1 and 10.9µg/L, respectively (plus any ABC of dissolved zinc; see Section 4.14.1) (<u>UK Government, 2015</u>). These EQSs are expressed as long-term means in freshwater.

All these thresholds used for the assessment are given in Table 4.14.7 and are used for the assessment here.

Table 4.14.7 Annual average environmental quality standards for dissolved cadmium in freshwater¹

Substance	Hardness (mg CaCO₃/L)	EQS (µg/L)
Dissolved cadmium	0 to <50	0.08
Dissolved cadmium	50 to <100	0.009
Dissolved cadmium	100 to <200	0.15
Dissolved cadmium	≥200	0.25

¹CaCO₃: calcium carbonate; EQS: environmental quality standard.

Typically, average site concentrations are used for comparison with the EQSs for the metals. These are based on available data for a 3-year period. The assessment here is based on site averages for the period 2020–2022. Very few sites had the maximum number of years' data available (2–17%) owing to reductions in monitoring in recent years (see Section 4.14.1).

Each site requires at least 3 samples per year to be included in the assessment; the number of samples per site varied between 3 and 38 for lead and cadmium and between 3 and 36 for nickel, copper and zinc.

For lead, 37 out of 291 sites (13%) had mean concentrations above the threshold of 1.2μ g/L. For cadmium, a slightly higher percentage of exceedance was seen: 60 out of 297 sites (20%) were above the relevant thresholds given in Table 4.14.7.

For nickel, 22 out of 253 sites (9%) had mean concentrations above the threshold of $4\mu g/L$. For copper, 28 out of 254 sites (11%) were above the EQS of $1\mu g/L$ for bioavailable copper. Zinc had the highest percentage of exceedance with 75 out of 257 sites (29%) above the threshold for the bioavailable fraction of the metal.

These percentage results are used for the corresponding entries in the dashboard and reflect the results for all sites.

It is noteworthy that the results above the EQSs were predominantly observed at WAMM sites for all metals indicating them to be key areas for improvement still. Very few non-WAMM sites were above the corresponding thresholds (1–4%). Approximately four-fifths of WAMM sites were above the EQS for zinc (68 sites out of 84), indicating that zinc concentrations present the highest potential risk at such sites compared with other metals. Cadmium, followed by lead, copper, and nickel showed potential risk at 64, 40, 32, and 25% of WAMM sites, respectively.

The results represent a slight increase in potential risk for all metals since the previous indicator report (<u>Environment Agency, 2021</u>), with zinc moving to a different category of risk.

However, in general, the current results are likely to be biased by changes to the monitoring over the last 3 years (see Section 4.14.1), particularly with reductions in non-WAMM sites (see Appendix G), and they should be viewed with this in mind.

4.15 Metals in freshwater fish: lead and cadmium

Lead

Cadmium



Data on lead and cadmium in fish in England have been provided by the Environment Agency. Data on concentrations in whole fish (roach, chub and brown trout) have been collected by the Environment Agency as part of its biota monitoring, which began in anticipation of requirements under the Water Environment Regulations 2017 (<u>UK</u> <u>Government, 2017</u>).

Individual sites are monitored once a year. Typically, 5 fish replicate samples are collected and analysed. However, the numbers in the past have varied from 3 to 8 samples for both substances.

The number of sites monitored is relatively low. Some sites have been sampled in multiple years. It should be noted that this data source is relatively new and a baseline data set relating to designated trend sites is still being established. The number of sites monitored in earlier years for cadmium and lead is low; no sites were monitored in 2020 and only a few sites since then, partly owing to the COVID-19 pandemic. We have considered all site data as part of this assessment.

A data summary is available for each year based on the total number of measurements made in a year – that is all data pooled from all sites (see Tables 4.15.1 and 4.15.2). Summaries are also available for each site per year for those sites that had more than 1 sample per year.

4.15.2 Data structure

Relevant data are available for the period 2016–2019, 2021 and 2022 for lead and cadmium. The data consist of a variable number of measurements of the substances, both in terms of the number of freshwater fish sampled at a site and the number of sites monitored per year across England.

Concentration data are reported as µg/kg wet weight in whole fish.

The LoDs given for lead vary with a value of 100µg/kg wet weight attributed to analysis of samples relating to 2016 and 2017. Following that, the LoDs were lower but based on dry weight samples analysed and converted into wet weight results. Around 17% of the results were reported as below the LoD for lead. There were very few cases for cadmium where

the result was below the LoD of approximately 2µg/kg wet weight. For lead and cadmium, results recorded as below the LoD were assigned a value that was half the LoD.

4.15.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.15.1 and 4.15.2 for lead and cadmium, respectively. The corresponding modelled trend information is shown in Figure 4.15.1.

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2016	3	12	151	143	88.5	50.0	525	50.0	220
2017	4	19	156	225	69.9	47.2	1010	50.0	163
2018	11	52	266	405	105	11.7	2330	49.8	321
2019	16	79	152	301	72.6	10.7	2450	33.8	166
2021	1	3	35.4	17.8	43.5	15.0	47.6	29.3	45.6
2022	8	34	135	95.3	128	11.5	416	49.4	207

Table 4.15.1 Summary statistic	s for concentrations of	lead in whole freshwater fis	sh (µg/kg
wet weight) ¹			

Table 4.15.2 Summary statistics for concentrations of cadmium in whole freshwater fis	۶h
μg/kg wet weight) ¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2016	3	12	18.7	7.73	15.9	9.36	35.0	14.0	22.7
2017	4	19	37.4	49.8	10.8	5.59	179	7.72	48.7
2018	11	52	13.8	15.5	6.92	1.86	61.0	4.01	16.9

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2019	16	79	14.4	23.3	7.11	0.940	153	4.00	12.1
2021	1	3	4.87	1.79	5.80	2.80	6.00	4.30	5.90
2022	8	34	8.76	5.64	7.11	1.92	24.0	5.67	10.7





To describe the changes over time, linear mixed-effects models were fitted to log10transformed concentrations for each metal, with decimal date of sampling as the main predictor. This corresponds to modelling the geometric mean of concentration. This approach was chosen because of the relatively low number of sample sites and samples available. As replicate data were available, a random effects structure of replicate sample within site-visit was used to ensure statistical power was as good as possible. This accounted for the inherent correlations between observations over time from any particular site, and between replicate samples collected on the same visit to a site. The fitted model was used to predict mean log10 concentrations for each year between 2016 and 2022 for lead and cadmium. Fitted values and their confidence intervals were back-transformed to the original scale of the data, and the significance of the linear trend term was then evaluated with reference to Satterthwaite's approximation for effective degrees of freedom (Kuznetsova, Brockhoff and Christensen, 2017).

Although some data on fish species were available, this is not recorded consistently so no separation by freshwater species was undertaken.

While data are available to report trends over time, the data availability is still relatively poor. In particular, the relative lack of data in recent years contributes to the wide confidence intervals for the current situation. Even so, the significance of the upward trend term for lead in fish is noteworthy. The analysis for cadmium shows a gradual but non-statistically significant downward trend.

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'increasing concentrations' is given for lead and 'no observed change in concentrations' for cadmium.

Continued collection of data over time will help improve future analysis.

4.15.4 Thresholds

There are no established thresholds for lead or cadmium in freshwater fish and, therefore, no threshold values are proposed for the corresponding assessment of potential risk. The entries in the dashboard reflect that there are no values available for comparison.

4.16 Metals in Eurasian otter: lead, cadmium and nickel



4.16.1 Data source

Data on metals in otter livers have been provided by the CUOP (<u>Cardiff University, 2023</u>). Livers have been collected from individuals found dead each year. Most animals died as a result of traffic collisions but some individuals died from other causes.

Individuals selected for chemical analysis were chosen to provide a balanced selection by sex and age class, and an even spatial distribution across England. All individuals were ≥900 mm in length, with 2 exceptions of 820 and 885mm length to ensure adequate sample size for analysis. Individuals excluded from selection included diseased, emaciated or decomposed otters, those with missing body length or weight data, and pregnant or lactating females (<u>Chadwick and Farrington, 2022</u>).

Chemical analysis of the samples was supported by the Environment Agency and has been conducted since the last round of reporting the indicator (<u>Environment Agency, 2021</u>) using archived tissue.

In the previous round of reporting, data for earlier years were used. However, these were selected using different criteria to that mentioned above; therefore, they are not directly comparable and have not been included here.

4.16.2 Data structure

The data consist of measurements of lead, cadmium and nickel concentrations in the livers from carcasses found each year from 2014 to 2021 in England. Concentrations are reported as mg/kg wet weight for all metals.

The LoDs were variable across samples and substance. For those results reported below the LoD, the LoDs ranged from 0.004 to 0.021 mg/kg wet weight for lead, 0.003 to 0.058 mg/kg wet weight for cadmium and 0.029 to 0.054mg/kg wet weight for nickel. For lead, cadmium and nickel, 4, 7 and 21 samples (2, 3 and 9%), respectively, were below their corresponding LoDs. All results below the LoD were assigned values that were half the LoD.

4.16.3 Exploration of change in chemical concentrations over time

The distribution of data for lead, cadmium and nickel by year is summarised in Tables 4.16.1 to 4.16.3 and shown in Figures 4.16.1 to 4.16.3, respectively.

Table 4.16.1 Summary statistics for concentrations of lead in the livers of Eurasian otter	S
(mg/kg wet weight) from England ¹	

Year	n	Mean	SD	Median	Min Max		Q1	Q3	
2014	10	0.0680	0.112	0.0303	0.0139	0.367	0.0278	0.0398	
2015	35	0.165	0.284	0.0489	0.0142	1.32	0.0289	0.123	
2016	40	0.104	0.207	0.0417	0.00916	1.21	0.0263	0.0798	
2017	36	0.164	0.324	0.0388	0.00908	1.83	0.0253	0.139	
2018	31	0.0447	0.0345	0.0331	0.00465	0.133	0.0193	0.0686	
2019	29	0.0786	0.107	0.0438	0.00803	0.542	0.0313	0.0831	
2020	30	0.115	0.395	0.0399	0.00511	2.16	0.0151	0.0564	
2021	15	0.0365	0.0316	0.0306	0.00698	0.112	0.0124	0.0453	

Table 4.16.2 Summary statistics for concentrations of cadmium in the livers of Eurasian
otters (mg/kg wet weight) from England ¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	10	0.117	0.0478	0.112	0.0699	0.200	0.0755	0.124
2015	35	0.142	0.237	0.0677	0.00345	1.28	0.0196	0.157
2016	40	0.113	0.131	0.0775	0.00754	0.641	0.0336	0.138
2017	36	0.0937	0.125	0.0541	0.00256	0.724	0.0366	0.104

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	31	0.0722	0.0696	0.0505	0.00710	0.282	0.0277	0.0813
2019	29	0.142	0.265	0.0496	0.0129	1.38	0.0320	0.110
2020	30	0.0994	0.151	0.0451	0.00473	0.709	0.0179	0.0771
2021	15	0.0769	0.0844	0.0583	0.0128	0.357	0.0439	0.0715

Table 4.16.3 Summary statistics for concentrations of nickel in the livers of Eurasian otter	S
(mg/kg wet weight) from England ¹	

Year	n	Mean	SD	Median	Min Max		Q1	Q3	
2014	10	2.79	7.73	0.124	0.0407	23.4	0.0600	0.545	
2015	35	0.166	0.331	0.0996	0.0464	1.950	0.0698	0.116	
2016	40	0.101	0.0734	0.0874	0.0130	0.412	0.0591	0.124	
2017	36	0.147	0.0632	0.145	0.0494	0.353	0.110	0.177	
2018	31	0.420	0.961	0.131	0.0374	4.910	0.0821	0.221	
2019	29	0.435	0.718	0.164	0.0261	3.250	0.0980	0.356	
2020	30	0.329	0.806	0.109	0.0214	4.470	0.0692	0.253	
2021	15	0.222	0.344	0.0908	0.0160	1.300	0.0618	0.168	

Figure 4.16.1 Box plots of lead concentrations in the livers of Eurasian otters (mg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (with 17 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)





Figure 4.16.2 Box plots of cadmium concentrations in the livers of Eurasian otters (mg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (with 7 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)



Figure 4.16.3 Box plots of nickel concentrations in the livers of Eurasian otters (mg/kg wet weight) from England representing median and lower/upper interquartile range values; data shown are for individuals; the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (with 10 extreme values across years omitted to improve the visualisation of the box plots) (top). Linear regression modelled plot of the change in concentrations over time with control for variation with otter sex; shaded ribbon indicates 95% confidence intervals (bottom) (diagrams courtesy of CUOP)







For all metals, a linear regression model was fitted. This used the concentration data with the year and otter sex information to assess changes over time and discern/control for any difference in concentration between sexes. No statistically significant difference was seen in concentrations between otter sexes for each metal (p > 0.05).

For lead, there was a statistically significant decline in concentrations over time (p = 0.003). Therefore, the assignment of 'decreasing concentrations' is given in the dashboard.

For cadmium and nickel, no statistically significant change in concentrations over time was observed (p = 0.225 and 0.378, respectively). Therefore, the assignment of 'no observed change in concentrations' is given in the dashboard.

4.16.4 Thresholds

There are no established thresholds for lead, cadmium or nickel concentrations in otter livers and, therefore, no threshold values are proposed for the corresponding assessment of potential risk. The entries in the dashboard reflect that there are no values available for comparison.

4.17 Metals in estuarine and coastal waters: lead, cadmium, nickel, copper and zinc



4.17.1 Data source

Data on dissolved lead, cadmium, nickel, copper, and zinc concentrations in estuarine and coastal waters from around the English coast have been provided by the Environment Agency from their statutory monitoring network.

Improvements were made to analytical techniques for metals in water samples in preparation for assessments under water quality reporting regimes, now covered by the Water Environment Regulations 2017 (<u>UK Government, 2017</u>). For this reason, maintaining consistency with the freshwater water assessment (see Section 4.14), we have selected the period from 2014 to 2022 for reporting here, although data are available prior to that.

Fewer sites were monitored and samples taken in recent years, particularly for 2020 owing to the COVID-19pandemic.

4.17.2 Data structure

Relevant data are available for the period 2014–2022 for dissolved metals. The monitoring varies both in terms of the number of measurements taken within a year per site and the number of sites monitored per year. Some sites have been sampled in multiple years.

A data summary is available for each year based on the total number of measurements made in a year – that is all data pooled from all sites (see Tables 4.17.1 to 4.17.5).

Summaries are also available for each site based on samples taken over the most-recent 3 years and for which there were at least 3 samples per year available for the purpose of the threshold assessment (see Section 4.17.4).

Concentration data are reported as μ g/L.

For those samples reported as below the LoD, the LoD values ranged from 0.04 to $0.2\mu g/L$ for dissolved lead, 0.03 to $0.3\mu g/L$ for dissolved cadmium, 0.3 to $2\mu g/L$ for dissolved nickel, 0.2 to $1\mu g/L$ for dissolved copper, and 0.4 and $2\mu g/L$ for dissolved zinc. Results recorded as below the LoD were assigned a value that was half the LoD. The large majority of these cases had LoDs at the lower end of the ranges given above.

4.17.3 Exploration of change in chemical concentrations over time

The distribution of data by year is summarised in Tables 4.17.1 to 4.17.5 for dissolved lead, cadmium, nickel, copper, and zinc, respectively. Modelled trend information is shown in Figure 4.17.1.

Table 4.17.1 Summary	statistics for concentrations	of dissolved lead in	estuarine and
coastal waters (µg/L) ¹			

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	155	1081	0.106	0.208	0.0500	0.0200	2.66	0.0200	0.0950
2015	153	1040	0.158	0.475	0.0550	0.0200	7.88	0.0200	0.116
2016	175	1216	0.127	0.299	0.0460	0.0200	4.95	0.0200	0.0982
2017	160	1200	0.0906	0.180	0.0416	0.0200	2.45	0.0200	0.0880
2018	155	1031	0.133	0.342	0.0569	0.0200	7.30	0.0200	0.118
2019	156	949	0.177	0.705	0.0490	0.0200	15.8	0.0200	0.110
2020	107	248	0.193	0.640	0.0400	0.0200	6.50	0.0200	0.130

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2021	106	417	0.170	0.385	0.0740	0.0200	3.80	0.0400	0.140
2022	119	1000	0.169	0.366	0.0540	0.0200	3.40	0.0200	0.130

Table 4.17.2 Summary statistics for concentrations of dissolved cadmium in estuarine and coastal waters $(\mu g/L)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2014	165	1186	0.0243	0.0280	0.0150	0.0150	0.479	0.0150	0.0150
2015	162	1130	0.0316	0.0291	0.0150	0.0150	0.150	0.0150	0.0398
2016	183	1311	0.0235	0.0189	0.0150	0.0150	0.156	0.0150	0.0150
2017	172	1295	0.0267	0.0227	0.0150	0.0150	0.192	0.0150	0.0330
2018	161	1122	0.0325	0.0310	0.0150	0.0150	0.377	0.0150	0.0412
2019	160	1031	0.0235	0.0265	0.0150	0.0150	0.460	0.0150	0.0150
2020	111	258	0.0197	0.0187	0.0150	0.0150	0.290	0.0150	0.0150
2021	107	417	0.0461	0.144	0.0150	0.0150	2.70	0.0150	0.0470
2022	118	1006	0.0263	0.0206	0.0150	0.0150	0.120	0.0150	0.0340

Table 4.17.3 Summary statistics for concentrations of dissolved nickel in estuarine and coastal waters $(\mu g/L)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	157	1114	1.25	1.22	0.806	0.150	13.5	0.482	1.56
2015	155	1072	1.21	1.10	0.806	0.150	11.4	0.456	1.58
2016	177	1262	1.14	1.13	0.847	0.150	15.4	0.446	1.55
2017	165	1250	1.09	1.05	0.781	0.150	19.5	0.484	1.36
2018	157	1080	1.63	7.96	1.06	0.150	260	0.518	2.03
2019	159	997	1.20	1.21	0.788	0.150	14.0	0.473	1.60
2020	109	252	1.22	0.993	0.935	0.150	6.00	0.500	1.70
2021	108	419	1.87	2.77	1.40	0.150	30.0	0.730	2.20
2022	124	1038	1.22	1.41	0.915	0.150	22.0	0.520	1.50

Table 4.17.4 Summary statistics for concentrations of dissolved copper in estuarine and
coastal waters (μg/L) ¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	179	626	1.43	1.21	1.13	0.100	11.6	0.674	1.80
2015	172	498	1.51	1.07	1.22	0.100	5.56	0.692	2.04
2016	190	677	1.34	0.948	1.07	0.100	5.16	0.588	1.90
2017	181	698	1.50	1.09	1.19	0.100	7.43	0.677	2.13
2018	169	490	1.64	1.26	1.28	0.100	10.4	0.730	2.30

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2019	168	438	1.45	1.16	1.08	0.100	5.85	0.633	1.88
2020	103	126	1.51	0.926	1.25	0.260	4.50	0.790	1.98
2021	92	336	2.10	1.17	2.00	0.270	6.40	1.10	3.00
2022	111	620	1.76	1.43	1.30	0.100	16.0	0.730	2.50

Table 4.17.5 Summary statistics for concentrations of dissolved zin	c in estuarine and
coastal waters (μg/L)¹	

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2014	170	580	3.59	3.02	2.75	0.200	19.7	1.56	4.55
2015	169	477	4.37	6.21	3.26	0.200	116	1.70	5.22
2016	188	660	3.97	4.03	2.68	0.200	19.6	1.17	4.72
2017	178	682	4.53	4.55	2.70	0.200	21.9	1.29	5.75
2018	172	508	4.75	4.45	3.31	0.200	25.5	1.62	6.15
2019	171	460	3.78	4.32	2.60	0.200	57.0	1.20	4.80
2020	107	131	4.09	2.68	3.30	0.410	16.0	2.20	5.55
2021	94	338	6.10	4.82	4.80	0.200	24.0	2.60	7.80
2022	110	614	5.24	5.69	3.55	0.200	70.0	2.10	6.48

Figure 4.17.1 Modelled trends for dissolved lead, cadmium, nickel, copper, and zinc concentrations in estuarine and coastal waters (μ g/L, log10 y-axis scale). The graphs show trends based on the predicted mean concentrations for all months together (left), with shading representing 95% confidence intervals, and for individual months coloured by season (right)



To consider changes over time, a generalised additive mixed model was fitted to the log10-transformed concentration data on a substance-by-substance basis with date – expressed as a decimal – and month of sampling as the main covariates. This corresponds to modelling the geometric mean of concentration. No spatial aggregation of the data was required. The model-fitting process allowed identification of any seasonality in the data, any trend in the data and also any trend in the seasonality itself. The model also accounted for the inherent correlation between observations over time from any particular site. These are more likely to be correlated with each other than with observations from other sites. This was achieved through specifying a random intercept for site identity. The fitted model was used to predict mean log10 concentrations for each month between 2014 and 2022. Fitted values and their confidence intervals were back-transformed to the original scale of the data.

Assessment of the data shows that there are no significant changes in concentrations between 2014 and 2022; however, during that period copper concentrations rose and fell again. All metals, apart from lead, appeared to show a slight decrease in concentrations since 2020, although this period is too short to deduce a trend and may be a consequence of monitoring changes.

All metals apart from cadmium appeared to show some unexplained changes in seasonality. Results for cadmium are likely influenced by the data set having a larger number of samples with concentrations below the detection limit. Lead and nickel exhibited a strong change in seasonality, with the central period of the data – from 2016 to 2019 – showing low seasonality, with higher seasonality at the beginning and end of the period.

The dashboard trend information is based on the overall national assessment; therefore, the corresponding entry is 'no observed change in concentrations'.

4.17.4 Thresholds

Annual average EQS values for dissolved lead ($1.3\mu g/L$), dissolved cadmium ($0.2\mu g/L$) and dissolved nickel ($8.6\mu g/L$) in surface waters other than inland ones are given in the Water Framework Directive (Standards and Classification) Directions 2015 (UK Government, <u>2015</u>). For copper and zinc, EQSs are also specified in the 2015 Directions for England and Wales (<u>UK Government, 2015</u>):

For dissolved copper, the EQS varies depending on DOC content at the sampling site: where DOC ≤ 1 mg/L, the EQS is 3.76µg/L; where DOC > 1mg/L, the EQS is 3.76 + (2.677 x ((DOC/2) - 0.5)) µg/L. This accounts for the fact that the ecotoxicity of copper has been shown to significantly reduce with increasing DOC (<u>Maycock, Merrington and Peters,</u> 2012).

For zinc, the EQS is $6.8\mu g/L$ over and above any ABC present (<u>UKTAG, 2013</u>). A saline ABC of $1.1\mu g/L$ was added to the EQS to give a threshold of $7.9\mu g/L$ for use as a comparison here.

Typically, average site concentrations are used for comparison with the EQSs for these metals. These are based on available data for a 3-year period. The assessment here is based on site averages for the period from 2020 to 2022. Not every site has the maximum number of years' data available; only 3 sites had data for 3 years and for only one or 2 metals. Each site requires at least 3 samples per year to be included in the assessment; the number of samples per site varied between 3 and 24 for lead, 3 and 28 for cadmium, 3 and 17 for nickel and zinc, and 3 and 25 for copper.

The number and proportion of sites with mean concentrations for 2020 to 2022 that exceed the above thresholds have been calculated. For lead, only 1 out of 11 sites (9%) had a mean concentration above the threshold of 1.3μ g/L. For cadmium, nickel and copper, none of the sites sampled were above the corresponding EQSs. For zinc, 5 out of 10 sites (50%) exceeded the threshold. The percentage results are used for the corresponding entries in the dashboard.

The results represent an increase in potential risk for lead and zinc since the previous indicator report (<u>Environment Agency, 2021</u>), with both metals moving up to a different category of risk. For nickel, there has been a slight improvement with this metal moving down a category in risk.

However, the changes in results for lead and nickel relate to a difference of only one site in each case. In addition, the current results for all metals are likely to be biased by changes to the monitoring over the last 3 years (see Section 4.17.1). The numbers of sites assessed against a threshold in this report are approximately a twentieth to a seventh of those considered in previous reporting (Environment Agency 2021), and the results should be viewed with this in mind.

4.18 Metals in blue mussel: lead, cadmium, nickel, copper, and zinc



4.18.1 Data source

Data on lead, cadmium, nickel, copper, and zinc in blue mussels (*Mytilus edulis*) in England have been provided by the Environment Agency. Concentration data in *Mytilus* flesh have been collected, since around 2000, as part of the UK-wide OSPAR CEMP, with analysis later expanded in anticipation of monitoring requirements under the Water Environment Regulations 2017 for lead and cadmium (<u>UK Government, 2017</u>).

Data used in this assessment are also submitted, as part of the wider UK data set, to the DOME (marine environment) data portal for the ICES (<u>ICES, 2023</u>).

The monitoring methodology is described in the CEMP programme manual, the Green Book (British Oceanographic Data Centre (<u>BODC, 2020</u>). Where feasible sites are monitored annually, with a target of 3 samples – consisting of pooled individuals – collected at each site on each sampling occasion. Samples are collected in the winter/early spring to avoid any seasonal influence from spawning.

For all substances, individual sites are sampled once a year. Fewer sites have been monitored since 2020, partly owing to the COVID-19 pandemic, and monitored sites have changed over time due to disappearing intertidal mussel beds in key locations. Change in in the balance of monitored catchments over time can influence the results of the trend and threshold assessments.

4.18.2 Data structure

Data on concentrations of metals in *Mytilus* flesh are available for the period 2000–2022, but only data from 2011 onwards are included in this assessment to eliminate the impacts of historical changes on the monitoring programme.

Data are reported as $\mu g/kg$ wet weight.

All reported lead and cadmium concentrations were above the minimum reporting value (MRV). For nickel, 18% of samples were recorded at an elevated MRV of <300 μ g/kg wet weight. For copper, 2 samples had an elevated MRV of <800 μ g/kg wet weight. All zinc data were above the MRV except for one result which was at an elevated value of <17,000 μ g/kg wet weight. All results with a less than (<) qualifier were assigned a value that was half the MRV.

4.18.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.18.1 to 4.18.5 for dissolved lead, cadmium, nickel, copper, and zinc, respectively. The corresponding modelled trend information is shown in Figure 4.18.1.

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	691	507	516	176	2010	339	852
2012	17	33	686	378	593	249	1750	383	930
2013	17	51	593	409	497	247	2750	336	744
2014	20	61	772	734	517	258	3990	363	834
2015	19	57	549	403	393	180	1940	318	620
2016	16	48	738	623	472	250	2790	378	707
2017	15	45	687	502	473	261	1890	346	797
2018	13	37	499	310	396	216	1290	300	547
2019	16	46	552	369	430	171	2030	310	710

Table 4.18.1 Summary statistics for lead in *Mytilus edulis* (µg/kg wet weight)¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2020	2	6	1510	467	1380	1080	2210	1140	1820
2021	6	18	863	495	696	289	1950	554	1060
2022	8	24	498	420	358	95.0	1630	255	516

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2011	17	47	198	115	144	84.4	447	106	278
2012	17	33	218	121	181	78.2	531	138	292
2013	17	51	153	99.7	120	73.0	498	93.6	158
2014	20	61	163	82.9	142	78.0	434	116	167
2015	19	57	209	138	148	75.9	633	122	242
2016	16	48	243	200	147	81.0	969	114	278
2017	15	45	191	112	130	70.2	473	103	244
2018	13	37	186	156	104	66.0	618	85.6	243
2019	16	46	199	151	158	69.4	665	106	212
2020	2	6	122	23.9	120	92.4	156	106	138
2021	6	18	181	115	137	90.2	442	108	182

Table 4.18.2 Summary statistics for cadmium in *Mytilus edulis* (µg/kg wet weight)¹

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2022	8	24	232	208	204	62.7	1110	122	257

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	245	132	150	150	606	150	323
2012	17	33	439	262	370	150	1340	261	529
2013	17	51	328	145	304	153	690	204	435
2014	20	61	674	444	624	150	2570	405	844
2015	19	57	264	137	150	150	589	150	345
2016	16	48	342	195	326	150	767	150	504
2017	15	45	353	113	350	151	584	261	454
2018	13	37	410	122	398	230	659	299	499
2019	16	46	294	114	260	141	640	202	378
2020	2	6	266	60.2	260	196	364	227	288
2021	6	18	365	138	324	208	684	264	433
2022	8	24	342	125	337	158	644	259	412

Table 4.18.3 Summary statistics for nickel in *Mytilus edulis* (µg/kg wet weight)¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	1610	1610	1120	583	8890	938	1400
2012	17	33	6630	11100	1570	967	38000	1350	2150
2013	17	51	1900	1870	1130	866	7450	991	1580
2014	20	61	2710	2240	2030	400	11400	1630	2550
2015	19	57	1180	312	1150	400	2250	990	1350
2016	16	48	1470	761	1260	836	4830	1010	1620
2017	15	45	1760	1540	1190	812	6490	952	1590
2018	13	37	1000	317	931	522	1670	773	1220
2019	16	46	1060	301	1000	540	1760	844	1140
2020	2	6	862	203	804	636	1110	722	1040
2021	6	18	2440	3340	1070	605	12000	890	1440
2022	8	24	9470	39500	1280	675	195000	964	1690

Table 4.1	8.4 Summarv	statistics fo	r copper in	Mvtilus	edulis	(ua/ka wet	weiaht) ¹
	or roannary	01010010010		, my and o	ouuno	(mg/ng not	

Table 4.18.5 Summary data for zinc in *Mytilus edulis* (µg/kg wet weight)¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2011	17	47	16500	4490	16400	8650	33800	13800	19300
2012	17	33	20200	6670	19400	10800	41700	15900	22100

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2013	17	51	20000	10900	15600	10700	51300	13800	19800
2014	20	61	19800	6780	17400	12100	42500	15900	20900
2015	19	57	21400	9880	17000	8580	55300	15300	25600
2016	16	48	22700	9270	20700	9400	48000	16300	26500
2017	15	45	19500	7260	18500	8930	38500	14300	22200
2018	13	37	22200	13300	15300	9510	54000	13500	25700
2019	16	46	21300	10500	18000	11700	61500	16000	21800
2020	2	6	20100	3780	20200	14400	25500	18500	22000
2021	6	18	17800	4360	17400	8500	25500	15400	20600
2022	8	24	69200	252000	17800	8650	1250000	14200	22300

Figure 4.18.1 Modelled trends for lead, cadmium, nickel, copper, and zinc in *Mytilus edulis* (μ g/kg wet weight) using 2 modelling approaches, shown as solid lines with shading representing 95% confidence intervals



Changes over time were assessed using the data for all individual samples analysed for each metal.

To describe potential trends over time, 2 complementary approaches were used. In both cases, models were fitted to log10-transformed concentration data with decimal date of sampling as the main predictor. This corresponds to modelling the geometric mean of concentration. The approaches used were:

- Linear mixed-effects models (Ime green lines in the graphs). The model structure specified random intercepts for replicate sample nested within sampling site. This approach should give better statistical power if the underlying trends are genuinely linear.
- 2. Generalised additive mixed models (gamm orange lines in the graphs). These allow the trend to follow the data in a curvilinear manner. This is a better option if the data length and quantity are sufficient, and if the true trend is non-linear. In this approach, a random intercept for sample site was specified; the replicate samples were averaged to give one value per site visit.

Use of random effects in the models accounts for the inherent correlations between observations over time from any particular site, and in the case of the linear mixed-effects model approach between replicate samples collected on the same visit to a site.

Fitted values and their confidence intervals were back-transformed to the original concentration scale of the data. For the linear trends, the significance of the linear trend term was then evaluated with reference to Satterthwaite's approximation for effective degrees of freedom (Kuznetsova, Brockhoff and Christensen, 2017).

The final assessment of trend was a combination of results from the linear and non-linear analyses. Where the results agreed this was flagged as 'higher certainty'; if there were some inconsistencies with the results, the result from the linear analysis was given precedence, but the result was flagged as 'lower certainty'.

Statistical confidence will also have been influenced by changes in the monitoring over time, particularly a reduction in numbers of samples in 2020 and relatively few sites sampled in 2021 and 2022.

For lead (decreasing), cadmium (no change) and zinc (increasing), there was close agreement between the trends from the two analyses, although for cadmium and zinc, the non-linear generalised additive mixed models approach yielded a slightly steeper trend line. For copper (decreasing) and nickel (no change), there was some disagreement between the two approaches so the results have been flagged as lower certainty. Table 4.18.6 summarises these results.
Table 4.18.6 Summary of the assessment of trends over time for metal concentrations in

 Mytilus edulis

Substance	Trend	Certainty	
Lead	Decreasing	Higher	
Cadmium	No trend	Higher	
Nickel	No trend	Lower	
Copper	Decreasing	Lower	
Zinc	Increasing	Higher	

The results in the dashboard represent the observed statistically significant trends. Therefore, the assignment of 'decreasing concentrations' is given for lead and copper, 'no observed change in concentrations' for cadmium and nickel, and 'increasing concentrations' for zinc. The certainty of these results should also be taken into account.

4.18.4 Thresholds

There are currently no established thresholds for lead, cadmium, nickel, copper, or zinc in *Mytilus* under OSPAR or derived EQSs. The entries in the dashboard reflect that there are no values available for comparison.

4.19 Metals in estuarine and coastal fish: lead, cadmium, nickel, copper, and zinc



4.19.1 Data Source

Data on lead, cadmium, nickel, copper, and zinc in estuarine and coastal fish in England have been provided by the Environment Agency. Data on concentrations in whole fish, primarily dab (*Limanda limanda*), but also flounder (*Platicthys flesus*) and plaice (*Pleuronectes platessa*), have been collected; other fish also have been monitored to a lesser degree. Data have been collected under the Water Environment Regulations 2017 (<u>UK Government, 2017</u>) for cadmium and lead, with those for nickel, copper and zinc provided as part of the same analytical suite.

Data are collected once a year at multiple sites. On each sampling occasion, multiple replicate samples are taken from each monitoring site. Generally, 3 samples are collected. Each sample consists of one or more fish of the same species; where more than one fish is needed for the required quantity for analysis, this typically comprises 2 or 3 fish, occasionally 4.

Survey teams are guided to collect data preferentially from a ranked list of fish species, based on what was previously found at each site.

4.19.2 Data Structure

Data are available from 2018 to 2022 for all the metals in estuarine and coastal fish.

Concentration data are reported as μ g/kg wet weight in whole fish.

The lowest reported wet weight values for lead, cadmium, nickel, copper, and zinc varied within the data sets because they are calculated from dry weight results and percentage dry matter. The dry weight LoD values for each metal were 0.1mg/kg for lead, 0.007mg/kg for cadmium, 0.3mg/kg for nickel, 0.8mg/kg for copper, and 40mg/kg for zinc. The percentage dry matter varies for each specimen collected and had an average result of 24% for the estuarine and coastal fish data set.

The dry weight results below their LoDs had corresponding reported wet weight results ranging from 18 to 52μ g/kg for lead, 0.182 to 2.63μ g/kg for cadmium, 6.6 to 274μ g/kg for nickel, 17.6 to 526μ g/kg for copper, and 10,000 to $12,400\mu$ g/kg for zinc. Approximately 7% of results were reported below the LoD for lead, 25% for cadmium, 60% for nickel, 6% for copper, and 4% for zinc. Results recorded as below the LoD were assigned a value that was half the LoD.

4.19.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Tables 4.19.1 to 4.19.5 for lead, cadmium, nickel, copper, and zinc, respectively.

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	16	34	174	228	78.4	12.1	1070	44.5	222
2019	25	73	190	212	92.4	9.00	1010	49.4	294
2020	17	38	156	167	83.1	12.5	621	53.2	184
2021	21	62	208	308	95.8	13.5	1980	64.6	215
2022	16	46	214	264	108	4.84	1230	48.6	255

Table 4.19.1 Summary statistics for concentrations of lead in estuarine and coastal fish $(\mu g/kg \text{ wet weight})^1$

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.19.2 Summary statistics for concentrations of cadmium in estuarine and coastal fish $(\mu g/kg wet weight)^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	16	34	6.50	6.46	4.46	0.715	34.5	2.37	8.58
2019	25	73	9.79	13.4	6.00	0.770	82.8	1.76	11.9
2020	17	38	4.76	4.78	2.56	0.840	20.2	0.910	7.99
2021	21	62	15.0	33.7	4.74	0.770	168	1.02	10.4
2022	16	46	9.69	18.1	2.88	0.0910	96.8	1.84	9.25

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.19.3 Summary statistics for concentrations of nickel in estuarine and coastal fisl	h
(μg/kg wet weight)¹	

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	16	34	68.2	71.5	38.1	30.3	366	34.1	69.6
2019	25	73	98.2	89.0	69.5	31.5	504	38.1	131
2020	17	38	67.7	39.9	41.2	30.0	188	37.5	97.2
2021	21	62	91.9	113	43.5	27.0	648	39.0	86.3
2022	16	46	801	1560	73.0	3.30	8640	34.9	1300

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.19.4 Summary statistics for concentrations of copper in estuarine and coastal fish $(\mu g/kg \text{ wet weight})^1$

Year	No. of sites	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	16	34	606	382	536	264	2190	361	633
2019	25	73	615	307	551	102	1300	396	821
2020	17	38	445	157	444	96.0	760	335	566
2021	21	62	540	323	446	108	1570	330	669
2022	16	46	587	338	522	8.80	1580	440	733

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Table 4.19.5 Summary statistics for concentrations of zinc in estuarine and coastal fish
(µg/kg wet weight) ¹

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2018	16	34	16300	3570	15800	9850	25300	14300	18500
2019	25	73	17900	4890	17500	8930	37100	14300	20900
2020	17	38	14000	5770	15700	5000	23300	10200	18500
2021	21	62	13900	4540	13400	6720	30600	10800	15400
2022	16	46	15800	6480	16000	1140	35200	13200	18100

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Unlike for freshwater fish (Section 4.15), species data are available for each sample. Data are available for 136, 73 and 40 samples of dab (*Limanda limanda*), flounder (*Platicthys flesus*) and plaice (*Pleuronectes platessa*), respectively. Therefore, species identity was used as a covariate in the trend analysis, and trends were identified for the 3 species

individually and together. Data for un-named species and a very small number of samples of sole and whiting also available were excluded from the trend analysis. The corresponding modelled trend information is shown in Figure 4.19.1. The overall trend is based on the result for all species together.





To describe changes over time, the data analysis approach was identical to that undertaken for PBTs in estuarine and coastal fish tissue detailed in Section 4.8.

The results of the trend analyses are shown in Figure 4.19.1 and Table 4.19.6. All conclusions are conditional on the short length of the available records. For lead and cadmium, there is no evidence of any statistically significant trends. For nickel, there is a clear statistically significant upward trend, both overall and for each species. For copper and zinc, there are slight statistically significant downward trends; however, these are marginal given the uncertainty in the data arising from the relatively short record length, the numbers of samples and the variation between replicates. The overall downward trends in plaice specifically.

The significance of the limited variation in the concentrations of copper and zinc in estuarine and coastal fish is not yet clear. These values may be a reflection of naturally regulated concentrations in fish as the metals are essential elements.

Further research is required to understand these patterns.

Table 4.19.6 Summary of the trends over time based on the limited data available for lead, cadmium, nickel, copper, and zinc in estuarine and coastal fish tissue, showing trend information for all species together and whether mean concentrations and trends and differ among species

Metal	Trend all species	Difference in mean concentration among species	Difference in trend among species
Lead	No trend	No	No
Cadmium	No trend	No	No
Nickel	Increasing	No	No
Copper	Decreasing (marginal)	No	Yes
Zinc	Decreasing (marginal)	No	Yes

For all substances, the minimum requirements for reporting a trend are not met (see Section 3.1.2). Therefore, the entry in the dashboard reflects that data are available, but insufficient to report a trend assessment.

4.19.4 Thresholds

There are currently no established threshold concentrations for lead, cadmium, nickel, copper, and zinc in estuarine and coastal fish. The entries in the dashboard reflect that there are no values available for comparison.

4.20 Metals in offshore fish: lead, cadmium, nickel, copper, and zinc



4.20.1 Data source

Data on concentrations of lead, cadmium, nickel, copper, and zinc in fish livers are available for dab (*Limanda limanda*). These data for offshore marine fish are collected as part of UK Marine Strategy Regulations–OSPAR monitoring for assessing good environmental status. The data are collected and held by Cefas and are submitted to the national MERMAN database.

Data used in this assessment are also submitted, as part of the wider UK data set, to the DOME (marine environment) data portal for the ICES (<u>ICES, 2023</u>).

Stations – around which sampling is conducted – are selected on the basis that they reliably support dab populations that can be sampled for analysis and that there are no direct impacts from local point sources so that they are representative of the overall sub-region. There are a minimum of 3 stations required within each OSPAR hydro-geographical sub-region (OSPAR Commission, 2023).

Between 2008 and 2010, sampling around the country was done annually. From then onwards, fish were collected on alternate sides of the country each year with sampling around east coast stations occurring in odd years and west coast ones in even years. A couple of west coast sites were also included in the 2011 monitoring. Up to 17 stations can be monitored in odd years and up to 10 in even ones.

All data relate to designated English waters, except for those from a Welsh station in the Bristol Channel as this is a shared water body in which fish are likely to move freely across territorial water.

Typically, 5 or fewer pools of fish were sampled around each station. Each pool comprised 5 fish.

Sampling is typically carried out in mid-summer, but monitoring deviated to winter for 2020 and 2022, and to spring for 2021. Reasons for this include the COVID-19 pandemic and vessel problems.

4.20.2 Data structure

The data consist of measurements of all the metal concentrations in offshore dab for 2008 to 2022.

The data summaries that were provided comprise results from individual pool samples taken around the stations. These individual samples were used in the trend and threshold assessments rather than station means for the purposes of the dashboard indicator. This is because the pooled samples are already representative of a mean of 5 fish and this approach allows assessment of trends across the stations and nationally.

Data are for lead, cadmium, nickel, copper, and zinc concentrations in liver. All concentration data are reported in mg/kg wet weight.

The LoDs varied within the data sets of 996 samples. For lead and cadmium, 33 and 19 samples were reported below LoDs of 0.01 to 0.09 and 0.01 to 0.14mg/kg wet weight, respectively. One hundred and forty nickel samples (14%) were reported below LoDs of 0 to 0.23mg/kg wet weight. Only one sample for both copper and zinc was reported below LoDs of 0.04 and 3.21mg/kg wet weight, respectively. All concentrations below the LoD were assigned a value that was half the LoD.

4.20.3 Exploration of change in chemical concentrations over time

Summary data for lead, cadmium, nickel, copper, and zinc concentrations in dab livers analysed across the period are given in Tables 4.20.1 to 4.20.5, respectively.

The measured concentrations of lead, cadmium and nickel were converted into Ln values for the purpose of assessing trends. For copper, square root transformations of the data were used; for zinc, the data were used untransformed. Plots of the overall change over time of these lead, cadmium, nickel, copper, and zinc values in dab livers from 2008 to 2022 are shown in Figures 4.20.1 to 4.20.5, respectively. For cadmium, the plot seems to be cyclic and reflects the higher values seen on the east coast compared with those on the west (Figure 4.20.2 and Table 4.20.2).

Table 4.20.1 Summary statistics for samples of lead concentrations in dab livers (mg/kg wet weight)¹

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2008	23	114	0.22	0.33	0.10	0.015	2.5	0.070	0.23
2009	23	115	0.17	0.22	0.080	0.010	1.2	0.040	0.21
2010	16	79	0.20	0.33	0.10	0.010	2.4	0.040	0.20
2011	15	79	0.14	0.27	0.070	0.0050	2.0	0.033	0.10
2012	8	40	0.42	0.48	0.26	0.050	2.4	0.090	0.60
2013	15	74	0.20	0.28	0.070	0.020	1.2	0.050	0.21
2014	9	45	0.29	0.22	0.24	0.060	1.1	0.12	0.40
2015	14	66	0.29	0.39	0.10	0.020	1.6	0.050	0.25
2016	8	37	0.26	0.29	0.13	0.050	1.5	0.080	0.33
2017	15	75	0.30	0.56	0.080	0.020	3.0	0.040	0.18
2018	9	45	0.227	0.278	0.142	0.0473	1.77	0.0895	0.264
2019	15	71	0.250	0.465	0.0648	0.0198	2.76	0.0437	0.181
2020	10	42	0.203	0.213	0.122	0.0346	0.926	0.0681	0.184
2021	15	75	0.145	0.161	0.0855	0.0277	0.877	0.0480	0.176
2022	9	39	0.570	0.534	0.412	0.0155	1.90	0.186	0.814

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.20.1 Scatterplot of lead concentrations (in units of mg/kg wet weight, log10 y-axis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Lead in Fish

Table 4.20.2 Summary statistics for samples of cadmium concentrations in dab livers (mg/kg wet weight)¹

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2008	23	114	0.23	0.22	0.16	0.020	1.8	0.10	0.31
2009	23	115	0.23	0.22	0.15	0.0050	1.2	0.095	0.29
2010	16	79	0.27	0.33	0.21	0.020	2.00	0.10	0.31
2011	15	79	0.27	0.30	0.20	0.030	2.2	0.11	0.32
2012	8	40	0.14	0.084	0.13	0.030	0.40	0.068	0.18
2013	15	74	0.49	0.56	0.34	0.050	3.7	0.23	0.53
2014	9	45	0.13	0.089	0.11	0.040	0.38	0.060	0.17
2015	14	66	0.49	0.46	0.36	0.050	2.0	0.17	0.57

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2016	8	37	0.17	0.013	0.13	0.030	0.68	0.080	0.19
2017	15	75	0.48	0.45	0.38	0.070	3.1	0.24	0.55
2018	9	45	0.0863	0.0323	0.0784	0.0432	0.188	0.0626	0.107
2019	15	71	0.427	0.509	0.245	0.0414	2.76	0.168	0.369
2020	10	42	0.106	0.0573	0.0931	0.0310	0.276	0.0609	0.144
2021	15	75	0.550	0.508	0.424	0.102	3.58	0.315	0.590
2022	9	39	0.143	0.0593	0.125	0.0642	0.315	0.105	0.168

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.20.2 Scatterplot of cadmium concentrations (in units of mg/kg wet weight, log10 yaxis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Cadmium in Fish

Table 4.20.3 Summary statistics for samples of	f nickel concentrations in dab livers (mg/k	g
wet weight) ¹		

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2008	23	114	0.14	0.10	0.12	0	0.56	0.060	0.19
2009	23	115	0.069	0.074	0.045	0.015	0.53	0.025	0.090
2010	16	79	0.065	0.070	0.050	0.0050	0.38	0.010	0.095
2011	15	79	0.22	0.49	0.10	0.0050	3.4	0.070	0.15
2012	8	40	0.12	0.19	0.075	0.020	1.2	0.050	0.10
2013	15	74	0.16	0.12	0.14	0.0080	0.53	0.080	0.20
2014	9	45	0.25	0.39	0.13	0.0080	2.0	0.070	0.21
2015	14	66	0.28	0.34	0.19	0.030	2.4	0.11	0.29
2016	8	37	0.08	0.047	0.070	0.030	0.23	0.040	0.090
2017	15	75	0.11	0.062	0.090	0.030	0.35	0.060	0.15
2018	9	45	0.0662	0.0289	0.0624	0.0210	0.158	0.0465	0.0783
2019	15	71	0.268	0.743	0.106	0.0269	6.08	0.0620	0.215
2020	10	42	0.0488	0.0245	0.0408	0.0135	0.111	0.0341	0.0640
2021	15	75	0.163	0.144	0.130	0.0469	1.14	0.0952	0.167
2022	9	39	0.445	1.31	0.0624	0.00708	6.18	0.0416	0.169

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.20.3 Scatterplot of nickel concentrations (in units of mg/kg wet weight, log10 y-axis scale) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Nickel in Fish

Table 4.20.4 Summary statistics for	samples of copp	er concentrations	in dab livers	(mg/kg
wet weight) ¹				

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2008	23	114	5.95	2.15	5.80	1.80	16.0	4.55	6.88
2009	23	115	5.45	2.54	4.90	0.0200	17.0	3.70	7.00
2010	16	79	4.51	1.90	4.20	1.60	12.0	3.15	5.30
2011	15	79	4.10	1.85	3.90	0.340	10.0	2.75	4.90
2012	8	40	5.55	2.78	4.95	2.60	16.0	3.90	6.15
2013	15	74	6.23	2.41	5.99	2.26	14.4	4.49	7.44
2014	9	45	5.85	2.18	5.50	3.10	13.0	4.30	6.40
2015	14	66	6.37	3.50	5.30	2.00	20.0	4.15	7.53

Year	No. of stations	n	Mean	SD	Median	Min	Max	Q1	Q3
2016	8	37	6.47	3.47	5.30	1.80	14.0	3.20	8.90
2017	15	75	5.47	2.16	5.20	1.80	13.0	3.95	6.55
2018	9	45	5.23	2.02	5.25	1.65	10.6	4.02	6.45
2019	15	71	5.05	2.39	4.61	1.59	11.4	3.09	6.80
2020	10	42	11.0	3.65	11.0	4.46	18.7	8.33	13.1
2021	15	75	5.38	2.38	4.77	1.52	14.1	3.60	6.72
2022	9	39	10.3	4.03	10.4	1.79	18.7	7.69	13.2

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.20.4 Scatterplot of square-root-transformed copper concentrations (original untransformed data are in units of mg/kg wet weight) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)





Table 4.20.5 Summary statistics for samples of zinc concentrations in dab livers (mg/kg wet weight)¹

Year	No. of stations	n	Mean	SD	Median	Min	Мах	Q1	Q3
2008	23	114	28.0	3.92	27.5	18.0	38.0	25.0	31.0
2009	23	115	23.3	5.12	23.0	1.61	43.0	20.0	25.5
2010	16	79	21.0	3.87	22.0	12.0	29.0	18.0	24.0
2011	15	79	22.7	4.89	23.0	3.50	34.0	21.0	25.8
2012	8	40	25.4	4.56	25.0	18.0	39.0	23.0	27.3
2013	15	74	26.3	3.37	26.4	20.1	34.0	24.0	28.5
2014	9	45	22.3	2.82	22.0	17.0	28.0	20.0	24.0
2015	14	66	26.8	7.17	25.0	18.0	46.0	22.0	28.0
2016	8	37	25.5	5.31	24.0	15.0	38.0	22.0	30.0
2017	15	75	25.6	2.77	25.0	20.0	35.0	24.0	27.0
2018	9	45	23.6	4.45	23.1	15.7	37.0	21.4	25.1
2019	15	71	23.7	3.67	23.8	16.6	33.7	21.4	25.3
2020	10	42	35.8	6.82	35.6	20.3	51.9	30.0	41.0
2021	15	75	27.1	3.22	27.0	17.4	33.9	25.1	29.6
2022	9	39	34.0	11.2	32.5	15.5	65.0	26.4	39.3

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.20.5 Scatterplot of zinc concentrations (mg/kg wet weight) in the livers of dab from marine waters around England between 2008 and 2022. Data shown are for individual samples. The solid red line shows the trend from a generalised additive model as a function of time (diagram courtesy of Cefas)



Zinc in Fish

The minimum data requirements for trend assessment are met (see Section 3.1.2), though the monitoring regime has altered over time (see Section 4.20.1). The same GAM (\underline{Wood} , 2017) approach and criteria as described for mercury in dab (see Section 4.9.3) was used to estimate trends.

The trends lines shown in Figures 4.20.1 to 4.20.5, based on all samples from all stations, were statistically significant for each metal (p < 0.001) owing to the large number of observations. However, only increases for lead, cadmium, copper, and zinc were supported using the criteria.

To determine overall trends for these substances for the dashboard, changes in concentrations over time at individual stations were assessed using the same GAM method.

Scatterplots of results for lead, cadmium, nickel, copper, and zinc in samples taken at these stations can be found in Appendix F, Figures F.4.20.1 to F.4.20.5, respectively. The statistic D for each metal was then calculated as also described for mercury in Section 4.9.3.

For lead, 6 stations in the east and 4 in the west showed upward trends and a station on each side of the country downward trends (see Appendix F, Figure F.4.20.1 and Table F.2). Similar results were observed for cadmium, with 7 stations in the east and 3 in the west showing upwards trends and one site in the west showing a downward trend (see Appendix F, Figure F.4.20.2 and Table F.2). The resulting D values of 33 and 38% for lead

and cadmium, respectively, support the assignment of 'increasing concentrations' for these 2 metals and this is used within the dashboard.

For nickel, 5 stations on the east coast and one on the west showed upward trends and 2 stations on the west coast showed downward trends (see Appendix F, Figure F.4.20.3 and Table F.2). The resulting D value (17%) supports the assignment of 'no observed change in concentrations' and this is used within the dashboard.

In the case of copper, 2 stations on the east coast showed upward trends and 4 showed downward ones; upward trends only were observed on the west coast at 6 stations (see Appendix F, Figure F.4.20.4 and Table F.2). For zinc, few sites depicted trends on the east coast: one an upward trend and 2 downward trends; similar to copper, only upward trends were observed in the west and these occurred at 4 stations (see Appendix F, Figure F.4.20.5 and Table F.2). The resulting D values of 17 and 13% for copper and zinc, respectively, support the assignment of 'no observed change in concentrations' for these 2 metals and this is used in the dashboard.

The significance of the limited variation in the concentrations of copper and zinc in dab livers with a slight increase in the west coast values in the last couple of sampling rounds – as shown by the mean values in Tables 4.20.4 and 4.20.5, respectively – is not yet clear. These values may be a reflection of naturally regulated concentrations in fish as the metals are essential elements.

For further context, national trends were determined for all metals based on data relating to individual stations from 2011 to 2022 – that is, the minimum data required for a trend assessment (see Section 3.1.2) rather than using the full data set. The results suggest the need to continue to review the situation over time as upward trends are observed.

4.20.4 Thresholds

There are no ecological thresholds either under the OSPAR framework or derived as statutory values. Therefore, assessment of the most recent data against thresholds for lead, cadmium, nickel, copper, and zinc is not possible and the dashboard entries indicate that there are no corresponding thresholds defined.

It is worth noting the distinct difference between the east and west coast concentrations in dab liver for cadmium. Should a threshold become available in future, it may be worthwhile determining any geographical differences in threshold exceedance, alongside a national view, for this substance.

4.21 Metals in harbour porpoise: lead, cadmium and nickel



4.21.1 Data source

Data on concentrations of lead, cadmium and nickel are available in liver tissue for harbour porpoise (*Phocoena phocoena*). These data are collected as part of the UK CSIP and the Scottish Marine Animal Stranding Scheme (SMASS) funded by Defra and the Devolved Administrations, as well as through Cefas, the NERC ChemPop project and other ad hoc funding obtained by the CSIP and the SMASS. The first samples were analysed in 1991 and a minimum of 20 UK samples are analysed each year.

Tissue samples are taken opportunistically from marine mammal stranding and bycatch incidents. A subset is chosen for analysis that contains an even split of trauma vs infectious disease as causes of death, adult vs juvenile and male vs female, with samples covering England, Wales and Scotland that are broadly in proportion with the number of individuals found.

The contaminant analysis is carried out and held by Cefas.

Data are for Great Britain and not restricted to the England level, as for most of the other metrics within this indicator. This is because the wider geographical data set maintains an even split between animal types in the data set – not biasing a certain type that may be more (or less) susceptible to accumulating contaminants, such as adult males or those dying from infectious disease or starvation. It also reflects that these species are likely to move more widely along the British coast and enables more robust trend determination because of the increased number of samples per year. This approach is consistent with other marine indicators within the 25-YEP Outcome Indicator Framework.

4.21.2 Data structure

Each sample is from a single individual. Data were provided for lead, cadmium and nickel for the years 2009–2021, excluding 2010. All concentration data are reported in mg/kg wet weight in liver.

The LoDs varied within the data sets of 241 samples per substance. Those samples that had results reported below the LoD had LoDs ranging 0.006–0.008, 0.002–0.016 and 0.008–0.014mg/kg wet weight for lead, cadmium and nickel, respectively. The number of samples below the LoD were 16 for lead, 8 for cadmium and 37 for nickel, that is between 3 and 15% of all samples. These samples were assigned a value that was half the LoD.

4.21.3 Exploration of change in chemical concentrations over time

The distribution of data by year is summarised in Tables 4.21.1 to 4.21.3 for lead, cadmium and nickel concentrations, respectively, in harbour porpoise livers. The measured concentrations were converted into Ln values for the purpose of assessing trends, and then back-transformed to the original concentration scale. Plots of the overall change over time for lead, cadmium and nickel concentrations in harbour porpoise livers from 2009 to 2021 are shown in Figures 4.21.1 to 4.21.3, respectively.

Year	n	Mean	SD	Median	Min	Мах	Q1	Q3
2009	23	0.0216	0.0307	0.00400	0.00350	0.110	0.00400	0.0400
2011	3	0.0603	0.0534	0.0310	0.0280	0.122	0.0280	0.122
2012	3	0.0210	0.0151	0.0160	0.00900	0.0380	0.00900	0.0380
2013	4	0.0630	0.0880	0.0285	0.00300	0.192	0.00500	0.156
2014	17	0.0206	0.0143	0.0134	0.00500	0.0552	0.00900	0.0323
2015	23	0.0737	0.241	0.0150	0.00700	1.17	0.00816	0.0269
2016	20	0.0374	0.0522	0.0128	0.00301	0.168	0.00968	0.0293
2017	29	0.0572	0.111	0.0118	0.00273	0.465	0.00721	0.0256
2018	29	0.0257	0.0346	0.00978	0.00176	0.154	0.00619	0.0362
2019	30	0.0446	0.0703	0.0136	0.00224	0.244	0.00556	0.0404

Table 4.21.1 Summary statistics for samples of lead concentrations in harbour porpois	е
ivers (mg/kg wet weight) ¹	

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2020	30	0.0752	0.171	0.0116	8.22 x 10 ^{−4}	0.607	0.00483	0.0361
2021	30	0.111	0.149	0.0353	0.00300	0.443	0.00881	0.219

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.21.1 Scatterplot of lead concentrations in the livers of harbour porpoise from marine waters around the UK between 2009 and 2021 (in units of mg/kg wet weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence interval (diagram courtesy of Cefas)



Table 4.21.2 Summary statistics for samples of cadmium concentrations in harbour porpoise livers (mg/kg wet weight)¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2009	23	0.329	0.402	0.230	0.0100	1.90	0.0900	0.400
2011	3	0.220	0.0144	0.216	0.208	0.236	0.0280	0.236
2012	3	0.164	0.121	0.219	0.0250	0.248	0.0250	0.248
2013	4	0.167	0.111	0.164	0.0360	0.306	0.0640	0.274
2014	17	0.217	0.238	0.112	0.00100	0.746	0.0153	0.331
2015	23	0.184	0.233	0.123	0.00150	0.953	0.0311	0.239
2016	20	0.335	0.394	0.146	0.0178	1.52	0.0749	0.555
2017	29	0.321	0.373	0.194	0.00208	1.48	0.0744	0.402
2018	29	0.297	0.405	0.160	0.00100	1.79	0.0935	0.359
2019	30	0.190	0.185	0.168	0.00100	0.656	0.0344	0.267
2020	30	0.259	0.316	0.124	0.00100	0.981	0.0335	0.331
2021	30	0.363	0.427	0.174	0.00800	1.27	0.0840	0.471

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.21.2 Scatterplot of cadmium concentrations in the livers of harbour porpoise from marine waters around the UK between 2009 and 2021 (in units of mg/kg wet weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence interval (diagram courtesy of Cefas)



Table 4.21.3 Summary statistics for samples of nickel concentrations in harbour porpoise livers (mg/kg wet weight)¹

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2009	23	0.129	0.306	0.0500	0.00700	1.50	0.0300	0.0700
2011	3	0.00767	0.00551	0.00500	0.00400	0.0140	0.00400	0.0140
2012	3	0.0645	0.0852	0.0270	0.00450	0.162	0.00450	0.162
2013	4	0.00675	0.00419	0.00500	0.00400	0.0130	0.00425	0.0110
2014	17	0.179	0.379	0.0570	0.00450	1.59	0.0179	0.174
2015	23	0.0742	0.224	0.0231	0.00450	1.10	0.0150	0.0418
2016	20	0.0596	0.0688	0.0503	0.00984	0.334	0.0275	0.0651
2017	29	0.139	0.354	0.0178	0.00112	1.51	0.00551	0.0479

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2018	29	0.0391	0.0603	0.0237	0.00235	0.327	0.00995	0.048
2019	30	0.0241	0.0341	0.00984	0.00386	0.145	0.00780	0.0218
2020	30	0.128	0.324	0.0121	8.04 x 10 ⁻⁴	1.15	0.00467	0.0466
2021	30	0.303	0.469	0.09013	0.00400	1.51	0.00400	0.371

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.21.3 Scatterplot of nickel concentrations in the livers of harbour porpoise from marine waters around the UK between 2009 and 2021 (in units of mg/kg wet weight, log10 y-axis scale). Data shown are for individual samples. The thick red line shows the trend from a generalised additive model as a function of time; the thinner red lines show the 95% confidence interval (diagram courtesy of Cefas)



The same GAM (<u>Wood, 2017</u>) approach and criteria as described for mercury in harbour porpoise (see Section 4.10.3) was used to estimate trends.

For lead, a statistically significant upward trend was observed based on the full data set (p = 0.03, p <0.01). This trend was also observed for the most-recent years, from the end of 2015 to the end of 2021 (p = 0.03, p = 0.02).

For cadmium, no statistically significant change in concentrations was found based on the full data set (p = 0.56, p = 0.48) or based on the last 5 years (p = 0.56, p = 0.61).

For nickel, no statistically significant change in concentrations was found based on the full data set because while the first criterion was met (p < 0.001), this was not confirmed for the second (p = 0.38). However, a statistically significant upward trend was observed for the results based on the last 5 years (p < 0.001, p = 0.02).

The results in the dashboard represent the observed trends from the full data sets. Therefore, the assignment of 'increasing concentrations' is given for lead and 'no observed change in concentrations' for cadmium and nickel.

4.21.4 Thresholds

There are currently no thresholds for lead, cadmium or nickel in harbour porpoise livers against which to compare the exposure levels detected. This is reflected in the dashboard entry.

4.22 Pesticides and biocides in freshwater: pesticides

Pesticides



4.22.1 Data source

Data on pesticides in freshwaters have been collected as part of the Environment Agency's Watch List surveillance monitoring and Catchment Sensitive Farming (CSF) monitoring, as well as through more-recent RSN monitoring and research monitoring looking at areas vulnerable to exposure from any chemical.

The resultant concentration data from the Watch List monitoring are available from 2016 and those from CSF from 2014, although limited earlier data from 2007 have been collected at fewer sites; the recent research monitoring is based on sites within these networks. Data from the RSN have only been available since 2021.

There were fewer samples taken in 2020 owing to the COVID-19 pandemic.

Since the previous round of reporting (Environment Agency), we have selected 2016 as a starting date for the current assessment as this represents when data for a greater number of sites were available. We have also looked at the data across all years, rather than combining those pre-2019.

Analysis involves gas chromatography–mass spectrometry (GCMS) and liquid chromatography–mass spectrometry (LCMS) semi-quantitative screening, capable of measuring a large suite of chemicals (including hundreds of pesticides) via comparison to a target database. For a few substances, both methods can be used. The majority of pesticide detects come from the LCMS target screen analyses; therefore, this section considers the LCMS data only as the richer data set and to avoid reporting twice for any pesticide measured in a sample by both methods.

Using these data allow the consideration of a far broader suite of pesticides over time than those historically monitored using traditional quantitative methods. However, it should be noted that the uncertainty of measurement in the analytical results from target semiquantitative screening is unknown in comparison with the fully quantitated methods for individual substances. In general, there is a favourable comparison between semiquantitative and fully quantitative results, however this is very substance specific and the semi-quantitative nature of the analysis should not be overlooked. Substances included in the suite have also increased over time.

For the purposes of this assessment, results for plant protection active substances with historical or current authorisations and their metabolites are considered (approximately 200 active substances). It is important to note that some of these substances are also, or may have been previously, approved for other uses – for example as veterinary

medicines. Emissions of these substances may, therefore, come from other exposure routes in addition to agricultural, horticultural or domestic use.

The assessment of the data used for the dashboard is based on a toxic units approach (<u>Bundschuh, Goedkoop and Kruger, 2014</u>). This involves conversion of pesticide concentrations into toxic units (TU) using an ecotoxicological endpoint. This effectively converts concentration data into a measure of the risk posed in a given sample by a given substance.

This TU approach does not rely on consistently evaluating data for the same pesticides each year, as the metric is the total toxic risk posed and not an absolute concentration/quantity of any particular active substance. Thus, the metric is robust to the future introduction or withdrawal of active substances from the market as these will not affect the usage of the indicator, although they may alter the magnitude of the value.

For this report, the ecotoxicological endpoint used was the lowest available chronic endpoint for each substance taking into consideration data for algae/macrophytes, aquatic invertebrates and fish, where readily available. This is a change from the previous indicator reporting approach, which exclusively used acute EC50 data for the invertebrate water flea *Daphnia magna* to derive the TU, and it is a move that addresses the proposal to consider the chronic effects of pesticides (Environment Agency, 2021). By considering data for algae/macrophytes, invertebrates and fish rather than data for the one specific species, it addresses the fact that invertebrates (represented by *Daphnia magna*) may not always be the most-sensitive organisms to a particular substance.

The University of Hertfordshire's Pesticide Properties Database (PPDB) (<u>University of</u> <u>Hertfordshire, 2020</u>) was used as the initial source of relevant ecotoxicological data. However, other information sources were also considered, principally the pesticide assessments published by the European Food Safety Authority and published substance assessments undertaken for classification and labelling of substances. The lowest relevant chronic value for a substance across these data sources was used as the relevant data point.

Chronic no-observed effect concentration (NOEC) values were used to derive TU values where available. The NOECs were chosen as a suitable chronic endpoint as they are widely used in regulatory assessments and are frequently reported. It is acknowledged that NOECs are a function of the test design, but as they are considered precautionary and are an accepted endpoint in regulatory assessments, they were determined to be a relevant endpoint to use. In addition, from a practical point of view, NOECs are frequently reported and, therefore, more available than other relevant endpoints, such as EC10s. This enabled relevant information to be readily gathered for the determination of the TU values for a large number of substances. In a few circumstances, other chronic endpoints, such as EC10s, such as EC10s, were used if a relevant NOEC was not available.

The TU for each active substance detected in the water column was calculated as:

TU = Detected concentration (μ g/L) / Lowest available chronic NOEC for algae, invertebrates or fish (μ g/L)

TUs were calculated for all pesticides detected in the LCMS target screen samples, provided that a chronic toxicity endpoint, typically a NOEC, was available from the sources considered.

For each water sample, the summed toxic units for all pesticides detected (TU_{sum}) can be calculated. This measure implies that different active substances may have additive toxic effects. Where a site has been sampled repeatedly within a year, the average (median or mean) and maximum TU_{sum} values across all samples for that site can be calculated. For the purposes of the current report, TU_{sum} values have been calculated for all identified pesticides with detectable concentrations in each sample and the trend and threshold assessments are based on this value.

4.22.2 Data structure

Relevant data are available from 2016 onwards.

In terms of numbers of samples, the data set is dominated by the monitoring for the 8 CSF sites. The geographical spread of the sites is shown in Figure 4.22.1. While much of England is covered, there is poor coverage of the south-west – Devon, Cornwall, Wessex and Solent, and South Downs areas – and the north-east and north-west – Cumbria and Lancashire and Northumbria areas.

Figure 4.22.1 Map showing the locations of Catchment Sensitive Farming (CSF) and non-Catchment Sensitive Farming sites



The data set considered did not contain less than values or non-detects as these are not recorded by the scan methods.

The number of substances detected each year across the samples ranged from 116 to 128 for each year from 2016 to 2022, apart from in 2020 when 98 pesticides were detected. A high proportion of the pesticides detected, however, were detected infrequently (less than 10 times per year). There was some consistency in the pesticides detected, with 100 detected in 5 or more of the years covered. The number of pesticides in a sample ranged from 1 to 53 across the period considered, but the median number of pesticides was very consistent between years and ranged from 24 to 27 pesticides in a sample each year.

A relevant chronic endpoint, that is a NOEC or EC10, was not located for 27 pesticides/metabolites detected between 2016 and 2022. However, for 15 of these substances, there were a relatively low number of detects: fewer than 10 detects were noted over the 7-year period. Several of the most commonly detected substances were degradation products, with 2,6-dichlorobenzamide, atrazine diisopropyl and atrazine desethyl being the most commonly detected. Owing to the lack of chronic data for these substances, they were not included in the calculation of the TU_{sum} value.

The TU_{sum} for each sample was often dominated by one or 2 pesticides, particularly fipronil and imidacloprid.

4.22.3 Exploration of change in chemical concentrations over time

The distribution of data by year for all samples at all sites is summarised in Table 4.22.1 for TU_{sum} concentrations.

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2016	21	585	4.12	16.4	2.22	0.0194	393	1.15	5.08
2017	20	294	2.66	2.55	1.84	0.0455	18.1	0.793	4.21
2018	26	669	4.87	6.73	3.29	0.00454	139	1.49	6.80
2019	105	410	3.89	4.24	2.24	6.35 x10 ^{−6}	27.8	0.815	5.55
2020	23	116	1.89	1.75	1.45	0.00776	10.8	0.596	2.88

Table 4 22 4 Summar	v statistics for TU	aanaantratiana of	naatiaidaa in	frachwater /u	مر/I \1
Table 4.22.1 Summar	y statistics for TU _{st}	im concentrations of	pesticides in	Tresnwater (µ	g/L)'

Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
2021	21	355	2.66	3.23	1.40	2.02 x 10 ^{−8}	23.7	0.559	3.67
2022	34	530	4.17	4.37	2.63	0.00319	29.6	1.06	6.35

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1 lower interquartile range value; Q3: upper interquartile range value.

Particularly high maximum values were noted in 2016 and 2018. These were much higher than values for the other samples and were due to a relatively high concentration of fipronil in those samples.

For the trend analysis, data were filtered to exclude sites which did not have at least one sample in at least four separate years, as those excluded sites would have minimal influence on any overall trend. The corresponding modelled trend information is shown in Figure 4.22.2.

The data analysis approach followed that adopted for other freshwater concentration data (see Sections 4.4 and 4.14). No spatial aggregation of data was necessary. A generalised additive mixed model was fitted to the log10-transformed TU_{sum} data. The model-fitting process allowed analysis of the trends over time, seasonality and trends in the seasonality within the data. The model also accounted for the inherent correlation between observations over time from any particular site. These are more likely to be correlated with each other than with observations from other sites. Separate trends were fitted to CSF and non-CSF data within the same model.

The resulting predicted mean concentrations for each month were back-transformed to the original concentration scale. The results are presented in Figure 4.22.2 for both CSF and non-CSF sites. There was a relatively similar pattern of seasonality across both CSF and non-CSF sites. The non-CSF sites followed a more accentuated pattern, which is logical: there is more similarity within CSF sites than non-CSF sites. Overall, there is considerable seasonality in both parts of the data set. Both CSF and non-CSF sites also showed highest values in the very earliest part of the data (January to February 2016) and there may be some uncertainty in the laboratory analysis for this earlier period. Given the limited number of sites monitored overall and the high seasonality, it is not possible to conclude there is any significant overall trend.

Figure 4.22.2 Modelled trends for pesticides in freshwater expressed as summed toxic units (TUsum) for Catchment Sensitive Farming (top) and non-Catchment Sensitive Farming (bottom) sites (log10 y-axis scale). The graphs show trends based on the predicted mean concentrations for all months together with shading representing 95% confidence intervals (left) and for individual months coloured by season (right)



The result in the dashboard for pesticides represents the observed statistically significant trends. Therefore, the assignment of 'no observed change in concentrations' is given.

4.22.4 Thresholds

For this analysis, a Uniform Principle value (UP) of 0.1 TU is taken as an indicative threshold as chronic effects have been considered. This value is based on the Uniform Principle stating that the 'toxicity/exposure ratio should be less than 10 for long-term exposure' (EC, 2011d).

A median TUsum value was calculated for 32 sites based on LCMS data for 2022. These represented sites for which there were sufficient samples in 2022 to enable the median TUsum value to be determined. Of the 32 sites, the majority (91%) were above the threshold of 0.1; only 3 sites were below the threshold. The percentage result is used for the corresponding entries in the dashboard.

The result indicates very high potential risk in freshwater from mixtures of plant protection active substances. Several factors need to be considered in relation to this: Some of the substances detected and included in the calculation of the TU_{sum} may be present as a result of uses other than within plant protection products. The 2 substances that contributed significantly to the high TU_{sum} observed at many of the sites considered were fipronil (and it metabolites) and imidacloprid. The use of both of these chemicals is now primarily as veterinary medicines rather than in plant protection products. In addition, the approach used for this assessment needs to be taken into account. For example, the method used assumes additive toxicity between the substances present and the analysis is based on screening rather than quantitative data (see Section 4.22.1).

4.23 Pesticides and biocides in red kite: secondgeneration anticoagulant rodenticides

Second-generation anticoagulant rodenticides



4.23.1 Data source

Red kites (*Milvus milvus*) are monitored for their exposure to SGARs because their prey includes rats, which are target species subject to control using SGARs. Secondary exposure in red kites is widespread in England and lethal secondary poisoning does occur (<u>Ozaki and others, 2023b</u>; <u>Walker and others, 2021</u>; <u>Walker and others, 2022</u>).

Livers were collected from individual red kites found dead throughout England and submitted to the PBMS or WIIS. The majority of animals died as a result of collisions or starvation, but some birds have died from other causes, such as rodenticide poisoning.

Under WIIS, red kite carcasses are submitted to the scheme as part of investigations into suspected poisoning incidents, although the suspected active ingredient involved may or may not have been a SGAR. The WIIS samples are not necessarily the absolute total number of suspected poisoning cases per annum, as submissions are dependent on animals being found and subsequently reported.

Necropsy data for red kites submitted to the PBMS have been conducted largely by the Institute of Zoology (IoZ), and post-mortem examinations of birds submitted to the HSE's WIIS include birds necropsied by APHA.

Data on SGARs in the livers of 170 red kites have been provided by the UKCEH from the PBMS and by Fera Science Ltd from WIIS (Fera, 2024) on 92 and 78 birds, respectively, and these have been collated as part of the PBMS (UKCEH, 2023). Data on concentrations of SGARs in red kites are reported by the UKCEH in a series of reports (Ozaki and others, 2023b; Walker and others, 2021; Walker and others, 2022).

The monitoring conducted by UKCEH has been financially supported by NERC, Natural England and the Campaign for Responsible Rodenticide Use. Chemical analysis has been supported by Natural England as part of H4.

Compared with the previous round of reporting the H4 indicator (<u>Environment Agency</u>, <u>2021</u>), some samples have been removed from the 2018 data as their country location was unknown.

4.23.2 Data structure

The data consist of measured concentrations of 5 SGARs – brodifacoum, bromadiolone, difenacoum, difethialone, and flocoumafen – in the livers of a variable number of

individuals. Summed SGAR concentrations (SUM SGARs) represent the summed concentrations of these 5 compounds.

Data are available for each year between 2015 and 2021 and are reported as $\mu g/kg$ wet weight.

The LoD for each individual SGAR was 1.7 μ g/kg wet weight in 2015 for the analyses by both Fera and UKCEH. For later years, the corresponding LoDs were between 0.6 and 0.8 μ g/kg wet weight for the Fera analysis. The UKCEH LoDs from 2016 ranged from 1.3 to 1.6 μ g/kg wet weight for all substances except for difethialone; for this substance, the LoDs ranged from 2.6 to 3.1 μ g/kg wet weight.

The median number of different compounds detected in the liver samples was 3 for each year, and there were only 2 samples – one in 2016 and one in 2019 – out of 170 birds in which no SGAR was detected. Non-detected concentrations were assigned a zero value when used in the calculation of the summed SGARs.

4.23.3 Exploration of change in chemical concentrations over time

The distribution of data by year for red kites is summarised in Table 4.23.1 and shown in Figure 4.23.1.

Year	n	Mean	SD	Median	Min	Max	Q1	Q3
2015	21	411	344	309	50.2	1267	127	638
2016	16	499	526	202	0	1800	111	749
2017	23	268	337	138	5.30	1150	74.0	297
2018	31	293	293	190	16.0	1218	134	319
2019	27	221	226	114	0	787	14.9	409
2020	17	524	300	490	15.7	1086	308	727
2021	35	519	555	386	68.0	3224	260	560

Table 4.23.1 Summary statistics for concentrations of SUM SGARs in the livers of red kites (μ g/kg wet weight) from England¹

¹n: number of samples analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.23.1 Scatterplot of concentrations of SUM SGARs in the livers of red kites (μ g/kg wet weight, log10 y-axis scale) from England from 2015 to 2021. Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year (diagram courtesy of UKCEH). The 2 samples with non-detected SUM SGARs concentrations in 2016 and 2019 are shown by white dots using a default value of 0.6 μ g/kg wet weight – the lowest LoD for a single SGAR – to aid their representation (diagram courtesy of UKCEH)



For the time trend analysis, the data for concentrations of SUM SGARs were logarithmically transformed. However, even the log-transformed data were not normally distributed, and the assumptions of a linear model, particularly the normality of residuals, were not met. The normality of residuals was not respected even for a GAM. Therefore, change in concentrations of SUM SGARs in the livers of red kites over time was analysed by non-parametric Spearman's rank correlation. The result showed no statistically significant time trend over the years from 2015 to 2021 (p = 0.06).

The results in the dashboard represent the observed long-term trends. Therefore, the assignment of 'no observed change in concentrations' for SUM SGARs is given in the dashboard.

4.23.4 Thresholds

There are no statutory threshold values established for SGARs in biota. However, the proportion of red kites in which SGARs are diagnosed as a contributory cause of death is a relevant metric that is considered suitable for use in the dashboard.

All of the red kites that were analysed were subject to a post-mortem examination conducted by wildlife veterinarians or trained pathology staff at the IoZ, UKCEH, APHA, and Fera Science Ltd. During the necropsy, non-trauma-related macroscopic haemorrhaging that was consistent with anticoagulant-rodenticide-induced anticoagulation was noted. Birds were classed as individuals in which SGARs were implicated as a contributory cause of death (an SGAR-poisoned bird) if such haemorrhaging was present
and if anticoagulant rodenticide residues (of any magnitude) were detected in the liver. Presence of signs of SGAR poisoning for individual samples was classed into 3 categories: yes, no or uncertain. Birds with haemorrhaging related to trauma and detected levels of SGARs may also have been detrimentally affected by exposure to SGARs, but would not be classified as SGAR-poisoned birds for the purposes of this metric.

The percentages of red kites in which SGARs were implicated as a contributory cause of death by year are given in Table 4.23.2. This proportion is calculated by dividing the number of poisoned birds by the number of samples analysed excluding uncertain cases. The number of uncertain cases was higher in 2021 than in the other years owing to a greater number of birds being in an advanced state of decomposition, hindering assessment of haemorrhaging.

Table 4.23.2 Summary of the percentages of red kites in which second-generation anticoagulant rodenticides were implicated as a contributory cause of death¹

Year	n	Yes ²	Uncertain ²	No ²	Percentage (%) of birds with SGARs implicated as a contributory cause of death ³
2015	21	7	1	13	35.0
2016	16	7	1	8	46.7
2017	23	4	0	19	17.4
2018	31	8	0	23	25.8
2019	27	2	0	25	7.4
2020	17	3	1	13	18.8
2021	35	4	5	26	13.3

¹n: number of samples analysed; SGARs: second-generation anticoagulant rodenticides.

²Yes, uncertain and no: categories denoting whether SGARs are implicated as a contributory cause of death for red kites.

³Calculated from the number of samples categorised as 'yes' divided by the total number of samples excluding uncertain cases.

The proportion of red kites in which SGARs were implicated as a contributory cause of death in 2021 - 13.3% – has increased from that previously reported of 7.4% for 2019 (Environment Agency, 2021). To assess the change in such percentage results from 2015 to 2021, a logistic regression model was fitted to the data. The result showed a statistically

significant decrease in the proportion of birds in which SGARs were implicated as a contributory cause of death over these years (p-value of analysis of deviance for GLM fits <0.01).

The proportion of red kites in which SGARs were implicated as a contributory cause of death in 2021 is used for the dashboard entry (13%).

However, it is worth noting that this threshold assessment approach is based on a correlation with an observed effect (that is, where SGAR poisoning is implicated as a contributory cause of death), as opposed to solely assessing measured concentrations in red kites against a threshold concentration. Therefore, the trend in potential risk will not necessarily match that relating to concentration levels over time. Indeed, a statistically significant decrease in potential risk is observed in contrast to the steady levels of SGAR concentrations seen in these birds (Section 4.23.3).

4.24 Pesticides and biocides in red fox: secondgeneration anticoagulant rodenticides

Second-generation anticoagulant rodenticides



4.24.1 Data source

The red fox (*Vulpes vulpes*) is an omnivore that eats small mammals, including rats and mice living in proximity to humans. They may be directly exposed to SGARs through eating unprotected bait and secondarily through eating rodents and other contaminated prey. Foxes, therefore, provide a measure of environmental exposure to SGARs across multiple uptake pathways.

Red fox livers from England were acquired by Fera Science Ltd (Fera) via two sources: (1) WIIS and (2) APHA.

Under WIIS, red fox carcasses are submitted to the scheme as part of investigations into suspected poisoning incidents, although the suspected active ingredient involved may or may not have been a SGAR. Investigations in England are conducted by Natural England and involve the collection of such animals. The samples are not necessarily the absolute total number of suspected poisoning cases per annum, as submissions are dependent on animals being found and subsequently reported. Foxes were found dead at various rural and urban locations. Livers were collected and analysed from individuals submitted to the WIIS each year.

The Animal and Plant Health Agency undertake surveillance of *Echinococcus multilocularis* in red foxes on an annual basis. The agency uses a network of land managers, who cull foxes for pest control purposes, to supply the required carcasses. Shooting for this survey typically occurs between October and early March. A subset of these shot foxes was selected by APHA – providing a spread of geographic location, gender, weight and overall condition of the fox – and their livers were used for the analysis of SGARs. Chemical analysis of these samples was supported by Natural England.

The use of these 2 existing opportunities to look at the exposure of red foxes to SGARs is in an exploratory phase to ascertain their suitability for informing the indicator. Previously, only WIIS information was available for consideration under the indicator, although there were not enough data to report a trend (<u>Environment Agency, 2021</u>). Since previous reporting, we have also reassigned some of the samples to different years of collection.

4.24.2 Data structure

The data consist of measured concentrations of 5 SGARs – brodifacoum, bromadiolone, difenacoum, difethialone, and flocoumafen – in the livers of a variable number of

individuals for the years from 2015 to 2022. Summed SGAR concentrations (SUM SGARs) represent the summed concentrations of these 5 compounds.

The WIIS samples cover the complete time period and were collected throughout the year, that is spanning several months.

Those samples collected by APHA are for 2020 and 2021. However, these years represent samples collected during targeted campaigns over a single winter period; that is, a single sample was collected in November 2020 and the rest throughout December 2020, January 2021 and the first week of February 2021. For some APHA locations, more than one sample was collected on a single occasion and/or within a year.

For consistency, the data are assigned to the different years in which they were collected, and the WIIS and APHA data are treated as separate entities within this report.

Data are reported as mg/kg wet weight.

For the WIIS fox data, the LoDs were variable between samples, and/or individual substance. The LoDs for individual substances were not reported as this is not a requirement of the scheme. An LoD was only reported for a sample for which there were no detections of all 5 SGARs; this applied to 6 samples and the LoDs for these ranged from 0.0006 to 0.03mg/kg wet weight.

For the APHA fox data, the LoDs for individual SGARs generally ranged from 0.002 to 0.001mg/kg wet weight, though some of the LoDs for bromadiolone and flocoumafen also reached down to 0.0002mg/kg wet weight and about two thirds of the results for difethiolone were below an LoD of 0.01mg/kg wet weight.

For the individual SGARs, brodifacoum, bromadiolone, difenacoum, difethialone, and flocoumafen were each detected in 85, 90, 58, 17, and 5% of samples, respectively.

In a sample where one or more SGARs were detected, the results for any individual SGARs reported as below the LoD were assigned a value of zero for the purposes of summing. The treatment of samples where no SGARs were detected is explained in Section 4.24.3.

4.24.3 Exploration of change in chemical concentrations over time

The distribution of data for SUM SGARs by year is summarised in Table 4.24.1 and shown in Figure 4.24.1. For those samples with no SGARs detected (n = 6), the concentration was recorded as zero for the calculations in Table 4.24.1; for visualisation of concentrations on a log scale (Figure 4.24.1), a value of 0.00000001mg/kg wet weight was used in these cases.

Observations below the LoD were not replaced with other values for estimating a trend over time. A linear model was fitted to the log of observations which maximised the likelihood of values at the observed concentration for results above the LoD, and maximised the likelihood of values below the reported LoD for samples in which SGARs were not detected.

Table 4.24.1 Summary statistics for concentrations of SUM SGARs in the livers of red foxes
(mg/kg wet weight) from England ¹

Sample source	Year	No. of sites	n	Mean	SD	Median	Min	Мах	Q1	Q3
WIIS	2015	3	3	0.138	0.121	0.190	0	0.224	0	0.224
WIIS	2016	2	3	0.314	0.437	0.120	0.00700	0.814	0.00700	0.814
WIIS	2017	6	7	0.674	0.679	0.608	0.0160	1.60	0.0190	1.33
WIIS	2018	8	10	1.04	1.31	0.520	0	3.07	0.00200	2.81
WIIS	2019	16	21	0.610	0.953	0.217	0	3.43	0.0630	0.678
WIIS	2020	18	21	1.88	4.48	0.176	0	16.4	0.0360	1.21
WIIS	2021	20	24	1.74	2.58	0.455	0	10.5	0.0350	3.39
WIIS	2022	7	7	1.10	1.40	0.503	0.0100	3.86	0.105	2.00
APHA	2020	18	32	0.559	0.794	0.111	0.00600	3.08	0.0610	0.875
APHA	2021	30	57	0.479	0.540	0.297	0.00110	2.69	0.0796	0.745

¹n: number of individuals analysed; mean: arithmetic mean; SD: standard deviation; min: minimum value; max: maximum value; Q1: lower interquartile range value; Q3: upper interquartile range value.

Figure 4.24.1 Box plots of concentrations of SUM SGARs in the livers of red foxes from England from 2015 to 2022 in samples from the Animal and Plant Health Agency (APHA) and the Wildlife Incident Investigation Scheme (WIIS); the boxes represent the median and first and third quartiles of observations on a log10 y-axis scale; the boundaries of the whiskers are at the minimum and maximum values that are within one and a half times the interquartile range of the first and third quartiles – observations outside of this range are shown as points (diagram courtesy of Fera)



The summed SGAR concentrations in the livers of red foxes from the APHA samples were broadly similar to those in the WIIS samples. There was no statistically significant difference found between the mean Ln-transformed APHA concentrations for 2020 and 2021 using a t-test (p >0.95).

Analysis of trend over time was conducted with the Ln-transformed concentrations against year using a Tobit regression model, assuming the results displayed a normal distribution on the log scale, to give a linear fit (Figure 4.24.2).

Figure 4.24.2 Scatterplots of the concentrations of SUM SGARs in the livers of red foxes from England in samples from the Animal and Plant Health Agency (APHA) for 2020 to 2021 and from the Wildlife Incident Investigation Scheme (WIIS) for 2015 to 2022 on a log10 y-axis scale; the black line across the plots for the different years represents a linear regression model applied to the data, with shading representing the 95% confidence interval (diagram courtesy of Fera)



At present there is insufficient knowledge on how representative the two different data sources are of the general fox population to allow inferences about trends – or lack of trends – in the fox population to be made based on those estimated from WIIS and APHA samples. Similarly, the relationship between APHA and WIIS samples and how, or if, trends estimated from the two sources can be combined is also unknown. Therefore, the trends for these sources have been considered separately.

There were insufficient years of data for the APHA foxes to interpret a trend over time.

For the WIIS data, all samples were included in the trend analysis. The result showed a statistically significant increase in the concentrations of SUM SGARs over the years from 2015 to 2022 (p = 0.034).

The results in the dashboard reflect the WIIS data, consistent with previous reporting (<u>Environment Agency, 2021</u>). Therefore, the assignment of 'increasing concentrations' for SUM SGARs is given in the dashboard.

The use of both WIIS and APHA samples to monitor the exposure of foxes to SGARs over time is still under investigation. Additionally, the following points must be taken into consideration when interpreting the results:

- 1. The APHA sample collection is confined to a specific sampling period in the year in comparison to WIIS samples and, therefore, seasonal differences would need investigating.
- 2. Samples are submitted to the WIIS scheme when there is a suspected case of poisoning, and rodenticides are a common means of poisoning. It follows that exposure to SGARs is expected to be higher in WIIS samples than non-WIIS samples, although this was not borne out by the current data set and further interrogation of the data is required to explore the usefulness of the WIIS data in monitoring exposure to SGARs e.g. in response to policy changes as the data are relative to each other year on year.
- 3. In relation to WIIS, there were only 3 samples from each year in 2015 and 2016 and 7 samples in each year in 2017 and 2022. These low sample numbers increase the uncertainty in the trend analysis.

4.24.4 Thresholds

Thresholds have not been established for summed or individual SGAR concentrations in fox livers. Therefore, no threshold value is proposed for this metric. The entry in the dashboard reflects that there is no value available for comparison.

5 Conclusion

To report our interim H4 indicator, we have updated our existing data sets, including new data for PCB 118 and PFAS, new species data for buzzards and estuarine and coastal fish, and enhancing existing data sets through the analysis of archived and newly collected samples.

There is some variability across the different assessments in terms of years assessed, congeners or substances reviewed for PBDEs, PCBs and PFAS and treatment of LoDs. There is also variability in the basis of the thresholds used. Our aim has been to make the assessment as comprehensive and consistent as possible using readily available data. The assessment for PFAS is considered under development, as this area is still evolving.

Many of our data sets are now showing statistically significant changes over time in chemical concentrations. For those that are not, this may be a consequence of some chemicals, such as PBT substances, being slow to respond to change, or that some management actions may be in their early stages of implementation. It could also indicate that further investigation is needed as to why levels are stable. Limited data has also affected the interpretation of results in some cases.

Potential risk is seen for all 3 chemical groups, based on comparison of chemical concentrations at sites or within individual animals against thresholds chosen for the purpose of this indicator. This is not unexpected given the choice of these substances as potential or known substances of concern.

For PBT substances, downward trends for PBDEs and PFOS are observed in freshwater and marine wildlife, except for PFOS in otters which shows no trend. The downward trend for PBDEs in mussels has lower certainty. Downward trends are also seen for PFOS in freshwater. No trends are observed for PCBs as a group; however, for the congener PCB 118, levels are decreasing in freshwater fish but upward trends are seen in harbour porpoise. An upward trend is also seen for mercury in mussels, though this may be influenced by recent reductions in monitored sites. It should be noted that the results for PBTs in offshore fish and harbour porpoise in the interim indicator are generally based on well-established data sets covering long periods (greater than 10 sampling years). Within those data sets, PBDEs and PCBs in offshore fish and PBDEs and PFOS in harbour porpoise show levelling off or increasing concentrations in more-recent years.

The percentage of sites or samples exceeding thresholds is very high for mercury in the freshwater and marine environments, although this is either not observed or not known for top predators in all compartments. The result for mercury in offshore fish (common dab), however, is based on a threshold that could be considered over-precautionary for the tissue examined. Medium to very high potential risk is presented by PCBs; thresholds were only available for the marine environment for this assessment. Low potential risk is observed for PBDEs and PFOS in offshore fish (common dab) and freshwater, respectively.

For metals, the trends over time are varied. Downward trends are observed for lead, cadmium, nickel, and zinc in freshwater, for lead in otters, and for lead and copper in mussels, though the result for copper in mussels has lower certainty. Lead also presents the majority of upward trends, which are seen in buzzards, freshwater fish, offshore fish (common dab), and harbour porpoise. Cadmium and zinc also have upward trends in offshore fish and mussels, respectively. Further investigation and increased monitoring may help provide a better understanding of the trends seen. The results for metals in offshore fish and harbour porpoise in the interim indicator are based on well-established data sets covering long periods – greater than 10 sampling years. Within those data sets, data for more-recent years for all metals in offshore fish, and for lead and nickel in harbour porpoise, suggest the need to review the situation over time as upward trends are observed.

The lack of thresholds relevant to many of the matrices covered in the indicator means it is often not possible to assess the potential risks that metals pose to wildlife. Recent levels of lead in buzzards and estuarine and coastal waters, and freshwater concentrations for lead, cadmium, nickel, and copper, show some but low potential risk. Zinc shows a medium to high percentage of sites exceeding thresholds in both water types. However, there has been more bias towards freshwater sites affected by abandoned metal mines in recent years in the freshwater monitoring, and the number of sites assessed for metals in estuarine and coastal waters is substantially lower compared with previous reporting.

The freshwater sites from which water samples are taken can be split into two types: those located in waters polluted by abandoned metal mines – as mentioned above – and those in other locations. Over the period from 2014 to 2022 for waters affected by abandoned metal mines, all metals show upward trends. For the same period in other waters not affected by abandoned metal mines, metal concentrations show overall downward trends. For waters affected by abandoned metal mines, their elevated levels of metals mean that they comprise a high proportion of those sites which exceed available thresholds; very few 'other' sites are above the corresponding thresholds.

Pesticides in freshwater and the biocidal SGARs in red kites show no statistically significant changes in concentrations over time. For SGARs in red foxes, a statistically significant upward trend is seen, although data for some years are few, increasing the uncertainty.

Percentage threshold exceedance suggests very high potential risk for pesticides in freshwater. However, there are some assumptions around the assessment, for example that additive toxicity occurs, to allow it to be based on exposure to multiple substances. In addition, some of these substances may have environmental presence because of sources other than their use within plant protection products, for example imidacloprid is now primarily used as a veterinary medicine. Potential risk is indicated for less than a quarter of individuals considered for assessing SGARs in red kites. In this case only, the risk is assessed using an approach which includes looking at related SGAR effects observed in the birds, as opposed to solely assessing exceedances of threshold concentrations. Therefore, the trend in potential risk does not necessarily match that relating to concentration levels over time. Indeed, a statistically significant decrease in

potential risk is observed in contrast to the steady levels of SGAR concentrations seen in these birds.

There remain data gaps for the terrestrial environment, and the baseline data for terrestrial species and estuarine and coastal fish are still being established. Representation of exposure at different trophic levels in the terrestrial environment needs improvement, although work such as that relating to honey monitoring and honeybees, for example, is starting to address this area. Exploration of the introduction of soil data remains a priority so that the entry point to exposure, at least to terrestrial wildlife, becomes known. This will also help contribute to the broader picture of the mobility of chemicals in the environment from source to receptor and their effects, in combination with other indicators under the Outcome Indicator Framework.

In addition, the specific monitoring activities that we depend on for these data have undergone challenges in recent years with the amount of available data decreasing. This is due to a range of issues, including pressures on the animals we monitor, the impact of the COVID-19 pandemic, rising costs to deliver the same monitoring, and extreme weather events that have stopped us from being able to do some of the surveys we depend on. Further work is needed to establish the optimal way to collect data to reflect changes in chemical presence in the environment owing to action taken to manage these substances.

When we last reported, we raised additional reporting improvements from assessing the previous data sets. These have been addressed through this round of reporting or are being considered as part of ongoing development on the indicator.

In particular, a whole suite of research work is underway on:

- Improving our sampling design and assessments to provide robust metrics.
- Improving our assessment of risk through the investigation of additional thresholds.
- Understanding emerging risks that may be of relevance to reporting and looking at ways to capture these across all compartments.
- Linking chemical exposure with observed effects on wildlife.
- Strengthening our terrestrial data further to improve the picture of chemicals in this environmental compartment.

We will continue to explore options for all points raised through work on the indicator and its 2020 independent review. We are working to find ways to integrate our data into other areas of scientific investigation and policy development, where possible. In particular, we will explore opportunities to link our chemical information with that relating to biodiversity, to understand the influences of chemicals on ecosystem health and help inform the picture around biodiversity protection.

Finally, we will take the indicator and its development back to expert committees for a second independent review before the next update.

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Appendix A Coverage of per- and polyfluoroalkyl substances under the 2024 indicator

PFAS name	PFAS	Buzzards	Red	Freshwater	Freshwater	Otters	Estuarine and	Offshore	Harbour
	acronym		fox		fish		coastal fish	fish	porpoise
Perfluorooctanesulfonic	PFOS	Yes	Yes	Yes	Yes	Yes	Yes	Yes ³	Yes ³
acid									
Perfluorooctanoic acid	PFOA	Yes	Yes	Yes	Yes	Yes		Yes ³	Yes ³
Perfluorononanoic acid	PFNA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorodecanoic acid	PFDA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluoroundecanoic acid	PFUdA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorododecanoic acid	PFDoA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorotridecanoic acid	PFTrDA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorotetradecanoic acid	PFTeDA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorooctanesulfona-	PFOSA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
mide									
8:2 Fluorotelomer sulfonic	8:2 FTS		Yes		Yes	Yes		Yes	Yes
acid									
Perfluorohexanoic acid	PFHxA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluorobutanoic acid	PFBA	Yes	Yes		Yes	Yes		Yes	Yes
Perfluorohexanesulfonic	PFHxS	Yes	Yes		Yes	Yes		Yes ³	Yes ³
acid									
Perfluorobutanesulfonic	PFBS	Yes	Yes		Yes	Yes		Yes ³	Yes ³
acid									
4:2 Fluorotelomer sulfonic	4:2 FTS		Yes		Yes	Yes		Yes	Yes
acid									
6:2 Fluorotelomer sulfonic	6:2 FTS		Yes		Yes	Yes		Yes	Yes
acid									

Table A.1 Per- and polyfluoroalkyl substances (PFAS) analysed in each matrix¹

PFAS name	PFAS	Buzzards	Red	Freshwater	Freshwater	Otters	Estuarine and	Offshore	Harbour
	acronym		fox		fish		coastal fish	fish	porpoise
Perfluorobutanesulfona- mide	FBSA		Yes		Yes	Yes		Yes	Yes
Perfluorohexanesulfona- mide	FHxSA		Yes		Yes	Yes		Yes	Yes
3-Perfluoroheptylpropanoic acid	7:3 FTCA		Yes		Yes	Yes		Yes	Yes
9-Chlorohexadecafluoro-3- oxanonane-1-sulfonic acid	F-53B								
Perfluoropentanoic acid	PFPeA	Yes	Yes		Yes	Yes		Yes	Yes
Perfluoroheptanoic acid	PFHpA	Yes	Yes		Yes	Yes		Yes ³	Yes ³
1-Propanaminium, N- (carboxymethyl)-N.N-	6:2 FTAB								
dimethyl-3-									
[[(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)sulfonyl]									
amino]-, hydroxide (Capstone B):									
2-(Perfluorohexyl)ethanoic acid	6:2 FTCA								
Perfluoropropanoic acid	PFPrA								
Trifluoroacetic acid	TFA								
Perfluorodecanesulfonic acid	PFDS	Yes	Yes		Yes	Yes		Yes ³	Yes ³
Perfluoropentanesulfonic acid	PFPeS		Yes		Yes	Yes		Yes	Yes
Perfluoropentanesulfonic acid	PFHpS		Yes		Yes	Yes		Yes	Yes
Perfluorononanesulfonic acid	PFNS		Yes		Yes	Yes		Yes	Yes
3:3 Fluorotelomer carboxylic acid	3:3 FTCA		Yes		Yes	Yes		Yes	Yes
5:3 Fluorotelomer carboxylic acid	5:3 FTCA		Yes		Yes	Yes		Yes	Yes
Perfluoro-4-ethylcyclohexane- sulfonic acid	PFECHS		Yes		Yes	Yes		Yes	Yes

PFAS name	PFAS	Buzzards	Red fox	Freshwater	Freshwater	Otters	Estuarine and	Offshore	Harbour
2-(<i>N</i> -Methylperfluorooctane-	NMeFOSAA		Yes		Yes	Yes	Coastal lish	Yes	Yes
2-(<i>N</i> -Ethylperfluorooctane- sulfonamido)acetic acid	NEtFOSAA		Yes		Yes	Yes		Yes	Yes
Hexafluoropropylene oxide dimer acid	HPFO-DA		Yes		Yes	Yes		Yes	Yes
Dodecafluoro-3 <i>H</i> -4,8- dioxanonanoic acid	ADONA		Yes		Yes	Yes		Yes	Yes
Perfluoro{2-[(6-chloro- hexyl)oxy]ethanesulfonic acid}	9CI- PF3ONS		Yes		Yes	Yes		Yes	Yes
Perfluoro(11-chloro-3- oxaundecanesulfonic acid) (F53B minor)	11CI- PF3OUdS		Yes		Yes	Yes		Yes	Yes
Bis(perfluorohexyl)phosphinic acid	6:6 PFPi		Yes		Yes	Yes		Yes	Yes
Perfluorohexyl(perfluorooctyl)- phosphinic acid	6:8 PFPi		Yes		Yes	Yes		Yes	Yes
Bis(perfluorooctyl)phosphinic acid	8:8 PFPi		Yes		Yes	Yes		Yes	Yes
10:2 Fluorotelomer sulfonic acid	10:2 FTS				Yes ²	Yes ²		Yes	Yes
10:2 Fluorotelomer sulfonic acid	CI-PFOS				Yes	Yes		Yes	Yes
2-(Perfluorodecyl)ethanoic acid	FDEA 10:2				Yes	Yes		Yes	Yes

PFAS name	PFAS acronym	Buzzards	Red fox	Freshwater	Freshwater fish	Otters	Estuarine and coastal fish	Offshore fish	Harbour porpoise
Perfluoro-2-ethoxyethane- sulfonic acid	PFEESA				Yes	Yes		Yes	Yes
Perfluoro(2-ethoxy-2- fluoroethoxy)acetic acid ammonium salt	EEA-NH4				Yes				

¹The individual PFAS shown in bold are the 26 substances identified by the Emerging Risks and Persistent, Bioaccumulative and Toxic Substances Working Groups as a recommended minimum for including in any analysis of monitoring samples.

²Introduced as an additional substance as part of the analysis conducted in 2022. However, some archived samples from earlier years were included in that analysis.

³Original substances under the Cefas analytical suite. The analytical suite has grown over time to incorporate the analyses of further PFAS. However, archived samples from earlier years have been included in such later analyses; therefore, the number of PFAS do not necessarily increase over time based on sample year alone.

Appendix B Thresholds used in the 2024 H4 indicator

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Terrestrial	Biota	Buzzard, <i>Buteo buteo</i>	Mercury	6.2mg/kg dry weight	Based on a minimum indicative mercury concentration in liver of 2mg/kg wet weight; lowest species geometric mean above which adverse effects on reproduction may occur in non- marine bird populations	<u>Shore and</u> others, 2011	Mean wet weight to dry weight conversion factor for buzzards of 3.1 applied (<u>Scanlon</u> , <u>1982</u> ; <u>Monclús</u> , <u>Shore</u> <u>and Krone</u> , <u>2020</u>). Threshold not specific to buzzards; derived based on data for multiple species.
Metals	Terrestrial	Biota	Buzzard, <i>Buteo buteo</i>	Lead	18.6mg/kg dry weight	Indicative threshold based on concentrations of lead in liver of >6mg/kg wet weight that are associated with clinical poisoning in individual Falconiformes	Fransome and Pain, 2011	Mean wet weight to dry weight conversion factor for buzzards of 3.1 applied (<u>Scanlon</u> , <u>1982; Monclús, Shore</u> <u>and Krone, 2020</u>). This conversion factor has been widely used in studies on raptors (for example, <u>Krone</u> , <u>2018; Fransome and</u> Pain, 2011).

Table B.1 Summary of information relating to the thresholds used in the 2024 H4 indicator

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
Metals	Terrestrial	Biota	Buzzard, <i>Buteo buteo</i>	Cadmium	139.5mg/kg dry weight	Indicative threshold of 45– 70mg/kg wet weight in liver suggested for adult birds. The exceedance of this may be associated with adverse physiological effects in eiders, mallards, Leach's storm petrels, and starlings	<u>Wayland and</u> <u>Scheuhammer,</u> <u>2011</u>	Mean wet weight to dry weight conversion factor for buzzards of 3.1 applied (<u>Scanlon</u> , <u>1982</u> ; <u>Monclús</u> , <u>Shore</u> <u>and Krone</u> , 2020 This conversion factor has been widely used in studies on raptors (for example, <u>Krone</u> , <u>2018</u> ; <u>Fransome and</u> <u>Pain</u> , 2011). Threshold for adult full-grown birds; threshold for growing birds not defined but may be lower. The lower value of the effect concentration range is used.

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Terrestrial	Biota	Eurasian sparrowhawk, <i>Accipiter</i> <i>nisus</i>	Mercury	7mg/kg dry weight	Indicative threshold based on an ecotox value of 2mg/kg wet weight in liver; lowest species geometric mean for residues associated with impaired reproduction in nonmarine bird populations.	<u>Shore and</u> others, 2011	Wet weight to dry weight conversion factor mean (± standard error) of 3.52± 0.02 based on measurements on 1454 livers (<u>Shore,</u> <u>2020</u>). Threshold not specific to sparrowhawk; derived based on data for multiple species.
Metals	Terrestrial	Biota	Eurasian sparrowhawk, <i>Accipiter</i> <i>nisus</i>	Lead	21mg/kg dry weight	Indicative threshold based on concentrations of lead in liver of >6mg/kg wet weight that are associated with clinical poisoning in individual Falconiformes	Fransome and Pain, 2011	Wet weight to dry weight conversion factor mean (± standard error) of 3.52± 0.02 based on measurements on 1454 livers (Shore, 2020).

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
Metals	Terrestrial	Biota	Eurasian sparrowhawk, <i>Accipiter</i> <i>nisus</i>	Cadmium	160mg/kg dry weight	Indicative threshold of 45– 70mg/kg wet weight in liver suggested for adult birds. The exceedance of this may be associated with adverse physiological effects in eiders, mallards, Leach's storm petrels, and starlings	Wayland and Scheuhammer, 2011	Wet weight to dry weight conversion factor mean (± standard error) of 3.52± 0.02 based on measurements on 1454 livers (<u>Shore</u> , <u>2020</u>). Threshold for adult full- grown birds; threshold for growing birds not defined but may be lower. The lower value of the effect concentration range is used.
Pesticides and biocides	Terrestrial	Biota	Red kite, <i>Milvus milvus</i>	SGARs	Birds in which SGARs are diagnosed a contributory cause of death	Determined by expert judgement (see notes).	NA	During necropsy, non- trauma-related macroscopic haemorrhaging that was consistent with anticoagulant rodenticides induced anticoagulation was noted. Birds were classed as individuals in which SGARs were implicated as a contributory cause of death if such haemorrhaging was

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
								present and if SGARs residues (of any magnitude) were detected in the liver.
PBTs	Freshwater	Water	NA	PFOS	0.019µg/L	Equivalent empirical water concentration value to QS _{sec pois} value of 33µg/kg wet weight/annual average	See Appendix E	
Metals	Freshwater	Water	NA	Lead	1.2µg/L bioavailable	EQS/annual average	<u>UK</u> <u>Government,</u> 2015	
Metals	Freshwater	Water	NA	Cadmium	0.25µg/L dissolved	EQS/annual average	<u>UK</u> <u>Government,</u> 2015	
Metals	Freshwater	Water	NA	Copper	1µg/L bioavailable	EQS/long-term mean	UK Government, 2015	
Metals	Freshwater	Water	NA	Zinc	10.9µg/L bioavailable	EQS/long-term mean	<u>UK</u> <u>Government,</u> <u>2015</u>	An added risk approach is used for this assessment, that is background concentrations are taken into account.
Metals	Freshwater	Water	NA	Nickel	4 μg/L bioavailable	EQS/annual average	<u>UK</u> <u>Government,</u> 2015	

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
Pesticides and biocides	Freshwater	Water	NA	Range of plant protection products	UP value of 0.1	Chronic risk limit	European Commission, 2011d	TU _{sum} compared with UP. The TU _{sum} is calculated based on comparison of concentrations against chronic endpoints, such as NOECs.
PBT	Freshwater	Biota	Roach, <i>Rutilus rutilus</i> ; brown trout, <i>Salmo trutta</i> ; chub, <i>Squalius</i> <i>cephalus</i>	Mercury	20µg/kg wet weight	Biota EQS/not specified	<u>UK</u> <u>Government,</u> <u>2015</u>	
PBT	Freshwater	Biota	Roach, <i>Rutilus rutilus</i> ; brown trout, <i>Salmo trutta</i> ; chub, <i>Squalius</i> <i>cephalus</i>	PBDEs	44µg/kg wet weight	QS _{sec pois} /not specified	European Commission, 2011c	
PBT	Freshwater	Biota	Roach, <i>Rutilus rutilus</i> ; brown trout, <i>Salmo trutta</i> ; chub, <i>Squalius</i> <i>cephalus</i>	PFOS	33µg/kg wet weight	QS _{sec pois} /not specified	European Commission, 2011b	

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Freshwater	Biota	Eurasian otter, <i>Lutra lutra</i>	Mercury	25mg/kg wet weight	Ecotox value in otter liver; threshold level above which some lethality and impaired reproduction may occur. Average for a sampled population.	<u>Shore and</u> others, 2011	
Metals	Marine	Water	NA	Lead	1.3µg/L dissolved	EQS/annual average	<u>UK</u> <u>Government,</u> <u>2015</u>	
Metals	Marine	Water	NA	Cadmium	0.2µg/L dissolved	EQS/annual average	<u>UK</u> <u>Government,</u> <u>2015</u>	
Metals	Marine	Water	NA	Copper	3.76µg/L where DOC is ≤1mg/L and 3.76+(2.677 x((DOC/2)– 0.5)) µg/L where DOC is >1mg/L	EQS/annual average	Maycock, Merrington and Peters, 2012; UK Government, 2015	
Metals	Marine	Water	NA	Zinc	7.9µg/L dissolved	EQS/annual average	<u>UK</u> <u>Government,</u> 2015	
Metals	Marine	Water	NA	Nickel	8.6µg/L dissolved	EQS/annual average	UK Government, 2015	

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Blue mussel, <i>Mytilus edulis</i>	Mercury	1.6µg/kg wet weight	Biota EQS converted by OSPAR Commission based on <i>Mytilus</i> being trophic level 2 rather than 4/not specified	OSPAR Commission, 2016	
PBT	Marine	Biota	Blue mussel, <i>Mytilus edulis</i>	PBDEs	BDE 28: 120µg/kg wet weight BDE 47: 44µg/kg wet weight BDE 99: 1µg/kg wet weight BDE 100: 1µg/kg wet weight BDE 153: 4µg/kg wet weight BDE 154: 4µg/kg wet weight	Canadian Federal Environmental Quality Guidelines adopted by OSPAR MIME as EACs/statistic not specified	Environment and Climate Change Canada, 2013; OSPAR Commission, 2020	Values are for fish and are adjusted for mussels based on their percentage lipid content against a value of 5% typical for fish

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Blue mussel, <i>Mytilus edulis</i>	PCBs	PCB 28: 67µg/kg lipid weight PCB 52: 108µg/kg lipid weight PCB 101: 121µg/kg lipid weight PCB 118: 25µg/kg lipid weight PCB 138: 317µg/kg lipid weight PCB 153: 1585µg/kg lipid weight PCB 180: 469µg/kg lipid weight	OSPAR EAC/statistic not specified	OSPAR Commission, 2023	
PBT	Marine	Biota	Mainly dab, Limanda limanda; flounder, Platicthys flesus; plaice, Pleuronectes platessa	Mercury	20µg/kg wet weight	Biota EQS/not specified	<u>UK</u> <u>Government,</u> <u>2015</u>	Estuarine and coastal fish

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Mainly dab, Limanda limanda; flounder, Platicthys flesus; plaice, Pleuronectes platessa	PBDEs	BDE 28: 120µg/kg wet weight BDE 47: 44µg/kg wet weight BDE 99: 1µg/kg wet weight BDE 100: 1µg/kg wet weight BDE 153: 4µg/kg wet weight BDE 154: 4 µg/kg wet weight	Canadian Federal Environmental Quality Guidelines adopted by OSPAR MIME as EACs/statistic not specified	Environment and Climate Change Canada, 2013; OSPAR Commission, 2020	Estuarine and coastal fish
H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
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РВТ	Marine	Biota	Mainly dab, Limanda limanda; flounder, <i>Platicthys</i> flesus; plaice, <i>Pleuronectes</i> platessa	PCBs	PCB 28: 67µg/kg lipid weight PCB 52: 108µg/kg lipid weight PCB 101: 121µg/kg lipid weight PCB 118: 25µg/kg lipid weight PCB 138: 317µg/kg lipid weight PCB 153: 1585µg/kg lipid weight PCB180: 469µg/kg lipid weight	OSPAR EAC/statistic not specified	OSPAR Commission, 2023	Estuarine and coastal fish

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Mainly dab, <i>Limanda</i> <i>limanda</i> ; flounder, <i>Platicthys</i> <i>flesus</i> ; plaice, <i>Pleuronectes</i> <i>platessa</i>	PFOS	33µg/kg wet weight	QS _{sec pois} /not specified	<u>EC, 2011b</u>	Estuarine and coastal fish
PBT	Marine	Biota	Dab, <i>Limanda</i> <i>limanda</i>	Hg	20µg/kg wet weight	Biota EQS/not specified	<u>UK</u> <u>Government,</u> <u>2015</u>	Offshore fish EQS relates to whole fish and indicator assessment is based on concentrations in dab muscle; therefore, the application of this threshold for the indicator can be considered an interim approach and over- precautionary

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Dab, <i>Limanda</i> <i>limanda</i>	PBDEs	BDE28: 2400µg/kg lipid weight BDE47: 880µg/kg lipid weight BDE99: 20µg/kg lipid weight BDE 100: 20µg/kg lipid weight BDE153: 80µg/kg lipid weight BDE 154: 80µg/kg lipid weight	Canadian Federal Environmental Quality Guidelines adopted by OSPAR MIME as EACs of BDE28: 120µg/kg wet weight BDE47: 44µg/kg wet weight BDE99: 1µg/kg wet weight BDE 100: 1µg/kg wet weight BDE153: 4µg/kg wet weight BDE 154: 4µg/kg wet weight	Environment and Climate Change Canada, 2013; OSPAR Commission, 2020	Offshore fish Thresholds converted from wet weight using a conversion factor of 20 based on a standard whole fish with a lipid content of 5% (EC, 2014)
PBT	Marine	Biota	Dab, <i>Limanda</i> <i>limanda</i>	PCBs	PCB 28: 67µg/kg lipid weight PCB 52: 108µg/kg lipid weight PCB 101: 121µg/kg lipid weight PCB 118: 25µg/kg lipid weight	OSPAR EAC/statistic not specified	OSPAR Commission, 2023	Offshore fish

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
					PCB 138: 317µg/kg lipid weight PCB 153: 1585µg/kg lipid weight PCB180: 469µg/kg lipid weight			
PBT	Marine	Biota	Dab, <i>Limanda</i> <i>limanda</i>	PFOS	33µg/kg wet weight	QS _{sec pois} /not specified	European Commission, 2011b	Offshore fish QS _{sec pois} is for whole fish and the threshold assessment is based on concentrations in liver, which are typically 3 times higher than for whole fish. Caution is therefore needed in interpreting this threshold assessment in terms of potential risk to predators as the result is likely to be over- precautionary.

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Harbour porpoise, <i>Phocoena</i> <i>phocoena</i>	PBDEs	1.5mg/kg lipid weight	Ecotox value; threshold level based on thyroid disruption in juvenile grey seals (<i>Halichoerus</i> <i>grypus</i>)/statistic not specified.	<u>Hall, Kalantzi</u> <u>and Thomas,</u> <u>2003</u>	
PBT	Marine	Biota	Harbour porpoise, <i>Phocoena</i> <i>phocoena</i>	PCBs (25 in total, including ICES-7)	9mg/kg lipid weight	Ecotox value for immunological effects in aquatic mammals	Kannan and others, 2000	A second threshold 41mg/kg lipid weight for reproductive effects in seals (<u>Helle, Olsson</u> <u>and Jensen, 1976</u>) is also considered in the assessment but is not used for the indicator dashboard.

H4 group	Environmental compartment	Matrix	H4 species	Chemical	Threshold value	Type of threshold/ statistic	Reference	Notes
PBT	Marine	Biota	Harbour porpoise, <i>Phocoena</i> <i>phocoena</i>	PFOS	1075µg/kg wet weight	Ecotox value; tentative critical concentration based on an effects of 775µg/kg wet weight in cetacean (dolphin) liver; see notes	<u>Lam and</u> others, 2016	Original value derived from NOAEL for rat with an assessment factor applied for cross- species extrapolation. This was based on a reference species with a mass of 185kg. The value has been converted into the threshold for the indicator based on harbour porpoises having an approximate average mass of 50kg.

¹ NA: not applicable; SGARs: second-generation anticoagulant rodenticides; EQS: environmental quality standards; UP: uniform principle; TU: toxic units; EC50: Half maximum effective concentration; PNEC: predicted no-effect concentration; NOEC: no-observed-effect concentration; QS_{sec pois}: second poisoning quality standard; DOC: dissolved organic carbon; FEQGs: Canadian Federal Environmental Quality Guidelines; OSPAR: Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic; MIME: Monitoring on Trends and Effects of Substances in the Marine Environment; EAC: environmental assessment criteria; NOAEL: no observed adverse effect level.

Appendix C Comparison of chemical concentrations in common buzzard with those in sparrowhawks

A study was carried out using existing data to investigate whether metal concentrations in common buzzard and sparrowhawks were similar both in their average concentrations and trends over time. There are pragmatic advantages of using buzzard rather than sparrowhawk as a sentinel species for the terrestrial environment, including the larger liver mass of buzzards, allowing a broader suite of chemical contaminant analysis to be carried out in an individual bird.

Mercury

Data on mercury concentrations in the livers of common buzzards and sparrowhawks collected over a similar time period were compared. Data on 20 non-starved, first-year female buzzards from 2006 to 2021 and 35 sparrowhawks of the same condition from 2005 to 2021 were used for this analysis. The data were transformed into natural logarithm values to correct the skewed distribution of the mercury concentrations, and the assumptions of a linear model were met after this transformation.

The changes in mercury concentrations over time were analysed with a linear model using the functions '*Im()*' and '*anova()*' from the 'stats' package of the software R (R Core Team, 2022). Moreover, the difference in concentrations between the two bird species was assessed with the Student's t-test with the function '*t.test()*' from the 'stats' package of the software R.

The model showed no statistically significant time trend for each of the two species over the years (Figure C.1). However, concentrations of mercury in the livers were significantly higher in sparrowhawks than buzzards (t = 4.91, p < 0.001).

Figure C.1 Scatterplots of concentrations of mercury (Hg) in the livers of 35 sparrowhawks and 20 buzzards (mg/kg dry weight, log10 y-axis scale) from England from 2005 to 2021; the data are for non-starved, first-year females. Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. Data for sparrowhawks are represented in blue, whereas those for buzzards are in brown (diagram courtesy of UKCEH)



Lead, cadmium and nickel

Data on lead, cadmium and nickel concentrations in the livers of common buzzards and sparrowhawks collected over a similar time period were compared. Data on 140 buzzards from 2006 to 2021 and 202 sparrowhawks from 2007 to 2021 were considered for the analysis of lead and nickel. However, 3 samples with extreme concentrations of lead in buzzard livers (>100mg/kg dry weight) were subsequently removed. For cadmium, data on 88 first-year buzzards from 2007 to 2021 and 125 first-year sparrowhawks from 2006 to 2021 were used. Data were log-transformed to correct the skewed distribution of the metal concentrations.

The assumptions of a linear model were met after the logarithmic transformation for lead and cadmium in buzzards and cadmium in sparrowhawks. The changes in these metal concentrations over time were analysed with a linear model using the functions '*lm()*' and '*anova()*' from the 'stats' package of the software R (<u>R Core Team, 2022</u>).

For nickel in buzzards and sparrowhawks and lead in sparrowhawks, change over time was analysed by the non-parametric Spearman's rank correlation test using the function *'cor.test()'* from the package 'stats' of the software R.

Moreover, the difference in concentrations of cadmium between the two bird species was assessed with the Student's t-test using the function '*t.test()*' from the 'stats' package of the software R. The corresponding differences for lead and nickel were reviewed with the non-parametric Wilcoxon Mann–Whitney test with the function '*wilcox.test()*' from the 'stats' package of the software R.

The models showed no statistically significant time trends for concentrations of the metals in each of the two species over the years (Figure C.2). For nickel, there was a decreasing trend observed for sparrowhawks, however this could be due to a difference in the LoDs between years. It is therefore difficult to draw a conclusion about the difference in the time trend of nickel concentrations between the two species (see also Section 4.12.3).

However, concentrations of lead and cadmium in the livers were significantly higher in buzzards than sparrowhawks (cadmium: t = 4.22, p <0.001; lead: U = 19776, p <0.001). There was no significant difference in nickel in the liver. However, the lack of statistical significance could be due to a high proportion of nickel concentrations below the LoDs.

Figure C.2 Scatterplots of concentrations of lead (Pb), cadmium (Cd) and nickel (Ni) in the livers of 202 sparrowhawks and 140 buzzards (mg/kg dry weight, log10 y-axis scale) from England from 2006 to 2021; lead values are restricted to 137 buzzards; cadmium values are restricted to 125 first-year sparrowhawks and 88 first-year buzzards. Box plots represent median and lower/upper interquartile range values, while the boundaries of the whiskers represent minimum and maximum values of concentrations by year. Data for sparrowhawks are represented in blue, whereas those for buzzards are in brown (diagrams courtesy of UKCEH)





Conclusion

These results suggest that buzzards might be used as an alternative environmental matrix for the time trend analysis of metals – except for nickel – in terrestrial predatory birds. In doing this, it is important to be aware that there are differences in the average metal concentrations in livers between the two species: sparrowhawks tend to have higher mercury concentrations but lower lead and cadmium concentrations than in buzzards.

However, the number of samples used to compare the changes in mercury concentrations over time was low. For the other metals, the majority of sparrowhawk samples were from the period 2007–2014, while the majority of buzzards were from 2016–2021. It is difficult to conclude from the current limited data whether exposure and the time trend differed between sparrowhawks and buzzards. Therefore, it would be informative to continue this comparison in the future.

Appendix D Perfluorooctanesulfonic acid, perfluorooctanoic acid and metals in freshwater: comparison of River Surveillance Network sites with other monitoring data

Metal, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) concentrations in freshwater taken at sites under different monitoring networks were examined. The site types were split into those under the River Surveillance Network (RSN), those relating to rivers affected by abandoned metal mines (WAMM sites) (only relevant to metals) and those remaining sites from other freshwater monitoring programmes ('other' sites).

Only 2 years of data were available under the RSN: for 2021 and 2022; baseline data are still being established. Additionally, the availability of non-WAMM, non-RSN data reduced after monitoring restarted in late 2020 following the first COVID-19 lockdown.

Analysis of the freshwater data showed that there were too few PFOS and PFOA data with limited geographical spread at other sites to make any comparisons at this stage.

The RSN samples had different metal concentrations compared with those from sites within the other networks; for RSN sites, annual geometric mean concentrations were lower for metals (Figure D.1), even compared with results from the 'other' sites. There are likely a range of reasons for this, primarily that the RSN is designed to represent the broadscale condition of the England river network, while conversely, the other sites – non-RSN and non-WAMM sites – are monitored under a range of other national and locally commissioned programmes, some of which are targeted towards likely impacted locations.

The handling of data for trend analysis is different to that described above. For trend analysis, the data are aggregated to a monthly time step and to a waterbody level, either with (Section 4.14.3) or without the RSN data. Trends were fitted for metals without the RSN data in the data set (Figures D.2 and D.3) to understand whether there would be major differences compared with the trends with RSN data included (see Section 4.14.3).

There were some differences in very recent trends between the analyses with and without the RSN data included. These did not affect the overall conclusions of the trend assessments. However, for zinc in particular, the overall downward trend in concentrations was stronger with the RSN data included, and conclusions were somewhat sensitive to assumptions about whether the seasonality pattern had changed in the period being considered (from 2014 to 2022). The complex seasonality pattern for zinc can be seen in the lower coloured plots in both Figure 4.14.3 and Figure D.3.

Further investigation is needed as the RSN network becomes established to understand any differences in overall concentrations and trends for the different monitoring network types. Figure D.1 Comparison of geometric mean metal concentrations at Environment Agency freshwater monitoring networks (μ g/L, log10 y-axis scale) – River Surveillance Network (RSN), Water and Abandoned Metal Mine (WAMM) related sites, and other sites; results are predicted values from a linear mixed-effects model with season, monitoring network ('group') and year as fixed effects and waterbody as a random effect. Each substance is described using a separate model; based on the bioavailable concentration for lead, nickel, copper, and zinc and the dissolved metal for cadmium



Figure D.2 Modelled trends for geometric mean dissolved cadmium and bioavailable lead concentrations (μ g/L, log10 y-axis scale) in freshwater for all samples and for those from WAMM and non-WAMM waterbodies (excluding RSN sites), shown as solid lines with shading representing 95% confidence intervals (top), and by season (bottom)



Figure D.3 Modelled trends for geometric mean bioavailable nickel, copper and zinc (µg/L, log10 y-axis scale) in freshwater for all samples and for those from WAMM and non-WAMM waterbodies (excluding RSN sites), shown as solid lines with shading representing 95% confidence intervals (top), and by season (bottom)



Spring 🛶 Summer 🛶 Autumn 🛶 Winter

Appendix E Derivation of an empirical water threshold for perfluorooctanesulfonic acid

As part of the EU EQS derivation process, QSs are derived for different protection goals. These may cover the protection of water- or sediment-dwelling communities, human health, or predators from secondary poisoning. Typically, the lowest QS indicating the most-sensitive protection goal is proposed as an environmental quality standard (EQS).

For PFOS, the EQS is a quality standard based on the protection of human health. However, to consider the risk to freshwater wildlife from PBT substances it is appropriate to use secondary poisoning quality standards (QS_{sec pois}). These standards help protect wildlife from the effects of eating prey contaminated by PBT substances.

A QS_{sec pois} for PFOS of $33\mu g/kg$ wet weight (<u>EC, 2011b</u>) has been derived through the EU EQS derivation process.

In the EQS dossier (<u>EC, 2011b</u>), equivalent water values to the QS_{sec pois} have been derived: 0.002μ g/L in freshwater and 0.00047μ g/L in marine waters. These values are considered tentative because of uncertainty around some of the data relating to biomagnification used for the conversion.

The Environment Agency has derived an approach to translate biota standards for PFOS into water concentration thresholds that equate to the same levels of protection. This is based on observations from co-located water and fish sampling data. PFOS is the only PBT substance for which a relationship between concentrations in water and fish was observed. This analysis applies to freshwater only.

Data from 65 freshwater locations sampled from 2015 to 2019 were used to derive the relationship, though not every site was monitored each year. Water samples were taken monthly. Fish were collected on one occasion per year at the same site, but not during the same visit as for water monitoring. The amount of fish data varied between sites: 40 sites had 1 year of data (between 3–5 samples), 8 sites 2 years (6–10 samples), 7 sites 3 years (11–15 samples), 9 sites 4 years (16–20 samples), and 1 site 5 years (21–25 samples) worth of data.

The data were plotted in two graphs (Figure E.1) and analysed using linear regression. The upper graph shown in Figure E.1 is based on overall site means – 1 point per site – and the lower is based on annual site means – 1 point per year per site. Additionally, these data were assessed using a Spearman's rank correlation analysis. The overall statistics from these analyses are given in Tables E.1 and E.2. Figure E.1 Overall site means (upper) and annual sites means (lower) of PFOS concentrations in freshwater and biota (fish) with linear regression analysis. The diagonal blue lines show the regression line with the grey shading either side giving the 95% confidence bands. Horizontal dashed lines mark the EQS (human health protection goal) and the $QS_{sec pois}$ of $33\mu g/kg$ wet weight. The vertical dotted lines indicate the water concentration corresponding to these thresholds based on the regression line.



Using the lines of best fit, an equivalent water concentration value of $0.019\mu g/L$ was derived for the $QS_{sec\ pois}$. There is slightly more variation in the lower plot (Figure E.1), but the results are very similar.

The linear models are statistically significant as both p-values are below the significance level of 5%. From the Spearman's rank correlation analyses, the correlation coefficients (r_s) show a strong relationship and the corresponding p-values indicate this is unlikely to be by chance (Tables E.1 and E.2).

Table E.1 Statistics from the linear regression model and Spearman's rank analysis of the overall sites means of PFOS concentrations in freshwater and biota (fish)

Test	Statistic	Result
Linear regression model	t-stat	8.449
Linear regression model	p-value	6.611 x10 ⁻¹²
Linear regression model	Model p-value	5.872 x10 ⁻¹⁵
Linear regression model	Multiple R-squared	0.5312
Spearman's rank correlation analysis	rs	0.7243
Spearman's rank correlation analysis	p-value	9.124 x10 ⁻¹²

Table E.2 Statistics from the linear regression model and Spearman's rank correlation analysis of the annual sites means of PFOS concentrations in freshwater and biota (fish)

Test	Statistic	Result
Linear regression model	t-stat	9.154
Linear regression model	p-value	6.061 x10 ⁻¹⁵
Linear regression model	Model p-value	5.617 x10 ^{−15}
Linear regression model	Multiple R-squared	0.4486
Spearman's rank correlation analysis	rs	0.7114
Spearman's rank correlation analysis	p-value	<2.2 x10 ⁻¹⁶

The water concentration value derived using this approach that is equivalent to the EQS is used as part of assessing classification in England, alongside the biota value. This is in agreement with the Water Framework Directive (Standards and Classification) Directions 2015 (<u>UK Government, 2015</u>), which allows for monitoring alternative biota or matrices

providing the equivalent level of protection is achieved. However, the EQS is based on the protection of human health and therefore not appropriate for use under H4.

A thresholds task and finish Group for the H4 indicator considered the use of the empirical water threshold corresponding to the $QS_{sec\ pois}$. In the sample data, there were fewer samples with high concentrations of PFOS in both matrices, which caused the confidence band width to increase on the regression plots as the values increased. Using the annual data as an example, the $QS_{sec\ pois}$ of $33\mu g/kg$ wet weight gives a 95% confidence range of approximately 0.0162 to 0.0232 $\mu g/L$ around the empirical value of 0.019 $\mu g/L$. Predicting the biota concentration from the empirical water standard value gives a 95% confidence range of between approximately 28 to 37.5 $\mu g/kg$.

The potential inclusion of the uncertainty from the 95% confidence band in the threshold was discussed because of the slight difference in results seen using the two different media. However, the use of the value derived from the line of best fit – or midline – was maintained as a more even approach for the following reasons:

- to reduce the chance of false positives and negatives
- because precaution is already incorporated into the QS_{sec pois}
- because it is consistent with the current compliance approach

A value of 0.019μ g/L is selected for use within the H4 indicator as a threshold for the protection of freshwater wildlife from the effects of secondary poisoning. This value is more stringent than that derived – through the EU EQS derivation process – to protect the freshwater community from the direct toxic effects of PFOS (<u>EC, 2011b</u>). It is therefore considered protective of wildlife from both routes of exposure.

Appendix F Marine stations map, station scatterplots and trend assessment p-values

The Clean Safe Seas Environmental Monitoring Programme (CSEMP) stations considered within this report are mapped in Figure F.1.

The map can be used alongside the scatterplots within this section to gain a spatial understanding of where the different trends are observed. The scatterplot figures are numbered here according to which main section the data are discussed within the report. For example, mercury in marine fish (dab) is covered under Section 4.9, therefore the corresponding diagrams can be found in Figure F.4.9.1. Stations numbered up to and including 494 are on the east coast; those numbered from 534 upwards are on the west coast. Trends for each station are assessed using 2 criteria (see Sections 4.9.3 and 4.20.3). The p-values for the first criteria are given with each corresponding station scatterplot in the figures here; those for the second are listed in Tables F.1 and F.2 and correspond to Sections 4.9.3 and 4.20.3, respectively.

Figure F.1 Map showing the Clean Safe Seas Environmental Monitoring Programme monitoring stations around the English coast; western stations are usually sampled in even-numbered years and eastern stations in odd-numbered years





Figure F.4.9.1 Scatterplot of Ln-transformed mercury concentrations in the muscle of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)









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Figure F.4.9.2 Scatterplots of Ln-transformed SUM 11PBDE residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)







Figure F.4.9.3 Scatterplots of Ln-transformed SUM 25PCB residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)





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8



2010 2012 2014 2016 2018

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Figure F.4.9.4 Scatterplots of Ln-transformed PCB118 residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)







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Figure F.4.20.1 Scatterplots of Ln-transformed lead residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)



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-4.5





a

-2.0

Figure F.4.20.2 Scatterplots of Ln-transformed cadmium residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)






2008

2012

2016

c

2020

-2.5 c 8 0 o

-3.5

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Figure F.4.20.3 Scatterplots of Ln-transformed nickel residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)









Figure F.4.20.4 Scatterplots of square-root-transformed copper residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)











Figure F.4.20.5 Scatterplots of zinc residues in the livers of dab at individual stations around England. The solid black line shows trends from a generalised additive model as a function of time (diagrams courtesy of Cefas)









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Table F.1 p-values for the second criteria of the trend assessments for persistent, bioaccumulative and toxic chemicals in offshore fish for each monitoring station

Station	Mercury	SUM 6PBDE	SUM 25PCBs	PCB 118
243	0.53	0.027	0.232	0.421
244	0.609	0.085	0.014	0.003
283	0	0	0.062	0.011
284	0.095	0.032	0.56	0.176
286	0.771	0	0	0
287	0	0.036	0.02	0.018
294	0	0.017	0.006	0.001
344	0.093	0.818	0.035	0.108
346	0.992	0.094	0.333	0.038
377	0.001	0.1	0.001	0.014
378	0.804	0.164	0.006	0.003
387	0.967	0.086	0.639	0.536
475	0.009	0	0.016	0.056
486	0.005	0.203	0	0
494	0.22	0.546	0.05	0.031
534	0.262	0.001	0.071	0.184
584	0.063	0.001	0	0
604	0.175	0.343	0.871	0.031
616	0.988	0	0	0

Station	Mercury	SUM 6PBDE	SUM 25PCBs	PCB 118
706	0.14	0	0	0
715	0.009	0.001	0.101	0.09
769	0.004	0.005	0.039	0.002
796	0.017	0.011	0.029	0.02
805	0.332	0	0	0

Table F.2 p-values for the second criteria of the trend assessments for metals in offshore fish for each monitoring station

Station	Nickel	Copper	Zinc	Cadmium	Lead
243	0.124	0.646	0.098	0.298	0.017
244	0.017	0.646	0.004	0.062	0
283	0.508	0	0.004	0.189	0.467
284	0.95	0.475	0.584	0.966	0.815
286	0.903	0.454	0.072	0.652	0.057
287	0.905	0.286	0.916	0.798	0.089
294	0.665	0.251	0.184	0.01	0.002
344	0	0	0.328	0.317	0.541
346	0.46	0.079	0.153	0.139	0.551
377	0	0.029	0	0.001	0
378	0.217	0	0.225	0	0.005
387	0.275	0	0.179	0	0.01

Station	Nickel	Copper	Zinc	Cadmium	Lead
475	0.021	0.179	0.121	0.007	0.882
486	0.002	0	0.365	0	0.059
494	0.35	0	0.848	0	0
534	0.292	0.29	0.084	0.005	0.085
584	0.092	0.045	0.913	0	0.012
604	0.028	0	0	0.897	0.386
616	0.003	0.004	0	0	0
706	0.006	0.413	0.236	0.891	0.027
715	0.333	0.349	0.203	0.201	0
769	0.066	0	0	0.004	0
796	0.512	0.011	0.007	0.881	0.38
805	0.411	0	0.458	0.114	0.365

Appendix G Water and Abandoned Metal Mines Programme sites

Figure G.1 Map showing the Water and Abandoned Metal Mines programme sites



WAMM sampling sites
Scottish and Welsh border



Table G.1 Number and percentage of Water and Abandoned Metal Mines Programme sites(WAMM) versus other sites (non-WAMM) monitored for lead in each year

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2014	122	942	11	89	1064
2015	114	1189	9	91	1303
2016	124	1108	10	90	1232
2017	119	810	13	87	929
2018	110	657	14	86	767
2019	104	671	13	87	775
2020	90	500	15	85	590
2021	136	332	29	71	468
2022	191	306	38	62	497

Table G.2 Number and percentage of Water and Abandoned Metal Mines Programme sites (WAMM) versus other sites (non-WAMM) monitored for cadmium in each year

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2014	125	1045	11	89	1170
2015	115	1213	9	91	1328
2016	125	1135	10	90	1260
2017	121	836	13	87	957
2018	112	686	14	86	798

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2019	105	690	13	87	795
2020	94	528	15	85	622
2021	136	345	28	72	481
2022	194	310	38	62	504

Table G.3 Number and percentage of Water and Abandoned Metal Mines Programme sites(WAMM) versus other sites (non-WAMM) monitored for nickel in each year

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2014	123	808	13	87	931
2015	114	1132	9	91	1246
2016	124	1070	10	90	1194
2017	118	774	13	87	892
2018	109	620	15	85	729
2019	104	658	14	86	762
2020	84	447	16	84	531
2021	132	209	39	61	341
2022	188	185	50	50	373

Table G.4 Number and percentage of Water and Abandoned Metal Mines Programme sites(WAMM) versus other sites (non-WAMM) monitored for copper in each year

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2014	124	853	13	87	977
2015	118	1210	9	91	1328
2016	128	1131	10	90	1259
2017	122	837	13	87	959
2018	113	690	14	86	803
2019	108	728	13	87	836
2020	85	499	15	85	584
2021	132	210	39	61	342
2022	188	187	50	50	375

Table G.5 Number and percentage of Water and Abandoned Metal Mines Programme sites(WAMM) versus other sites (non-WAMM) monitored for zinc in each year

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2014	124	854	13	87	978
2015	117	1198	9	91	1315
2016	127	1125	10	90	1252
2017	122	824	13	87	946
2018	112	677	14	86	789

Year	No. of WAMM sites	No. of non- WAMM sites	Percentage of WAMM sites (%)	Percentage of non-WAMM sites (%)	Total no. of sites monitored
2019	107	710	13	87	817
2020	85	493	15	85	578
2021	132	208	39	61	340
2022	188	193	49	51	381

List of abbreviations and acronyms

3:3 FTCA	3:3 fluorotelomer carboxylic acid (sometimes referred to as FPrPA 3:3)						
4:2 FTS	4:2 fluorotelomer sulfonic acid						
5:3 FTCA	5:3 fluorotelomer carboxylic acid (sometimes referred to as FPePA 5:3)						
6:2 FTAB tridecafluoroo	<i>N</i> -(carboxymethyl)- <i>N</i> , <i>N</i> -dimethyl-3-{[3,3,4,4,5,5,6,6,7,7,8,8,8- octyl)sulfonyl]amino}-1-propanaminium hydroxide (Capstone B)						
6:2 FTCA	2-(perfluorohexyl)ethanoic acid						
6:2 FTS	6:2 fluorotelomer sulfonic acid						
6:6 PFPi	bis(perfluorohexyl)phosphinic acid						
6:8 PFPi	perfluorohexyl(perfluorooctyl)phosphinic acid						
7:3 FTCA	7:3 fluorotelomer carboxylic acid (sometimes referred to as FHpPA 7:3)						
8:2 FTS	8:2 fluorotelomer sulfonic acid						
8:8 PFPi	bis(perfluorooctyl)phosphinic acid						
9CI-PF3ONS	perfluoro{2-[(6-chlorohexyl)oxy]ethanesulfonic acid}						
10:2 FTS	10:2 fluorotelomer sulfonic acid						
11CI-PF3OU	dS perfluoro(11-chloro-3-oxaundecanesulfonic acid) (F53B minor)						
25-YEP	25-Year Environment Plan						
ABC	ambient background concentration						
ADONA	dodecafluoro-3 <i>H</i> -4,8-dioxanonanoic acid						
APHA	Animal and Plant Health Agency						
ATSDR	Agency for Toxic Substance and Disease Registry						
BODC	British Oceanographic Data Centre						
CaCO₃	calcium carbonate						
Cd	cadmium						
Cefas	Centre for Environment, Fisheries and Aquaculture Science						
CEMP	Coordinated Environmental Monitoring Programme (OSPAR)						

CI-PFOS	perfluoro-8-chloroperfluorooctanesulfonic acid
CSF	Catchment Sensitive Farming
CSIP	Cetaceans Strandings Investigation Programme
Cu	copper
CUOP	Cardiff University Otter Project
Defra	Department for Environment, Food and Rural Affairs
DOC	dissolved organic carbon
EAC	environmental acceptable concentration
EC	European Commission
ECx	effect concentration for X% of the population
EEA-NH ₄	perfluoro(2-ethoxy-2-fluoroethoxy)acetic acid ammonium salt
EQS	environmental quality standard
F-53B acid	9-chloro-1,1,2,2,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-3-oxanonanesulfonic
FBSA	perfluorobutanesulfonamide (sometimes referred to as PFBSA)
FDEA 10:2	2-(perfluorodecyl)ethanoic acid
FHxSA	perfluorohexanesulfonamide (sometimes referred to as PFHxSA)
GAM	generalised additive model
gamm	generalised additive mixed model
GiA	grant in aid
GLM	generalised linear model
Hg	mercury
HPFO-DA	hexafluoropropylene oxide dimer acid
ICES	International Council for the Exploration of the Sea
loZ	Institute of Zoology
JNCC	Joint Nature Conservation Committee
KW	Kruskal–Wallis statistic

lme	linear mixed effects
Ln	natural logarithm
LoD	limit of detection
log10	logarithm to base 10
M-BAT	Metals Bioavailability Assessment Tool
max	maximum
MIME	OSPAR Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment
min	minimum
MRV	minimum reporting value
NERC	Natural Environment Research Council
NEtFOSAA	2-(N-ethylperfluorooctanesulfonamido)acetic acid
Ni	nickel
NMeFOSAA	2-(N-methylperfluorooctanesulfonamido)acetic acid
NOEC	no-observed effect concentration
OSPAR	The Convention for the Protection of the Marine Environment of the North- East Atlantic (OSPAR Convention)
р	p-value
Pb	lead
PBDE	polybrominated diphenyl ether
PBMS	Predatory Bird Monitoring Scheme
PBT	persistent, bioaccumulative and toxic
PCB	polychlorinated biphenyl
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid (sometimes referred to as PFBuA)
PFBS	perfluorobutanesulfonic acid (sometimes referred to as PFBuS)
PFDA	perfluorodecanoic acid (sometimes referred to as PFDcA)

- PFDoA perfluorododecanoic acid (sometimes referred to as PFDoDA)
- PFDS perfluorodecanesulfonic acid (sometimes referred to as PFDcS)
- PFECHS perfluoro-4-ethylcyclohexanesulfonic acid
- PFEESA perfluoro-2-ethoxyethanesulfonic acid
- PFHpA perfluoroheptanoic acid
- PFHpS perfluoroheptanesulfonic acid
- PFHxA perfluorohexanoic acid
- PFHxS perfluorohexanesulfonic acid
- PFNA perfluorononanoic acid
- PFNS perfluorononanesulfonic acid
- PFOA perfluorooctanoic acid
- PFODA perfluorooctadecanoic acid
- PFOS perfluorooctanesulfonic acid
- PFOSA perfluorooctanesulfonamide
- PFPeA perfluoropentanoic acid
- PFPeS perfluoropentanesulfonic acid
- PFPrA perfluoropropanoic acid
- PFTeDA perfluorotetradecanoic acid (sometimes referred to as PFTeA or PFTreA)
- PFTrDA perfluorotridecanoic acid (sometimes referred to as PFTriA)
- PFUdA perfluoroundecanoic acid (sometimes referred to as PFUnA)
- Q1 lower interquartile range
- Q3 upper interquartile range
- QS quality standard
- QSsec pois secondary
- rs Spearman's rank correlation coefficient
- RSN River Surveillance Network

SD	standard deviation
SGAR	second-generation anticoagulant rodenticide
SMASS	Scottish Marine Animal Stranding Scheme
TEQ	toxic equivalent
TFA	trifluoroacetic acid
UKCEH	UK Centre for Ecology and Hydrology
UK-SCAPE	UK Status, Change and Projections of the Environment
UKTAG	UK Technical Advisory Group
WAMM	Water and abandoned metal mines
WIIS	Wildlife Incident Investigation Scheme
Zn	zinc



Advanced materials

Materials – whether new or resulting from modifications to existing materials – that possess novel or enhanced properties compared with conventional materials resulting in superior performance.

Bioaccumulation

The movement of a substance into an organism from its environment.

Biocides

Biocidal products are used to protect people and animals, preserve goods, stop pests like insects or rodents, and control viruses, bacteria and fungi through a chemical or biological action.

Congener

One of a group of substances that are related in terms of origin and structure.

Dioxin-like PCBs

PCBs which have the same toxic action as 2,3,7,8-tetrachlorodibenzo-p-dioxin – the most toxic chlorinated dioxin congener – albeit at different potencies.

Dry weight

Weight of a biological sample after removing water.

Falconiformes

A taxonomic order of carnivorous birds.

False positive

An error where a result based on some data suggests the presence of a condition when in reality it is not present. For example, monitoring data may suggest a trend over time when in reality there is no trend. See p-value.

False negative

An error where a result based on some data indicates the absence of a condition when in reality it is present. For example, monitoring data may suggest no trend when in reality there is a trend. See statistical power.

ICES-7

Seven PCBs designated by the ICES as congeners commonly found the environment and therefore an indicator of the degree of contamination. The group include PCB118 which is the most toxic of the seven; without this congener the group is commonly referred to as the ICES-6. PCB118 is also one of a group of 12 PCBs known as dioxin-like PCBs.

Matrix

The type of sample in which the chemical is being measured, such as water or animal tissue.

Null hypothesis

An assumption that a particular effect in the underlying data is not present.

Order

Order is part of the taxonomic classification and is located between class and family.

OSPAR

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

Pesticides

Substances, also known as plant protection products, that are used to control pests, weeds and diseases. Examples include insecticides, fungicides, herbicides, molluscicides, and plant growth regulators.

p-value

The p-value is a reflection, expressed as a probability, of how incompatible some observed data (or a more extreme result) are with an assumed model of no effect (the null hypothesis). A lower p-value indicates greater incompatibility. A p-value is also conditional on all other assumptions of the null hypothesis model being correct.

For example, in the case of an indicator, the null hypothesis is that there is no change in concentration over time. In this report, generally a significance level of 5% is used to support decisions on whether there is no trend or a trend. If p is less than 0.05 then the data are fairly incompatible with the null hypothesis in its entirety. While the focus is often on the compatibility with the no change element of the null hypothesis, there are other implicit assumptions, for example independence of observations. The p-values are also dependent on the sample size of the study: the same magnitude of trend (effect size) may give a significant result with a larger sample size but a non-significant result with a smaller sample size.

The p-value represents the probability of the data given the model, not the probability of the model given the data. Therefore, while it is conventional to reject the null hypothesis when p<0.05, and thus accept the alternative hypothesis, p does not measure a probability

of the null hypothesis being true, nor is it a measure of an alternative hypothesis (in this instance a true underlying trend in the data) being true. In addition, the p-value does not reflect the size of an effect or the importance of a result.

Sample

In the context of this report, a sample is a physical piece of media, such as bird liver tissue, a volume of water, whole fish, etc., that is subsequently analysed for chemicals.

Statistical significance

See p-value.

Statistical power

Statistical power is the probability that, given a stated null hypothesis, and some observed data, one would correctly reject the null hypothesis of no effect. In the context of trend analysis, low statistical power typically means there is not enough evidence to correctly reject the null hypothesis, even when there is a genuine trend. Increasing sample size generally increases power and typically, power analysis is used prior to a study, given assumptions about the sample size and data. Greater unexplained variation in the data decreases power, however as with significance, power to correctly reject the null hypothesis is dependent on the form of the model as some components of overall variation in the data (for example, consistent differences between sites) do not necessarily reduce power to detect trend.

There is an intrinsic relationship between power and any significance criteria chosen for the p-value of the null hypothesis test: the lower the p-value, the greater the sample size required to achieve a specified power.

Stratified sampling

Where a subset of data proportionally reflects any different groups in the full data set.

TEQ

A system of toxic equivalents used to derive a quantity of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and PCB congeners as a single value based on the relative toxicity of all the congeners to the most harmful derivative, 2,3,7,8-tetrachlorodibenzo-p-dioxin. There are two systems commonly used: I-TEQ adopted by NATO in 1989 and WHO-TEQ which was published in 1998 and updated in 2005. We have used the TEQs for the PCBs only here to express concentrations in the environment in a way that is proportional to their toxicity.

Tobit regression model

A generic term for linear regression models fitted to censored data: where some observations are known only to be below or above a certain value. In the context of this

report, the most common situation is that some observations are below the limit of detection (LoD) for the analytical technique used.

Trophic level

A position within a hierarchy of levels that represents the feeding relationships of all organisms within an ecosystem; a stage in a food chain.

Waterbody

Surface waters and groundwaters are divided into subunits for the purpose of assessing water condition under the Water Environment (Water Framework Directive) Regulations 2017; these subunits are called waterbodies. Those referred to in this report relate to surface waters in a freshwater environment.

Wet weight

Whole weight, fresh weight and wet weight refer to the sample as it is received, regardless of whether it is a whole organism or parts of the organism.

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