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This report presents the results of marine and freshwater scientific work carried out by Marine Scotland Science.

A Review of Hazardous Substances in the Scottish Marine Environment: Update 2021

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Summary

1. This review is an update of the review undertaken in 2010 to identify what data is currently held for the Scottish marine environment on hazardous substances included on OSPAR and WFD lists and identify any gaps in information that may require further monitoring or method development.
2. The UK Clean Seas Environment Monitoring Programme (CSEMP) is operated so as to ensure a uniform monitoring programme across the United Kingdom providing the necessary data to fulfil the UK's obligations under the OSPAR Coordinated Environmental Monitoring Programme (CEMP) and for the Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)/UK Marine Strategy (MS).
3. OSPAR and MSFD/UK MS monitoring still focuses on the legacy contaminants and there has been no changes to contaminant monitoring requirements since the 2010 MSS review. A considerable amount of data is available for the legacy OSPAR Coordinated Environment Monitoring Programmes (CEMP) determinands (polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and the trace metals cadmium, mercury and lead) which are monitored annually in biota and sediment around Scotland. The legacy contaminant data was assessed recently as part of the Scottish Marine Assessment (SMA) 2020.
4. There are a number of national and international initiatives aimed at identifying Contaminants of Emerging Concern (CEC) which should be considered for inclusion in future monitoring programmes.
5. The ICES Working Group on Marine Sediment (WGMS) and the Marine Chemistry Working Group (MCWG) identified nine contaminants/contaminant groups that should be given consideration for addition to the OSPAR List of Contaminants of Concern/ Priority Action. OSPAR's Lists of Substances of Possible Concern and Priority Action has not changed for many years, but

should be updated in 2022/23. The contaminant groups being considered by MCWG/WGMS are: dechloranes, alternative brominated flame retardants, phosphorous flame retardants, antifoulants, per- and polyfluorinated substances (PFAS), benzotriazoles, siloxanes, anticorrosion agents and pharmaceuticals.

6. PFAS (including longer chain compounds) are still considered a priority, with PFOS the only PFAS to be currently included on the OSPAR pre-CEMP List, and also highlighted by OSPAR as a contaminant group that needs continued monitoring. The recent German specimen bank study focussing on the MCWG/WGMS CECs, highlighted PFAS and dechloranes as CECs to be considered for inclusion in monitoring programmes. In addition, the MSS 2010 hazardous substances review highlighted PFAS as the priority contaminant for method development and monitoring in Scotland.
7. The results from the screening of mussel samples for Phase 1 of the CONnECT project (CONtaminants of Emerging Concern and Threat in the marine environment) wide scope target and suspect screening initiative are now available, with further analysis being planned. It is hoped that the outcome of this project will inform the update of the OSPAR Lists of Contaminants of Concern/Priority Action. Contaminants detected in the Scottish mussels included methyl paraben (personal care product) and alkyl amines and quaternary alkylammonium surfactants. Neither contaminants have previously been highlighted by OSPAR or ICES as contaminants to be considered for inclusion in monitoring programmes
8. A recent study on pharmaceutical contaminants in the Clyde and Forth, showed that these were present in marine waters, with concentrations highest for caffeine and paracetamol. A global initiative looking at pharmaceuticals identified the 25 worldwide areas with highest concentrations for pharmaceuticals, a site in the Clyde was number 25 on this list. Again across the globe highest concentrations were for caffeine and paracetamol. Although pharmaceuticals were not detected in Scottish mussels from the CONnECT project, they were detected in English mussel samples.

Recommendations

1. PFAS are a potential issue for the Scottish marine environment and are still highlighted as priority CEC in a number of different forums. The development of a method for the analysis of PFAS was initiated at MSS in 2010, but due to a lack of staff resources this work stopped. However, this work should be finalised in 2021 and sediment and fish liver from the Clyde should be

analysed for PFAS to establish if they are present in the Scottish marine environment.

2. Dechloranes have also been highlighted for possible addition to monitoring programmes, from ICES work and the German specimen bank study. It may be possible to analyse dechloranes using a method similar to that already used at MSS for PCBs and PBDE analysis. MSS will investigate if it is possible to add dechloranes to our existing PCB/PBDE methods.
3. From the CONnECT project the CECs of most concern in Scottish mussel samples were methyl paraben and alkyl amines and quaternary alkylammonium surfactants, although not previously highlighted in other CEC initiatives. MSS should participate in any follow up work for the CONnECT project and consider if method development for methyl paraben and alkyl amines and quaternary alkylammonium surfactants is a priority.
4. Although not detected in Scottish mussels, pharmaceuticals have been detected in water samples from the Forth and Clyde and English mussel samples. MSS should consider if additional pharmaceutical monitoring is required in Scottish sediment and biota, taking into account future outputs from the SEPA initiative- One Health Breakthrough partnership (OHBP), which will link prescription practices to what we find in the environment.

Introduction

The marine environment acts as a sink for many hazardous substances, including persistent organic pollutants (POPs) and trace metals. Many of these compounds are toxic, persistent, and bioaccumulative and can be prone to long range transport. Their sources and pathways into the marine environment are diverse with most hazardous substances being produced by anthropogenic activities. Some are, or have been, produced intentionally (such as brominated flame retardants (BFRs)) whilst others are by-products of industrial processes (such as polycyclic aromatic hydrocarbons (PAHs) and dioxins). Direct or indirect release to rivers, from industrial discharges and from sewage works discharges, are a major source of a range of hazardous substances. Historically the biggest sources of hazardous substances to the Scottish environment were from heavy industry (steelworks, mining and gasworks), however increased regulation and closure of some of these industries has reduced contaminant inputs from these sources. Run-off from urban areas and atmospheric deposition continue to be diffuse sources of hazardous substances to the marine environment. Due to the persistent nature of many hazardous substances, high concentrations can still be found in the sediments of industrialised and urbanised estuaries as a result of historical inputs.

There are a number of regulations aimed at preventing hazardous substances entering the environment. Within the EU, the Directive for Regulation, Evaluation, Authorization and Restrictions of Chemicals (REACH; No. 1907/2006) concerns usage and production of chemicals. The EU REACH was brought into UK law on 1 January 2021 and is now known as UK REACH. The aim of REACH is to improve the protection of the environment and human health against potential risks posed by chemicals through early flagging. REACH requires the registration of substances, which are either imported or manufactured at a volume above one tonne per year. Substances which are likely to cause an unacceptable risk on human health and the environment may either become authorized or restricted. Substances which present an unacceptable risk to human health and the environment are classed as Substances of Very High Concern (SVHC) and are required to be phased out. If economically and technically feasible SVHCs will undergo a process of authorization to be replaced with less hazardous substances.

Although thousands of substances will enter the marine environment, only a few are included in national monitoring programs. Some contaminants have been monitored for many years and are called legacy contaminants. Those include trace metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Despite reductions in inputs, many legacy contaminants are still of concern, as they persist in the marine environment for many years. Others contaminants recently highlighted as cause for concern but not yet regulated are known as Contaminants of Emerging Concern (CECs). Over the last few years the ICES Working Group on Marine Sediment (WGMS) and the Marine Chemistry Working Group (MCWG) have included a term of reference dedicated to the review and occurrence of CECs in the marine environment, which is being considered to be an emerging issue. To date this non exhaustive list of CECs includes pharmaceuticals and personal care products (PCPs), per- and polyfluoroalkyl substances (PFAS), plasticizers, alternative flame retardants and organophosphate pesticides.

This review is an update of the review undertaken in 2010 (Webster *et al*., 2010) by MSS to identify the hazardous substances monitoring requirements, what hazardous substance data is currently held for the Scottish marine environment and identify any gaps in information that may require further monitoring or method development, taking into account current CEC identification and prioritisation work being undertaken nationally and internationally.

Hazardous substances monitoring requirements

Monitoring of hazardous substances in the Scottish marine environment is required to enable Scotland to assess what measures and actions are required in order to enable the Scottish vision of clean and safe seas to be delivered. In addition, such monitoring is required in order to ensure that Scotland fulfils its international obligations to OSPAR, the Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD)/UK Marine Strategy (MS) (OSPAR Commission, 1998, Water Framework Directive, 2000).

Analyses undertaken for the Clean Seas Environment Monitoring Programme (CSEMP) by Marine Scotland or the Scottish Environment Protection Agency (SEPA) aims to fulfil many of Scotland’s marine monitoring commitments under OSPAR, the WFD and MSFD/UK MS. The various CEC initiatives will also be reviewed with the aim of identifying CECs monitoring priorities for the Scottish marine environment. Early identification of these substances is important due to the time it takes to develop analytical methods and initiate monitoring programmes. In addition it can take years to gather enough data to make an assessment of any new CEC, at least 3 years of data is needed for a status assessment, longer for trend assessments. Furthermore there will be little toxicology data for many CECs. All this contributes to the significant lag from when a substance is identified as a CEC and determining its occurrence and impact on the marine environment.

Current drivers for contaminant monitoring

Stockholm Convention

The Stockholm Convention, a global treaty to protect human health and the environment, identified a list of 12 priority persistent organic pollutants (POPs) which governments are required to take measures to eliminate or reduce the release of into the environment (Stockholm Convention, 2008). The Stockholm Convention on POPs entered into force on 17 May 2004 and was signed by 151 Countries with the objective to protect human health and the environment from these particularly harmful organic pollutants. The UK ratified the treaty on 17 April 2005. The initial list of priority POPs includes eight pesticides (dieldrin, endrin, aldrin, chlordane, heptachlor, dichlorodiphenyltrichloroethane (DDT), mirex and toxaphene), two industrial chemicals (PCBs and hexachlorobenzene) and two unintentionally produced chemicals (polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzodifurans (PCDFs)). Since 2009, a further 16 POPs have been added to the list, including PBDEs, pentachlorobenzene (PeCB), hexachlorocyclohexane (HCH), perfluorooctane sulphonate (PFOS), short chain chlorinated paraffins (SCCPs), hexabromocyclododecane (HBCD) and endosulphan. Of these, PCBs and PBDEs are monitored routinely as part of CSEMP, with others being monitored as part of the Water Framework Directive (WFD).

Water Framework Directive (WFD)

The Water Framework Directive (2000/60/EC) was adopted by the European Parliament and the Council of the European Union on 22 December 2000. The Directive became law in Scotland during 2003 through the Water Environment and Water Services (Scotland) Act 2003 (the WEWS Act) which sets out the new arrangements for the protection of the water environment in Scotland. The WFD monitoring programme became operational in Scotland in 2007. The majority of monitoring for WFD is undertaken in Scotland by SEPA. The WFD has been retained in UK law following the UK’s exit from the European Union.

The WFD requires member states to monitor a range of priority substances (PS) discharged into the water environment with the objective being to reduce emissions of all priority substances and cease emissions of priority hazardous substances.

There are 45 PS, 21 of these are designated as priority hazardous substances (PHS). The Priority Substances Directive (2013/39/EU) sets out the Environmental Quality Standards (EQS) for PS for the different water body types (fresh, transitional and coastal) and is the boundary between a Good and Less Than Good standard. An additional requirement of WFD is that member states identify substances which are released in significant quantities in their waters, and to set appropriate WFD 'specific' pollutants (SP) EQSs for these substances. Concentrations of SPs in the environment are compared to the EQS and reported as part of overall ecological status. The priority substances and specific pollutants monitored in Scotland include metals, pesticides, industrial chemicals and pharmaceuticals. The over-all objective of the WFD is to achieve a good chemical status and a good ecological status. Exceedance of the EQS in a water body for a priority substance or specific pollutant will result in a less than good classification.

Measures are put in place as part of River Basin Management Planning (RBMP) to limit the release of contaminants to the water environment from point and diffuse sources (e.g. runoff from agricultural land). Depending on the substance, marketing and usage restrictions are also used to limit releases of priority substances to the water environment (e.g. plant protection products under European legislation 1107/2009).

SEPA are responsible for licensing discharges to the water environment, both freshwater and directly to transitional (bodies of water in the vicinity of river mouths that are saline in character) and coastal waters out to three nautical miles. SEPA monitors concentrations of contaminants in the water environment where they are considered to be an environmental pressure and compares the data to the EQS to determine the water quality status of the water body. WFD monitoring is discontinued where there is no risk of failing EQSs. In practice, concentrations of trace organic contaminants in Scottish marine waters are often below the analytical limit of detection. However, since the introduction of the EQS for biota for eleven lipophilic contaminant groups, future WFD monitoring will require biota monitoring.

A further requirement of the WFD is to collect data on substances included on the Watch List to confirm if these substances are widespread in the environment. This list includes substances that are suspected of posing significant risk to the aquatic environment. This list is updated every two years with the latest update done in 2020 (EUR-Lex - 32020D1161 - EN - EUR-Lex (europa.eu)). This list includes the following added chemicals:

- The sulphonamide antibiotic sulfamethoxazole and the diaminopyrimidine antibiotic trimethoprim;
- The antidepressant venlafaxine and its metabolite O-desmethylvenlafaxine
- A group of three azole pharmaceuticals (clotrimazole, fluconazole and miconazole)
- Seven azole pesticides (imazalil, ipconazole, metconazole, penconazole, prochloraz, tebuconazole, tetraconazole), and the fungicides famoxadone and dimoxystrobin.

SEPA are collecting data on Watch List Substances, though this data is not currently available.

UK Marine Strategy

The Marine Strategy Framework Directive (MSFD) took effect 17 June 2008 (Directive 2008/56/EC). Contaminant monitoring previously required for MSFD will continue as part of the UK Marine Strategy (MS), following the UK's exit from the EU. The aim of UK MS was to achieve Good Environmental Status (GES) in our seas by 2020. UK MS has three parts. Part 1: assessment of marine waters, sets out objectives for GES and targets and indicators to measure progress towards GES; Part 2: monitoring programmes to monitor progress against the targets and indicators; and Part 3: programme of measures and actions for achieving GES. The assessment to determine whether GES has been achieved is due to be published in 2024. Descriptor 8 (contaminants and their effects) is one of the eleven qualitative descriptors for determining GES. To monitor compliance with GES for Descriptor 8, common indicators for contaminants and biological effects should be measured in environmental samples and compared to assessment criteria. Descriptor 8 states that 'concentrations of contaminants are at levels not giving rise to pollution effects'. For hazardous substances the common indicators are heavy metal inputs, PCBs, PAHs, PBDEs and metals in sediment and biota, and organotins in sediment.

OSPAR

OSPAR is the convention for the protection of the marine environment of the North-East Atlantic. The Convention entered into force on 25 March 1998. Under the OSPAR Joint Assessment and Monitoring Programme (JAMP), contracting parties are committed to monitor specific chemicals in the marine environment (water, sediment and biota) (OSPAR, 2014). There are six OSPAR strategies; Assessment and Monitoring, Biological Diversity and Ecosystems, Eutrophication, Hazardous

Substances, Offshore Oil & Gas Industry and Radioactive Substances. The OSPAR Strategy for Hazardous Substances has a strategic objective which is:

- To prevent pollution of the OSPAR maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim to achieve concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances.

OSPAR list of substances of possible concern and priority action

There are currently 315 substances on the List of Substances of Possible Concern. These substances were selected due to their persistence, potential to bioaccumulate and toxicity using the OSPAR Dynamic Selection and Prioritisation Mechanism for Hazardous Substances (DYNAMEC) (OSPAR Commission, 2006). This procedure identified substances of concern using a set of cut-off values for persistence in the environment, tendency to bioaccumulate and toxicity, known as the PBT criteria. Persistence (P) reflects the potential for the substance to reach the marine environment and to be transported to remote areas as well as the potential for long-term exposure of organisms. P can be measured as the half-life ($T_{1/2}$) and if greater than 50 days in water is considered persistent. A substance is not considered to meet this criterion if both of the following conditions are met: (i) the half-life of the parent compound is less than 50 days and (ii) the resulting metabolites are not PBT chemicals.

Liability to bioaccumulate (B) can be predicted from the octanol water partition coefficient (Log K_{ow})[i], or from the bioconcentration factor (BCF)[ii]. Bioaccumulation is the sum of bioconcentration and biomagnification. The DYNAMEC criteria state that a Log K_{ow} greater than four and BCF greater than 500 l/kg indicate that there is a potential to bioaccumulate.

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[i] The octanol-water partition coefficient has been shown to correlate well with the adsorption of pesticides to soil and sediments. Unless other factors operate (such as rapid biodegradation), compounds with high K_{ow} values, such as organochlorine compounds, tend to bioaccumulate in the fat portion of organisms. K_{ow} was chosen to represent the solubility of a pesticide in fat. A compound is designated as fat-soluble when log K_{ow} exceeds four (with several exceptions) and is not so designated when log K_{ow} is less than three. Interpretation varies for values between three and four. High K_{ow} is known to be typical for persistent compounds that are largely (bio) accumulated in the fat portion of organisms. The ability of a compound to enter the cuticle of plants (the distribution of residues in plants) is also indicated by the K_{ow} value.

[ii] BCF is associated with hydrophobic chemicals having a tendency to partition from the water column and bioconcentrate in aquatic organisms. BCF is given by the concentration of the chemical in the organism at equilibrium divided by the concentration of the chemical in water. Bioconcentration is the result of direct uptake by the tissues exposed to water: the gills, lamellae and skin.

Toxicity is defined as the capacity of a substance to cause toxic effects to organisms or their progeny. Effects from toxic compounds can be either acute or chronic. These toxic effects include (a) reduction in survival, growth and reproduction (b) carcinogenecity, mutagenecity and tetragenecity and (c) adverse effects as a result of endocrine disruption. Acute toxicity is measured in the laboratory as lethal or sublethal toxicity resulting from intermittent or continuous exposure of a substance for a period of time shorter than the life cycle of the organism. This can be measured as the median Lethal Concentration (LC$_{50}$); using DYNAMEC procedures, LC$_{50}$ values of 1 mg l^{-1} should give rise to concern. Long-term chronic effects are defined as sublethal toxicity resulting from intermittent or continuous exposure of a substance for a period during a substantial proportion of the life cycle. This can be measured as the no-observable adverse effect concentration (NOEC) and the cut off value, using the DYMANEC procedure, is $\leq$ 0.1 mg l^{-1} (OSPAR, 2006).

However, since 2004 the DYNAMEC procedure has not been used to select or de-select substances from the OSPAR Lists. Due to the regulation of hazardous substances via REACH and work on identifying hazardous substances as part of the EU WFD processes, OSPAR decided to discontinue the DYNAMEC procedure and the OSPAR List of Substances of Possible Concern was temporarily suspended. However, in 2019 OSPAR undertook a review of the OSPAR List of Chemicals for Priority Action, to identify which substances needed additional action (OSPAR, 2019). Following this review it was decided that an update to the OSPAR List of Chemicals for Priority Action should be carried out in 2022/23.

The OSPAR List of Chemicals for Priority Action contains groups of compounds as well as specific compounds (see below). The 2019 OSPAR review of the OSPAR List of Chemicals for Priority Action has highlighted those substances that required continued monitoring (in bold), those that do not fulfil the PBT criteria (in italics), with all others requiring no further OSPAR action[iii]:

- **polycyclic aromatic hydrocarbons (PAHs)**
- **polychlorinated biphenyls (PCBs)**
- alkyl phenols
- **polychlorinated dibenzodioxins, dibenzofurans (PCDDs, PCDFs)**
- pesticides/biocides (endosulfan, hexachlorocyclohexane (HCH) isomers, methoxychlor, pentachloropnenol (PCP), trifluralin)

[iii] The MSS hazardous substance review includes information on the uses and sources of these substances.

- **metals (cadmium, lead, mercury)**
- **organometallic compounds including tributyltin (TBT)**
- musk xylene
- phthalates
- **brominated flame retardants (tetrabromobisphenol-A, hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs))**
- short chain chlorinated paraffins (SCCPs)
- *clotrimazole*
- **perfluorooctane sulphonates (PFOS)**
- *4-(dimethylbutylamino)diphenylamine (6PDD)*
- *Neodecanoic acid, ethenyl ester*
- Trichlorobenzenes

Six groups of substances require no additional OSPAR action (OSPAR, 2019) despite being considered to be hazardous as they are sufficiently regulated through REACH, WFD and the Stockholm Convention. This group includes pesticides/biocides (methoxyhlor, dicofol, endosulphan, trifluralin, pentachlorophenol (PCP), lindane), SCCPs, musk xylene and other musks, certain phthalates, trichlorobenzenes (TCB) and alkyl phenols (nonylphenol and nonylphenol ethoxylates (NP/NPE) and octylphenol). These are summarised below, and more information can be found in the OSPAR Review (OSPAR Commission, 2019) and the MSS hazardous substances review (Webster *et al.*, 2010).

The pesticides/biocides group includes active substances in plant protection and biocidal products, i.e. lindane, methoxychlor, trifluralin, dicofol, endosulphan and pentachlorophenol (PCP) and its salts and esters. These are banned for use on the European Market and the Stockholm Convention requires that these are phased-out globally.

SCCPs have been produced over the last 40 years for use in metal working fluids (70%), as plasticisers in paints, coatings (9%) and sealants (5%), and as flame retardants in rubbers (10%) and textiles (1.5%) and in leather processing (3%). Since 2017 SCCPs are identified as POPs under the Stockholm Convention and are identified as SVHC under REACH. Furthermore SCCPs are classed as PHS under the WFD.

The main use of nitro musks is in the fragrance industry; however they are not produced in Europe. They are used in a wide range of products including cosmetics, detergents and cleaning products. Musk xylene is primarily used in detergents and soaps. It was identified as a SVHC substance under REACH, however, it is not registered for use on the European Market. In addition there is currently no evidence to suggest other synthetic musks pose a risk to the marine environment.

Phthalate esters are widely distributed in the environment because of their properties and their common usage as plasticisers. The main sources of phthalates into the marine environment are through release *via* wastewater from production and processing activities and release from use and disposal of materials containing phthalate esters, including losses of plasticiser during the lifetime of products or during incineration or landfilling of refuse and other waste. Phthalates can leach from plastics and evaporate directly into the air and spread into the environment. However, phthalates do not meet the PBT-criteria nor do they in general present a risk to the marine environment, given the present level of exposure. However, some phthalate compounds are potential endocrine disruptors and are classed as SVHC under REACH which has led to restrictions on their use in place. In addition phthalates are classed as a PHS under WFD.

Nonyl- and octylphenol ethoxylates are part of a group of alkyl phenol ethoxylates (APEs) which were commonly used as emulsifiers and non-ionic surfactants for both domestic and industrial use until they were phased out in 1995. APEs were deposited in sewage sludge and subsequently ended up in the marine environment. Another use of APEs is in the formulation of drilling muds where they have been used in oil based muds (OBM) as surfactants in demulsifier formulations and as flow improvers. In the United Kingdom the use of nonylphenols (NPs) and nonylphenol ethoxylates (NPEs), as well as other known endocrine disrupters, in the offshore sector were phased out in 1999. Alkyl phenols (APs) are formed by the degradation of APEs but have also been used as an intermediate in the production of other substances such as APEs. Their use is restricted under REACH while nonylphenol is classed as a PHS under the WFD and octylphenol a PS.

Historically trichlorobenzenes (TCBs) were used as dye carriers, which adsorb into polyester fibres. During dying, a significant amount of TCBs could be discharged to waste waters. Today TCBs are used as intermediates in the production of herbicides and pesticides. TCBs have also been used as an additive to mixtures for insulating and cooling dielectric fluids. TCBs may be released into the marine environment, directly from the production site, from waste disposal, from products treated with

TCB (i.e. textiles) and from degradation of higher chlorinated benzenes. There is only one producer of TCB in Europe (located in Germany) which sells and uses TCBs as intermediates. Furthermore TCBs have been phased out in a number of uses, such as dielectric fluids, lubricants and heat transfer fluids, as solvents, as components in synthetic oils, in abrasive formulations, in degreasing agents and cleaning agents for septic tanks. 1,2,4-TCB is the only TCB which has restrictions on its use in place under REACH, and TCBs are classed as a WFD PS.

The OSPAR review recommended three substances for removal from the OSPAR List of Chemicals for Priority Action. This includes the pharmaceutical clotrimazole, neodecanoic acid, ethynyl ester (used in the synthesis of polymers to make them more hydrolytically and UV-stable), and 4-(dimetyhylbutylamino)diphenylamine (6PPD used as a protective agent (anti-ozonant and antioxidant) in the rubber industry) as they do not fully fulfil the OSPAR DYNAMEC PBT criteria.

The substances that were recommended for continued monitoring were PAHs, PCBs, brominated flame retardants (including PBDEs), trace metals (Cd, Hg and Pb), organotins, dioxins, including polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and perfluorooctanyl sulphonic acid and its salts (PFOS). PCDFs, PCDFs and PFOS are not included in the OSPAR's Co-ordinated Environmental Monitoring Programme (CEMP) and therefore are not routinely monitored in Scotland.

The OSPAR CEMP is currently focussed on monitoring the concentrations and effects of the following contaminants, from the List of Chemicals for Priority Action, in the marine environment. This list has not changed for many years:

- metals (cadmium, mercury and lead) in sediment and biota;
- PAHs (anthracene, benz[*a*]anthracene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, fluoranthene, ideno[1,2,3-*cd*]pyrene, pyrene and phenanthrene) in biota (shellfish) and sediment;
- PCBs (ICES7- CB28, 52, 101, 118, 138, 153 and 180) in biota and sediment
- brominated flame retardants (HBCD and BDE28, 47, 66, 85, 99, 100, 153, 154 and 183 in biota and sediment, and BDE 209 in sediment);
- tributyltin (TBT) in sediment.

Further substances are classed as pre-CEMP. Contracting Parties are preparing to monitor these in a co-ordinated manner through the development of monitoring guidance, quality assurance procedures and/or assessment tools. Currently the pre-CEMP includes the following, and again has not been updated for many years:

- planar PCBs (CB77, 126 and 169) in biota;
- alkylated PAHs C1-, C2-, and C3-naphthalenes, C1-, C2- and C3-phenanthrenes, and C1-, C2- and C3-dibenzothiophenes and the parent compound dibenzothiophene in biota and sediment;
- TBT in biota;
- PFOS in sediment, biota and water;
- dioxins and furans in biota and sediment.

Under the OSPAR Joint Assessment and Monitoring Programme (JAMP), periodic assessments of the presence and effects of the chemicals in the CEMP (PAHs, PCBs, PBDEs, HBCD and trace metals) are required. This includes a Quality Status Report for the OSPAR Maritime Area, the latest one of which is due for publication in 2023 (QSR 2023). The QSR 2023 will require the OSPAR common indicators to undergo a status and trend assessment. The common indicators for contaminants include PAHs in sediment and shellfish, PCB in sediment and biota, PBDEs in sediment and biota and trace metals in sediment and biota. For effects, imposex is the only common indicator. Scotland is required to monitor substances detailed in the OSPAR CEMP in sediment, fish and shellfish. This includes PAHs (9 parent PAHs[iv]), PCBs (ICES7) and trace metals (Hg, Cd and Pb) and PBDEs.

Monitoring under the UK Clean Seas Environment Monitoring Programme (CSEMP) and other research and monitoring programmes in Scotland

Analyses of OSPAR CEMP contaminants are undertaken by both MSS and SEPA as part of the UK Clean Seas Environment Monitoring Programme (CSEMP). The main focus of the CSEMP to date has been to meet the temporal trend monitoring requirements of the OSPAR Convention and for compliance with the WFD and the MSFD/UK MS.

MSS's CSEMP monitoring is described in Webster *et al.* (2013), with the focus still on the analysis of the OSPAR CEMP determinands and common indicators for MSFD/UK MS assessments. Since 2010 the main change to the Programme has

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[iv] The 9 CEMP parent PAHs are anthracene, benz[*a*]anthracene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, fluoranthene, indeno[1,2,3-*cd*]pyrene, pyrene, phenanthrene. The ICES7 CBs are CB28, 52, 101, 118, 138, 153, 180.

been to try and improve the spatial coverage for regional assessments of these legacy determinands (and key biological effects). The current Scottish sediment and biota sampling design uses stratified sampling where the strata are the WFD water bodies in transitional and coastal waters, and larger strata in offshore waters. Biota samples are typically taken at fixed locations. However, sediment samples are often collected using random sampling and can be widely dispersed throughout a water body. The samples are collected in areas of fine sediment only; British Geological Survey maps showing sediment type were used to identify suitable areas.

OSPAR and MSFD/UK MS assessments are carried out at the scale of the eight UK biogeographic areas, and the recent Scottish Marine Assessment (SMA) 2020 (Moffat *et al.*, 2020) also used the four Scottish biogeographic regions (Irish Sea, Minches and West Scotland, Scottish Continental Shelf and Northern North Sea). A minimum of three stations with sufficient geographic spread is required to make a robust regional assessment.

Regional Marine Planning required the creation of Scottish Marine Regions (SMRs). Under the Marine (Scotland) Act 2010, Scottish Ministers were given the power to identify the boundaries of SMRs. Eleven SMRs were created which cover sea areas extending out to 12 nm. Regional Marine Plans will be developed for SMRs by the relevant Marine Planning Partnerships, allowing more local ownership and decision making about specific issues within their area. Assessments on the state of the environment will be needed for each SMR. For SMA 2020 there was a requirement to use this new reporting regime for Scottish waters based on the SMRs as detailed in the National Marine Plan. Outside 12 nautical miles new Offshore Marine Regions, proposed by Scotland’s Seas Data and Assessment Steering Group (SSDAG) should be used.

There is currently insufficient stations to undertake assessments of contaminants and biologicals effects in sediment and biota at the scale of the SMRs/OMRs. OSPAR and MSFD assessments have focused on having sufficient coverage for the 4 Scottish biogeographic regions, however even at this scale sampling sufficient stations has been difficult. Therefore, for SMA 2020 the four Scottish biogeographic regions were used for the regional assessment of contaminants and effects in biota and sediment (and also seafloor litter).

To try and improve biota regional assessments, new sites have been proposed for future monitoring of contaminants and effects in fish, mussels and dog whelks, to try and ensure there are three stations for each indicator in each of the four biogeographic regions, with one site in each SMR. For sediment this is not possible as samples should be collected in areas of fine sediment only; in many SMRs the sediment is sandy and not appropriate for contaminant monitoring and even in some of the biogeographic regions there is limited areas of suitable sediment type. Marine Scotland has undertaken the sediment and biota (fish and shellfish) analyses for the four biogeographic regions; the contaminant and biological effects data (1999-2018) from the CSEMP has been reported as part of SMA 2020 (Moffat *et al*., 2020).

Contaminants of Emerging Concern (CECs)

In recent years there has been an increased awareness in CECs as a major environmental issue and it is recognised that there is a need to identify and prioritise relevant CECs. The identification of substances which are not listed as WFD or OSPAR priority substances, but that entail a significant risk to the marine environment is part of the provisions under the MSFD. Within the UK, freshwater laboratories have or are developing target, non-target and suspect screening methods to identify CECs in water. These methods are based on non-selective methods of extraction coupled with high resolution mass spectrometry (HR-MS), coupled with either gas chromatography (GC) or liquid chromatography (LC). There is a bigger driver in freshwater and coastal waters to develop screening methods to identify CECs with a likely wider range of substances at higher concentrations compared to marine waters. In addition the UK Chemical Strategy there is a commitment to run a Prioritisation and Early Warning System (PEWS) to identify emerging chemical issues across different media (water, air and soil) with the aim of improving our understanding of the risk posed by emerging substances present in surface waters and ground waters. PEWS is currently only being used in England with no equivalent in Scotland, but SEPA have provided data to this process. SEPA have also recently developed scanning methods for freshwater, and hope to expand this to sediment and biota.

ICES/OSPAR

OSPAR is invested in better understanding the diversity and extent of CECs in the marine environment. The OSPAR CEMP list has not changed for many years, with PBDEs being the last addition in 2008 and PFOS being the latest addition on the pre-CEMP. However, it has been recognised there is a need to update the OSPAR List of Chemicals for Priority Action which is expected to happen in 2022/23.

In addition, there is a requirement in EU legislation for member States to establish a list of other relevant contaminants, i.e. from offshore sources, that may lead to pollution in the marine region or sub-region. Following on from an OSPAR request for advice on CECs in 2017, the Marine Chemistry Working Group (MCWG) and the Working Group on Marine Sediment (WGMS) both have terms of references (ToR) relating to CECs.

MCWG's ToR is to *"Assemble and synthesise new information on chemical substances of emerging concern in ICES area and beyond, including residuals in higher trophic level marine species."*

WGMS ToR is to "To review and inform on the occurrence of substances of emerging concern in sediments, including platinum group and rare earth elements, as well as organic contaminants"

Both Groups have been working together to gather available data and information on CECs. Nine substance groups with critical chemical properties (e.g., bioaccumulation potential, persistence, toxicity-PBT criteria) that may be of emerging concern in the marine environment, were identified for further investigation: dechloranes, alternative brominated flame retardants, phosphorous flame retardants, antifoulants, per- and polyfluorinated substances, benzotriazoles, siloxanes, anticorrosion agents and pharmaceuticals. These nine substances/groups of substances are summarised below. To date ICES MCWG/WGMS has received CEC data from 11 countries with most data being for PFASs and pharmaceuticals with limited data for phosphorous flame retardants, and alternative flame retardants.

Alternative flame retardants- Dechloranes

The ban on the use of brominated flame retardants (PBDEs) has led to the development of alternative flame retardants such as dechloranes. Dechloranes are a class of highly chlorinated norbornene compounds, synthesized by the Diels-Alder reaction of hexachlorocyclopentadiene with various substrates. Dechloranes were initially developed as substitutes for the pesticide Mirex, which was banned worldwide in the 1970s under the Stockholm Convention. Dechlorane Plus (DP) and related compounds (Dechloranes 602, 603 and 604) are used as flame retardant in plastics, electric and electronic devices, and building materials (Feo *et al.*, 2012). DP is produced in the US (Oxychem, Buffalo, USA) and China (Anpon Electrochemical

Co., Ltd, Jiangsu, China) with an estimated annual production volume of 5000 t. Dechloranes enter the marine environment through rivers carrying contaminated wastewater and via atmospheric transport. DP has been classified as a SVHC under REACH. There is little information on production and usage for Dechloranes 602, 603 and 604. Dechloranes are hydrophobic (Log K_{ow} >5) and have the potential to bioaccumulate and biomagnify. However, there is a lack of data on their persistence or toxicity so it is not clear if they fully meet the PBT criteria (Feo *et al.*, 2012).

Analysis and presence in the environment

Extractions methods used for other organic contaminants, such as PCBs and PBDEs, can also be used to extract dechloranes from environmental samples (Feo *et al.*, 2012). This includes soxhlet, and pressurised liquid extraction (PLE), the latter being currently by MSS for the extraction of PCBs and PBDEs from sediment and biota. Detection methods reported for DPs include GC-HRMS and GC-MS/MS (Neugebauer *et al*., 2018).

Current environmental studies on concentrations of dechloranes have focussed on areas where they are being produced (North America and China). However, there have been few studies in other regions of the world (e.g., Korea, Spain). DP was first identified in the environment in the Great Lakes (Hoh *et al*., 2006). Data suggests that Dec-602 may be found in fish and sediment samples at levels similar to or even higher than DP and Mirex, while related compounds Dec-603, Dec-604 and Chlordene Plus (CP) are often not found above the limit of detection. Long-range atmospheric transportation of DP has been observed with DP being found in remote areas. A recent study of marine samples from the German environmental specimen bank found Dec-602 was the only emerging flame retardant that was found above detection limits in all samples (Fliedner *et al*., 2020). The conclusion from this paper was that dechloranes (as well as PFAS) should be considered for inclusion in future monitoring programmes.

Alternative brominated flame retardants (aBFR)

Brominated flame retardants (BFRs) such as polybrominated biphenyls (PBBs), PBDEs, hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) have been studied for many years and due to concerns about their persistence, potential to bioaccumulate and toxicity were increasingly regulated. Due to the ban on the use of these established BFRs, alternative brominated flame retardants (aBFR) were developed. aBFRs are the biggest group of CECs in terms of production volumes, and contain a diverse range of compounds. aBFRs include compounds such as 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), tris(2,3-dibromopropyl) phosphate (TDBPP) and dibromoneopentyl glycol (DBNPG) (EFSA, 2012). Similar to established BFRs, aBFR can enter the environment during production (of the commercial product as well as of products containing aBFRs), use (i.e. release from aBFR-containing products) and disposal. Fisk *et al.* (2003) evaluated the uses and environmental risks of various flame retardants including some aBFRs. aBFRs similar to the traditional BFRs are hydrophobic, persistent and toxic with most fulfilling the PBT criteria. The highly brominated compounds are less likely to bioaccumulate but will be more persistent (Howard and Muir, 2010).

Analysis and presence in the environment

aBFRs are extracted using similar methods as used for other organic contaminants such as PBDEs and PCBs. Quantification methods used include GC–MS/MS and gas chromatography (GC) coupled with magnetic sector high resolution mass spectrometry (HRMS). The German environmental specimen bank study found aBFRs in coastal marine biota (mussels and eelpout) at similar concentrations to PBDEs (Fliedner *et al*., 2020), with most showing decreasing trends. Tao *et al.* (2019) demonstrated that some aBFRs such as pentabromotoluene (PBT) and pentabromoethylbenzene (PBEB) biomagnified, with biomagnification factors (BMFs) similar to PBDEs, and therefore these contaminants may pose a significant risks to aquatic organisms. Some aBFRs have been detected in the Arctic (mainly in air and seawater), confirming that they can undergo long range atmospheric transport (AMAP, 2017).

Organo-phosphorous flame retardants (OPFR)

Organo-phosphorous flame retardants (OPFR) have increased in use due to the phasing out of many brominated flame retardants. OPFRs are widely used as additive flame retardants to prevent the risk of fire in various consumer products including electronics, textiles, industrial materials and furniture. They are also utilized as plasticizers, antifoaming or anti-wear agents in lacquers, hydraulic fluids and floor polishing agents. The global production of organophosphate esters (OPEs) was approximately 680,000 tons in 2015, and reached 1 million tons in 2020 (He *et al.*, 2020; Zhang *et al*., 2020). Additive flame retardants are not chemically bonded to the product and therefore may be released to the environment. OPFRs have a wide range of physical (Log K_{OW}, vapour pressure) and physiological properties (BCFs), depending on their molecular structure. Those with longer side chains and more branches are more hydrophobic with higher octanol-water partition coefficients (Log K_{OW}). Some OPFRs can act as endocrine disruptors which can, therefore, result in health risks to neurodevelopment, liver and behavioural abnormalities. In addition some OPFR are suspect carcinogens. Compared to BFRs, OPFRs are less persistent and bioaccumulative, OPFRs are rapidly metabolized with relatively short half-lives.

Analysis and presence in the environment

Liquid chromatography-mass spectrometry (LC/MS) is the most traditional method for detecting OPFR residues in the environment, although GC-MS and GC-MS/MS have also been used (Pantelaki and Voutsa, 2019; Yang *et al.*, 2019). Extraction methods include microwave, sonication and PLE. Studies have shown OPFRs to be present in a variety of environmental matrices, including water and sediment (Wang *et al*., 2020). However, environmental concentrations are generally below the exposure doses of OPEs determined to be toxic in toxicological studies (Wang *et al.*, 2020). OPFRs have also been detected in Arctic sediment far from known sources, confirming their long range transport (Vorkamp *et al.,* 2019). However, concentrations in Arctic biota were generally low, probably due to metabolic transformation. In summary as OPFRs are less persistent and biocuumulative with low environmental concentrations, they are not seen as a priority for addition to monitoring programmes.

Antifoulants (Irgarol (cybutryn), Sea-Nine (4,5-dichloro-2-n-octyl-4-isothialozin-3-one), diuron and pyrithione (both Zn and Cu)

Antifouling paints containing tributyltin (TBT) were first painted on ships in the 1970s and were subsequently used on aquaculture infrastructure to protect against biofouling. In 2003 the International Maritime Organisation (IMO) banned the sale and application of antifouling paints containing TBT due to associated environmental issues (imposex in dog whelks; Gibbs *et al*., 1991). This resulted in the introduction of alternative antifoulants such as copper salts with copper oxide (Cu_2O) and copper thiocyanate (CuCHNS) being the main alternatives to TBT in many antifoulants (Tornero and Hanke, 2016). However, some organisms are resistant to copper, and therefore booster biocides were developed to be added to copper based paints to improve their effectiveness. The most commonly used booster biocides in antifouling paints are Sea-Nine 211, Diuron, Irgarol 1051 and Zinc Pyrithione and Copper Pyrithione, although there are limitations on their use. In the UK Irgarol 1051 and diuron antifoulants are banned.

Analysis and presence in the environment

There is a lack of information and data on the types and quantities of booster biocides used around the world. A UK Defra study (2000- 2003) investigated the fate and bioavailability of eight booster biocides in harbours, docks and marina dredge material (Defra, 2003). Of those tested only Irgarol 1051 and diuron were regularly detected in coastal surface water and sediment samples. Sea-Nine 211, zinc pyrithione and dichlofluanid were found to rapidly degrade under both aerobic and anaerobic conditions. A UK study investigating the impact of this legislation demonstrated that water concentrations of Irgarol 1051 had reduced considerably. In the same study, other booster biocides were screened (chlorothalonil, dichlofluanid and Sea-Nine 211®) and were found to be below the detection limit (<1 ng/l) in all samples (Creswell *et al*., 2006). Data on booster biocides in the marine environment is still very limited and there is no clear evidence that these substance pose a threat to the marine environment.

Per- and polyfluoroalkyl substances (PFAS) other than PFOS and PFOA

Per- and polyfluoroalkyl substances (PFAS) are widely used as surfactant aids in the manufacture of fluoropolymers which have a number of industrial and consumer applications, including non-stick surfaces for cookware and water-repellent outdoor clothing. Perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) were the most widely studied PFASs due to their high production volumes and PBT (persistence, bioaccumulation and toxicity) criteria. The main producer of PFOS and PFOA was the US Company, 3M. In 2002, 3M voluntarily ceased producing PFOS and PFOA. Furthermore the use of PFOS in major applications has been restricted. However, the ban and restrictions on these first-generation PFAS products has led to the development of similar substances, with now 1400 replacement PFAS in use (Glüge *et al*., 2020).

PFAS can enter the environment during manufacturing, usage and disposal with the main inputs into the marine environment being through rivers and atmospheric deposition. PFASs are exceptionally stable to both metabolic and environmental degradation. PFOS and PFOA have been shown not to hydrolyse, photolyse or biodegrade in any environmental condition tested (OECD, 2002). PFAS environmental behaviour is dependent on the length of their carbon chain. Long chain (>8) PFAS are bioaccumulative, while short-chain PFAS tend to be mobile in sediments and waters. Moreover, some PFAS are toxic and/or endocrine disruptors. A number of long-chain PFAS are classified as SVHC under the REACH regulation. Although PFOS is already included on the OSPAR pre-CEMP (and is also a WFD PHS) other PFAS could also be of concern (OSPAR Commission, 2006). In 2009, PFOS (and related chemicals) were added to the Stockholm Convention, with PFOA added in 2020.

Although 3M ceased producing PFOS and PFOA in 2002, due to their extreme persistent they are still found in the marine environment. In addition, there are other PFAS compounds that are not currently restricted, although they are being considered under REACH. PFOS is included on the OSPAR List of Chemicals for Priority Action and analysis of PFOS in sediment, biota and water is included on the pre-CEMP so monitoring is likely to become a OSPAR statutory requirement in the future.

Analysis and presence in the environment

Various methods have been applied to determine PFAS in water, sediment and biota, and they generally involve extraction with polar solvents, clean-up steps and LC-MS analysis. Guidelines on the analysis of PFASs in sediment and biota have been prepared through the ICES Marine Chemistry Working Group (MCWG) (Ahrens *et al.,* 2010). Although most studies have focused on PFOS and PFOA, MCWG recommend that longer- and shorter-chained PFASs should be included in the analysis.

In recent years there have been an increasing number of publications on PFASs in the environment. The available data shows that these compounds are present in the marine environment and often at high concentrations, particularly in biota. PFAS differ from other persistent organic contaminants in that they do not accumulate in the fat tissue but bind to proteins in the blood and liver. Therefore, for fish monitoring, analysis of the liver is recommended.

A French study investigating PFASs showed widespread contamination in shellfish from the French coast with a shift from PFOS to long-chain PFAS (Munschy *et al.*, 2019). PFAS were found in the Norwegian Arctic, in water, sediment and biota samples, with the firefighting training stations at Svalbard airport and diffuse release from the local settlement being the major sources (Ali *et al.*, 2021). Concentrations in biota of different trophic levels indicated that these substances were biomagnifying. The German environmental specimen bank study found PFAS in blue mussels and eelpout filet and liver, with PFAS concentrations higher in samples from the North Sea compared to the Baltic Sea (Fliedner *et al.*, 2020). In addition, increasing trends were observed at some sites, and the conclusion from this paper was that PFAS (including long chain compounds) should be considered for inclusion in monitoring programmes.

PFAS have been found in remote areas such as the Arctic, indicating atmospheric transportation is a source of these compounds (Muir *et al.*, 2019). PFAS concentrations were detected at a range of trophic levels in Arctic biota, with some time series showing increasing trends. It was though that these increases were due to continued emissions of long-chain Perfluoroalkyl carboxylic acids (PFCAs) and their precursors and inflows to the Arctic Ocean, particularly from the North Atlantic.

As part of a recent UK (CEFAS) study on PFAS in estuarine and coastal sediments, samples were analysed for 31 PFAS, and total organic carbon as a normaliser (Barber *et al.*, 2021). PFAS were found in 85 of the 103 samples analysed. However, many of the sediment samples analysed were sandy, and, therefore, were less likely to accumulate PFAS. Most PFAS were below detection limits with PFOS having the highest detection frequency (60/103), followed by PFOA (33/103). Highest concentrations were found in samples from the Thames and Severn. Overall concentrations were low, below Dutch assessment thresholds. This study confirmed that sediment was maybe not the best matrix for PFAS analysis, with fish being the preferred matrix for monitoring long chain compounds and water for shorter chain compounds.

A MSS review of hazardous substances in 2010 (Webster et al., 2010) highlighted that currently PFAS are not routinely monitored in Scotland but may be of concern. A method development programme for PFAS was initiated at MSS**,** including longer chain (>8 carbons) PFASs. The extraction method involved extraction by sonication in acetonitrile, followed by clean-up through freezing out of interferences and filtration and analysis by LC-MS/MS. However the method development work was not completed due to staffing issues. Therefore it is still considered a priority to complete the method validation and instigate a monitoring programme.

Benzotriazoles

Benzotriazoles (BZTs) are a class of organic compounds that have been used as metal anticorrosive, antifoulants and as ultraviolet (UV) light stabilizer additives in plastics and polymers. Some BZT compounds exhibit behaviours characteristic of persistent organic pollutants and have low volatility, so may persist in the aquatic environment (Herrero *et al*., 2014). BZTs are a suspected human carcinogen and have estrogenic effects in fish. Consequently, BZTs are considered to be CECs.

Analysis and presence in the environment

Analytical methods for BZTs have been reviewed (Kim *et al.*, 2011; Herrero *et al*., 2014). Extraction methods include solid phase extraction (SPE), solid-phase microextraction (SPME), dispersive liquid-liquid microextraction (DLLME) and stir-bar sorptive extraction (SBSE) for water, and pressurised liquid extraction (PLE) for sediment/soils, followed by silica clean up. Analytical techniques include LC or GC coupled with MS/MS, with LC UV-Vis or fluorescence detection also having been used. The most frequently used analytical method is LC-MS/MS, GC being less suitable as BZTs are polar and not volatile, so better suited to LC separation methods.

BZTs are more water soluble than other organic contaminants and are therefore detected more frequently in water samples (Alotaibi *et al*., 2015). BZTs have also been detected in sediment and biota, although there are few studies in the marine environment. There is limited information currently available on the presence and impact of BZTs on the marine environment and therefore these substances are not a priority for addition to monitoring programmes.

Siloxanes

Siloxanes comprise a large group of chemicals which have in common multiple uses including for biomedical and cosmetic applications as well as in waxes and polishes. Substantial amounts are also used for the production of siloxane polymers. In case of the cyclic volatile methyl siloxane (cVMS) D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane), the side chains consist of methyl groups. They can be emitted during industrial processes or from the use of products, and have the potential to enter the environment via air and waste water. Under the REACH regulation D4, D5 and D6 are classified as SVHC because of their environmental persistence, and potential to bioaccumulate. Available data on the bioaccumulation of siloxanes is mixed with some studies showing no evidence of bioaccumulation or biomagnification (Hong *et al*., 2014). One study showed some weak evidence of D4 being a weak endocrine disruptor (Quinn *et al.*, 2007).

Analysis and presence in the environment

Siloxanes have been determined by GCMS, following solvent extraction and SPE clean up. There are few studies on the presence of siloxanes in the marine environment. However, methyl siloxanes have been detected in seawater, sediment and bottom fish samples collected from marine environment in Northeast China, with sewage being the main source of these substances in the area studied (Hong *et al.*, 2014). Studies have shown some siloxanes can bioaccumulate, and can undergo long range atmospheric transport.

Siloxanes (mainly D5 and D6) have been detected in seaweed samples in the central and North Atlantic coastline of Portugal as well as in the Mediterranean coastlines of the Spanish Region of Murcia and South of France, with higher concentrations found in areas with higher urban and industrial pressures (Rocha *et al*., 2019). Siloxanes were also measured in the German marine specimen bank study (Fliedner *et al*., 2020). Eelpout filet samples collected in 2018 were analysed for cVMS (D4, D5 and D6) and were found to be below detection limits in all samples. Low concentrations were found in marine fish from the Norwegian coast and from the Baltic Sea, with the limit of detection (LoD) being lower than in the German study (Powell *et al*., 2018).

There is limited data on siloxanes and from the PBT criteria and environment concentrations, no real evidence that this contaminant group is a priority for addition to monitoring programmes.

Anticorrosion agents (especially those applied in offshore windmill parks)

Corrosion inhibitors are used in a multitude of applications, however, those applied in offshore windfarms could be a significant source of these contaminants in the marine environment (Kirchgeorg *et al*., 2018). Offshore wind energy is a new and fast growing green energy source. However, offshore wind structures are also an additional pressure for the marine environment and environmental impact assessments are a requirement of the windfarm approval process. Wind farm structures require corrosion protection systems to protect the steel construction against corrosion in the marine environment. Epoxy resins and polyurethane based coatings are a commonly used corrosion protection technique in a wide range of marine applications (harbour, shipping, offshore industry). Metals (zinc and aluminium) associated with sacrificial anodes might also be released into the marine environment.

Analysis and Presence in the environment

Currently there is limited data available for these substances in the marine environment. Little is known about the behaviour and impact of corrosion inhibitors such as epoxy resins and polyurethane based coatings in the marine environment. Therefore further research is needed on the release of corrosion inhibitors from resins and anodes, and on the concentrations and effects of these on the marine environment.

Pharmaceuticals

Unlike other contaminant groups such as PCBs and PBDEs, pharmaceuticals have diverse and complex structures and properties, although most will be polar. The estimated global medicine use for 2020 was 4.5 trillion doses (IMS Institute, 2015), with the pattern of usage varying by country. Incomplete removal during waste water treatment has led to their detection in environmental samples. Over the last 20 years, pharmaceutical and their metabolites have been identified in environmental matrices across the globe and their occurrence has raised concerns over potential impacts on ecosystem and human health. Although most pharmaceuticals are not persistent and will degrade in the aquatic environment, their continuous influx from a range of sources renders many to be pseudo-persistent. Knowledge of pharmaceutical prescription information should allow pharmaceutical concentrations in rivers to be predicted. A new SEPA initiative, One Health Breakthrough partnership (OHBP), is hoping to link prescription practices to what we find in the environment.

Analysis and presence in the environment

A global study of pharmaceuticals their metabolites in tap, surface, wastewater treatment plant (WWTP) influent and WWTP effluent water was undertaken by York University (Wilkinson *et al.*, 2019). High-Performance Liquid Chromatography-Tandem Mass Spectrometry was used for the quantification of 61 active pharmaceutical ingredients (APIs). APIs were selected for this study to include: (a) compounds of high usage across the world; (b) compounds with known or suspected ecological or human health concern; and (c) compounds of expected high use due to regional disease pressures (e.g., antimalarials). Areas with greatest pharmaceutical concentrations were characterised by political instability, highly populated, poor waste water treatment, inadequate sewage and a dry climate. Sites with highest concentrations were found in Latin America, Asia, Africa, and also several sites in Europe too. The main substances found were painkillers, antimicrobial, anti convulsants, anti-diabetic drugs with the highest concentrations for caffeine and paracetamol. A site in the Clyde was in the top 25 of sites with highest concentrations of pharmaceuticals (number 25).

A recent Robert Gordon University paper on the development of methodologies for emerging drug contaminants and the application of this method to seawater samples from the Clyde and Forth, highlighted that these pharmaceuticals are present in Scottish waters and further investigation on their presence and effects is required (McKenzie *et al*., 2020). However, pharmaceuticals were not detected in mussels samples analysed as part of the CONnECT project (see below).

CONnECT- CONtaminants of Emerging Concern and Threat in the Marine Environment

The OSPAR Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) is considering new substances for inclusion in the OSPAR Coordinated Environmental Monitoring Programme (CEMP). To help identify emerging substances of concern in the OSPAR region a wide scope target and suspect screening initiative (CONnECT- CONtaminants of Emerging Concern and

Threat in the Marine Environment) has been organised through the NORMAN network (Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances). The first phase of this initiative focussed on mussel samples, from impacted and background sites, although some Danish fish samples were also provided. Mussel samples were analysed by a central lab with the aim of generating listings of potential contaminant threats at both a local Contracting Party level but also on an OSPAR regional basis. In addition this list of contaminants will be linked to the NORMAN ecotoxicological databases, to complete a prioritisation listing integrating concentrations measured to their potential for harmful effects. This process will aid in the selection of hazardous substances of concern to be further considered by OSPAR and, potentially, the EU WFD and MSFD for inclusion in priority list of substances.

Thirty-two biota samples (mainly mussels, but also some fish samples) were provided by eight different OSPAR partners and screened for several thousands of organic pollutants and their transformation products by wide-scope target (> 2,500 substances) and suspect (>65,000 substances) screening methodologies. Substances screened for included industrial chemicals, pharmaceuticals, antipsychotic and antidepressant drugs, Personal Care Products (PCPs), stimulants, Plant Protection Products (PPPs), preservatives and sweeteners. At a minimum, OSPAR participating countries provided an impacted and a reference mussel sample. UK mussel sites sampled in 2020 included two from Scotland (impacted site, Aberdeen Harbour; clean site, Ythan) and two from England (impacted site, Canvey Island; clean site, The Exe).

Overall, 67 contaminants were detected in the 32 samples tested. There was little difference in the number of contaminants detected at the impacted and clean sites. In the two Scottish mussel samples, concentrations for most compounds were below the limit of detection (LoD), with only 14 compounds being detected in Scottish samples; 1 PCP (parabens) and 13 industrial contaminants (PAHs and alkyl amines and quaternary alkylammonium surfactants). In both Scottish samples, all pharmaceuticals were below the LoD, though some pharmaceuticals (Mexiletine, Phenazone, Reproterol, Sotalol) were detected in the English samples. Across the OSPAR area the pharmaceutical found most frequently was Antipyrine- 4-Acetamido which was found in 71.9% of the samples analysed. Antipyrine- 4-Acetamido is a metabolite of metamizole which is an anti-inflammatory medication which is banned in the UK, and was < LoD in Scottish and English mussel samples. PFOS was not detected in UK samples, however PFAS do not accumulate in the fat tissue but bind to proteins in the blood and liver, and therefore mussels are not the best matrix for PFAS monitoring.

The mussel sample from the Ythan contained methylparaben (15.1 µg/kg wet weight), as did both CEFAS samples (23.5, 29.1 µg/kg wet weight). Overall, most samples (98.3%) analysed contained this compound with concentrations ranging from <LoD to 641 µg/kg in a Swedish mussel sample. However, it was above the LoD but below the limit of quantification (LoQ) in the Aberdeen mussel sample. Parabens are esters of para-hydroxybenzoic acid, with an alkyl (such as a methyl group in the case of methylparaben) or a benzyl group and are considered as a CEC despite being in use since the 1920s. They are mainly used as preservatives in foodstuffs, cosmetics and pharmaceutical drugs. Parabens may act as weak endocrine disruptor chemicals, but controversy still surrounds the health effects of these compounds. They were first detected in water samples in 1996. Although they are biodegradable, they are ubiquitous in surface water and sediments, due to the wide-spread use of paraben-based products and their continuous introduction into the environment.

Alkyl amines and quaternary alkylammonium surfactants are cationic surfactants used in a wide variety of consumer products and industrial processes such as hair care products, fabric softeners, and hydraulic fracturing fluids. These compounds were found in both the Ythan and Aberdeen mussels, though more compounds were detected in Aberdeen and concentrations were higher. N,N-Dimethyldodecylamine N-oxide was found at a concentration of 165 µg/kg in the Aberdeen mussel sample. This was the highest concentration across all sites involved in the study, however it was only found in 6.3% of sites. Across all OSPAR sites N,N-Dimethyldodecylamine was found more frequently being detected in 68.8% of sites. At the CEFAS sites, alkyl amines were mainly below detection limits with only N,N-Dimethyltetradecylamine and N,N-Dimethyldodecylamine above the LoD at the Exe estuary site, though concentrations were at the lower end of those found across all sites.

Risk assessment

A prioritisation of the CECs was also undertaken by comparing the concentrations found to Predicted No Effect Concentrations (PNECs) or Environmental Quality Standards (EQS), and considering the Frequency of Exceedance (FoE) and Extent of exceedance (EoE). PNEC values for biota were derived from existing PNECs for freshwater.

Thirty-two chemicals were flagged as being a potential risk across the OSPAR region and for the UK 16 out of 28 detected CECs in UK samples exceeded the respective EQS or PNEC values. Most of these were for pharmaceuticals in English mussel samples. Five out of 14 emerging contaminants detected in Scottish mussel samples exceeded their respective EQS or PNEC values. The frequency and extent of PNECs exceedance in the Aberdeen and Ythan mussel samples were significantly lower compared to the samples provided by other OSPAR partners. Two parabens, methyl- and butyl- paraben presented the highest FoE, as they were detected above their PNECs in both samples. Methylparaben seems to be of high environmental concern, as its concentration exceeded the PNEC (0.64 µg/kg) value in 24 of all samples across the OSPAR area. However, it should be noted that the PNEC is lower than the LoD and LoQ.

Butylparaben and didecyldimethylammonium (DADMAC (C10:C10)) exceeded their ecotoxicological thresholds 10-fold, whereas N,N-dimethyldodecylamine and N,N-dimethyltetradecylamine concentrations in the Aberdeen mussel sample were 11 and 15-fold higher than their respective PNECs. The highest EoE was for methylparaben and N,N-dimethyldodecylamine.

Phase 2 of the CONnECT project is likely to look at widening the matrix types and trophic levels of samples to be analysed, and possibly additional sites. The results of Phase 1 will be included as case study for the QSR 2023.

Conclusions

1. The OSPAR List of Chemicals for Priority Action has not been updated for many years and the same groups of contaminants continue to be monitored routinely for UK CSEMP, to fulfil the requirements for OSPAR and MSFD/UK MS.
2. There are a number of initiatives looking at CEC both nationally and internationally, although there is a lack of consistency between monitoring authorities approaches to CEC monitoring. Within the UK, the Environment Agencies are using labour intensive screening methods for CEC identification in freshwater and in England PEWS is being used to identify CECs. Less is being done on CECs in the UK marine environment.
3. ICES MCWG/WGMS are collating data and information from member states on nine key CECs identified as of interest due to their PBT criteria. A German specimen bank study investigated the presence of most of these nine CECs in the marine environment, and concluded that the CECs most likely to be of

interest in the marine environment were the alternative flame retardants (including dechloranes) and PFAS.

4. As part of a MIME/Norman project (CONnECT) mussel samples were screened for contaminants to try and identify CECs priorities. The UK provided mussels from 4 sites sampled in 2020, two from Scotland (impacted site, Aberdeen Harbour; clean site, Ythan) and two from England (impacted site, Canvey Island; clean site, The Exe).
5. From the risk assessment of the results from the CONnECT project methyl paraben and alkyl amines and quaternary alkylammonium surfactants were of most concern in Scottish mussels. Neither contaminant groups have previously been considered as CECs.
6. PFAS was not detect in the mussel samples for the CONnECT project, although this is not unexpected as mussels are not a suitable matrix for PFAS monitoring.
7. Although pharmaceuticals have been found in water samples from the Clyde and Forth, they were not detected in Scottish mussels analysed as part of the CONnECT project, although pharmaceuticals were found at concerning levels in English mussels.
8. Of the CEC work (ICES, CONnECT) to date there is no clear priority for monitoring in marine biota or sediment at either the OSPAR or UK level. Future work on the CONnECT project is likely to look at other sample matrices and additional sites, MSS should consider samples to be included in this to help inform CEC prioritisation. MSS should also complete their method development programme for PFAS analysis as this contaminant group is still considered a priority for monitoring, and investigate the possibility of including dechloranes in our existing methods.

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