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Identification of marine chemical contaminants released from sea-based sources

A review focusing on regulatory aspects

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Abstract

The monitoring of chemical contaminants, as required by the Marine Strategy Framework Directive (MSFD) Descriptor 8, should allow for the seamless protection of the marine environment against chemical pollution. A list of priority substances (PS) at EU level is provided under the Water Framework Directive (WFD) for coastal and territorial waters. EU Member States may also identify in their coastal waters substances of national or local concern (River Basin Specific Pollutants, RBSP). The MSFD provisions foresee the consideration of contaminants that are not covered by the WFD, but entail a significant risk to, or via, the marine environment. A close collaboration with Regional Sea Conventions is crucial, as contaminants cross national and EU borders.

Chemical substances occurring in the marine environment might derive from specific sea-based sources, such as shipping, mariculture, offshore oil and gas production, marine renewable energy devices, seabed mining, dredging of sediments, dumping of dredged material and historical dumping. This report consists of a scientific review of the literature to compile a list of marine specific contaminants potentially entering the marine environment from these sea-based sources. It also provides an overview of the environmental policy instruments and frameworks in place to oversee and regulate these substances within the EU.

The resulting list should support Member States in setting-up of monitoring approaches, including hotspots screening, and therefore, help guide the selection of relevant substances for MSFD Descriptor 8 implementation and also contribute to the work done in RSCs.

1 INTRODUCTION

The Water Framework Directive (WFD, 2000/60/EC¹) sets out the framework for the protection of surface waters against chemical pollution. The first step was to establish a first list of substances of European Union (EU)-wide concern (the priority substances, PS) as a means to assess the chemical status of water bodies up to 12 nautical miles from the straightened coastline (Decision 2455/2001). This first list was replaced by the Directive on Environmental Quality Standards (EQSD, 2008/105/EC²), which sets environmental quality standards (EQS) for these substances as well as for eight other pollutants already regulated under the scope of the Directive 86/280/EEC³. The WFD requires the Commission to review periodically the list, and in 2012 it put forward a proposal for a Directive amending the WFD and the EQSD as regards to PS (Directive 2013/39/EU⁴). The next WFD priority substances review is currently ongoing and completion is expected by 2016. In addition, the WFD requires the selection by Member States of substances of national or local concern (river basin specific pollutants, RBSP), which form part of the quality elements for "good ecological status" up to 1 nautical mile.

The Marine Strategy Framework Directive (MSFD, 2008/56/EC⁵) aims to achieve Good Environmental Status (GES) for Europe's marine waters by 2020. It completes the coverage of marine waters by provisions for substance selection in the areas covered by European legislation (fig. 1). The input of contaminants into the marine environment is considered under MSFD Descriptor 8 "*Concentrations of contaminants are at levels not giving rise to pollution effects*" as one of the anthropogenic pressures which needs to be assessed by EU Member States. According to MSFD requirements (Commission Decision 2010/477/EU⁶), Member States have to take into consideration the relevant provisions of the WFD in territorial and/or coastal waters to ensure proper coordination of the implementation of the two legal frameworks. Moreover, Member States have to consider also substances or groups of substances which are not listed as PS or RBSP but may entail significant risks to the marine environment. Hence, Member States should have also regard to the information and knowledge gathered and approaches developed in Regional

¹ Directive 2000/60/EC of the European parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy. http://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF

² Directive 2008/105/EC of the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0105&from=EN>

³ Council directive of 12 June 1986 on limit values and quality objectives for discharges of certain dangerous substances included in List I of the Annex to Directive 76/464/EEC (86/280/EEC). <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:1986L0280:20090113:EN:PDF>

⁴ Directive 2013/39/EU of the European parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:EN:PDF>

⁵ Directive 2008/56/EC of the European parliament and of the council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive). <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:164:0019:0040:EN:PDF>

⁶ Commission decision of 1 September 2010 on criteria and methodological standards on good environmental status of marine waters. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:232:0014:0024:EN:PDF>

Sea Conventions (RSCs) which cover EU marine regions or sub-regions: OSPAR⁷, HEL-COM⁸, Barcelona Convention⁹, and Bucharest Convention¹⁰.

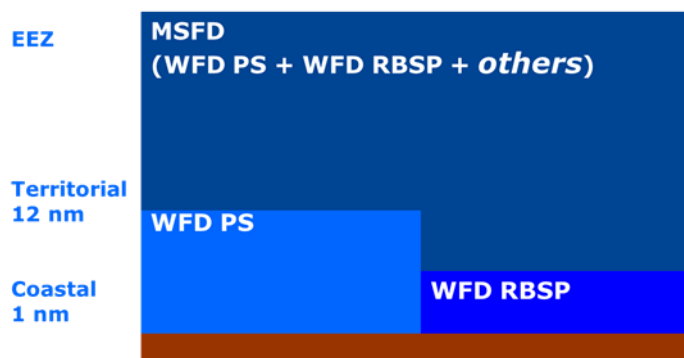


Fig. 1. Coverage of substances in marine waters by WFD and MSFD.

The aim of this report is, therefore, to compile a list of chemical substances that might be released from major sea-based human activities (shipping, mariculture, offshore operations, seabed mining, dredging and dumping at sea, and shipwrecks) and occur in the marine environment. It is important to bear in mind that the substances are listed without taking into account their toxicological properties and/or marine concentrations, so this report should not be regarded as a risk assessment.

The report also provides an overview of the relevant policies and regulations and RSC programmes dealing with the identified substances, thus allowing the analysis of their management and control in European marine waters. The outcome list might provide support for setting-up of monitoring approaches, e.g. through target screening schemes, and thus help guide the selection of relevant substances for MSFD Descriptor 8 implementation. Likewise, provisions of the RSCs are in place to identify substances of concern also in non-EU waters.

⁷ OSPAR Convention for the protection of the marine environment of the North-East Atlantic. <http://www.ospar.org/>

⁸ Baltic marine environment protection commission. <http://www.helcom.fi/>

⁹ Barcelona Convention for the protection of the marine environment and the coastal region of the Mediterranean. <http://www.unepmap.org/index.php?module=content2&catid=001001004>

¹⁰ Convention on the Protection of the Black Sea against Pollution. <http://www.blacksea-commission.org/>

2 MATERIAL AND METHODS

This report is largely based on the information provided recently by Tornero and Hanke (*in press*), which performed an extensive review of the available literature regarding chemical substances entering the sea from sea-based human activities. This report includes additional, complementary information in order to have a more complete picture of potential sea-sourced pollutants.

3 CHEMICAL CONTAMINANTS RELEASED FROM SEA-BASED SOURCES

This section compiles information on the basis of the sea-based human activities potentially resulting in the release of contaminants into the marine environment. According to Tornero and Hanke (*in press*), the highest number of discharged substances derive from the offshore oil and gas industry, followed by shipping, mariculture, dredging and dumping activities, offshore renewable energy devices, shipwrecks and seabed mining (fig. 2).

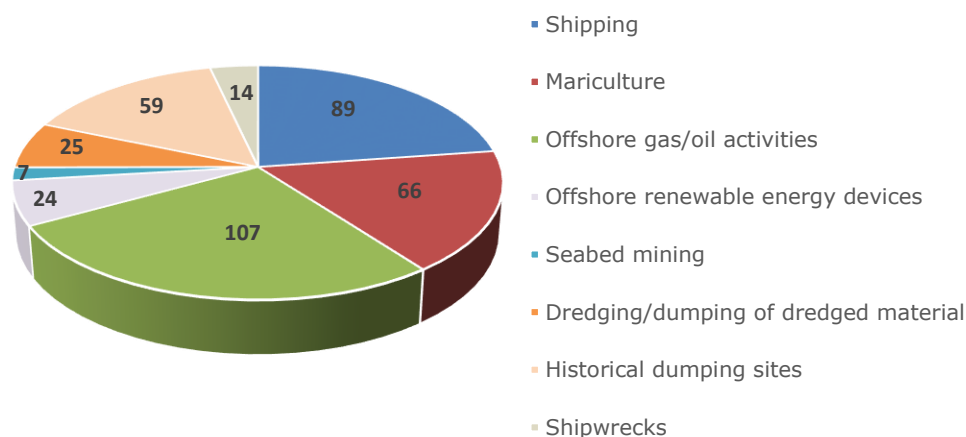


Fig. 2. Number of substances identified as potentially entering the marine environment from different sea-based sources (*from Tornero and Hanke, in press*).

3.1 OFFSHORE OIL AND GAS EXPLORATION AND PRODUCTION

Offshore installations are the means by which the oil and gas industry is able to explore, extract and transport oil and gas reserves from the geologic layers situated under the seabed. In European waters there are over 1000 offshore oil and gas installations, the majority of which are concentrated in the North Sea (UK, Norway, Netherlands), while others are located in the Adriatic Sea, around the Iberian Peninsula and the Black Sea. Most of these offshore installations operate in shallow waters of less than 300 meters in depth. Furthermore, intensive prospection activities are planned in the Maltese and Cypriot sectors. Exploration also takes place in the close vicinity of the EU, off the coasts of Algeria, Croatia, Egypt, Israel, Libya, Tunisia, Turkey and Ukraine (EMSA, 2013b).

Offshore operations can be divided into two main activities: exploration (all of the work required to site and drill a well) and production (ARPEL, 1999). Rock cuttings from drilling (drill cuttings) and formation water brought up with the hydrocarbons (produced water) are considered as the major sources of contaminants entering the sea from regular operations (Bakke et al., 2013). Additionally, offshore activities also entail the risk of discharges of oil and chemicals due to accidental spills. Pollution from normal operations and from accidents should be clearly distinguished and consequently are regulated by different instruments. Operation discharges are regulated by international conventions (such as OSPAR, HELCOM and the Barcelona Convention), while accidental risks are regulated by

national legislation or the European Safety of Offshore Oil and Gas Operations Directive¹¹ (Christou and Konstantinidou, 2012).

The use and discharge of hazardous substances in the offshore oil and gas industry have been identified as a cause for great concern. However, there is limited monitoring of quantities and consequent inputs to marine ecosystems. Within the OSPAR Maritime area, 752 offshore installations were discharging to the marine environment in 2012. The total quantity of chemicals discharged on that year was 222 414 tonnes, out of which almost 86% (wt.) were on the PLONOR¹² list (considered to have limited environmental impact) and another 13 % (wt.) were chemicals not containing candidates for substitution. Less than 1% (wt.) of the discharged substances were Priority Action chemicals¹³ (expected to cause adverse impact in the marine environment) or substances which are candidates for substitution (OSPAR, 2014a).

Tornero and Hanke (*in press*) identified 107 substances potentially released from the offshore oil and gas exploration and production. However, a better understanding of the chemicals used in both drilling and production processes and their potential impacts on the environment is still required, especially taking into account that the oil and gas industry is shifting to deeper regions of the ocean, where even less data are available and where appropriate monitoring and management can be more problematical (Roose et al., 2011; Science for Environment Policy, 2012).

3.1.1 Operational discharges: drilling waste and produced waters

The major components of drill muds are a base fluid (water, oil, or another organic fluid) and a weighting material, commonly barite (barium sulfate). Various additives (viscosifiers, biocides, corrosion inhibitors, shale inhibitors, emulsifiers, lubricants, wetting agents, surfactants, detergents, salts and organic polymers) are also utilized to improve the technical performance of the mud. The total number of ingredients in most drilling fluids is about 8–12 (Holdway, 2002), although there are more than 1000 products available for formulating drilling fluids. Several metals and metalloids are also present in most water-based drilling muds. Those of greatest concern, because of their potential toxicity and/or abundance in drilling fluids, include arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, nickel, and zinc (ARPEL, 1999; Neff, 2005).

Operational discharges nowadays practically only occur from drilling using water-based drilling muds, since the releases of oil-based and synthetic muds were gradually phased out from mid-1990s for environmental reasons (Neff, 2005; Bakke et al., 2013). As an example, in the OSPAR region, the amount of oil and other organic-phase fluids discharged via cuttings were significantly reduced from 342 tonnes to 5 tonnes over the 2003 to 2012 period (OSPAR, 2014a).

Drill cuttings produced during drilling with water-based drilling muds may contain small amounts of petroleum hydrocarbons and radionuclides such as ²²⁶Ra, ²²⁸Ra, and ²¹⁰Pb (Neff, 2005; Breuer et al., 2004).

The accumulations of drill cuttings (cuttings piles) represent an additional potential anthropogenic source of pollutants. Extensive discharges of oil-based cuttings were commonplace in the past and led to the formation of large waste deposits of polluted drilling

¹¹ Directive 2013/30/EU of the European parliament and of the council of 12 June 2013 on safety of offshore oil and gas operations and amending Directive 2004/35/EC. <http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32013L0030>

¹² OSPAR Agreement 2013-06. OSPAR List of Substances Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment (PLONOR). <http://www.ospar.org/convention/agreements>

¹³ OSPAR List of Chemicals for Priority Action (Revised 2013). (Reference number 2004-12)

cuttings beneath and around the oil and gas platforms. Although the discharges are currently regulated and no longer have oil, there is a risk of leakage of contaminants from old cuttings piles (e.g. hydrocarbons and heavy metals) resulting from physical disturbance during platform activities, storms, or trawling as well as of generation of potentially toxic compounds (e.g. complex esters and organic acids) resulting from biodegradation and other diagenetic processes over the years (Breuer et al., 2004; Bakke et al., 2013).

Produced water is considered a major source of marine pollution due to the sheer volume discharged in the offshore production activities (Meier et al., 2010; Brooks et al., 2011). Concerns over its ocean disposal have led the Norwegian government to enforce a strict “zero environmental harmful discharge” policy for all oil exploration activities in the Norwegian Arctic areas. Similarly, the OSPAR Recommendation 2001/1 (amended by the OSPAR Recommendation 2011/8)¹⁴ aims at preventing and eliminating pollution by oil and other substances caused by discharges of produced water into the sea.

The composition of produced waters vary considerably from well to well and over time in individual wells (Roose et al., 2011). This wide variation makes it difficult to establish routine monitoring, so area specific studies might be necessary to understand the potential risks to the environment caused by the discharge of produced waters (Neff et al., 2011). The OSPAR Agreement 2014-05¹⁵ provides a list of the naturally occurring substances usually being analyzed to characterize produced water samples along with their established PNECs. Compounds include PAHs and other dissolved hydrocarbons, alkylphenols, metals, organic acids, and radioactive isotopes. In addition, treatment chemicals such as scale and corrosion inhibitors, biocides, antifoams, and flocculants are also common constituents in produced waters (ARPEL, 1999; Meier et al., 2010; Neff et al., 2011).

The table 1 compiles the main chemical substances present in drilling muds and produced waters from the offshore gas and oil industry. Nonetheless, the specific chemicals and quantities are not generally publically available and only the legally obligatory health and safety data are usually indicated on material safety data sheets (McCormack et al., 2001). Therefore, there is still need for a better understanding of the constituents, environmental fate and potential effects of oilfield products (Neff et al., 2011; Bakke et al., 2013).

¹⁴ OSPAR Recommendation 2011/8 amending OSPAR Recommendation 2001/1 for the management of produced water from offshore installations. <http://www.ospar.org/convention/agreements>

¹⁵ Background Document. Establishment of a list of Predicted No Effect Concentrations (PNECs) for naturally occurring substances in produced water (OSPAR Agreement 2014-05). <http://www.ospar.org/convention/agreements>

Table 1. Main chemical constituents of drill muds and produced waters from the offshore gas and oil industry.

| Drilling muds | | Produced waters | |
|-------------------------------------|---|--|---|
| Weighting materials | Barite Calcite Ilmenite Hematite | PAHs | Acenaphtene Acenaphtylene Anthracene Benz(a)anthracene Benzo(g,h,i)perylene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Chrysene Dibenzo(a,h)anthracene Dibenzothiophene Fluoranthene Fluorene Indeno(1,2,3,-cd)pyrene Naphthalene Phenanthrene Pyrene |
| Viscosifiers | Bentonite Carboxymethyl cellulose Hydroxyethyl cellulose | BTEX | Benzene Toluene Ethylbenzene Xylene |
| Biocides | Glutaraldehyde | Phenols/ alkylphenols | Dimethylphenols Methylphenols Nonylphenol Octylphenol Phenol |
| Shale inhibitors | Glycol Lime Potassium chloride Sodium hydroxide | Organic acids | Acetic acid Benzoic acid Butyric acid Formic acid Hexanoic acid Isobutyric acid Isovaleric acid Malonic acid Naphthenic acid Oxalic acid Propionic acid Valeric acid |
| Thinners and dispersants | Lignites Lignosulfonates Tannins | Biocides | (e.g. Kathon and MB554) |
| Salts | Sulfonated salts of asphalt or gilsonite | Corrosion inhibitors | Amines Amides Imidazolines Quaternary Ammonium compounds |
| Lubricants | Diesel fuel Glycerin Graphite | Process scale inhibitors | (e.g. SP250 and SP 2945) |
| Emulsifiers | Alkylphenol polyethoxylate Alkylacrylate sulfonate derivatives Polyethylene oxide | Well treatment scale inhibitors | (e.g. S432) |
| Corrosion inhibitors | Amines Ammonium bisulfite Phosphate | Antifoams | (e.g. polydimethylsiloxane) |
| Inorganic sulfide scavengers | Basic zinc carbonate Triiron tetraoxide Zinc oxide | Flocculants | (e.g. ML 2317 W) |
| Defoamers | Aluminum stearate Tributyl phosphate | Gas treatment chemicals | Glycol Methanol |
| Metals/metalloids | Arsenic Barium Cadmium Copper Chromium Iron Lead Mercury | Metals/metalloids | Arsenic Barium Cadmium Chromium Copper Iron Lead Manganese |

| | | | |
|----------------------|-------------------------|----------------------|--|
| | Nickel Zinc | | Mercury Molybdenum Nickel Vanadium Zinc |
| Radioisotopes | 226Ra 228Ra 210Pb | Radioisotopes | 40K 224Ra 226Ra 228Ra 210Pb 210Po 222Rn 228Th 235U 238U |

3.1.2 Accidental spills

In the past three decades, at least 11 major offshore disasters have occurred around the world, and several lesser incidents could have escalated into such¹⁶. Disasters such as the Deepwater Horizon spill in the Gulf of Mexico in 2010 represent perhaps the greatest threat to marine and coastal environments from offshore activities. This kind of events prompted the restart of discussions on risk management in offshore oil and gas operations. Under the Safety of Offshore Oil and Gas Operations Directive, the EU has put in place a set of rules to help prevent accidents, as well as respond promptly and efficiency should one occur. Accidental oil spills from offshore installations can differ significantly from ship-sourced oil spills, mainly due to the potentially higher amount and prolonged discharge of fresh oil (EMSA, 2013b).

The use of chemical dispersants to combat oil spills at sea can be regarded as another source of pollutants into the marine environment. This has been a topic of particular interest in recent years, especially after the explosion of the Deepwater Horizon oil platform, where roughly two million gallons of dispersants were used at the water's surface and a mile below the surface as a method to disperse the spilled crude oil. Although chemical dispersants can accelerate dilution and biodegradation of the oil and so reduce the potential environmental and economic impacts, their application can also lead to increased short-term toxicity to aquatic organisms and risk of exposure to coastal populations and emergency responders (Graham et al., 2016; Major et al., 2016).

Within the EU, the European Maritime Safety Agency (EMSA)¹⁷ publishes since 2005 an "Inventory of national policies regarding the use of oil spill dispersants in the EU Member States", which is updated at regular intervals (EMSA, 2014). Policies vary greatly across the EU. In most Member States, the use of dispersants is secondary to mechanical containment and recovery, and in many countries, particularly in the Baltic region, it is either not permitted or highly restricted. In other states, where the use of dispersants is in practice allowed, they have not been used for more than one decade (Chapman et al., 2007).

Dispersants consist of a formulation containing a mixture of substances including, but not limited to, surfactants (anionic/nonionic) and solvents that helps break oil into small droplets which dilute throughout a very large volume of water, facilitating the natural biodegradation process (EMSA, 2010, 2016; Graham et al., 2016; Major et al., 2016). The table 2 shows the typical surfactants and solvents present in today's formulations.

¹⁶ Commission staff working paper executive summary of the impact assessment accompanying the document proposal for a regulation of the European parliament and of the council on safety of offshore oil and gas exploration and production activities, 2011

¹⁷ European Maritime Safety Agency (EMSA). <http://www.emsa.europa.eu/>

Table 2. Typical surfactants and solvents in chemical oil dispersants.

| Surfactants | | Solvents | |
|--|--|------------------------------------|---|
| Fatty acid esters or sorbitan esters | Sorbitan, mono-(9Z)-9-octadecenoate | Light petroleum distillates | Hydrotreated light (SP 250) |
| Ethoxylated fatty acid esters (PEG esters) or ethoxylated sorbitan esters | Fatty acids, fish-oil, ethoxylated Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives | Glycol ethers | 2-Butoxyethanol Di-propylene glycol butyl ether Di-propylene glycol monomethyl ether Ethylene glycol Propylene glycol |
| Sodium di-iso-octyl sulphosuccinate (DOSS) | | | |

Besides major offshore accidents, the occurrence of frequent minor spills is not to be neglected. 1205 tonnes of chemicals were accidentally spilled in 2012 in the OSPAR area, the majority of which were on the PLONOR list (84%) or were chemicals not containing candidates for substitution (12%) (OSPAR, 2014a).

3.1.3 Atmospheric emissions

Atmospheric inputs from offshore oil and gas activity, mainly due to flaring, may also be substantial. Inputs are mainly nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon oxide and VOCs (Roose et al., 2011). Although this issue deserves further in-depth research, the analysis of contaminants entering the sea through atmospheric transport is beyond the scope of this report.

3.1.1 Decommissioning of offshore installations

The decommissioning of offshore oil or gas fields is a complex process which can consist in complete removal and re-processing of the materials, partial removal of the surface structure, or toppling or dismantling the structure and placement of the materials on the seabed (Techera and Chandler, 2015). This issue is particularly pressing in some parts of the world like the OSPAR area, where thousands of installations are reaching the end of their operational life (OSPAR, 2010a).

There is a subtle line between decommissioning and dumping. The controversy over the disposal of redundant oil and gas installations in European waters was re-opened in 1995 when the UK government authorized the sinking of the entire Brent Spar oil platform at a deep water site in the North Atlantic Ocean¹⁸. Nowadays, there are many different regulatory frameworks around the world relevant for decommissioning operations (e.g. UNCLOS¹⁹, London Dumping Convention, IMO, OPGGSA²⁰), but there is no clear consensus on what best practices should be (Testa, 2014; Techera and Chandler, 2015). In European waters, the OSPAR Decision 98/3²¹ establishes the general rule that "dumping, and the leaving wholly or partly in place, of disused offshore installations within the maritime area

¹⁸ Communication from the Commission to the Council and the European Parliament on Removal and Disposal of Disused Offshore Oil and Gas Installations, 1998

¹⁹ United Nations Convention on the Law of the Sea (UNCLOS). http://www.un.org/depts/los/convention_agreements/texts/unclos/UNCLOS-TOC.htm

²⁰ Commonwealth Offshore Petroleum and Greenhouse Gas Storage Act 2006. <https://www.comlaw.gov.au/Series/C2006A00014>

²¹ OSPAR Decision 98/3 on the Disposal of Disused Offshore Installations. <http://www.ospar.org/convention/agreements?q=98%2F3&t=32282&a=&s=>

is prohibited". Only some heavy steel installations or gravity based concrete structures, and subject to an assessment, may be allowed to be left in place (OSPAR, 2010a). Similarly, the Baltic Convention obliges the contracting parties to ensure that all abandoned offshore units are essentially removed and brought ashore under the responsibility of the owner. Anything left behind (i.e., partial removal) would be considered dumping (Hamzah, 2003).

Any removal choice can result in the remobilization of contaminants from re-suspended sediments or from the cuttings piles accumulated on the seabed (Schroeder and Love, 2004; OGP, 2012). Likewise, any structure left over might eventually deteriorate and release into the surrounding environment contaminants such as PCB's, residual oil and heavy metals (Lakhal et al., 2009; Adedayo, 2011).

3.2 SHIPPING

As shipping lanes become more and more congested, the risk of pollution caused by shipping increases (Tournadre, 2014). In 1973, the International Maritime Organization (IMO)²² adopted the International Convention for the Prevention of Pollution from Ships (known as the MARPOL Convention 1973–78)²³. The MARPOL Convention is the main international convention covering prevention of pollution of the marine environment by ships from operational or accidental causes as well as pollution by chemicals, goods in packaged form, sewage, garbage and air pollution. Even though regulations are strict, the discharges of polluting substances into the sea still happen, often illegally (EMSA, 2012).

Tornero and Hanke (*in press*) identified 89 chemical substances potentially released into the sea from shipping activities, including accidental spills, operational discharges and release of antifouling chemicals from boats.

3.2.1 Accidental spills of oil and other chemicals

The number of maritime incidents causing significant oil spills seems to have decreased in recent years, but major accidental oil tanker spills still happen in European waters. Moreover, as oil production and consumption are increasing, as are net imports of oil to the EU, the risk of oil spills also increases (EEA, 2008). MARPOL regulates the construction, design and operation of vessels with the goal of reducing the amount of oil released to the sea.

Crude oil is composed of thousands of chemicals and there are thousands of different kinds of crude and refined oils (Coppock and Dziwenka, 2014). Of the hydrocarbon compounds common in petroleum, the polycyclic aromatic hydrocarbons (PAHs) appear to pose the greatest toxicity to the environment and normally provide insight into the general distribution of petroleum hydrocarbons in the environment associated with a spill. Other oil-related compounds include Volatile Organic Compounds (VOCs) (e.g. hexane, heptane, octane, nonane, benzene-toluene-ethylbenzene-xylene isomers, BTEX), acids, esters, ketones, phenols and metals (e.g. iron, nickel, copper, chromium, and vanadium) (Bennett and Larter, 2000; NRC, 2003; Neuparth et al., 2012; Sammarco et al., 2013).

Furthermore, as said above, chemical dispersants can be used as a response option to oil spills and hence they can also be listed as substances potentially released into the marine environment from shipping activities.

²² International Maritime Organization (IMO). <http://www.imo.org/>

²³ International Convention for the Prevention of Pollution from Ships (MARPOL). [http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Prevention-of-Pollution-from-Ships-\(MARPOL\).aspx](http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Prevention-of-Pollution-from-Ships-(MARPOL).aspx)

Shipping is also the main way of transport of Hazardous and Noxious Substances (HNS), which are defined as substances other than oil, which if introduced into the marine environment are likely to create hazards to human health, to harm living resources and other marine life, to damage amenities and/or to interfere with other legitimate uses of the sea (IMO, 2000). Approximately 2000 different chemicals used by man are estimated to be regularly transported by sea, either in bulk or in packaged form (Purnell, 2009). However, information on transportation volumes is limited and decentralized, and the exact quantities of different substances transported and spilled are usually not available (Posti and Häkkinen, 2012; EMSA, 2013a). The most important conventions governing the transportation of HNS are the International Convention for the Safety of Life at Sea (SOLAS)²⁴ and MARPOL. The MARPOL Annex II contains the "Regulations for the Control of Pollution by Noxious Liquid Substances in Bulk" and includes some 250 substances graded into four categories according to the hazard they present to marine resources, human health or amenities. Regulations concerning chemicals transported in packaged form are MARPOL Annex III.

In European waters, incidents resulting in HNS release occur frequently (EMSA 2007, 2008, 2009, 2010). During 1978-2013, the most released substances were styrene, sulphuric acid, benzene, and phosphoric acid, the majority carried by single cargoes in bulk form (EMSA, 2013a). According to the HASREP project (Response to Harmful Substances spilled at sea) and the Chembaltic project (Risks of Maritime Transportation of Chemicals in Baltic Sea), the bulk HNS most transported in and along European waters are palm and other vegetable oils, methanol, benzene and its mixtures, sodium hydroxide solution, xylenes, styrene, methyl tert-butyl ether (MTBE), molasses, ammonia, ethanol, phenol, phosphoric acid, sulphuric acid, acetic acid, and animal fat (HASREP, 2005; Posti and Häkkinen, 2012).

The prioritization of the HNS posing the highest risk to the marine environment, based on their volumes transported, their reported incidents, their physico-chemical properties and their toxicity to marine biota, would be necessary when developing emergency response plans in the event of a chemical spill (Neuparth et al., 2012). The table 3 presents the HNS prioritized in European waters according to the ARCOPOL²⁵ platform and the RAMOCS²⁶ project (Neuparth et al., 2011; Radovic et al., 2012).

²⁴ International Convention for the Safety of Life at Sea (SOLAS). [http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-\(SOLAS\),-1974.aspx](http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-(SOLAS),-1974.aspx)

²⁵ ARCOPOL (Atlantic Region-Coastal Pollution Response). <http://www.arcopol.eu/>

²⁶ RAMOCS (Implementation of risk assessment methodologies for oil and chemical spills in the European marine environment). <http://www.idaea.csic.es/ramocs/>

Table 3. Ship-sourced hazardous and noxious substances (HNS) posing the highest risk to European marine waters according to the ARCOPOL and RAMOCS projects.

| ARCOPOL project | RAMOCS project |
|------------------------------------|--------------------------------|
| Benzene | Sulfuric acid |
| Styrene | Phosphoric acid |
| Xylenes | Styrene monomer |
| Cyclohexane | Phenol |
| Toluene | Sodium hydroxide |
| Nonene (All Isomers) | Ammonia |
| Aniline | Methanol |
| Acrylonitrile | Xylene |
| Nitrobenzene | Aniline |
| Isononanol | Benzene |
| Alkyl (C5–C8, C9) Benzenes | Palm oil |
| Nonylphenol Poly(4–12) Ethoxylates | Propylene oxide |
| Octane (all Isomers) | Nitrobenzene |
| 1-Nonanol (Nonyl Alcohol) | Toluene |
| Butyl Acrylate (All Isomers) | Cyclopentadiene |
| Di (2-Ethylhexyl) Adipate | Acetic acid |
| Trichloroethylene | 1-Nonanol |
| Hexane (All Isomers) | Acrylonitrile |
| Heptane (All Isomers) | Animal oil |
| 1-Dodecanol | Methyl tert-butyl ether (MTBE) |
| Cresols (All Isomers) | |
| Decanoic acid | |

Marine toxicological data are scarce for most priority HNS (Neuparth et al., 2013). The Marine Intervention in Chemical Emergencies Network (MAR-ICE)²⁷ and the Marine Chemical Information Sheets (MAR-CIS)²⁸ are the EMSA information tools for HNS pollution response. Both products aim at providing specific information on diverse substances selected on the basis of their maritime transport and involvement in past incidents within European waters and their risks to the marine environment and hazards to human health. Datasheets of approximately 200 substances are expected to be soon available for distribution to Member States.

3.2.2 Operational discharges

Operational discharges include releases of bilge water from machinery spaces and ballast water of fuel oil tanks. At the global IMO level, several measures have been taken to reduce deliberate and "routine" spills. For example, the so-called Crude Oil Washing (COW)²⁹ has been made mandatory for new vessels under MARPOL. Although environmental regulations for these operations are quite strict, especially in MARPOL special areas, compliance rates are low in some areas of the world (Kachel, 2008). Operational discharges are still quite frequent and represent one of the largest anthropogenic inputs of oil and oily wastes into the marine environment, thus becoming a major issue to be addressed (NRC, 2003; EMSA, 2008; Hassler, 2011). Detergents and cleaners, lubricants, chemicals from refrigerating equipment and fire-extinguishers are also frequently discharged. However, information on pollutants associated with shipping operational discharges is scarce (Honkanen et al., 2013; McLaughlin et al., 2014).

The United States Environmental Protection Agency (EPA)³⁰ analyzed various operational discharge types from various vessel classes and provided a list with the detected pollutants which might represent a risk to the marine environment (USEPA, 2010). The table 4 presents the substances found in this study.

Table 4. Pollutants frequently detected in operational discharges from different vessels.

| | |
|---|---|
| Metals and metal-loids | Arsenic Aluminum Cadmium Copper Iron Lead Manganese Zinc |
| Semivolatile organic compounds (SVOCs) | Bis(2-ethylhexyl) phthalate |
| VOCs | Benzene |
| Surfactants | Long- or short-chain nonylphenol and octylphenol ethoxylates |
| Nutrients | Phosphorus and nitrogen compounds |
| Pathogens | |

3.2.3 Release of biocides from antifouling paints

The accumulation of biofouling can reduce the performance of vessels and increase fuel consumption. Traditionally, biocides have been used in antifouling paints to prevent the

²⁷ <http://emsa.europa.eu/hns/mar-ice-network/item/1613.html>

²⁸ <http://www.emsa.europa.eu/about/faq/300-hazardous-noxious-substances-hns-operational-support/2166-what-is-mar-cis.html>

²⁹ <http://www.imo.org/en/OurWork/Environment/PollutionPrevention/OilPollution/Pages/Crude-Oil-Washing.aspx>

³⁰ United States Environmental Protection Agency (EPA). <http://www.epa.gov/>

growth of potential fouling organisms such as bacteria, fungi, algae, mussels, barnacles and other invertebrates. However, the use of biocides in the marine environment has proved to be harmful to non-target organisms. For many years the organotin tributyltin (TBT), which has an endocrine disrupting effect, was the most widely used active component in antifouling paints was (Dafforn et al., 2011). The EU Regulation (EC) No. 782/2003³¹ banned the application of TBT-paints on all EU-flagged vessels from 2003 and the global prohibition on all vessels was ratified under the IMO Convention on the Control of Harmful Anti-fouling Substances in 2008.

The main alternatives to TBT have been biocides such as copper(I) salts (e.g. copper oxide and copper thiocyanate). The use of Cu-based antifouling coatings is currently allowed in all countries. In many developed countries, biocidal active ingredients and products must pass a rigorous review before they can be sold and used (Blossom, 2014). A restriction put in place by Sweden in the Baltic Sea, classified as a Particularly Sensitive Sea Area by the IMO, was recently lifted based on an improved understanding of the effects of copper (Swedish Chemicals Agency, 2011).

Cu-based paints have now been supplemented by 'booster biocides', to improve its performance against certain more resistant algal fouling (Cima and Ballarin, 2012). The list of potential booster biocides is substantial, although not all compounds are marketed (Price and Readman, 2013). Moreover, detailed up-to-date data on the quantities and types of biocides used around the world or even at national level is limited (ACE, 2002; Readman, 2006). Typical tin-free booster biocide in recent years include non-metallic organic compounds (e.g. irgarol and diuron) and organometallic compounds (e.g. copper pyrithione and zinc pyrithione) (Dafforn et al., 2011; Diniz et al., 2014). The table 5 shows the most commonly biocides used in antifouling paints along with specific information on their concentrations in the marine environment compartments, bioaccumulation potential, ecotoxicity data, and available quality standards or thresholds for their assessment.

The European Union is establishing a regulatory framework for the placing of biocidal products on the market, with a view to ensuring a high level of protection for humans, animals and the environment. The new EU-Biocide-Regulation (BPD, No 528/2012³² and amendment No 334/2014³³) repeals the Directive 98/8/EC³⁴ and states that all biocidal products require an authorization before they can be placed on the market, and the active substances contained in that biocidal product must be previously approved. Hence, a list of active substances agreed for inclusion in biocidal products are listed in Annexes I and IA and classified under 22 different biocidal product types, including antifouling agents (product type 21). For some existing active substances, such as diuron and ziram, a decision of non-inclusion into Annexes I or IA has been adopted. Thus, these substances and the biocidal products containing these active substances shall be removed from the market within 12 months of the entering into force of such decision. However, active substances

³¹ Regulation (EC) No 782/2003 of the European parliament and of the council of 14 April 2003 on the prohibition of organotin compounds on ships. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:115:0001:0011:EN:PDF>

³² Regulation (EU) No 528/2012 of the European parliament and of the council of 22 May 2012 concerning the making available on the market and use of biocidal products. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012R0528&from=EN>

³³ Regulation (EU) No 334/2014 of the European parliament and of the council of 11 March 2014 amending Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products, with regard to certain conditions for access to the market. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32014R0334&from=EN>

³⁴ Directive 98/8/EC of the European parliament and of the council of 16 February 1998 concerning the placing of biocidal products on the market. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0008&from=EN>

under the review programme, such as dichlofluanid and irgarol, can be placed on the market while awaiting the final decision on the approval. New active substances, such as tralopyril that are still under assessment are also allowed on the market. The European Chemicals Agency (ECHA)³⁵ will in particular be responsible for the assessment of applications for the Union authorization of biocidal products. Before the BPD only a handful of European countries regulated the use of antifouling products so the implementation of the BPD in all member states has changed the market drastically.

3.2.1 Air pollution

Exhaust emissions from vessels' engines are a significant and increasing source of air pollution, principally in the form of NO_x, particulate matter, SO_x, and carbon oxide. Once in the air, these substances may also reach the marine environment, contributing to acidification of water, eutrophication and global warming. Some VOCs (mainly methane, propane, and butane) may also be released from tankers underway or during loading and offloading activities, contributing to the total inputs of hydrocarbons to the sea (OSPAR, 2009a). Recently adopted strict IMO emission control standards are expected to help progressively reduce these emissions. However, as said above for offshore-related pollution, the analysis of atmospheric contaminants is beyond the scope of this report.

³⁵ European Chemicals Agency (ECHA). <http://echa.europa.eu/>

Table 5. Overview of the most common biocides used in ship antifouling paints (as published in Tornero and Hanke, *in press, supplementary material*).

| Substance | Concentrations in the marine environment | Bioaccumulation Bioconcentration | Toxicity in the marine environment | PNEC for the marine environment | Quality benchmarks | Remarks |
|---|---|---|--|---|--|---|
| Capsaicin 8-methyl-N-vanillyl-6-nonenamide | MEC: Not available. PEC: <i>Marina:</i> 0.0935-0.768 µg/L (Oliveira et al., 2014); 0.0249 µg/L (Wang et al., 2014b). <i>Commercial harbor:</i> 0.00663 µg/L (Wang et al., 2014a); 0.00399 µg/L (Wang et al., 2014b). <i>Sediment:</i> 0.000208 mg/Kg (Wang et al., 2014a). | Log Kow = 3.04. BCF <1000 from 219 aquatic species (Wang et al., 2014b). | <i>Invertebrates:</i> 48h EC50 = 3.868 µg/L (<i>Mytilus galloprovincialis</i>); 5.248 µg/L (<i>Paracentrotus lividus</i>). 48h LC50 = 1.252 µg/L (<i>Tisbe battagliai</i>). NOEC = 10 µg/L (<i>Mytilus galloprovincialis</i>); 1 µg/L (<i>Paracentrotus lividus</i>); 600 µg/L (<i>Tisbe battagliai</i>) (Oliveira et al., 2014). | <i>Water:</i> 0.0629 µg/L (Oliveira et al., 2014); 0.490 µg/L (Wang et al., 2014a). <i>Sediment:</i> 0.0138 mg/Kg (Wang et al., 2014a). | | Natural, processed vegetable matter that has been part of the human diet for many years. Become of interest as biocide over the last few years, although it has limited international use (with the exception of China). Not supported through any national or international registration for antifouling use. Very few data publicly available on its environmental fate and effects, but initial assessments suggest that it will bind to the surface of sediments and suspended solids (Thomas and Brooks, 2010) and poses relatively low risk to the marine environment (Wang et al., 2014b). |
| Chlorothalonil 2,4,5,6-tetra-chloroisophthalonitrile | MEC: <i>Water:</i> from undetectable levels (LOD = 0.8 ng/L) to 10.9 ng/L (Atlantic coast of France and UK) (ACE, 2002); 360-1380 ng/L (UK commercial estuary) (Konstantinou and Albanis, 2004). <i>Sediment:</i> 16-34.3 ng/g (UK commercial estuary) (Konstantinou and Albanis, 2004); 8-165 µg/Kg dwt (Greek marinas/harbors) (ACE, 2002). PEC: 1.4 µg/L (Bellás, 2006). | Log Kow = 2.6–4.4 (Van Wezel and Van Vlaardingen, 2004). | <i>Algae:</i> 24h EC50 = 190 µg/L (<i>Pyrocystis lunula</i>). 96h EC50 = 13 µg/L (<i>Skeletonema costatum</i>); 4.4 µg/L (<i>Thalassiosira pseudonana</i>) (Bao et al., 2011). <i>Invertebrates:</i> EC10 = 4.5 µg/L (<i>Mytilus edulis</i> , embryonic development); 4.3 µg/L (<i>Paracentrotus lividus</i> , embryonic development). EC50 = 8.8 µg/L (<i>Mytilus edulis</i> , embryonic development); 6.6 µg/L (<i>Paracentrotus lividus</i> , larval growth) (Bellás, 2006). | <i>Water:</i> 0.45 µg/L (<i>Mytilus edulis</i>); 0.043 µg/L (<i>Paracentrotus lividus</i> , embryo); 0.05 µg/L (<i>Paracentrotus lividus</i> , larval growth); 1.2 µg/L (<i>Ciona intestinalis</i> , embryo); 2.9 µg/L (<i>Ciona intestinalis</i> (larval settlement) (Bellás, 2006); 0.69 µg/L (Yamada, 2006). | 530 ng/L (ERL water); 50.6 µg/kg (ERL sediment) (Van Wezel and Van Vlaardingen, 2004). 0.36 µg/L (protection of marine life, Canadian Council Ministers of the Environment) (Konstantinou and Albanis, 2004). | Commonly used in recent years and afterwards subject to restrictions. Sporadically found in European coasts, mainly in the Mediterranean, but in isolated cases at high levels. The usually low concentrations (mostly below limit of detection) are probably due to the lack of persistence in the water column (half-lives between 1.8 and 8 days) (Thomas and Langford, 2009). Amongst the most toxic biocides to aquatic organisms (Bellás, 2006; Voulvoulis, 2006; Cui et al., 2014). It has |

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|---|---|--|--|--|--|---|
| | | | <p>24h LC50 = 1 mg/L (<i>Artemia salina</i>) (Koutsaftis and Aoyama, 2007). 48h LC50 = 12 µg/L (<i>Hydrodroides elegans</i>, larvae). 96h LC50 = 67µg/L (<i>Elaemopus rapax</i>, juvenile); 91 µg/L (<i>Tigriopus japonicus</i>, adult) (Bao et al., 2011). 96h EC50 = 0.005 mg/L (<i>Crassostrea virginica</i>) (Van Wezel and Van Vlaardingen, 2004). Fish: 96h LC50 = 0.033 mg/L (<i>Cyprinodon variegatus</i>) (Van Wezel and Van Vlaardingen, 2004); 69-76 µg/L (<i>Oncorhynchus mykiss</i>); 73 µg/L (<i>Gasterosteus aculeatus</i>) (Yamada, 2006); 22.6 µg/L (<i>Pimephales promelas</i>) (Mochida and Fujii, 2009a); 110 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011).</p> | | | <p>immunosuppressive potential which, although counterbalanced by their short half-life, can lead to biocoenosis dismantling through rapid bioaccumulation by filter-feeding non-target benthic organisms (Cima et al., 2008).</p> |
| <p>Chromium trioxide <i>Trioxochromium</i></p> | <p>Typical Cr-total natural concentrations 0.1-5 µg/L, and generally <1 µg/L (water); 0-100 mg/kg (sediments). MEC (Cr-total): Water: 145 µg/L (Irish estuary). Sediment: 30 ppm (Galician estuary, Spain). Biota: 0.71-4.23 µg/g dwt (<i>Mytilus edulis</i>, France); 0.30-3.38 µg/g dwt (<i>Mytilus galloprovincialis</i>, France); 3-26 ppm (<i>Mytilus galloprovincialis</i>, Galicia); 0.45-2.34 µg/g dwt (<i>Crassostrea gigas</i>, France); 1-508 ppm (<i>Scrobicularia plana</i>, Galicia); 11-</p> | <p>Log Kow not applicable. BCF for Cr (VI) in fish is relatively low at around 1 L/kg. Once in the organism, reduction of Cr (VI) to Cr (III) appears to occur, resulting in accumulation of Cr-total to a factor of approximately 100 times the original concentration in water. Uptake of Cr by other organisms appears to be</p> | <p><i>Invertebrates</i> (Cr VI): 96h LC50 = 8 mg/L (<i>Capitella capitata</i>, larvae); 5 mg/L (<i>Capitella capitata</i>, adults); >1.0 mg/L (<i>Neanthes arenaceodonta</i>, juvenile, adults). 28d LC50 = 0.28 mg/L (<i>Capitella capitata</i>, adults); 0.70 mg/L (<i>Neanthes arenaceodonta</i>, juvenile); 0.55 mg/L (<i>Neanthes arenaceodonta</i>, adults). 21d NOEC = 0.5 mg/L (<i>Ophryotrocha diadema</i>, adult) (EC, 2005). Fish:</p> | <p><i>Surface water</i>: 3.4 µg/L (Cr VI); 4.7 µg/L (Cr III). <i>Sediment</i>: 31 mg/kg ww (EC, 2005).</p> | <p>15 µg Cr-total/L (UK AA-EQS for the protection of saltwater life). 10 µg Cr-total/L (German water quality criterion for aquatic communities) (EC, 2005).</p> | <p>Substance of very high concern (SVHC) according to Regulation (EC) No. 1907/2006 (REACH). Very toxic to aquatic life with long lasting effects. Usual source of Cr (VI) and excess of Cr (VI) in biological systems has been implicated in specific forms of cancer (EC, 2005).</p> |

| | | | | | | |
|--------|---|---|--|---|--|---|
| | 100 ppm (<i>Cerastoderma edule</i> , Galicia); 3-409 ppm (<i>Nereis diversicolor</i> , Galicia) (EC, 2005). | higher than for fish. In mussels, BCFs up to around 9,100 L/kg dwt for Cr (VI) and 2,800 L/kg dwt for Cr (III) (EC, 2005). | 96h LC50 = 1-10 mg/L based on the most sensitive species, Atlantic salmon (CEPA, 2011). | | | |
| Copper | <p>Typical background concentrations 0.5–3 µg/L; up to 21 µg/L in contaminated areas (Brooks and Waldoock, 2009).</p> <p>MEC: <i>Water:</i> 0.7-7.8 µg/L (UK marinas) (Boxall et al., 2000); 0.62-3.89 µg/L (Finnish marina) (Thomas and Brooks, 2010); 10 µg/L (France); 20.7 µg/L (Greece) (Dafforn et al., 2011). <i>Sediment:</i> 10-161 mg/kg (UK commercial harbor); 4.8-30 mg/kg (UK estuarine moorings); 9-57 mg/kg (UK marinas) (Brooks and Waldoock, 2009); 80.4 µg/g (Greece) (Dafforn et al., 2011); 16-3100 mg/kg (aquaculture farms) (Simpson et al., 2013); 98.73 mg/kg (aquaculture farms) (Nikolaou et al., 2014). <i>Biota:</i> 2-5.6 µg/g dwt (<i>Caulerpa taxifolia</i>, France); 7.9-22 µg/g dwt (<i>Posidonia oceanica</i>, NW Mediterranean); <8-88 µg/g dwt (sponges, Portugal); 150-3110 µg/g dwt (<i>Crassostrea angulata</i>, Portugal); 3.7-33 µg/g dwt <i>Paracentrotus lividus</i> (NE Mediterranean); <0.15-4.4 µg/g dwt (deep sea fish, North Atlantic); 1.7-104 µg/g dwt (loggerhead turtle tissues, France); 1-272 µg/g dwt (stripped dolphin</p> | <p>Log Kow not applicable. BCF = 185 (<i>Argopecten irradians</i>); 4420-7730 (<i>Mytilus edulis</i>); 33400-57000 (<i>Crassostrea gigas</i>); 27800 (<i>Crassostrea virginica</i>); 2491-4915 (<i>Mytilus galloprovincialis</i>) (USEPA, 2003). However, Cu is an essential metal, which is actively regulated within animal cells, so bioaccumulation is not directly related to the environmental concentration and BCFs are considered unsuitable for describing Cu bioaccumulation (Thomas and Brooks, 2010).</p> | <p><i>Algae:</i> 96h EC50 = 770 µg/L (<i>Thalassiosira pseudonana</i>); 290 µg/L (<i>Skeletonema costatum</i>). 24h EC50 = 140 µg/L (<i>Pyrocystis lunula</i>) (Bao et al., 2011). 21d NOEC = 11-46 µg/L (<i>Fucus vesiculosus</i>, zoospore). 7d NOEC = 1.1-18 µg/L (<i>Ulva reticulata</i>, adult) (Van Sprang et al., 2008). <i>Invertebrates:</i> L(E)C50 = 200-1090 µg/L (<i>Hediste diversicolor</i>); 3.8-9.5 µg/L (<i>Mytilus spp.</i>, embryo); 11.5-560 µg/L (<i>Crassostrea gigas</i>, embryo, adult); 15.1-18.7 µg/L (<i>Crassostrea virginica</i>, embryo); 153-181 µg/L (<i>Americamysis bahia</i>) (USEPA, 2003). 48 h LC50 = 120 µg/L (<i>Hydroides elegans</i>); 110 µg/L (<i>Elasmopus rapax</i>) (Bao et al., 2008); 100 µg/L (<i>Hydroides elegans</i>, larvae) (Bao et al., 2011); >1000 µg/L (<i>Tigriopus japonicus</i>) (Bao et al., 2013). 48h NOEC = 6.6 µg/L (<i>Artemia franciscana</i>, cysts); 6.2 µg/L (<i>Mytilus edulis</i>, embryo); 5.9-9.7 µg/L <i>Mytilus galloprovincialis</i>,</p> | <p><i>Water:</i> 5.6 µg/L (Brooks and Waldoock, 2009); 2.6 µg/L (SCHER, 2009). <i>Marine sediment:</i> 338 mg/kg dwt. <i>Estuarine sediment:</i> 144 mg/kg dwt (SCHER, 2009).</p> | <p>3.76 µg/L (UK AA-EQS where DOC ≤ 1 mg/L); 3.76 µg/L + (2.677 x ((DOC/2) - 0.5)) (UK AA-EQS where DOC > 1 mg/L (SEPA, 2014). 1.0 µg/L (OSPAR ecotoxicological assessment criterion for ionic Cu in seawater) (Cima and Ballarin, 2012). 65 mg/kg (Australian lower SQGs to protect against acute effects) (Simpson et al., 2013).</p> | <p>Most commonly used biocide in antifouling paints for a long time (Yebra et al. 2004) and probably still today. In certain European countries, banned from use on recreational vessels, although so far this is restricted to inland freshwaters. Yet, many countries are beginning to re-evaluate current risk assessments in marine coastal waters (Brooks and Waldoock, 2009). Antifouling coatings on ship hulls are one main source of Cu to the marine environment and are estimated to account for 15,000 tons Cu/ year input into the marine environment globally (Bao et al., 2008, 2013). Although Cu is an essential metal for many organisms, it becomes toxic at high concentrations; it is immunotoxic to molluscs and teleosts and alters fertilization and early life stages of bivalves and corals (Cima and Ballarin, 2012). There are relatively few studies that specifically relate to the effect of Cu-based antifouling paints on the marine environment and these point to evidence of elevated levels of Cu in the vicinity of shipyards and dry docks (Thomas and Brooks, 2010). It has</p> |

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| | <p>tissues, NE Atlantic); 1.3-44 µg/g dwt (sperm whale tissues, North Sea) (Neff, 2002); 26 mg/ kg dwt (<i>Sparus aurata</i>, Mediterranean farms); 28.50 mg/ kg dwt (<i>Dicentrarchus labrax</i>, Mediterranean farms) (Nikolaou et al., 2014).</p> <p>PEC: <i>UK marinas:</i> 0.9-134 µg/L (Boxall et al., 2000). <i>Regional Worst-Case ambient for different European countries:</i> 0.8-2.7 µg/L (dissolved); 4.2-55.3 mg/kg dwt (sediments) (SCHER, 2009).</p> | | <p>embryo); 8.8-16.5 µg/L (<i>Paracentrotus lividus</i>, embryo) (Van Sprang et al., 2008).</p> <p><i>Fish:</i> LC50 or EC50 = 418 µg/L (<i>Cymatogaster aggregata</i>, adult); 2.6-8.08 µg/L (<i>Morone saxatilis</i>) (USEPA, 2003). 96h LC50 = 7300 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011). 32d NOEC = 57.8 µg/L (<i>Cyprinodon variegatus</i>, embryo-larvae). 12d NOEC= 55-123 µg/L (<i>Atherinops affinis</i>, early blastula embryo) (Van Sprang et al., 2008).</p> | | <p>also been suggested low bio-availability of Cu in antifouling paints (Simpson et al., 2013).</p> |
| <p>Copper pyrithione (CuPT) <i>Bis(1-hydroxy-1H-pyridine-2-thionato-O,S)copper</i></p> | <p>So far, only detected in harbor sediments and not in water (Mochida and Fujii, 2009a).</p> <p>PEC: <i>New Zealand harbors and marinas (based on average leaching rate):</i> 0.0408-0.469 µg/L (maximum); 0.0272-0.269 µg/L (average) (EPA, 2012). <i>Sediment:</i> suggested that the sediment compartment is not a concern for CuPT, as concentrations are extremely low (likely to be below the limit of determination for current analytical measurement) (ACP, 2005b).</p> | <p>Log Kow = 2.44 (EPA, 2012).</p> | <p><i>Algae:</i> 96h EC50 = 1.8 µg/L (<i>Skeletonema costatum</i>) (Bao et al., 2011); 50 µg/L (<i>Amphora coffeaeformis</i>, growth) (Mochida and Fujii, 2009a). 72h EC50 = 0.0284 mg/L (<i>Skeletonema costatum</i>) (Yamada, 2006); 1.5 µg/L (<i>Skeletonema costatum</i>, growth) (Mochida and Fujii, 2009a). <i>Invertebrates:</i> 96h EC50 = 0.011 mg/L (<i>Crassostea virginica</i>) (ACP, 2005b). 96h LC50 = 0.0436 mg/L (<i>Penaeus japonicus</i>) (Yamada, 2006); 30 µg/L (<i>Tigriopus japonicus</i>); 11 µg/L (<i>Elasmopus rapax</i>, juvenile) (Bao et al., 2011); 2.5 µg/L (<i>Heptacarpus futillirostris</i>) (Mochida and Fujii, 2009a).</p> | <p><i>Water:</i> 22 ng/L (Yamada, 2006); 0.046 µg/L (EPA, 2012).</p> | <p>Currently in widespread use. High toxicity to aquatic organisms, equivalent to that of the TBT compounds. Considered to degrade rapidly (Readman, 2006; Yamada, 2006) and unlikely to bioconcentrate in aquatic organisms (EPA, 2012). The absence of CuPT monitoring data means that experimental data have yet to be confirmed in the field and some uncertainty exists as to whether CuPT is as rapidly removed from the environment as predicted (Thomas and Brooks, 2010). Long-term exposure to CuPT can induce skeletal deformities and inflammatory mass formation in mummichog larvae (<i>Fundulus heteroclitus</i>). The mechanism of induction of skeletal anomalies is simi-</p> |

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| | | | <p>24h LC50 = 0.83 mg/L (<i>Artemia salina</i>) (Koutsafitis and Aoyama, 2007); 63 µg/L (<i>Balanus amphitrite</i>, larvae).</p> <p>48h LC50 = 5.7µg/L (<i>Hydrodroides elegans</i>, larvae) (Bao et al., 2011).</p> <p>96h NOEC = 6.9 µg/L (<i>Crassostrea virginica</i>, growth) (ACP, 2005b).</p> <p><i>Fish:</i></p> <p>96h LC50 = 0.00767 mg/L (<i>Pagrus major</i>) (Yamada, 2006); 9.3 µg/L (<i>Pagrus major</i>) (Mochida and Fujii, 2009a); 8.2 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011).</p> <p>7d LC50 = 0.0076 mg/L (<i>Oncorhynchus tshawytscha</i>).</p> <p>14d LC50 = 0.003 mg/L (<i>Oncorhynchus tshawytscha</i>).</p> <p>21d LC50 = 0.0017mg/L (<i>Oncorhynchus tshawytscha</i>).</p> <p>28d LC50= 0.0013 mg/L (<i>Oncorhynchus tshawytscha</i>) (Yamada, 2006).</p> <p>NOEC generally 1.5 µg/L or lower (Okamura et al., 2002).</p> | | | <p>lar to that proposed for organophosphorus insecticides, that is, it is thought to have neuromuscular blocking properties through its ability to inhibit acetylcholinesterase (AChE) activity, thus causing muscular contraction that can lead to abnormal axial contortion (Mochida and Fujii, 2009a).</p> |
| Copper (I) thiocyanate | <p>Total dissolved Cu (I) in coastal seawater ranges between 0.15-0.8 µg/L, increasing to values exceeding 2.6 µg/L in marinas, especially during the tourist season; for instance, a maximal concentration of 3.8 µg/L was found in Stockholm harbor (Cima and Ballarin, 2012).</p> | | <p><i>Invertebrates:</i></p> <p>96h LC50 = 1 µg/L (<i>Craginotus crangon</i>, mortality).</p> <p><i>Fish:</i></p> <p>96h LC50 = 6-24 µg/L (<i>Pleuronectes platessa</i>, mortality) (Pesticide Ecotoxicity Database, 2000).</p> | | | <p>Commonly used in Europe (ACE, 2002). Very highly toxic to fish and moderately toxic to crustaceans (Pesticide Ecotoxicity Database, 2000). There are insufficient data on water pollution potential (PAN pesticide database, 2014).</p> |

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| Dichlofluanid <i>N</i> -dichlorofluoromethylthio- <i>N,N'</i> -dimethyl- <i>N</i> -phenylsulfamide | <p>MEC: <i>Water:</i> not detected (LOD = 0.24 ppb) (UK estuary); not detected (LOD = 9.5 ng/L)-284 ng/L (Greek marinas) (Konstantinou and Albanis, 2004); not detected (LOD = 0.1-0.2 ng/L) (harbors and marinas from Gran Canaria Island, Spain) (Sánchez-Rodríguez et al., 2011b). <i>Sediment:</i> 7.2-688.2 ng/g (Blackwater estuary, UK); <1.6-11 ng/g (Mediterranean coast of Spain); not detected (LOD = 2.5-3 ng/g)-195 ng/g dwt (Greek marinas) (Konstantinou and Albanis, 2004); not detected (LOD = 0.3 ng/g)-16.6 ng/g (harbors and marinas of Gran Canaria Island) (Sánchez-Rodríguez et al., 2011a). <i>Biota:</i> not detected (LOD = 0.01 mg/Kg) (mussels, Australia) (Department of Water, 2009). PEC: 5.8 µg/L (Bellás, 2006); 0.56-16.3 ng/L (Mukherjee et al., 2009). <i>New Zealand harbors and marinas (based on average leaching rate):</i> 0.0147-0.17 µg/L (maximum); 0.00761-0.044 µg/L (average) (EPA, 2012). <i>Sediment:</i> 0.00027 ng/g dwt (Mukherjee et al., 2009).</p> | Log Kow = 3.7 (Konstantinou and Albanis, 2004). | <p><i>Invertebrates:</i> EC10 = 52 µg/L (<i>Mytilus edulis</i>, embryonic development); 277 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 206 µg/L (<i>Paracentrotus lividus</i>, larval growth). EC50 = 81 µg/L (<i>Mytilus edulis</i>, embryonic development); 627 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 282 µg/L (<i>Ciona intestinalis</i>, embryonic development) (Bellás, 2006).</p> | <p><i>Water:</i> 5.2 µg/L (<i>Mytilus edulis</i>); 28 µg/L (<i>Paracentrotus lividus</i>, embryo); 21 µg/L (<i>Paracentrotus lividus</i>, larval growth); 22 µg/L (<i>Ciona intestinalis</i>, embryo); 3.2 µg/L (<i>Ciona intestinalis</i> (larval settlement) (Bellás, 2006); 0.0265 µg/L (EPA, 2012).</p> | Highly unstable in the water phase, so it is recommended to base the ERLs on the metabolites formed and not on the parent compound (Van Wezel and Van Vlaardingen, 2004). | <p>Commonly used in Europe (ACE, 2002). Detected in saline coastal waters at concentrations higher than in freshwaters, suggesting that its use in antifouling products may be of significance (Voulvoulis, 2006). Extremely toxic effects to aquatic organisms, such as embryotoxicity in sea urchin (<i>Glyptocidaris crenularis</i>) (Guardiola et al., 2012). However, in water it hydrolyses rapidly to DMSA (N,N-dimethyl-N'-phenylsulfamide), which has a low toxicity (Assessment report, 2006). The occurrence of dichlofluanid in Greek and other sediments and surface waters has been challenged by a repeat study which suggest that previous reports may be the result of 'false positives' arising from the use of non-specific detectors or inappropriate confirmation ions when using gas chromatography-mass spectrometry (Thomas and Brooks, 2010). Whenever dichlofluanid is measured in the field, this points to a severe situation that probably results in toxicity (Van Wezel and Van Vlaardingen, 2004).</p> |
| Diuron <i>N</i> -(3,4-dichlorophenyl)- <i>N,N</i> -dimethylurea | <p>MEC: <i>Water:</i> 10.5-768 ng/L (UK marinas) (Boxall et al., 2000); 6.7 µg/L (UK); 1.13 µg/L (Netherlands); 2 µg/L (Spain) (Dafforn et al.,</p> | Log Kow = 2.8 (Konstantinou and Albanis, 2004). BCF = 75 and 22 (Thomas and Brooks, 2010). | <p><i>Algae:</i> 96h EC50 = 5.9 µg/L (<i>Skeletonema costatum</i>); 4.3 µg/L (<i>Thalassiosira pseudonana</i>).</p> | | 0.2 µg/L (WFD AA-EQS); 1.8 µg/L (WFD MAC-EQS). | <p>Increased use since restrictions on the use of TBT. Persists in the marine environment anywhere from between a month to a year. However, significant contam-</p> |

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| | <p>2011); 2.3-203.6 ng/L (harbors and marinas from Gran Canaria Island) (Sánchez-Rodríguez et al., 2011b).</p> <p><i>Sediment</i>: 1.42 µg/g (UK); <1 µg/g (Netherlands); 0.136 µg/g (Spain) (Dafforn et al., 2011); not detected (LOD = 0.2 ng/g)-21.3 ng/g (harbors and marinas of Gran Canaria Island) (Sánchez-Rodríguez et al., 2011a).</p> <p>PEC: <i>UK marinas</i>: 48.4-17000 ng/L (Boxall et al., 2000).</p> | | <p>24h EC50 = 43000 µg/L (<i>Pyrocystis lunula</i>) (Bao et al., 2011).</p> <p><i>Invertebrates</i>: 24h LC50 = 12.01 mg/L (<i>Artemia salina</i>) (Koutsafitis and Aoyama, 2007); 21000 µg/L (<i>Balanus amphitrite</i>, larvae). 48h LC50 = 16000 µg/L (<i>Hydroides elegans</i>, larvae). 96h LC50 > 3000 µg/L (<i>Elasmopus rapax</i>, juvenile); 11000 µg/L (<i>Tigriopus japonicus</i>, adult).</p> <p><i>Fish</i>: 96h LC50 = 7800 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011).</p> | | | <p>ination is more likely attributable to agricultural run-off rather than antifouling usage (Dafforn et al., 2011).</p> <p>Photosynthetic system II (PSII) inhibitor and highly toxic to autotrophic aquatic species such as cyanobacteria, algae, macrophytes and symbiotic dinoflagellates in corals (Bao et al., 2011).</p> |
| <p>Folpet <i>N-(trichloromethylthio)phthalimide</i></p> | <p>MEC: <i>Water</i>: <1-2 ng/L (Northern Adriatic) (Readman et al., 1997). <i>Sediment</i>: not detected (LOD = 10 ng/g dwt) (major ports and marinas of the Cote d'Azur, France) (Cassi et al., 2008).</p> | <p>Log Kow = 3.02. BCF = 56 (PPDB, 2013).</p> | <p><i>Invertebrates</i>: 96h LC50 = 12.1 mg/L (<i>Americamysis bahia</i>) (PPDB, 2013).</p> <p><i>Fish</i>: 96h LC50 = 675 ppb (bluegill sunfish) (USEPA, 1999).</p> | | | <p>Characterized as being highly toxic to both cold water and warm water fish. Data from a study with a typical end-use product of folpet indicate that it is also toxic to aquatic invertebrates (USEPA, 1999). Non-persistent compound (PPDB, 2013).</p> |
| <p>Irgarol 1051 (Cybutryne) <i>N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine</i></p> | <p>MEC: <i>Water</i>: 5.6-201 ng/L (UK marinas) (Boxall et al., 2000); 1.4 µg/L (UK); 0.09 µg/L (Netherlands); 1 µg/L (Spain); 0.09 µg/L (Greece) (Dafforn et al., 2011); 2.4-146.5 ng/L (harbors and marinas from Gran Canaria Island) (Sánchez-Rodríguez et al., 2011b); <1 ng/L-1.7 µg/L (European coasts and other world countries) (Cima and Ballarin, 2012); 2 ng/L and 8 ng/L (two samples out of 31 in the remotest part of the Indian</p> | <p>Log Kow = 3.95 (Loos, 2012). BCF = up to 150,000 ml/g (<i>Tetraselmis suecica</i> under laboratory conditions) (Thomas and Brooks, 2010); 250 (whole fish) (Assessment report, 2011).</p> | <p><i>Algae</i>: 96h EC50 = 0.57 µg/L (<i>Skeletonema costatum</i>); 0.38 µg/L (<i>Thalassiosira pseudonana</i>). 24h EC50 >15000 µg/L (<i>Pyrocystis lunula</i>) (Bao et al., 2011). 120h NOEC = 0.146 µg/L (<i>Skeletonema costatum</i>, growth inhibition) (Assessment report, 2011).</p> <p><i>Invertebrates</i>: EC10 = 797 µg/L (<i>Mytilus edulis</i>, embryonic development); 2904 µg/L (<i>Para-</i></p> | <p><i>Water</i>: 80 µg/L (<i>Mytilus edulis</i>); 290 µg/L (<i>Paracentrotus lividus</i>, embryo); 187 µg/L (<i>Paracentrotus lividus</i>, larval growth (Bellas, 2006); 1.46 ng/L; 5.8 ng/L (Assessment report, 2011). <i>Sediment</i>: 4.4 ng/g dwt (Assessment report, 2011).</p> | <p>0.0025 µg/L (WFD AA-EQS); 0.016 µg/L WFD MAC-EQS). 24 ng/L (ERL, water); 1.4 µg/kg (ERL, sediment) (Van Wezel and Van Vlaardingen, 2004).</p> | <p>First introduced in Europe in the mid-1980s since the partial regulatory restrictions on TBT. It has been banned on pleasure crafts (<25 m in length) in the UK and Denmark, but still widely used in other parts of the world. Detected in all European coasts and other world countries, indicating widespread pollution. It can be linked to vessel activity since it is not used as an herbicide. Interestingly, also detected in Australia, despite not being used</p> |

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| | <p>Ocean) (Price and Readman, 2013).</p> <p><i>Sediment</i>: 1.011 µg/g (UK); <1 µg/g (Netherlands); 0.088 µg/g (Spain); 0.69 µg/g (Greece) (Dafforn et al., 2011); not detected (LOD = 0.1 ng/g)-23.9 ng/g (harbors and marinas of Gran Canaria Island) (Sánchez-Rodríguez et al., 2011a).</p> <p>PEC:</p> <p><i>UK marinas</i>: 2.5-7670 ng/L (Boxall et al., 2000); 4.0 µg/L (Bellas, 2006).</p> | | <p><i>centrotus lividus</i>, embryonic development); 1868 µg/L (<i>Paracentrotus lividus</i>, larval growth). EC50 = 1540 µg/L (<i>Mytilus edulis</i>, embrionic development); 4021 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 6032 µg/L (<i>Paracentrotus lividus</i>, larval growth); 2115 µg/L (<i>Ciona intestinalis</i>, embryonic development) (Bellas, 2006). 96h EC50 = 480 µg/L (<i>Mysidopsis bahia</i>) (Assessment report, 2011). 48h LC50 = 2600 µg/L (<i>Hydroides elegans</i>, larvae) (Bao et al., 2011); >4000 µg/L (Bao et al., 2013). 96h LC50 = 1000 µg/L (<i>Elasmopus rapax</i>, juvenile); 2400 µg/L (<i>Tigriopus japonicus</i>, adult) (Bao et al., 2011); 1800 µg/L (<i>Tigriopus japonicus</i>) (Bao et al., 2013). 28d NOEC = 110 µg/L (<i>Mysidopsis bahia</i>, reproduction) (Assessment report, 2011). LOEC= 940 µg/L (<i>Tigriopus japonicus</i>). NOEC= 188 µg/L (<i>Tigriopus japonicus</i>) (Bao et al., 2013).</p> <p><i>Fish</i>:</p> <p>96h LC50 = 1760 µg/L (<i>Menidia beryllina</i>, mortality) (Assessment report, 2011); 1000 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011).</p> | | <p>in Australia's boating industry, and in remote areas (Dafforn et al., 2011; Price and Readman, 2013). Relatively highly stable and persistent in the marine environment (Assessment report, 2011; Bao et al., 2013). Considered to be non-biodegradable and its degradation in seawater is slow, with half-life of about 100 days (Konstantinou and Albanis, 2004). Photosynthetic system II (PSII) inhibitor and highly toxic to autotrophic aquatic species such as cyanobacteria, algae, macrophytes and symbiotic dinoflagellates in corals (Bao et al., 2011).</p> |
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| | | | 33d NOEC = 170 µg/L (<i>Cyprinodon variegatus</i> , grotwh) (Assessment report, 2011). | | | |
| Maneb <i>Manganese ethylene bisdithiocarbamate</i> | | Log Kow = -0.45 High potential of bioconcentration (PPDB, 2013). | <i>Invertebrates:</i> 96h LC50 = 2400 µg/L (<i>Americamysis bahia</i>) (PPDB, 2013). | | 3 µg/L (UK AA-EQS); 30 µg/L (UK MAC-EQS) (SEPA, 2014). | On the market in the United States. Very few data available. Moderately soluble in water and undergoes hydrolysis. Not seen as a likely contaminant of surface water and has not been monitored (Downing, 2000). |
| Medetomidine 4-[1-(2,3-dimethylphenyl)ethyl]-3Himidazole | PEC: <i>Marina:</i> 1.5 ng/L. <i>Harbor:</i> 1.1 ng/L. <i>Shipping lane:</i> 0.00034 ng/L. <i>Baltic harbors and marinas:</i> 0.0042 ng/L-57 ng/L. <i>Sediment:</i> 0.013 ng/Kg (harbor); 0.073 ng/Kg (marina). <i>Baltic harbors and marinas:</i> 0.0000027-0.78 ng/Kg dwt (Ohlauson, 2013). | Log Kow = 3.13 (Wendt, 2013), Log Kow = 2.9 (Ohlauson, 2013). BCF = 2.8 (<i>Crangon crangon</i>), 134 (<i>Mytilus edulis</i>) (Hilvarsson et al., 2009). | <i>Algae:</i> 72h EC50 = 100000 nM (<i>Ulva lactuca</i> , inhibition of settling and growth) (Wendt, 2013). EC50 = 2.145 µg/L (green alga) (Cui et al., 2014). <i>Invertebrates:</i> 24h EC50 = 86 µg/L (<i>Abra nitida</i> , burrowing response); 0.9µg/L (<i>Abra nitida</i> , sediment reworking activity) (Bellás et al., 2006). 48h LC50 = 540 nM (<i>Acartia tonsa</i> , mortality). 48h EC50 = 720 nM (<i>Acartia tonsa</i> , egg production). 24h LOEC = 42 nM (<i>Corophium volutator</i> , search behavior) (Wendt, 2013). <i>Fish:</i> LC50 = 14.043 µg/L (Cui et al., 2014). | <i>Water:</i> 50 µg/L (Ohlauson, 2013). | | Already approved in Japan and Korea. In Europe, even though it has yet to be registered as an antifouling biocide, a number of studies have been published on its effects on non-target organisms. Estimated to be toxic and persistent, though it has not yet been detected in the environment (Lennquist et al., 2010; Cui et al., 2014). Significant effects on burrowing and sediment reworking activity of <i>Abra nitida</i> were found, although after 24h recovery of exposed animals in clean sea water and sediment, a reversibility of the effects was detected (Bellás et al., 2006). Effects also observed on the respiration rate and color adaptation in juvenile turbot exposed to sublethal concentrations, although the effects were induced above PEC (Hilvarsson et al., 2007; Ohlauson, 2013). Its low ecotoxicity when compared to other biocides suggests it is a promising anti-fouling. Nevertheless, there |

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| | | | | | are still large knowledge gaps of the ecotoxicological effects, bioaccumulation potential, degradation pathways and metabolites, and leakage rates of this compound in the marine environment (Hivarsson et al., 2007, 2009; Wendt, 2013). |
| DCOIT (Sea-Nine 211) 4,5-dichloro-2-octylisothiazol-3(2H)-one | <p>MEC: <i>Water:</i> >3.3 µg/L (Spanish marinas) (Martínez et al., 2000); <1-3700 ng/L (Spanish marinas); <1-3 ng/L (Swedish marinas); <1 ng/L (UK and Greek marinas and ports) (ACE, 2002); 2.55 µg/L (Chen et al., 2014). <i>Sediment:</i> not detected (LOD < 1.6 µg/Kg dwt)-2 µg/Kg dwt (Greece and Spain) (ACE, 2002); 0.04-150 µg/Kg dwt (Japan) (Onduka et al., 2013); <0.04-2.4 µg/Kg dwt (coastal areas of Spain, Denmark, and Japan) (Ito et al., 2013). PEC: 3.7 µg/L (Bellas, 2006); 0.000423 µg/l (Wang et al., 2014a). <i>New Zealand harbors and marinas (based on average leaching rate):</i> 0.0279-0.337 µg/L (maximum); 0.0187-0.204 µg/L (average) (EPA, 2012). <i>Sediment:</i> 0.000187 mg/kg (Wang et al., 2014a).</p> | Log Kow = 2.8 (Wang et al., 2014a). BCF = 750 (bluegill sunfish, whole body) (Assessment report, 2014). | <p><i>Algae:</i> 48h EC50 = 0.34 µg/L (<i>Hormosira banksii</i>, germination); 0.43 µg/L (<i>Hormosira banksii</i>, rhizoid growth) (Myers et al., 2006). 24h EC50 = 0.48 µg/L (<i>Skeletonema costatum</i>) (Assessment report, 2014). EC50 = 18 µg/L (<i>Skeletonema costatum</i>) (Wang et al., 2014a). NOEC = 0.48 µg/L (<i>Skeletonema costatum</i>) (Assessment report, 2014). <i>Invertebrates:</i> EC10 = 7.1 µg/L (<i>Mytilus edulis</i>, embryonic development); 5.9 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 1.7 µg/L (<i>Paracentrotus lividus</i>, larval growth). EC50 = 11 µg/L (<i>Mytilus edulis</i>, embryonic development); 12.1 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 21 µg/L (<i>Paracentrotus lividus</i>, larval growth) (Bellas, 2006). LC50 = 24 µg/L (<i>Crassostrea virginica</i>) (EPA, 2012).</p> | <p><i>Water:</i> 0.71 µg/L (<i>Mytilus edulis</i>); 0.59 µg/L (<i>Paracentrotus lividus</i>, embryo); 0.17 µg/L (<i>Paracentrotus lividus</i>, larval growth) (Bellas, 2006); 0.0068 µg/L (Assessment report, 2014); 0.024 µg/L (Wang et al., 2014a). <i>Sediment:</i> 0.01 mg/Kg dwt (0.0034 mg/Kg ww) (Assessment report, 2014); 0.003 mg/Kg (Wang et al., 2014a).</p> | <p>One of the most popular alternative biocides, it has been used worldwide (Thomas and Brooks, 2010). Data regarding its toxicity for marine organisms are accumulating, however its occurrence is rarely reported. These studies revealed toxic effects on embryogenesis and larval growth of sea urchins, crustaceans, bivalve, and ascidians (Bellas, 2006; Guardiola et al., 2012), apoptosis in the testicular germ cells of mummichogs (<i>Fundulus heteroclitus</i>) (Ito et al., 2013), hepatic oxidative stress, affected brain neurotransmission, and impaired homeostasis of sex hormones in the plasma of adult marine medaka (<i>Oryzias melastigma</i>), which adversely affected the reproductive success of the offspring (Chen et al, 2014). Toxicity models performed in New Zealand marinas found DCOIT to pose very high risks to the aquatic environment and therefore may need to be reduced (EPA, 2012). Toxic effects on some sensitive species residing in the coastal areas of Japan have also been</p> |

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| | | | <p>96h LC50 = 4.7 µg/L (<i>Myxidopsis bahia</i>).</p> <p>48h EC50 = 3.2 µg/L (<i>Crassostrea virginica</i>, static); 411 µg/L (<i>Mytilus edulis</i>, static) (Assessment report, 2014).</p> <p>L(E)C50 = 2.7 µg/L (<i>Mytilus edulis</i>); 9.4 µg/L (<i>Crassostrea virginica</i>); 1700 µg/L (<i>Uca pugilator</i>); 27.2µg/L (<i>Penaeus aztecus</i>); 2.4 µg/L (<i>Paracentrotus lividus</i>) (Wang et al., 2014a).</p> <p>NOEC = 0.8 µg/L (<i>Crassostrea virginica</i>) (EPA, 2012); 18 µg/L (<i>Crassostrea virginica</i>); 207 µg/L (<i>Mytilus edulis</i>); 0.63 µg/L (<i>Americamysis bahia</i>); 0.1 mg/Kg dwt (<i>Leptocheirus plumulosus</i>) (Assessment report, 2014).</p> <p><i>Fish:</i></p> <p>96h LC50 = 20.5 µg/L (<i>Cyprinodon variegatus</i>) (Mochida and Fujii, 2009a).</p> <p>NOEC = 6.0 µg/L (<i>Cyprinodon variegatus</i>) (Assessment report, 2014).</p> | | | <p>suggested, although the ecological risk appears to be confined to a limited area of Japanese coastal waters (Onoduka et al., 2013). Overall, the risk in the marine environment is considered to be relatively low (Wang et al., 2014a). DCOIT is proposed to be approved as an active substance for use in product type 21, subject to some specific conditions (Assessment report, 2014).</p> |
| TCMS pyridine (Densil 100) 2,3,3,6-tetrachloro-4-(methylsulfonyl) pyridine | MEC: <i>Water:</i> not detected (LOD = 5 ng/L) in UK marinas (Konstantinou and Albanis, 2004). | Log Kow = 1.95 (Cui et al., 2014). | Only freshwater data. | | | <p>Previously used as leather tanning additive, it is one of the more recent antifouling compounds introduced to the market (Guardiola et al., 2012) and still little used (Thomas and Langford, 2009). Introduced as a booster in various antifouling paints in commerce in the northern Adriatic Sea (Menin et al., 2008). Removed on</p> |

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| | | | | | | <p>yachts <25 m in many European countries (Price and Readman, 2013).</p> <p>Very few available data concerning its toxicity. Found to cause immunotoxic effects at concentrations higher than 10 µM in haemocyte cultures of the colonial ascidian <i>Botryllus schlosseri</i>: i) deep changes in the cytoskeleton that irreversibly affect cell morphology and phagocytosis, ii) induction of DNA damage, iii) leakage of oxidative and hydrolytic enzymes due to membrane alteration (Menin et al., 2008).</p> <p>Its environmental characteristics are similar to TBT and has been registered as highly toxic for freshwater fish and aquatic invertebrates, thus caution against its use has been suggested. However, appropriate risk assessments are still required (Voulvoulis et al., 2002; Menin et al., 2008).</p> |
| TCMTB (Busan) <i>2-thiocy-anatomethyl-thio-benzothiazole</i> | <p>MEC: <i>Water:</i> not detected (LOD = 1 ng/L) in UK marinas (Konstantinou and Albanis, 2004).</p> <p>PEC: <i>Estuaries:</i> 0.8-27.5 µg/L. <i>Open marinas:</i> 18.1-604.5 µg/L (ACP, 2005a). <i>Sediment:</i> 2.1x10⁻⁶-6.9x10⁻⁵ µg/g (estuaries); 3.8x10⁻⁵-1.3x10⁻³ µg/g (open marinas) (ACP, 2005a).</p> | <p>Log Kow = 3.1 (Van Wezel and Van Vlaardingen, 2004). Log Kow = 3.3 (Voulvoulis, 2006). BCF = 184 (bluegill sunfish, whole body) (ACP, 2005a).</p> | <p><i>Invertebrates:</i> 24h LC50 = 63 µg/L (<i>Myxidopsis bahia</i>). 48h LC50 = 23 µg/L (<i>Myxidopsis bahia</i>). 96h LC50 = 21 µg/L (<i>Myxidopsis bahia</i>) (ACP, 2005a). 48h EC50 = 13.9 µg/L (<i>Mercenaria mercenaria</i>) (USEPA, 2006). 96h NOEC = <7.8 µg/L (<i>Mysidopsis bahia</i>) (ACP, 2005a). NOEC = <13 µg/L (<i>Mercenaria mercenaria</i>) (USEPA, 2006).</p> | <p><i>Water:</i> 0.021 µg/L (ACP, 2005a).</p> | <p>380 ng/L (ERL, water) (Van Wezel and Van Vlaardingen, 2004).</p> | <p>Frequently used in the past in many countries worldwide (Konstantinou and Albanis, 2004). Currently, it is not permitted on yachts <25 m in many European countries (Price and Readman, 2013). Limited information to allow for any accurate assessment of the actual amounts used (ACP, 2005a). Environmental characteristics similar to TBT, although toxicity data are very limited and mostly restricted to freshwater organisms (Van Wezel and Van Vlaardingen, 2004; ACP,</p> |

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| | | | <p><i>Fish:</i> 96h LC50 = 60 µg/L (<i>Cyprinodon variegatus</i>, although the low oxygen concentrations of this study reduces confidence in the results). 96h NOEC = 36µg/L (<i>Cyprinodon variegatus</i>) (ACP, 2005a).</p> | | | <p>2005a). It may cause sublethal effects in fish, resulting in an increase in predation and a decreased ability to survive. Indications of endocrine disruption (USEPA, 2006). Limited data are on its sorption characteristics, although the sediment compartment seems not to be a concern for this compound (ACP, 2005a; USEPA, 2006). The lack of information on their fate, behavior and toxicity makes accurate risk assessment difficult (Voulvoulis, 2006).</p> |
| <p>Thiram <i>Bis(dimethylthiocarbamoyl) disulfide</i></p> | <p>MEC: Not detected in water (<0.1 µg/L) and marine invertebrates (<0.1 mg/Kg) (ACE, 2002; Department of Water, 2009). <i>Sediment:</i> very low concentrations in Western Australian coasts (<0.1-3.4 mg/kg dwt) (Department of water, 2009). PEC: <i>New Zealand harbors and marinas:</i> 0.0961-0.16 µg/L (maximum); 0.065-0.757 µg/L (average) (EPA, 2012).</p> | <p>Log Kow = 1.73 (EPA, 2012).</p> | <p><i>Invertebrates:</i> L(E)C50 = 4.7 µg/L (<i>Crassostrea virginica</i>). NOEC = <1.3 µg/L (<i>Crassostrea virginica</i>). <i>Fish:</i> L(E)C50 = 46 µg/L (<i>Onchorhynchus mykiss</i>). NOEC = 9.6 µg/L (<i>Onchorhynchus mykiss</i>) (EPA, 2012).</p> | <p><i>Water:</i> 0.01 µg/L (EPA, 2012).</p> | | <p>Relatively frequent use. Exhibits strong toxic effects, and has teratogenic properties in some teleost species and reproductive toxicity in mammals (Mochida and Fujii, 2009b). It is also a suspected endocrine disruptor. Toxicity models performed in New Zealand marinas found thiram to pose very high risks to the aquatic environment and therefore may need to be reduced (EPA, 2012). However, data are mostly restricted to freshwater organisms. It is necessary to gather and analyze additional data on the toxic effects on marine organisms in addition to monitoring their occurrence in the marine environment (Mochida and Fujii, 2009a, b).</p> |
| <p>Tolylfluanid <i>N-(dichlorofluoromethylthio)-N',N'-dimethyl-N-p-tolylsulfamide</i></p> | <p>MEC: Not detected in sediments in a water-sediment study (BPC, 2014). PEC:</p> | <p>Log Kow = 3.9 (Wendt, 2013).</p> | <p><i>Invertebrates:</i> EC10 = 49 µg/L (<i>Mytilus edulis</i>, embryonic development); 219 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 193</p> | <p><i>Water:</i> 0.0265 µg/L (EPA, 2012).</p> | | <p>Frequently used. Rapidly hydrolyzed and biodegraded in water. The risks to aquatic organisms by the presence of its main two me-</p> |

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| | <p><i>Visakhapatnam Harbor (India)</i>: 1.08-6.72 ng/L (Mukherjee et al., 2009).</p> <p><i>New Zealand harbors and marinas (based on average leaching rate and arbitrarily chosen worst case leaching rates equal to those for diuron)</i>: 0.027-0.303 µg/L (maximum); 0.0157-0.0967 µg/L (average) (EPA, 2012).</p> | | <p>µg/L (<i>Paracentrotus lividus</i>, larval growth). EC50 = 74 µg/L (<i>Mytilus edulis</i>, embryonic development); 405 µg/L (<i>Paracentrotus lividus</i>, embryonic development); 986 µg/L (<i>Paracentrotus lividus</i>, larval growth); 217 µg/L (<i>Ciona intestinalis</i>, embryonic development) (Bellas, 2006).</p> | | <p>tabolites (N,N-dimethylsulphamide and N,N-dimethyl-N'-p-tolylsulphamide) are deemed low (EPA, 2012). It is not considered to have endocrine disrupting properties. The limit of quantification of the existing method in seawater does not fulfil the requirements based on the PNEC. No method for fish and shellfish is available. Studies on sorption at marine environmentally relevant conditions (concentrations µg/L to ng/L, pH ~8, DOC not too high, etc.) are recommended (BPC, 2014).</p> |
| <p>TPBP (KH101)</p> <p><i>Triphenylborane-pyridine</i></p> | <p>MEC: <i>Water</i>: 4.8–21 pg/L (coastal areas of Hiroshima Bay) (Mochida et al., 2012).</p> <p>PEC: <i>Marina</i>: 0.0881-0.736 µg/L (Oliveira et al., 2014). <i>Commercial harbor</i>: 0.176 µg/L. <i>Sediment</i>: 2.24 mg/kg (Wang et al., 2014a).</p> | <p>Log Kow = 5.52 (for triphenylborane, TPB) (Wendt, 2013).</p> | <p>Algae: 72h EC50 = 4.4 µg/L (<i>Chaetoceros calcitrans</i>); 140 µg/L (<i>Dunaliella tertiolecta</i>); 2.9 µg/L (<i>Tetraselmis tetrahele</i>); 2.2 µg/L (<i>Skeletonema costatum</i>). 72h NOEC = 0.3 µg/L (<i>Skeletonema costatum</i>) (Mochida et al., 2012). Invertebrates: 48h LC50 = 130 µg/L (<i>Artemia salina</i>) (Okamura et al., 2009); 31 µg/L (<i>Hemicentrotus pulcherrimus</i>) (Tsunemasa et al., 2013); 14 µg/L (<i>Tisbe battagliai</i>) (Oliveira et al., 2014). 24h LC50 = 32 µg/L (<i>Portunus trituberculatus</i>); 6.6 µg/L (<i>Tigriopus japonicus</i>) (Mochida et al., 2012); 6.3 µg/L (<i>Crassostea gigas</i>) (Tsunemasa et al., 2013).</p> | <p>Water: 0.0629 µg/L (Oliveira et al., 2014); 0.0002 µg/L (Wang et al., 2014a). Sediment: 0.0019 mg/Kg (Wang et al., 2014a).</p> | <p>In use over the last decade in certain Asian countries like Japan and China. Appears to have the potential to harm the environment. It exerts effects at very low concentrations in oyster and sea urchin species (Oliveira et al., 2014). However further data are essential to better understand the fate and effects of this biocide in natural marine environment (Mochida et al., 2012; Oliveira et al., 2014). Although the potential for bioaccumulation has not yet been fully clarified (Mochida et al., 2012), the Log Kow for TPB suggest it has a strong potential to bioaccumulate (Wang et al., 2014a).</p> |

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| | | | NOEC = 4 µg/L (<i>Tisbe battagliai</i>) (Oliveira et al., 2014). | | | |
| Tralopyril (Econeal) 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile | MEC: Not available. PEC: <i>Marina:</i> 0.0844-0.714 µg/L (Oliveira et al., 2014). | BCF <3.2 (<i>Cyprinus carpio</i>) (Kempen, 2011). | <i>Invertebrates:</i> 24h LC50 = 950 µg/L (<i>Balanus Amphitrite</i>) (Kempen, 2011). 48h EC50 = 3.1 µg/L (<i>Mytilus galloprovincialis</i>); 3 µg/L (<i>Paracentrotus lividus</i>); 0.9 µg/L (<i>Tisbe battagliai</i>). NOEC = 0.1 µg/L (<i>Mytilus galloprovincialis</i>); 1 µg/L (<i>Paracentrotus lividus</i>); 0.8 µg/L (<i>Tisbe battagliai</i>) (Oliveira et al., 2014). | <i>Water:</i> 0.009 µg/L (Oliveira et al., 2014). | | Already approved by US EPA. Paints reported to be available from late 2009. Very scarce information with respect to toxicity besides that provided by the manufacturer. It appears to have the potential to harm the environment, so further data are essential to better understand the fate and effects of this biocide (Oliveira et al., 2014). |
| Zinc pyrithione (Zinc Omadine) Bis[1-hydroxy-2(1H)-pyridinethionato-o,s]-T-4 zinc | MEC: <i>Water:</i> not detected (LOD < 20 ng/L) in UK marinas (Konstantinou and Albanis, 2004). <i>Sediment:</i> 58-560 mg/Kg (aquaculture farms) (Simpson et al., 2013); 166.47 mg/kg (maximum mean Zn-total in Mediterranean farms treated with antifouling). <i>Biota:</i> 330.20 mg/kg dwt (<i>Sparus aurata</i> , maximum Zn-total in Mediterranean farms treated with antifouling); 435.30 mg/kg dwt (<i>Dicentrarchus labrax</i> , maximum Zn-total in Mediterranean farms treated with antifouling) (Nikolaou et al., 2014). PEC: <i>Pleasure craft harbor:</i> 1.7 µg/L (including photolysis); 0.56 µg/L (ignoring photolysis). <i>Navigation route:</i> 0.022 µg/L (including photolysis); 0.0053 µg/L (ignoring photolysis) (Madsen et al., 2000). | Log Kow = 0.9 (EPA, 2012). | <i>Algae:</i> 96h EC50 = 30 µg/L (<i>Amphora coffeaeformis</i>) (Mochida and Fujii, 2009a); 0.51 µg/L (<i>Thalassiosira pseudonana</i>) (Bao et al., 2011). 72h EC50 = 1.6 µg/L (<i>Skeletonema costatum</i>) (Mochida and Fujii, 2009a). 48h EC50 = 0.21 µg/L (<i>Hormosira banksii</i> , germination), 0.31 µg/L (<i>Hormosira banksii</i> , rhizoid growth) (Myers et al., 2006). 24h EC50 = 4.4 µg/L (<i>Pyrocystis lunula</i>) (Bao et al., 2011). <i>Invertebrates:</i> 96h EC50 = 0.0063 mg/L (<i>Mysidopsis bahia</i>); 0.022 mg/L (<i>Crassostrea virginica</i>) (ACP, 2003); 120 µg/L (<i>Heptacarpus futilirostris</i>) (Mochida and Fujii, 2009a). | <i>Water:</i> 0.0026 µg/L (ACP, 2003); 0.115 µg/L (<i>Mytilus edulis</i>); 0.016 (<i>Paracentrotus lividus</i>) (Bellas et al., 2005); 0.046 µg/L (EPA, 2012). | 200 mg/kg (Australian lower SQGs to protect against acute effects) (Simpson et al., 2013). | Widely used in Europe (8246 kg/year maximum amount distributed/used in UK; 4248 kg/year quantities of biocide sold in France) (ACE, 2002; Willemsen, 2005). Very few monitoring surveys in Europe. Appears to be (along with zineb) the least hazardous options for the aquatic environment, being photodegradable within a short time frame. However, analytical constraints for these latter booster biocide compounds render environmental assessment difficult (Price and Readman, 2013). Moreover, it may not be a significant degradation process in lower depths even in coastal environments such as in marinas and harbors, where the influence of light is limited (Marcheselli et al., 2010; EPA, 2012). Similarly, it is not sure that a drastic reduction in ZnPT toxicity occurs under light conditions, so |

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| | <p><i>Open marina</i>: 2-53.5 ng/L (usually below limit of detection of 5 ng/L quoted by the Centre for Environment, Fisheries & Aquaculture Science, CEFAS) (ACP, 2003).</p> <p><i>New Zealand harbors and marinas (based on average leaching rate)</i>: 0.0727-0.835 µg/L (maximum); 0.0485-0.48 µg/L (average) (EPA, 2012).</p> <p><i>Sediment</i>: extremely low, 6.2×10^{-11}-1.6×10^{-9} µg/g (ACP, 2003).</p> | | <p>48h EC50 = 2.6 µg/L (<i>Mytilus edulis</i>); 2.5 µg/L (<i>Paracentrotus lividus</i>).</p> <p>24h EC50 = 72-187 µg/L (<i>Ciona intestinalis</i>, larval morphological abnormalities) (Bellas et al., 2005).</p> <p>24h LC50 = 3.17 mg/L (<i>Artemia salina</i>) (Koutsafitis and Aoyama, 2007).</p> <p>96h LC50 = 2.47 µg/L (<i>Dinophilus gyrociliatus</i>, dark conditions); 3.66 (<i>Dinophilus gyrociliatus</i>, 12h light/12h dark conditions) (Marcheselli et al., 2010).</p> <p>48h LC50 = 7.6 µg/L (<i>Hydroides elegans</i>, larvae).</p> <p>96h LC50 = 170 µg/L (<i>Tigriopus japonicas</i>) (Bao et al., 2011).</p> <p><i>Fish</i>:</p> <p>96h LC50 = 0.40 mg/L (<i>Cypridon variegatus</i>) (ACP, 2003); 98.2 µg/L (<i>Pagrus major</i>) (Mochida and Fujii, 2009a); 43 µg/L (<i>Oryzias melastigma</i>, larvae) (Bao et al., 2011).</p> | | <p>a great uncertainty still exists concerning the actual persistence of the biocide in the marine environment (Marcheselli et al., 2010). It poses potential ecological threat even at the very low tested concentrations (Bellas et al., 2005; Marcheselli et al., 2010, 2011; Bao et al., 2011). It shows strong toxicity to the germination and rhizoid growth of a macroalgal species (<i>Hormosira banksii</i>) and is extremely toxic to the embryonic development of sea urchins (<i>Anthocidaris crassispina</i>) (Mochida and Fujii, 2009b). It has been also found vulnerability of adult mussels (<i>Mytilus galloprovincialis</i>) to non-lethal concentrations, which rapidly induce a marked stress response and loss of genomic integrity (Marcheselli et al., 2011).</p> <p>There is need for monitoring the levels of ZnPT in seawater, sediment and biota, in order to improve the availability of environmental data (Marcheselli et al., 2010, 2011).</p> |
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| <p>Zineb Zinc ethylenebis(dithiocarbamate)(polymeric)</p> | <p>MEC: Not detected (LOD < 1 ng/L) in water and sediments (Assessment report, 2013). PEC: New Zealand harbors and marinas (based on average leaching rate): 0.0125-0.142 µg/L (maximum); 0.00506-0.0277 µg/L (average) (EPA, 2012). Commercial harbor: 0.0714 µg/l (Wang et al., 2014a).</p> | <p>Log Kow = 0.32 (Assessment report, 2013). Log Kow = 0.8 (Cui et al., 2014). BCF = 34 (measured, fish); 1.41 (estimated, fish) (Assessment report, 2013).</p> | <p>Algae: 72h EC50 = 0.49 mg/L (<i>Hormosira banksii</i>) (Myers et al., 2006); 0.036 mg/L (<i>Skeletonema costatum</i>). 72h NOEC = 0.022 mg/L (<i>Skeletonema costatum</i>, measured) (Assessment report, 2013).</p> | <p>Water: 0.044 µg/L (EPA, 2012); 0.0219 mg/L (Assessment report, 2013); 0.036 µg/L (Wang et al., 2014a).</p> | <p>Largely used in Europe, EEUU, Japan and Australia. Few available data on the toxicity to marine organisms. Found to have teratogenic properties and reproductive toxicity in mammals (Mochida and Fujii, 2009b). The ecological risk of antifouling paint using zineb onto ships in the marine environment is considered relatively high in China (Wang et al., 2014a). There is need to accumulate more data on the toxic effects, especially on reproduction in marine organisms, and to monitor their occurrence (Mochida and Fujii, 2009a, b). Data on the occurrence in the marine environment are limited, perhaps because the methodology for its monitoring is less clearly defined than for other booster biocides (Readman, 2006).</p> |
| <p>Ziram Zinc bis(dimethyldithiocarbamate)</p> | <p>PEC: New Zealand harbors and marinas: 0.0484-0.529 µg/L (maximum); 0.0308-0.222 µg/L (average) (EPA, 2012).</p> | <p>Log Kow = 1.65 (EPA, 2012).</p> | <p>Invertebrates: L(E)C50 = 77 µg/L (<i>Crassostrea virginica</i>). NOEC = 15 µg/L (<i>Crassostrea virginica</i>) (EPA, 2012).</p> | <p>Water: 0.02 µg/L (EPA, 2012).</p> | <p>9.7 ng/L (ERL, water); 0.011 µg/kg (ERL, sediment) (Van Wezel and Van Vlaardingen, 2004). Frequently used in the past on yachts <25 m in Greece and Netherlands. No longer approved, although some may be in the supply chain (ACE, 2002). No strong estrogenic response (ACE, 2002). Strong toxic effects on teleost species in early life stages and teratogenic properties, but there are no data on the toxicity to marine organisms. Thus, additional data on the toxic effects as well as its occurrence in the marine environment are needed (Mochida and Fujii, 2009a, b).</p> |

MEC: Measured environmental concentrations; PEC: Predicted environmental concentrations; dwt: dry weight; wwt: wet weight; LOD: Limit of detection.
Log Kow (log octanol/water partition coefficient) reflects the chemical's tendency to bioaccumulate in organisms.

BCF (Bioconcentration Factor) reflects the extent to which pollutants concentrate from water into aquatic organisms.

EC10: Effective Concentration of a toxic substance at 10% inhibition; EC50: Median effective concentration; LC50: Median lethal concentration; LOEC: Lowest observed effect concentration; NOEC: No effect concentration; PNEC: Predicted no effect concentration.

ERLs: Environmental risk limits; EQS: Environmental quality standards; AA: Annual average; MAC: Maximum allowable concentration; SQG: Sediment quality guidelines.

3.3 MARICULTURE

Aquaculture is one of the pillars of both the Common Fisheries Policy and the Blue Growth agenda of the European Commission³⁶. Although significant efforts are being made to promote sustainable aquaculture, the fast development of this sector may also have some adverse effects on the surrounding environment. Several chemicals such as antibiotics, pesticides and antifoulants are commonly utilized by farmers in order to control disease, parasites and algae (Guardiola et al., 2012). Tornero and Hanke (*in press*) identified 66 chemicals potentially released from marine aquaculture activities, including medicinal products (antibiotics, parasiticides, anaesthetics and disinfectants), food additives and contaminants, and antifouling biocides. Despite the fact many of these substances may affect non-target organisms, there are few data on the quantities applied and their levels and effects on the aquatic environment. Consequently, recent reviews have recognized the chemical inputs from aquaculture activities as an area requiring further research (BurrIDGE et al., 2010; Grigorakis and Rigos, 2011).

3.3.1 Medicinal products

Fish farmers must have access to a variety of properly authorized medicines to ensure animal health and consumer safety. The European Commission addresses this issue by establishing and periodically reviewing Maximum Residue Levels (MRL) for all food and animal feed. An MRL is defined as the maximum concentration of residue resulting from the use of a veterinary medicinal product that may be accepted to be legally permitted or recognized as acceptable on a food (EC, 1990). These MRLs are listed in Table 1 of Commission Regulation (EU) No. 37/2010³⁷.

The setting of an MRL is only a preliminary step towards achievement of full marketing authorization. The requirement to carry out an assessment of the environment safety of any veterinary medicinal product was introduced by Directive 92/18/EC³⁸. The Veterinary Medicinal Products Directive 2001/82/EC³⁹ (as amended) introduced mandatory risk assessments for all new and renewal authorizations for medicines used in mariculture and is applicable in all European Member States. The regulatory framework for veterinary medicines in the EU and, in particular how it affects their use in aquaculture, is well described by Alderman (2009).

In European marine aquaculture, the number of medicinal products fully authorized and approved for use is limited because of the high cost of development and licensing for a small market relative to other markets for pesticides and medicinals. Furthermore, the list of pharmaceuticals licensed varies a lot among countries. Interestingly, third countries exporting products into the EU are also required to comply with these regulations. Nevertheless, it seems that many compounds are still legally available and even if not fully

³⁶ http://ec.europa.eu/fisheries/cfp/aquaculture/index_en.htm

³⁷ Commission Regulation (EU) No 37/2010 of 22 December 2009 on pharmacologically active substances and their classification regarding maximum residue limits in foodstuffs of animal origin. http://ec.europa.eu/health/veterinary-use/maximum-residue-limits/developments_en.htm

³⁸ Commission directive 92/18/EEC of 20 March 1992 modifying the Annex to Council Directive 81/852/EEC on the approximation of the laws of Member States relating to analytical, pharmacotoxicological and clinical standards and protocols in respect of the testing of veterinary medicinal products. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31992L0018&from=EN>

³⁹ Directive 2001/82/EC of the European parliament and of the council of 6 November 2001 on the Community code relating to veterinary medicinal products. http://ec.europa.eu/health/files/eudralex/vol-5/consol_2004/dir_2001_02-dir_2004_28-cons_en.pdf

licensed, they can be used on an off-label basis (Daniel, 2009; Rodgers and Furones, 2009).

Antibiotics commonly used in marine aquaculture are oxytetracycline, oxolinic acid and flumequine, although the pattern of medicinal use is continually changing (Marine Institute for SWRBD, 2007). Concerns about the use of antibiotics are numerous. Antibacterial drugs may persist in water and sediments, sometimes long after their use has ceased, which can lead to the contamination of indigenous, non-target organisms (Grigorakis and Rigos, 2011; Samuelsen et al., 2014). Furthermore, antibiotics in medicated fish feed have the potential to induce drug resistance in microbial and other wild populations. Evidence suggests that these antibiotic-resistant organisms in the marine environment will, in turn, pass their antibiotic resistance genes to other bacteria including human and animal pathogens (Burridge et al., 2010). Nevertheless, adequate field studies regarding the effects of chemicals of aquaculture origin are almost lacking, especially for those species which are consumed extensively only in some European countries (Lucchetti et al., 2004).

Antiparasitic agents habitually utilized include pyrethroids (e.g. cypermethrin and deltamethrin), organophosphates (e.g. azamethiphos), benzamide and avermectins (e.g. flubenzurons and emamectin benzoate) (Olsvik et al., 2014; Samuelsen et al., 2014).

Most common anaesthetic agents are benzocaine, quinaldine and tricaine methanesulphonate (MS-222) (GESAMP, 1997; Costello et al., 2001). They are seldom used and in low quantities, so no great environmental damage is expected from their application, although little is known about their tolerance and related behavioral responses by fish (Burridge et al., 2010; Readman et al., 2013).

Formalin and iodophors are the main disinfectants used in aquaculture in Europe (Costello et al., 2001). Disinfectant formulations often contain surfactants of which the actual compounds used may not be listed on the label. Some of these compounds may have negative effects on marine organisms. Nevertheless, there are very few data available concerning the levels and effects of disinfectants in the marine environment and there seem to be no regulations in place to control their use (Burridge et al., 2010).

The table 6 presents information on the main medicinal products used in the marine aquaculture industry.

Table 6. Summary of main medicinal products used in the marine aquaculture industry (as published by Tornero and Hanke, *in press, supplementary material*).

| Substance | Concentrations in marine aquaculture environments | Bioaccumulation Bioconcentration | Toxicity in the marine environment | PNEC for the marine environment | Quality benchmarks | Remarks |
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| Antibiotics | | | | | | |
| Amoxicillin (2 <i>S</i> ,5 <i>R</i> ,6 <i>R</i>)-6-[[<i>(2R)</i> -2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid | | Log Kow = -0.12 (Martínez Bueno et al., 2009). Log Kow = 0.91 (Muñoz et al., 2010). | <i>Algae</i> : EC50 = 3108 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999). Did not exert toxic effects on <i>Phaeodactylum tricornutum</i> and <i>Isochrysis galbana</i> (de Orte et al., 2013). | | 50 µg/kg (MRL, fin fish muscle plus skin in natural proportions). | Used in aquaculture for many years in Japan and in the UK since 1990. Used in other European countries like Italy. Typical dosage in aquaculture is 80-160 mg active ingredient/kg fish day, for a standard period of 10 days. Very limited studies available on its pharmacokinetics and residue depletion. No effective against vibriosis and motile aeromonads are inherently resistant. Because of this and its relatively high cost, is rarely used now in aquaculture (GESAMP, 1997; Marine Institute for SWRBD, 2007). Very short environmental half-life (hours). Environmental concerns with respect to persistence of the β-lactam group of antibiotics are minimal (Armstrong et al., 2005). |
| Chloramphenicol 2,2-dichloro- <i>N</i> -[1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl]acetamide | MEC: <i>Biota</i> : 0.23-0.83 µg/kg ww, mean value 0.57µg/g ww (fish muscle, Sicilian aquaculture plant) (Conti et al., 2015). | | <i>Algae</i> : 96h EC50 = 41 mg/L (<i>Isochrysis galbana</i>); 4 mg/L (<i>Tetraselmis chui</i>) (Lai et al., 2009). <i>Invertebrates</i> : 24h LC50 = 2042 mg/L (<i>Artemia salina</i>) (Boxall et al., 2002). | | MRL cannot be established (prohibited substance). | Banned in Europe, but its use continues in other countries. The major environmental hazard is its potential to increase drug resistance (GESAMP, 1997). Serious toxic effects in humans in the form of bone marrow depression, particularly severe in the form of fatal aplastic anaemia (Evangelopoulou |

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| | | | | | | and Samanidou, 2013). Illegal uses are still being reported (Lai et al., 2009; Conti et al., 2015). |
| Enrofloxacin 1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid | MEC: Water: not detected (LOD = 0.07 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009). Biota: not detected (<0.1 µg/Kg wwt)-0.25 µg/kg wwt, mean value 0.14 µg/g wwt (fish muscle, Sicilian aquaculture plant) (Conti et al., 2015). | Log Kow = 1.10 (Martínez Bueno et al., 2009). | | | 100 µg/kg (MRL, sum of enrofloxacin and ciprofloxacin, fin fish muscle plus skin in natural proportions). | Widely used in Europe, Asia and Latin America. Like all fluoroquinolones, it strongly sorbs to sludge, soil or sediment, and therefore to determine its presence in the environment, both bottom water and sediment samples should be analyzed (Borecka et al., 2015). Few available studies on its potential deleterious effects on aquatic organisms. It causes very small changes in the oxidative stress status of shrimps (Tu et al., 2008). |
| Erythromycin (3R,4S,5S,6R,7R,9R,11R,12R,13S,14R)-6- {[(2S,3R,4S,6R)-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy}-14-ethyl-7,12,13-tri-hydroxy-4- {[(2R,4R,5S,6S)-5-hydroxy-4-methoxy-4,6-dimethyloxan-2-yl]oxy}-3,5,7,9,11,13-hexamethyl-1-oxacyclopentadecane-2,10-dione | MEC: Water: 0.01.-0.03 ng/L (fish farm, southeast Spain) (Martínez Bueno et al., 2009); 1.10-50.9 ng/L (vicinity of oyster bases and shrimp farms of China); 4.7-1900 ng/L (harbor in Hong Kong); <4 ng/L (UK estuaries) (Zheng et al., 2012). PEC: Fish farm, southeast Spain: 0.0073 ng/L (water); 3.3x10 ⁻⁷ mg/Kg wwt (fish) (Muñoz et al., 2010). | Log Kow = 1.98 (Martínez Bueno et al., 2009). Log Kow = 3.06 (Muñoz et al., 2010). BCF = 45.31 (Muñoz et al., 2010). | Invertebrates: 48 hr NOEC <10 mg/L (<i>Artemia</i>) (Boxall et al., 2002). 2d NOEC = 4.9 mg/L (<i>Penaeus vannamei</i>) (Muñoz et al., 2010). Fish: Low acute toxicity in yellowtails (LD50 > 2g/kg). No abnormalities noted at repeated doses of 100 mg/kg/day for 10 days (Armstrong et al., 2005). | Water: 0.02 µg/L (Muñoz et al., 2010). | 200 µg/kg (MRL, fin fish muscle and skin in natural proportions). | Not licensed for use in aquaculture in Europe but used elsewhere. Typical dosage in aquaculture is 50-100 mg active ingredient/kg fish day, for approximately 21 days. The environmental effects may be more related to antibiotic resistance than to persistence since the ether linkages within the molecules will be susceptible to reduction or oxidation by physicochemical or biological processes (Armstrong et al., 2005). |
| Florfenicol 2,2-dichloro-N- [(1R,2S)-3-fluoro-1-hydroxy-1-(4-methanesulfonylphenyl)propan-2-yl]acetamide | PEC: 0.0035 µg/L (water); 224 µg/kg (fish) (Marine Institute for SWRBD, 2007). | | Algae: 72h IC50 = 11.31 mg/L (<i>Tetraselmis chuii</i> , growth). 96h IC50 = 6.06 mg/L (<i>Tetraselmis chuii</i> , | | 1000 µg/kg (MRL, sum of florfenicol and its metabolites measured as | Authorized in many countries for use in aquaculture, including Japan, Canada, Norway and UK. Typical dosage is 10-30 mg active ingredient/kg fish day, usually 10 days. |

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| | | | <p>growth) Ferreira et al., 2007).</p> <p>96h EC50 = 8 mg/L (<i>Isochrysis galbana</i>); 1.3 mg/L (<i>Tetraselmis chui</i>) (Lai et al., 2009).</p> <p>Invertebrates:</p> <p>Did not cause mortality of <i>Artemia parthenogenetica</i> after 24h of exposure, and only 30% of mortality was recorded after 48 h of exposure to the highest concentration tested (889 mg/L) (Ferreira et al., 2007).</p> | | <p>florfenicolamine, fin fish muscle and skin in natural proportions).</p> | <p>Not known to be significantly bioaccumulated (Marine Institute for SWRBD, 2007). Degrades rapidly in the sediment with a half-life of 4.5 days and displays low toxicity to aquatic organisms (Marine Institute for SWRBD, 2007; Ferreira et al., 2007). However, it presents a serious environmental concern in terms of induction of resistance (Armstrong et al., 2005). Moreover, recent research suggests that water-borne pharmaceutical mixtures as low as ng/L levels may still have potential risks to aquatic life (Lai et al., 2009). Despite their wide use, its toxicity to marine algae and invertebrates has been scarcely investigated and the need for more studies on long-term and mixture effects has been pointed out (Ferreira et al., 2007).</p> |
| <p>Flumequine</p> <p>7-fluoro-12-methyl-4-oxo-1-azatricyclo[7.3.1.0^{5,13}]trideca-2,5,7,9(13)-tetraene-3-carboxylic acid</p> | <p>MEC:</p> <p><i>Water:</i> 0.13 ng/L (fish farm, southeast Spain) (Martínez Bueno et al., 2009).</p> <p><i>Sediment:</i> not detected (<0.012 µg/Kg dwt)-578.8 µg/kg dwt (sea-bass farms, Italy) (Lalumera et al., 2004).</p> <p><i>Biota:</i> 0-1.12 µg/g (wild fish muscle, vicinity of fish farms in Norway) (Ervik et al., 1994).</p> <p>PEC:</p> <p><i>Fish farm, southeast Spain:</i> 0.011 ng/L (water); 3.5x10⁻⁸ mg/Kg ww (fish) (Muñoz et al., 2010).</p> | <p>Log Kow = 1.60 (Martínez Bueno et al., 2009).</p> <p>BCF = 3.162 (Muñoz et al., 2010).</p> | <p>Algae:</p> <p>EC50 = 18 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999).</p> <p>Invertebrates:</p> <p>24h LC50 = 477 mg/L (<i>Artemia salina</i>).</p> <p>48h LC50 = 308 mg/L (<i>Artemia salina</i>).</p> <p>72h LC50 = 96 mg/L (<i>Artemia salina</i>) (OSPAR, 2009a).</p> <p>EC50 = 31.0 mg/L (<i>Paracentrotus lividus</i>, embryo) (Carballeira et al., 2012).</p> | <p><i>Water:</i> 1.59 µg/L (OSPAR, 2009a); 0.00032 mg/L (Muñoz et al., 2010).</p> | <p>600 µg/kg (MRL, fin fish muscle and skin in natural proportions).</p> | <p>Widely used in aquaculture in Europe, Japan and other countries in Asia and Latin America. Typical dosage is 1 g/100 kg fish day, for 10 days.</p> <p>Potential to accumulate in aquatic environments (Armstrong et al., 2005). High efficacy and relatively low toxicity (Armstrong et al., 2005). Research studies suggest that, apart from peak concentrations following treatments, the chronic presence of flumequine in sediments inside and out-</p> |

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| | | | 3d EC50 = 96.35 mg/L (<i>Artemia sp.</i>) (Muñoz et al., 2010). | | | side farms must be considered (Lalumera et al., 2004). |
| Nalidixic acid 1-ethyl-7-methyl-4-oxo-[1,8]naphthyridine-3-carboxylic acid | | | | | | Commonly used in the aquaculture industry. Parent compound of the quinolone antibiotic class and has a narrow antibacterial spectrum (Van Doorslaer et al., 2014). Potential to accumulate in aquatic environments. High efficacy and relatively low toxicity (Armstrong et al., 2005). |
| Oxolinic acid 5-ethyl-8-oxo-5,8-dihydro[1,3]dioxolo[4,5-g]quinoline-7-carboxylic acid | MEC: <i>Water:</i> not detected (LOD = 0.03 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009). <i>Sediment:</i> 0.05-0.2 µg/g (maximum concentrations found below fish farms in the southwest coast of Finland) (Boxall et al., 2002), <i>Biota:</i> 4.38 µg/g and 0.42 µg/g (mean in wild fish muscle caught within 400 m of two farms, with maximum concentration of 12.51 µg/g in coalfish); 0.02-3.77 µg/g (maximum concentrations in crab muscle); 0.05-1.48 µg/g (homogenised tissue from mussels) (vicinity of fish farms in Norway) (Samuelsen et al., 1992); 0.58-4.89 µg/g (mean in wild fish muscle, with maximum concentration of 15.74 µg/g in saithe) (vicinity of fish farms in Norway) (Ervik et al., 1994). | Log Kow = 0.94 (Martínez Bueno et al., 2009). | <i>Algae:</i> EC50 = 10 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999). | <i>Water:</i> 0.42 µg/L (OSPAR, 2009a); | 100 µg/kg (MRL, fin fish muscle and skin in natural proportions). | Widely used in Europe, Japan and other countries in Asia and Latin America. Typical dosage is 1 g/100 kg fish day, for 10 days. Potential to accumulate in aquatic environments. High efficacy and relatively low toxicity (Armstrong et al., 2005). Found to be very persistent in sediments. In the deeper layer of the sediment hardly any degradation occurred after 180 days and a calculated half-life of more than 300 days was estimated. The residues in the top layer of the sediment disappeared more rapidly (OSPAR, 2009a). |
| Oxytetracycline 2-naphthacenecarboxamide, 4-(dimethylamino)- | MEC: | Log Kow = -2.07 (Martínez Bueno et al., 2009). | <i>Algae:</i> EC50 = 1.6 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999). | | 100 µg/kg (MRL, sum of parent drug and its 4-epimer, fin | Probably the most widely used antibiotic in aquaculture. Typical dosage is 50-125 mg active ingredient/kg |

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| 1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexahydroxy-6-methyl-1,11-dioxo-, [4S-(4 alpha,4a alpha,5 alpha,5a alpha,6 beta,12a alpha)] | <p>Water: not detected (LOD = 0.60 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009).</p> <p>Sediment: not detected (<0.061 µg/Kg dwt)-4.2 µg/kg dwt (sea-bass farms, Italy) (Lalumera et al., 2004); <10-240 µg/g (Armstrong et al., 2005); not detected (< 1 µg/g)-19000 µg/kg dwt (beneath Atlantic salmon farms) (Mayor et al., 2008).</p> <p>Biota: present in oysters, crabs and benthic macro-invertebrates near salmon farms in British Columbia, with maximum of 3.8 µg/g ww in rock crab (Armstrong et al., 2005); 0.1-12.5 µg/g (tissues of wild mussels, crabs, and fish in the adjacent areas of farming sites outside the Mediterranean) (Grigorakis and Rigos, 2011).</p> | | <p>96h IC50 = 11.18 mg/L (<i>Tetraselmis chuii</i>, growth) (Ferreira et al., 2007).</p> <p>Invertebrates: 24h LC50 = 0.16 mg/L (<i>Panneus vannamei</i>) (Boxall et al., 2002); 871 mg/L (<i>Artemia parthenogenetica</i>) (Ferreira et al., 2007). 48h LC50 = 0.16-0.2384 mg/L (<i>Panneus vannamei</i>) (Boxall et al., 2002); 806 mg/L (<i>Artemia parthenogenetica</i>) (Ferreira et al., 2007). 10d LC50 = 414 µg active ingredient/kg wet sediment (<i>Corophium volutator</i>) (Mayor et al., 2008).</p> <p>Fish: LD50 >4000 mg/kg (Armstrong et al., 2005).</p> | | <p>fish muscle and skin in natural proportions). 2 µg/ g (US FDA guideline for seafood) (US FDA, 2013).</p> | <p>fish day, for a 4–10 day treatment period. The ultimate sink for this compound seems to be in dissolved and particle-associated phases in the water column (Armstrong et al., 2005). It can persist for relatively long periods in sediments (half-lives in marine sediments were found to be 151 days in the top layer, 0–1 cm, and more than 300 days at 5–7 cm deep). It also persists in fish tissues. It has a low bioavailability when administered orally and immunosuppressive effects on fish and may cause liver damage. Furthermore, a high incidence of bacterial resistance has been observed. For these reasons it has been increasingly replaced by other drugs (Fisheries and Oceans Canada, 2003; Ferreira et al., 2007).</p> |
| Piromidic acid 8-ethyl-5-oxo-2-pyrrolidin-1-yl-5,8-dihydro-pyrido[2,3-d]pyrimidine-6-carboxylic acid | | | | | | <p>Commonly used in the aquaculture industry. Potential to accumulate in aquatic environments. High efficacy and relatively low toxicity (Armstrong et al., 2005).</p> |
| Sarafloxacin 6-fluoro-1-(4-fluorophenyl)-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid | | Log Kow = -0.67 (Van Doorslaer et al., 2014). | <p>Algae: EC50 = 24 mg/L (<i>Rhodomonas salina</i>) (Boxall et al., 2002).</p> | | <p>30 µg/kg (MRL, Salmonidae muscle and skin in natural proportions).</p> | <p>Widely used in Europe, Japan and other countries in Asia and Latin America. Typical dosage is 10 mg active ingredient/kg fish day, for a period of 5 days. Very persistent in sediments with half-life higher than 80 days. Rapidly photodegraded in water with half-life <1h.</p> |

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| | | | | | | Assigned to the 'highest risk' category with respect to the relative potential for veterinary medicines to cause harm (Boxall et al., 2002). |
| Sulfadiazine 4-amino-N-pyrimidin-2-yl-benzenesulfonamide | MEC: Water: not detected-3.41 ng/L (vicinity of oyster bases and shrimp farms of China) (Zheng et al., 2012). | Log Kow = -0.09 (Drugbank, 2013). | <i>Algae:</i> EC50 = 403 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999); 0.11 mg/L (<i>Phaeodactylum tricornutum</i>); 1.44 mg/L (<i>Isochrysis galbana</i>) (de Orte et al., 2013). <i>Invertebrates:</i> EC50 = 12.7 mg/L (<i>Arbacia lixula</i> , embryo) (Carballeira et al., 2012). | | 100 µg/kg (MRL, Salmonidae muscle and skin in natural proportions). | Typical dose for sulfadiazine: trimethoprim (in a 5:1 ratio) is 30-75 mg/kg, for 5-10 days. The environmental implications of release of this type of antibiotic into the environment are unknown (Armstrong et al., 2005). However, given its broad spectrum and the fact that may be degraded slowly, it may affect bacteria of the marine sediments and fish pathogens selecting for resistance (Burridge et al., 2010). It is more persistent than trimethoprim, with which it is commonly combined (Marine Institute for SWRBD, 2007). |
| Sulfathiazole 4-amino-N-(1,3-thiazol-2-yl)benzenesulfonamide | | Log Kow = 0.05 (Leston et al., 2014). | | | | Exhibits high stability in seawater. The effects to non-target organisms may include changes in growth rate, reproduction and even lethal toxicity. It is not expected that the tested prophylactic and therapeutic concentrations will have a severe impact on macroalgal growth in the concentrations usually reported for environmental waters, which are in the ng/L to µg/L range (Leston et al., 2014). |
| Sulfamethoxazole 4-amino-N-(5-methylisoxazol-3-yl)benzenesulfonamide | MEC: Water: not detected (LOD = 0.02 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009); not detected- | Log Kow = 2.44 (Martínez Bueno et al., 2009). | | | | Commonly used in human medicine. Marine bacteria are affected by chronic exposure, while acute tests using the marine |

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| | 10.4 ng/L (vicinity of oyster bases and shrimp farms of China); not detected-47.5 ng/L (harbor, Hong Kong); <20 ng/L (UK estuaries) (Zheng et al., 2012). | Log Kow = 0.89 (Johansson et al., 2014). | | | | bacterium <i>Vibrio fischeri</i> (EC50 >395 nmol/L) fail to detect any toxicity. This underlines the need for evaluating the environmental hazards of antibiotics in chronic assays. Conclusions on the risks for the marine environment are hampered by the paucity of actual monitoring data, in particular there are no data published for European coastal environments (Johansson et al., 2014). |
| Trimethoprim 5-(3,4,5-trimethoxybenzyl)pyrimidine-2,4-diamine | MEC: Water: 0.03 ng/L (fish farm, southeast Spain) (Martínez Bueno et al., 2009); 0.23 ng/L (fish farm, southeast Spain) (Muñoz et al., 2010); not detected-3.37 ng/L (vicinity of oyster bases and shrimp farms of China); 2.6-216 ng/L (harbor, Hong Kong); <4-569 ng/L (UK estuaries) (Zheng et al., 2012). PEC: Fish farm, southeast Spain: 0.2 ng/L (water); 6.3x10 ⁻⁸ mg/Kg ww (fish) (Muñoz et al., 2010). | Log Kow = 1.36 (Martínez Bueno et al., 2009). Log Kow = 0.91 (Muñoz et al., 2010). BCF = 3.162 (Muñoz et al., 2010). | <i>Algae:</i> EC50= 16 mg/L (<i>Rhodomonas salina</i>) (Lützhøft et al., 1999). | <i>Water:</i> 0.016 mg/L (Muñoz et al., 2010). | 50 µg/kg (MRL, fin fish muscle and skin in natural proportions). | One of the most widely used antibiotics in aquaculture (synergistically in combination with sulphonamides). Typical dose for sulfadiazine: trimethoprim (in a 5:1 ratio) is 30-75 mg/kg d, for 5-10 days. The environmental implications of release of this type of antibiotic into the environment are unknown (Armstrong et al., 2005). However, given its broad spectrum and the fact that may be degraded slowly, it may affect bacteria of the marine sediments and fish pathogens selecting for resistance (Burridge et al., 2010). |
| Bactericides | | | | | | |
| Bronopol 2-bromo-2-nitropropane-1,3-diol | MEC: Not detected in water (LOD = 0.05 µg/L), sediment (LOD = 10-17 µg/Kg dwt) or fish (LOD = 10 µg/Kg fwt) from Swedish environment (Remberger et al., 2006). | Log Kow = -0.64. BCF = 3.2 (Remberger et al., 2006). | | <i>Water:</i> 0.78 µg/L (Remberger et al., 2006); 5.90 µg/L (OSPAR, 2009a). | MRL not required. | The European Agency for Evaluation of Medicinal Products (EMA) enrolls bronopol as a safe chemical for aquaculture and it has been used in European countries. Typical dosage in aquaculture is 50-500 mg/L. |

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| | | | | | | It is moderately to highly toxic to estuarine/marine invertebrates and slightly toxic to estuarine/marine fish. It undergoes rapid hydrolysis and biodegradation, which could explain its absence in environmental samples (Remberger et al., 2006). |
| Malachite green [4-[alpha-[4-(dimethylamino)phenyl]benzylidene]cyclohexa-2,5-dien-1-ylidene]dimethylammonium chloride | MEC: <i>Water:</i> not detected (LOD = 0.02 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009). <i>Biota:</i> Detectable levels, albeit at very low concentrations in edible tissues of free ranging wild eels in Germany (Burridge et al., 2010); not detected (<0.2 µg/Kg wwt)-1.21 µg/kg wwt, mean value 0.48 µg/g wwt (fish muscle, Sicilian aquaculture plant) (Conti et al., 2015). | Log Kow = 3.50 (Martínez Bueno et al., 2009). | | | 0.5 µg/L (UK AA-EQS, interim guideline); 100 µg/L (UK MAC-EQS, interim guideline) (SEPA, 2014). Zero tolerance level for food fish is in place in most countries (Burridge et al., 2010). | Banned from use in EU and US aquaculture because dietary exposure highlighted significant mutagenic and carcinogenic effects in rat. It and its metabolite leucomalachite green are suspected of being capable of causing gene damage and cancer. Despite its use has been banned, several reports identify instances of misuse in aquaculture internationally (Conti et al., 2014). It has been also suggested that it may be a ubiquitous contaminant in industrialized areas and calls into question the ability to enforce zero tolerance guidelines (Burridge et al., 2010). |
| Parasiticides-Bath treatment | | | | | | |
| Azamethiphos 6-chloro-3-(dimethoxyphosphorylsulfanylmethyl)-[1,3]oxazolo[4,5-b]pyridin-2-one | MEC: Not detected (<50 pg/L) in water from a salmon farming area in Canada (Haya et al., 2005). | Log Kow = 1.05 (Fisheries and Oceans Canada, 2003). | <i>Invertebrates:</i> 48h LC50 = 3.57-1.39 µg/L (<i>Homarus americanus</i> , larval/adult) (Fisheries and Oceans Canada, 2003). 24h LC50 > 10 µg/L (<i>Temora longicornis</i>) (Haya et al., 2005); 8.9 µg/L (<i>Homarus americanus</i> , stage I); 2.8 µg/L (<i>Homarus americanus</i> , adult); 191 µg/L (<i>Crangon</i> | | MRL not required. 250 ng/L (3h SEPA AA-EQS); 150 ng/L (24h SEPA MAC-EQS); 40 ng/L (72h SEPA MAC-EQS) (SEPA, 2014). | Used in the UK. Typical dosage in aquaculture is 0.1-0.2 mg/L for 60 minutes. Unlikely to accumulate in tissues (Fisheries and Oceans Canada, 2003) or in sediments (Haya et al., 2005). It decomposes by hydrolysis in natural water with a half-life of 8.9 days. Dispersion studies indicated that after release of an experimental treatment, the concentration was below detection |

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| | | | <p><i>septemspinosa</i>); 12.5 µg/L (<i>Mysid sp.</i>) (Burridge et al., 2014). 96h LC50 = 0.5 µg/L (<i>Homarus gammarus</i>, larvae); 0.52 µg/L (<i>Mysidopsis bahia</i>) (Haya et al., 2005). 10d LC50 = 182 µg active ingredient/kg wet sediment (<i>Corophium volutator</i>) (Mayor et al., 2008). 120min NOEC = 1 µg/L (lobster, larval/adult).</p> | | | <p>(0.1 µg/L) in a short period of time (hours) (Burridge et al., 2014). Highly toxic to crustaceans and many marine invertebrates; its effects on fish are less well characterized (PAN pesticide database, 2014). No negative effect on survival of non-target organisms except when held within the treatment cage (Burridge et al., 2010).</p> |
| <p>Cypermethrin [Cyano-(3-phenoxy-phenyl)methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate</p> | <p>MEC: Water: decreases rapidly on release from a cage site after treatment: 187 ng/L (highest concentration, 25 min after release at 25 m); >0.031 ng/L (up to 50 min after release); >0.074 ng/L (up to 30 min) (Haya et al., 2005). Sediment: not detected-7 µg/Kg dwt (beneath Atlantic salmon farms) (Mayor et al., 2008); not detected-0.15 µg/kg dwt (Scottish marine fish farms) (BIO Intelligence Service, 2013). Biota: 133 µg/g (mussels exposed inside a treated cage at 5 ug/L); 9.2 ng/g (mussels at 2 m from cages after seven treatments); occasionally detectable (100 m from the cage) (Haya et al., 2005).</p> | <p>Log Kow = 6.6 (Mayor et al., 2008).</p> | <p>Invertebrates: 96h LC50 = 0.016 µg/L (<i>Palaemonetes pugio</i>); 0.016µg/L (<i>Crangon septemspinosa</i>); 0.04 µg/L (<i>Homarus americanus</i>); 0.005-0.056 µg/L (<i>Americamysis bahia</i>). 24h LC50 = 0.14 µg/L (<i>Homarus americanus</i>, adult). 48h EC50 = 2.3 mg/L (oyster, larval development) (Haya et al., 2005). 10d LC50 = 5 µg active ingredient/kg wet sediment (<i>Corophium volutator</i>) (Mayor et al., 2008). Fish: 96h LC50 = 2 µg/L (<i>Salmo salar</i>); 1 µg/L (<i>Cyprinodon variegatus</i>) (Haya et al., 2005).</p> | <p>Water: 0.016 µg/L (OSPAR, 2009a).</p> | <p>50 µg/kg (MRL, Salmonidae muscle and skin in natural proportions, sum of isomers). 8x10⁻⁶µg/L (WFD AA-EQS); 6x10⁻⁵ µg/L WFD MAC-EQS). 0.05 ng/L (SEPA AA-EQS); 16 ng/L (3h SEPA MAC-EQS); 0.5 ng/L (24h SEPA MAC-EQS) (SEPA, 2014).</p> | <p>Applied in Europe, relatively more often in countries like Scotland. Typical dosage in aquaculture is 5 µg/L for 60 minutes. Weakly antiestrogenic and antiandrogenic. It may degrade to produce oestrogenic residues (Costello et al., 2001). Unlikely to be accumulated to a significant degree in fish and aquatic food chains since it is rapidly metabolized. However, it can persist in sediments for weeks and may be desorbed and affect benthic invertebrates. Large amount of ecotoxicological data for freshwater environments, but limited knowledge for marine species. Field studies indicated that it is lethal to lobsters and some planktonic crustaceans, but not to mussels, sea urchins or planktonic copepods (Haya et al., 2005). Although showed an immediate reduction of plankton</p> |

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| | | | | | | density and diversity in lab studies, in open systems concentrations are expected to drop quickly and that plankton migration and immigration would lead to recovery of the community (Burridge et al., 2010). |
| Deltamethrin [(S)-cyano-(3-phenoxyphenyl)-methyl] (1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate | MEC: <i>Sediments:</i> not detected-0.3 µg/kg dwt (Scottish marine fish farms) (BIO Intelligence Service, 2013). | Log Kow = 4.6 (Burridge et al., 2014). | <i>Invertebrates:</i> 24h LC50 = 0.8 ng/L (<i>Homarus americanus</i> , stage I); 0.6 ng/L (<i>Homarus americanus</i> , stage II); 1.7 ng/L (<i>Homarus americanus</i> , stage IV); 15 ng/L (0.8 ng/L (<i>Homarus americanus</i> , adult); 27 ng/L (<i>Crangon septemspinosa</i>); 1.4 ng/L (<i>Mysid sp.</i>). 96h LC50 = 3.4 µg/L (<i>Homarus americanus</i> , stage I); 18.8 ng/L (<i>Homarus americanus</i> , adult); 142 ng/L (<i>Crangon septemspinosa</i>); 1.7-8 ng/L (<i>Eohaustorius estuaries</i>); 13.9 ng/L (<i>Mysid sp.</i>) (Burridge et al., 2014). <i>Fish:</i> 96h LC50 = 0.4-2.0 µg/L (OSPAR, 2009a). | <i>Water:</i> 0.00024 µg/L (OSPAR, 2009a). | 10 µg/kg (MRL, fin fish muscle and skin in natural proportions). 0.3 ng/L (SEPA AA-EQS); 9 ng/L (3h SEPA MAC-EQS); 6 ng/L (6h SEPA MAC-EQS); 4 ng/L (12h SEPA MAC-EQS); 2 ng/L (24h SEPA MAC-EQS); 1 ng/L (48h SEPA MAC-EQS) (SEPA, 2014). | Used in countries like Norway and Chile. Typical dosage in aquaculture is 2-3 µg/L for 40 minutes. Much of the available information comes from the freshwater literature although recent publications have addressed its use in marine waters. It has an affinity for organic material, so exposure of non-target species from a single cage treatment may be via sediment, through ingestion of contaminated organic particles, as well as from water. It is extremely toxic to crustaceans. It seems it could remain in the marine environment for some time. This, coupled with the low lethal thresholds, suggests that it could pose great risk when used in an aquaculture setting, particularly where sensitive non-target organisms are present (Burridge et al., 2014). However, field studies have shown that this high potential toxicity is not realized. It is not mobile in the environment because of its strong adsorption on particles, its insolubility in water, and very low rates of application (OSPAR, 2009a). |

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| Dichlorvos <i>2,2-dichlorovinyl dimethyl phosphate</i> | MEC: <i>Water:</i> not detected (LOD = 0.10 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009). | Log Kow = 1.47 (Martínez Bueno et al., 2009). | <i>Fish:</i> LC50= 0.2->40 mg/L, with the lowest value 0.122 mg/L for larvae of herring (OSPAR, 2009a). | | 6x10 ⁻⁵ µg/L (WFD AA-EQS); 7x10 ⁻⁵ µg/L WFD MAC-EQS). 0.04 µg/L (UK AA-EQS) (SEPA, 2014). | Widely used in the past, but its use is no longer permitted. Degrades relatively rapidly in biologically active waters, with half-life from <1 to <25 days (Boxall et al., 2002). Unlikely to bioaccumulate (Burridge et al., 2010). Highly to moderately toxic to fish and aquatic arthropods are more sensitive than fish (OSPAR, 2009a). |
| Trichlorfon <i>(RS)-dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate</i> | | | No effects observed in <i>Chlorella vulgaris</i> (Coelho et al., 2011). | | | Widely used in seabass and sea bream aquaculture in the Mediterranean and in shrimp farms in many south-east Asian countries. The widespread use in aquaculture for a long time is generating concerns about the impact on public and environmental health (Coelho et al., 2011). Degrades into the more toxic and effective dichlorvos, but the rate of transformation is dependent on water temperature and pH. The inconsistency of this transformation, the acute toxic risk to salmon and the increase in use of dichlorvos resulted in the gradual cessation of use of trichlorfon (Haya et al., 2005). |
| Parasiticides-In-feed additives | | | | | | |
| Diflubenzuron <i>N-[(4-chlorophenyl)carbamoyl]-2,6-difluorobenzamide</i> | MEC: <i>Water:</i> not detected (LOD = 1.25 µg/L) (fish farm, south-east Spain) (Martínez Bueno et al., 2009). <i>Sediment:</i> not detected (<0.5 µg/kg ww) -1.6 µg/kg ww (Scottish lochs) (SEPA, 2009). | Log Kow = 3.89 (Martínez Bueno et al., 2009). | <i>Invertebrates:</i> 96h LC50 = 1.1-200 µg/L (<i>Palaemonetes pugio</i> , various stages). 48h LC50 = 2.2 µg/L (<i>Eurytemora affinis</i>) (Haya et al., 2005). EC50 = 130 mg/L (oyster, larvae); 250 | | 1000 µg/kg (MRL, Salmonidae muscle and skin in natural proportions). 0.005 µg/L (UK AA-EQS); 0.1 µg/L (UK MAC- | Moderate potential for bioaccumulation. Few marine studies suggest that sediment is a significant sink in the marine environment. It is stable and persistent in anoxic marine sediments under laboratory conditions (Haya et al., 2005). |

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| | <p><i>Biota</i>: traces of the metabolites are found in fish when water is contaminated with diflubenzuron (OSPAR, 2009a).</p> | | <p>mg/L (oyster, juveniles (OSPAR, 2009a). LC50 = 1 mg/L (<i>Uca pugilator</i>); 1200 mg/L (<i>Homarus americanus</i>) (PPDB, 2013).</p> <p><i>Fish</i>: 96h LC50 = 33 mg/L (<i>Fundulus heteroclitus</i>) (Haya et al., 2005); 255 mg/L (salt-water minnow) (OSPAR, 2010b). LC50 = 50000 mg/L (<i>Salmo salar</i>); 71.5 mg/L (<i>Cyprinodon variegatus</i>) (PPDB, 2013).</p> | | <p>EQS (SEPA, 2014).</p> | <p>Practically nontoxic to fish and aquatic invertebrates. Arthropods are most susceptible in the premolting stage. Monthly and bimonthly application of 10 µg/L were reported to reduce zooplankton abundance and species richness, causing algal biomass to increase because of decreases in invertebrate grazing (OSPAR, 2009a).</p> |
| <p>Emamectin benzoate (4''R)-4''-deoxy-4''-(methylamino)avermectin B1 benzoate</p> | <p>MEC: <i>Water</i>: not detected (LOD = 0.25 µg/kg) (field trial under EB commercial use conditions, Atlantic salmon farm, northwest Scotland) (Telfer et al., 2006). 8 day exposure to 0.1 mg/kg sediment-associated EB resulted in approximately 0.5 g/L in the overlying sea water (Veldhoen et al., 2012). <i>Sediment</i>: not detected (LOD = 0.25 µg/kg) to a maximum post-treatment level of 2.73 µg/kg after 4 months (field trial) (Telfer et al., 2006); not detected-28 µg/Kg dwt (beneath Atlantic salmon farms) (Mayor et al., 2008); not detected (<0.08 µg/Kg wwt)-44 µg/kg wwt (Scottish lochs) (SEPA, 2009). <i>Biota</i>: detectable levels in mussels one week after treatment, in crustaceans during and immediately after treatment, in scavengers</p> | <p>Log Kow = 5 (Fisheries and Oceans Canada, 2003). BCF = 69 (whole fish) (USEPA, 2009).</p> | <p><i>Invertebrates</i>: 96h LC50 = 0.983 mg/L (<i>Nephrops norvegicus</i>); 0.665 (<i>Crassostrea virginica</i>); 0.242 mg/L (<i>Crangon crangon</i>) (Boxall et al., 2002). 10d LC50= 153 µg/Kg wwt (<i>Corophium volutator</i>); 1368 µg/Kg wwt (<i>Hediste diversicolor</i>) (Mayor et al., 2008). EC50= 490 µg/L (<i>Crassostrea virginica</i>, shell deposition or embryo-larvae). LC50 = 0.04 µg/L (<i>Americamysis bahia</i>) (USEPA, 2009). Significant mortality in <i>Pandalus platyceros</i> within 8 days of treatment at concentrations between 0.1-0.8 mg/kg and no effect on molting (Veldhoen et al., 2012).</p> | <p><i>Water</i>: 0.00022 µg/L (OSPAR, 2009a). <i>Sediment</i>: 1.11 ppb (derived from <i>Arenicola marina</i> exposed in sediment); 6820 ppb (derived from <i>Nephrops norvegicus</i> exposed to medicated feed) (Marine Institute for SWRBD, 2007).</p> | <p>100 µg/kg (MRL, fin fish muscle and skin in natural proportions). 0.22 ng/L (SEPA MAC-EQS). 0.763 µg/kg wwt (SEPA MAC-EQS_{sediment}, 5 cm core depth outside zone of effects area. 100 m from edge of cages, increased up to 150 m where strong directional currents exist) (SEPA, 2014).</p> | <p>Widely used. Typical dosage in aquaculture is 0.05 mg active ingredient/kg fish day for 7 days. Moderate to high bioaccumulation potential (Telfer et al., 2006). Likely to be rapidly bound to particulate material or surfaces, so potential impacts could be predicted on sediment dwellers or fauna which feed on suspended particulate material, such as filter feeders. However, no evidence of toxic impacts on organisms in either water column or sediments around fish farm cages after treatment was found (Telfer et al., 2006). Induces molting in lobsters (Fisheries and Oceans Canada, 2003). Feeding to Atlantic salmon at up to ten times the recommended treatment dose resulted in no mortality. However, signs of toxicity, lethargy, dark</p> |

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| | several months after treatment (field trials) (Haya et al., 2005); not detected (LOD = 0.25 µg/kg)-1.99 µg/kg wwt (<i>Munida rugose</i>); not detected-5 µg/kg wwt (<i>Pagurus spp.</i>); not detected-1.08 µg/kg wwt (<i>Buccinum undatum</i>); not detected-0.61 µg/kg wwt (<i>Asterias rubens</i>); not detected-1.23 µg/kg wwt (<i>Scyliorhinus canicula</i>); not detected (<i>Conger conger</i>) (Telfer et al., 2006); 0.45±0.15 g/kg wwt (<i>Pandalus platyceros</i> , muscle) (Veldhoen et al., 2012). | | NOEC = 0.115 mg/kg (<i>Arenicola marina</i>); 0.056 mg/kg (<i>Corophium volutator</i>) (Telfer et al., 2006); 0.018 µg/L (<i>Americamysis bahia</i>) (USEPA, 2009). <i>Fish</i> : 96h LC50 = 1.34 mg/L (<i>Cyprinodon variegatus</i>) (Boxall et al., 2002). | | | coloration and lack of appetite were observed at the highest treatment concentration (Haya et al., 2005). Sort-term exposure can impact biological processes in spot prawn (<i>Pandalus platyceros</i>) (Veldhoen et al., 2012). Based on the current state of knowledge and monitoring requirements, it has the highest risk quotient because of the very low PNEC, but measured concentrations in sediments close to the farm indicate a much smaller localised risk (OSPAR, 2009a). |
| Ivermectin 22,23-dihydroavermectin B1a + 22,23-dihydroavermectin B1b | MEC: <i>Sediment</i> : not detected (<0.2 µg/kg wwt) (Scottish lochs) (SEPA, 2009); 1.4-6.8 ng/g (under and adjacent to salmon cages approx. 1 km off-shore on the west coast of Ireland) (Boxall et al., 2002). | Log Kow = 3.22 (Haya et al., 2005). BCF = 74 (fish); 750 (mussels) (Haya et al., 2005). | <i>Invertebrates</i> : 96h LC50 = 7.75 mg/L (<i>Nereis diversicolor</i>); 580 mg/L (<i>Littorina littorea</i>); 390 mg/L (<i>Nucella lapillus</i>); 300 mg/L (<i>Pecten maximus</i>); 400 mg/L (<i>Mytilus edulis</i>); 80-100 mg/L (<i>Crassostrea gigas</i> , larvae); 54 mg/L (<i>Palaemonetes varians</i>); 0.07 mg/L (<i>Nemomysis integer</i>); 9.57 mg/L (<i>Carcinus maenas</i>); >10000 mg/L (<i>Hydrobia ulvae</i>) (Boxall et al., 2002). 10d LC50 = 180 µg/kg dwt (<i>Corophium volutator</i>); 23 µg/kg dwt (<i>Arenicola marina</i>); 23600 µg/kg dwt (<i>Asterias rubens</i>) (Haya et al., 2005). NOEC = 0.05 mg/kg (<i>Corophium volutator</i>); 5 mg/kg (<i>Asterias</i> | <i>Sediment</i> : 2 mg/Kg (derived from <i>Arenicola marina</i> exposed in sediment) (Davies et al., 1998). | Has an MRL, but not established for fish. 0.0001 µg/L (UK AA-EQS); 0.001 µg/L (UK MAC-EQS) (SEPA, 2014). | Limited use. Employed to control sea lice in salmon culture grow-out operations in the UK and Ireland. Veterinarians can prescribe ivermectin if no other effective licensed product is available. Expected to be associated with sediments and particles and to show low mobility. It is highly toxic to several non-target organisms, particularly to crustaceans (BIO Intelligence Service, 2013). Behavioral changes, such as cessation of feeding and lethargy, were observed in Atlantic salmon exposed to this compound (Haya et al., 2005). |

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| | | | <p><i>rubens</i>) (Davies et al., 1998).</p> <p><i>Fish:</i> 96h LC50 = 17 µg/L (<i>Salmo salar</i>) (Haya et al., 2005).</p> | | | |
| <p>Teflubenzuron 1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea</p> | <p>MEC: <i>Water:</i> Not detected (salmon cages after treatment) (Haya et al., 2005). <i>Sediment:</i> Not detected (<0.2 µg/kg wet wt)-1.4 µg/kg ww (Scottish lochs) (SEPA, 2009); measurable concentrations at 1000 m from the cage, in line with the current flow, but 98% of the total load degraded or dispersed by 645 days after treatment (Haya et al., 2005). <i>Biota:</i> 0.2-11.3 ng/g (deep-water prawns, 1-5 km away from the farms); 185.7 ng/g (maximum concentration in brown crab, 100-300 m from the farms) (Langford, 2011); 200 ng/g (deepwater prawns); 319 ng/g (Norway lobster); 393 ng/g (squat lobster); 865 ng/g (king crab) (within an area of 300 m from a commercial farm under treatment) (Samuelson et al., 2014).</p> | <p>Log Kow = 4.3. BCF = 640 (PPDB, 2013).</p> | <p><i>Invertebrates:</i> Members of <i>Capitella</i> sp. reduce their feeding activity at 8.4 to 41.8 mg/g in sediments (Méndez, 2006).</p> | | <p>500 µg/kg (MRL, Salmonidae muscle and skin in natural proportions). 6 ng/L (SEPA AA-EQS); 30 ng/L (SEPA MAC-EQS). 2 µg/kg ww (SEPA MAC-EQS_{sediment}, 5 cm core depth outside zone of effects area. 100 m from edge of cages, increased up to 150 m where strong directional currents exist) (SEPA, 2014).</p> | <p>Apparently no longer produced as an anti-louse treatment. Typical dosage in aquaculture is 10 mg active ingredient/kg fish day, for 7 days or 2-3 mg active ingredient/kg fish day, for 14 days. Around 90% of the ingested teflubenzuron is evacuated from fish via faeces in the period immediately following treatment, with the remainder entering the environment in the form of uneaten waste feed (Méndez, 2006). Few marine studies suggest that sediment is a significant sink in the marine environment. Some indication of resuspension and redistribution of sediment after several weeks, suggesting risk to indigenous sediment dwelling crustaceans, such as crab or lobster. However, the mussels eliminated teflubenzuron readily. It is relatively non-toxic to marine species of birds, mammals and fish, due to its mode of action, but it is potentially highly toxic to any species which undergo molting within their life cycle (Haya et al., 2005). Variation in sensitivity between individuals made it difficult to determine a break point (Samuelson et al., 2014).</p> |

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| Fungicides | | | | | | |
| Trifluralin 2,6-dinitro- <i>N,N</i> -dipropyl-4-(trifluoromethyl)benz enamine | | Log Kow = 5.27. BCF = 2280-11500 (different fish species) (OSPAR, 2005). | <i>Invertebrates:</i> LC50 = 7.97mg/L (<i>Penaeus merguensis</i> , post larval stage 10); 9.98 mg/L (<i>Penaeus merguensis</i> , post larval stage 20); 13.3 mg/L (<i>Penaeus merguensis</i> , post larval stage 30) (Chan et al., 2013). <i>Fish:</i> 4d LC50 = 88 µg/L (<i>Oncorhynchus mykiss</i>). 166d NOEC = 1.3 µg/L (<i>Cyprinodon variegatus</i>). 48d NOEC = 1.14 µg/L (<i>Oncorhynchus mykiss</i>) (OSPAR, 2005). | | 0.03 µg/L (WFD AA-EQS). 1 µg/kg (Japanese MRL of Japan Food Chemical Research Foundation) (Chan et al., 2013). | Banned in Europe, but still widely use in other parts of the world. High potential for bioaccumulation and biomagnification and very toxic to aquatic organisms, especially towards fish. It is persistent in the environment and has a short half-life in water (OSPAR, 2005). As it undergoes extensive photodecomposition in aqueous media, the parent compound might not be the most appropriate marker of residue for detecting use. Information regarding its environmental concentrations, uptake, depuration, and metabolism for aquatic organisms is very limited (Chan et al., 2013). |
| Anaesthetics | | | | | | |
| Benzocaine Ethyl 4-aminobenzoate | | | Only freshwater data. | <i>Water:</i> 210 µg/L (OSPAR, 2009a). | MRL not required. | Widespread use. Not suspected to be persistent or bioaccumulative (CEPA, 2008). Shown to Induce increased blood glucose and serum cortisol levels on gilthead seabream (<i>Sparus aurata</i>). In addition, it depressed lysozyme activity, production of reactive oxygen species and pinocytosis activity (Bressler and Ron, 2004). It has been also seen that zebrafish are aversive to benzocaine, and recommended that in future this compound should perhaps be used only in exceptional circumstances (Readman et al., 2013). |

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| Tricaine methane sulphonate (MS-222) <i>Ethyl 3-aminobenzoate methanesulfate</i> | | | | | MRL not required. | Worldwide use. Typical dosage in aquaculture is 15-300 mg/L. No adverse environmental effects are foreseen with its use (Fisheries and Oceans Canada, 2003). It is assumed to be biodegradable but it is recommended not to discard it into the environment (OSPAR, 2009a). Several authors illustrated that it could significantly alter fish blood plasma chemistry, but this has not been adequately investigated in marine species (Popovic et al., 2012). It elicited an aversive response in zebrafish at 50% of the effective dose, supporting the anecdotal evidence of its aversive nature put forward for salmonids and other species (Readman et al., 2013). |
| Disinfectants | | | | | | |
| Formalin <i>Methanal</i> | | | <i>Invertebrates:</i> EC50 = 1.78 mg/L (<i>Paracentrotus lividus</i> , embryo); 1.79 mg/L (<i>Arbacia lixula</i> , embryo) (Carballeira et al., 2012). | | MRL not required. | Global use. Prohibited from commercial applications within the EU. Typical dosage in aquaculture is 150-250 ppm for 30 to 60 minutes. Not known to be significantly bioaccumulated (Marine Institute for SWRBD, 2007). Highly toxic to aquatic life at low concentrations, even found to be more toxic than antibiotics (Carballeira et al., 2012; de Orte et al., 2013). Chronic effects are unlikely to occur because of the intermittent nature of treatment and the relatively low persistence (GESAMP, 1997). |

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| Hydrogen peroxide | | Log Kow = <1 (Burridge et al., 2014). | <i>Invertebrates:</i> 24h LC50 = 800 mg/L (<i>Artemia salina</i>); 1637 mg/L (<i>Homarus americanus</i> , stage I); >3750 mg/L (<i>Homarus americanus</i> , adult); 3182 mg/L (<i>Crangon septemspinosa</i>); 973 mg/L (<i>Mysid sp.</i>) (Burridge et al., 2014). | | MRL not required. | Not in common use. Typical dosage in aquaculture is 500 mg/L for up to 20 minutes. There is little information of the toxicity to marine organisms. There is evidence that the concentrations used in sea lice treatments can cause gill damage and reduced growth rates for 2 weeks post treatment (Haya et al., 2005). Although is toxic to some aquatic organisms, including marine phytoplankton and crustacean, the rates of dilution and dissociation encountered on fish farms ensure that harmful effects on the environment are minimised and therefore this compounds seems to be of low regulatory priority (Marine Institute for SWRBD, 2007; Burridge et al., 2014). |
| Iodophoros | | | | | MRL not required. | Widespread use. May cause long term adverse effects on the aquatic environment. Formulations may contain compounds harmful or toxic to aquatic biota (Fisheries and Oceans Canada, 2003; Marine Institute for SWRBD, 2007). |

MEC: Measured environmental concentrations; PEC: Predicted environmental concentrations; dwt: dry weight; wwt: wet weight; LOD: Limit of detection.

Log Kow (log octanol/water partition coefficient) reflects the chemical's tendency to bioaccumulate in organisms.

BCF (Bioconcentration Factor) reflects the extent to which pollutants concentrate from water into aquatic organisms.

EC50: Median effective concentration; LC50: Median lethal concentration; LD50: Median lethal dose; IC50: Half maximal inhibitory concentration; NOEC: No effect concentration; PNEC: Predicted no effect concentration.

MRL: Maximum Residue Levels established in the Commission Regulation (EU) No 37/2010.

WFD EQS: Environmental quality standards set in the Directive 2008/105/EC (EQS Directive) and amendments (Directive 2013/39/EU); AA: Annual average; MAC: Maximum allowable concentration; SEPA EQS: Operational water and sediment Quality Standards applied by the Scottish Environmental Protection Agency (SEPA) for regulating the use of chemicals in aquaculture.

3.3.2 Food additives and contaminants

Food additives include artificial and natural pigments (e.g. astaxanthin and canthaxanthin), vaccines, antioxidants (e.g. butylated hydroxytoluene and ethoxyquin), and immunostimulants (e.g. vitamins C and E). These compounds are usually accepted as safe (GESAMP, 1997; Fisheries and Oceans Canada, 2003). The rules for the authorization, supervision and labelling of feed additives are set by the Regulation (EC) No 1831/2003⁴⁰.

On the other hand, the consumption of feed can lead farmed organisms to be exposed to pollutants such as polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), PAHs, hexachlorobenzenes (HCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides like DDT (Grigorakis and Rigos, 2011). Moreover, metal pollution in sediments under fish cages is often related to the fact that fish food formulations are supplemented with various trace elements, such as copper, zinc, iron, manganese, cobalt, magnesium and selenium (CIESM, 2007; Burridge et al., 2010; Grigorakis and Rigos, 2011; Simpson et al., 2013).

3.3.3 Antifouling biocides

The fish farming industry suffers significantly from the effects of biofouling, so the application of antifouling biocides is common in aquaculture. Antifouling compounds widely used include chorothalonil, copper pyrithione, dichlofuanid, DCOIT (sea-Nine 211), diuron, irgarol-1051, TCMS pyridine, zinc pyrithione, and zineb (Guardiola et al., 2012).

Antifoulants are not directly used on food-producing fish, so an MRL is not applicable to them. As mentioned above, their regulatory procedure comes within the scope of the Biocides Directive.

3.4 DREDGING AND DUMPING OF DREDGED MATERIAL

Dredging and dumping are common regulated human activities which can contribute to the input of sea-sourced substances. Dredging operations and associated re-suspension of bottom sediments may lead to large scale increases in water column pollutant levels (Hedge et al., 2009; Katsiaras et al., 2015). Nonetheless, dredging is essential to maintain ports and harbors and navigational access, and therefore dredging processes have increased worldwide (Wasserman et al., 2013).

Under UNCLOS and other relevant international maritime conventions, ocean dumping is defined as “any deliberate disposal of wastes or other matter from vessels, aircraft, platforms or other man-made structures at sea”. Disposal at sea of dredged material may also damage the marine environment (Parnell et al., 2008). Dredged material is not specifically tackled under any EU legislation, but several EU Directives have a direct or indirect impact on the management of dredged material (e.g. the Waste Framework Directive⁴¹, Natura

⁴⁰ Regulation (EC) No 1831/2003 of the European parliament and of the council of 22 September 2003 on additives for use in animal nutrition. <http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32003R1831>

⁴¹ Directive 2008/98/EC on waste (Waste Framework Directive). <http://ec.europa.eu/environment/waste/framework/>

2000 areas under the Birds⁴² and Habitat⁴³ Directives, the WFD, and the MSFD). Nowadays, the deliberate disposal of dredged material into the sea is fundamentally regulated by the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972 (London Convention) and its 1996 Protocol (London Protocol)⁴⁴. Guidelines for the management of dredged material, including its chemical characterization, are also provided on a regional level by OSPAR, HELCOM, the Barcelona and Bucharest Conventions. The OSPAR Agreement 2014-06e⁴⁵ recommends the consideration of trace metals and metalloids (arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc), PCBs (PCB congeners - IUPAC 28, 52, 101, 118, 138, 153 and 180), PAHs (anthracene, benzo[a]anthracene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, fluoranthene, indeno[1,2,3-cd]pyrene; pyrene, and phenanthrene), and organotin compounds. Based upon local information of sources of contamination or historic inputs, other substances may also require analysis: other chlorobiphenyls, organochlorine pesticides, organophosphorus pesticides, triphenyl tin (TPhT), other anti-fouling agents, petroleum hydrocarbons, PCDDs/PCDFs, and phthalates.

The London Protocol enumerates in its Annex 1 other wastes or matter that are currently legally acceptable for dumping, which includes sewage sludge, fish wastes, vessels and platforms, inert, inorganic geological material (such as mining wastes), organic material of natural origin, and bulky items (primarily comprising iron, steel and concrete). Nevertheless, dumping sewage sludge and vessels or aircrafts was phased out in the OSPAR area in 1998 and 2004, respectively. Throughout the Baltic Sea all dumping is prohibited, except for dredge spoil. Therefore, properly managed dredged material appear to be essentially all material currently dumped into the sea (OSPAR, 2009c). However, already-dumped material, as well as some allowed or unregulated dumping activities, can still represent a substantial environmental hazard. Illegal dumping and associated contamination may also be a problem in different parts of the world, including Europe (Frank, 2007).

3.5 HISTORICAL DUMPING SITES

Previously and until the prohibition with the London Convention, all types of wastes were ocean dumped, which led to areas with high levels of contaminants, such as PAHs, titanium dioxide waste, and heavy metals (Vethaak and Van Der Meer, 1991; Leipe et al., 2013; Liehr et al., 2013). Historical dumpsites are spread over the sea bottom and may still represent a serious threat to the marine environment (OSPAR, 2010b, 2010c).

Radioactive waste from nuclear power plants, reprocessing plants, nuclear powered vessels, industries, hospitals, scientific research centers, and nuclear weapons facilities was also routinely dumped into the sea worldwide (OSPAR 2010b). Information on the date and location of the disposal operations, the type, number and weight or volume of the disposed containers has been collected by the International Atomic Energy Agency (IAEA)⁴⁶, although complete data on radionuclide composition of the waste is usually lacking (IAEA, 1999, 2015).

⁴² Directive 2009/147/EC of the European Parliament and of the Council of 30 November 2009 on the conservation of wild birds. http://ec.europa.eu/environment/nature/legislation/birdsdirective/index_en.htm

⁴³ Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora. http://ec.europa.eu/environment/nature/legislation/habitatsdirective/index_en.htm

⁴⁴ London Convention and Protocol. <http://londonprotocol.imo.org>

⁴⁵ OSPAR Guidelines for the Management of Dredged Material at Sea (Agreement 2014-06). <http://www.ospar.org/convention/agreements>

⁴⁶ International Atomic Energy Agency (IAEA). <https://www.iaea.org/>

In the OSPAR high seas areas of the North-East Atlantic, approximately 98% of the disposed radioactive waste is considered to consist of beta and gamma emitters, mainly tritium (^3H) and others such as ^{90}Sr , ^{134}Cs , ^{137}Cs , ^{55}Fe , ^{58}Co , ^{60}Co , and ^{14}C . The rest 2% consists principally of plutonium and americium isotopes (OSPAR, 2014b). Information on radionuclide composition in other European marine regions is difficult to access or lacking (IAEA, 1999; HELCOM, 2003; Coll et al., 2012).

3.5.1 Munitions and chemical weapons

The Chemical Weapons Convention (CWC)⁴⁷ was ratified by most world countries in 1993 mandating the destruction of Chemical Warfare Agents (CWA) by 2012. However, previously and until the prohibition with the London Convention, dumping was the preferred destruction method. In effect, dumping at sea of chemical weapons and conventional munitions was commonplace in European waters after World Wars I and II, principally in the Baltic Sea, near the island of Bornholm and in the Gotland basin (Roose et al., 2011; Bełdowski et al., 2016). Large amounts were also dumped in the OSPAR Maritime Area (OSPAR, 2010c) and in the Mediterranean Sea, particularly in the Southern Adriatic, which was also more recently affected by the Balkans War (Frank, 2007). Warfare agents constitute, therefore, a class of legacy contaminants produced and dumped decades ago. Yet in many cases, accurate information on the quantities, locations and current condition of the dumpsites is unavailable because the original documentation has been lost or destroyed, dumping took place outside of official designated areas and/or the material has been moved or buried by natural or anthropogenic activities (Benn et al., 2010).

Chemicals originating from warfare materials can eventually leak into the sea and spread from the sites of disposal over more distant areas. Leakage of toxic compounds from the corroded munitions has been recently suggested in dumpsites of the Baltic (Missiaen et al., 2010; Baršienė et al., 2014) and Adriatic Sea (Amato et al., 2006; Della Torre et al., 2013), and there are predictions that corrosion will lead to maximal leakage periods in the middle of the 21st century (Roose et al., 2011). Furthermore, the increasing demand for marine activities such as offshore wind farms and pipelines as well as changes in fishing practices raise new issues since these activities could also alter undisturbed munitions. Hence, warfare agents and their degradation products represent a significant threat for the marine environment. Despite this, little is still known about their persistence, bioaccumulation and adverse effects on humans and biota (OSPAR, 2009d; Sanderson et al., 2012). Due to the increasing concern over sea-dumped CWA, several programmes and projects have been put in place over the past few decades to assess the extent of dumping and its potential impacts (e.g. OSPAR Recommendation 2010/20⁴⁸, HELCOM MUNI⁴⁹, HELCOM SUBMERGED⁵⁰, MERCW⁵¹ project, CHEMSEA⁵² project, and RED COD⁵³ project).

⁴⁷ Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction. <https://www.opcw.org/chemical-weapons-convention/>

⁴⁸ OSPAR Recommendation 2010/20 on an OSPAR framework for reporting encounters with conventional and chemical munitions in the OSPAR Maritime Area. <http://www.ospar.org/convention/agreements?q=2010%2F20&t=32283&a=&s=>

⁴⁹ HELCOM Expert Group to update and review the existing information on dumped chemical munitions in the Baltic Sea (HELCOM MUNI). <http://www.helcom.fi/baltic-sea-trends/hazardous-substances/sea-dumped-chemical-munitions/helcom-actions/>

⁵⁰ HELCOM Expert Group on Environmental Risks of Hazardous Submerged Objects (SUBMERGED). <http://www.helcom.fi/helcom-at-work/groups/response/submerged/>

⁵¹ MERCW (Modeling of Environmental Risks related to sea-dumped Chemical Weapons). <http://www.mercw.org/>

⁵² CHEMSEA (Chemical Munitions, Search and Assessment). <http://www.chemsea.eu/>

⁵³ RED COD (Research on Environmental Damage caused by Chemical Ordnance Dumped at sea). <http://ibimold.ibim.cnr.it/matranga/REDCODfinalreport-October%202006.PDF>

About 70 different chemicals have been used or stockpiled as CWA in the 20th century (CHEMSEA, 2013), although the actual composition in many dumping incidents is unknown (Beddington and Kinloch, 2005). Conventional munitions constitute the main proportion of dumped material and are predominantly composed of nitroaromatics explosives (e.g. TNT and DNT) and nitramines explosives (e.g. RDX). Besides the explosive material, conventional ammunition consists of metals (e.g. copper, iron, nickel, tungsten, tin, lead, aluminum and zinc), propellants, plasticizers, and stabilizers (e.g. nitroglycerin and nitrocellulose) (Liebezeit, 2002; Lotufo et al., 2013; Smith et al., 2013). Large numbers of incendiary munitions (e.g. containing white phosphorus) have been also commonly dumped at sea (Amato et al., 2006; OSPAR, 2010c; HELCOM, 2013a).

The main CWA dumped into the sea are blistering agents (e.g. sulfur mustard gas and arsenic-containing compounds), nerve agent organophosphates (e.g. Tabun), choking agents (e.g. phosgene), and lachrymatory agents (e.g. α -chloroacetophenone) (Sanderson et al., 2012; HELCOM, 2013a; Baršienė et al., 2014). Hazardous additives such as aromatic and chlorinated solvents (e.g., benzene, chlorobenzene, tetrachloromethane) are also frequent constituents of the dumped warfare material (HELCOM, 2013a). The table 7 presents an overview of the main warfare agents believed to have been dumped at sea at one time or another.

Table 7. Summary of main constituents of warfare material dumped at sea (as published by Tornero and Hanke, *in press, supplementary material*).

| Substance | Concentrations at sea dumpsites | Bioaccumulation Bioconcentration | Toxicity in the marine environment | Quality benchmarks | Remarks |
|---|--|---|---|--------------------|--|
| Chemical warfare agents (CWA) | | | | | |
| <i>Blister agents (vesicants)</i> | | | | | |
| Sulfur mustard (yperite) <i>Bis(2-chloroethyl) sulfide</i> | <p>MEC: Parental compound and metabolites not detected (LOD = 0.5 mg/kg dwt) in fish tissues in dumping areas of the Adriatic Sea, confirming low bioaccumulation and bioconcentration capacities (Amato et al., 2006). Not detected in sediments and porewater of the Bornholm dumpsite (Baltic Sea) (Sanderson et al., 2012). Derivatives or oxidation products found in sediments of the Baltic and Adriatic Seas (Amato et al., 2006; CHEMSEA, 2013).</p> <p>PEC: <i>Water:</i> 127 µg/L (Sanderson et al., 2008).</p> | Log Kow = 1.37 - 2.4 (Amato et al., 2006; HELCOM, 2013a). BCF = 14.3 (Sanderson et al., 2007). | Predicted LC50 = 6.7 mg/L (fish); 4.4 mg/L (algae) (Sanderson et al., 2007). HC5 = 100 µg/L (fish community) (Sanderson et al., 2008). | | CWA produced and dumped in the largest volume (accounts for 63% of all CWA dumped in the Baltic Sea). However, there is significant lack of information for marine biota. Persistent in water, dissolves extremely slow. Once dissolved, hydrolyzes quickly to thiodiglycol and hydrochloric acid (Baršienė et al., 2014). Enriched presence of special bacteria capable of degrading the hydrolysis products isolated from dumpsite areas in the Baltic (Medvedeva et al., 2009). Exposure related to high number of histological lesions in fish from a CWA dumpsite in the Adriatic (Amato et al., 2006). Shown to induce tissue and cell damaging and increased detoxification activities in marine fish (Della Torre et al., 2013). High chronic toxicity, among the most risky CWA with regard to the potential human consumption of contaminated fish (HELCOM, 2013a). |
| Nitrogen mustard <i>Tris(2-chloroethyl)amin</i> | No historical evidence of nitrogen mustard-filled warfare materials or break-down products in the Baltic Sea (HELCOM, 2013a). | Log Kow = 3.12 (Theobald, 2002). | 1-10 mg/L (acute toxicity for algae, crustaceans and fish (Theobald, 2002). | | Lower water solubility than sulfur mustard, also taking longer to hydrolyze in water. |
| Lewisite <i>Dichloro(2-chlorovinyl)arsine</i> | MEC: | Log Kow = 2.56 BCF = 18.6 | Predicted LC50 = 1.8 mg/L (fish); 15.6 | | Potentially persistent (Sanderson et al., 2007). Hydrolyzes |

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| | <p>Not detected in sediments and porewater of the Bornholm dumpsite, but oxidation products detected in trace and quantifiable amount in sediments (mean concentration 15 µg/Kg dwt) (Sanderson et al., 2012).</p> <p>Parental compound and metabolites not detected (LOD = 0.5 mg/kg dwt) in fish tissues in dumping areas of the Adriatic Sea. However, arsenic levels very high in sediments (up to 44.81 mg/Kg dw) and fish (up to 29.69 mg/kg dw in muscle), suggesting leakage from CWA (Amato et al., 2006).</p> | (Sanderson et al., 2007). | mg/L (algae) (Sanderson et al., 2007). | | <p>quickly in contact with water, producing toxic organic and inorganic arsenic compounds (Amato et al., 2006).</p> <p>Exposure related to high number of histological lesions in fish from a CWA dumpsite in the Adriatic (Amato et al., 2006).</p> |
| Irritant agents | | | | | |
| <p>Adamsite <i>Diphenylaminechloroarsine</i></p> | <p>MEC: <i>Water:</i> Not detected in porewater (Sanderson et al., 2012). Oxidation products detected in porewater (HELCOM, 2013a). <i>Sediment:</i> 0.9-354 µg/kg dwt (oxidation products) (HELCOM, 2013a); 0.032 mg/kg dwt (mean); 0.2 mg/kg dwt (max.) (Bornholm dumpsite) (Sanderson et al., 2012). PEC: <i>Water:</i> 25.8 µg/L (Sanderson et al., 2008).</p> | <p>Log Kow = 4.05 BCF = 262 (Sanderson et al., 2007).</p> | <p>Predicted LC50 = 0.44 mg/L (fish); 0.7 mg/L (algae) (Sanderson et al., 2007). HC5 = 10 µg/L (fish community) (Sanderson et al., 2008).</p> | | <p>Very low water solubility, it sticks to sediments. Hydrolyzes very slowly. Degradation products persistent and with high bioaccumulation potential. Expected to spread well outside of dumping grounds (HELCOM, 2013a). No information on exact effects in fish and relative intake and detoxification rates in fish tissues or other marine organisms, such as mussels (CHEM-SEA, 2013).</p> |
| <p>Clark I <i>Diphenylarsine chloride</i></p> | <p>MEC: <i>Water:</i> No measurable quantities of parent</p> | <p>Log Kow = 4.52</p> | <p>Predicted LC50 = 0.162 mg/L (fish); 0.33 mg/L (algae)</p> | | <p>Not readily water soluble. Adsorbs easily onto sediments. Main degradation products</p> |

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| | <p>compounds or degradation products in the water column (HELCOM, 2013a).</p> <p><i>Sediment:</i> 0.016 mg/kg dwt (mean); 0.051 mg/kg dwt (max.) (Bornholm dumpsite) (Sanderson et al., 2012); 990 µg/Kg dwt (degradation products); 240 µg/Kg dwt (oxidation products) (HELCOM, 2013a).</p> <p>PEC: <i>Water:</i> 12.9 µg/L (Sanderson et al., 2008).</p> | BCF = 600 (Sanderson et al., 2007). | (Sanderson et al., 2007). HC5 = 10 µg/L (fish community) (Sanderson et al., 2008). | | with same toxicity as parent compound (Baršienė et al., 2014). Highly toxic. No information on exact effects in fish and relative intake and detoxification rates in fish tissues or other marine organisms, such as mussels. Also component in dumped arsine oil (CHEMSEA, 2013). |
| Clark II <i>Diphenylarsine cyanide</i> | <p>MEC: <i>Water:</i> No measurable quantities of parent compounds or degradation products in the water column (HELCOM, 2013a).</p> <p><i>Sediment:</i> Derivatives or oxidation products found in sediments of the Baltic Sea (CHEMSEA, 2013).</p> | Log Kow = 3.29 BCF = 68 (Sanderson et al., 2007). | Predicted LC50 = 1.8 mg/L (fish); 1.9 mg/L (algae) (Sanderson et al., 2007). | | Not readily water soluble. Adsorbs easily onto sediments. Highly toxic. Main degradation products with same toxicity as parent compound (Baršienė et al., 2014). |
| Phenyldichloroarsine | <p>MEC: <i>Water:</i> Not detected (porewater)</p> <p><i>Sediment:</i> 0.036 mg/kg dwt (mean); 0.606 mg/kg dwt (max) (Bornholm dumpsite) (Sanderson et al., 2012).</p> <p>PEC: <i>Water:</i> 18.4 µg/L (Sanderson et al., 2008).</p> | Log Kow = 3.06 (Missiaen et al., 2010). BCF = 45.6 (Sanderson et al., 2009). | HC5 = 100 µg/L (fish community) (Sanderson et al., 2008). | | |
| Trichloroarsine | <p>MEC: <i>Water:</i> Not detected (porewater)</p> <p><i>Sediment:</i> 0.019 mg/kg dwt (mean); 0.09</p> | Log Kow = 1.61 (Missiaen et al., 2010). BCF = 3.5 (Sanderson et al., 2009). | HC5 = 100 µg/L (fish community) (Sanderson et al., 2008). | | Gives rise to inorganic arsenic compounds upon hydrolysis, which are indistinguishable from any naturally occurring arsenic compounds (HELCOM, 2013a). |

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| | mg/kg dwt (max) (Bornholm dumpsite) (Sanderson et al., 2012). PEC: <i>Water:</i> 1.8 µg/L (Sanderson et al., 2008). | | | | |
| Triphenylarsine | MEC: <i>Water:</i> Not detected (porewater) <i>Sediment:</i> 0.01 mg/kg dwt (mean); 0.017 mg/kg dwt (max) (Bornholm dumpsite) (Sanderson et al., 2012). PEC: <i>Water:</i> 1.8 µg/L (Sanderson et al., 2008). | Log Kow = 5.97 (Missiaen et al., 2010). BCF = 7901 (Sanderson et al., 2009). | HC5 = 0.5 µg/L (fish community) (Sanderson et al., 2008). | | High tendency to adsorb to sediments. Not prone to hydrolysis. Considered as a signature compound for arsine oil (HELCOM, 2013a). Thought to pose the highest risk to the fish community among CWA dumped in the Baltic. No information on exact effects in fish and relative intake and detoxification rates in fish tissues or other marine organisms, such as mussels (CHEMSEA, 2013). |
| <i>Lachrymatory agent</i> | | | | | |
| Tear gas <i>α-chloroacetophenone</i> | Not detected in sediments and porewater of the Bornholm dumpsite (Sanderson et al., 2012). PEC: <i>Water:</i> 9.3 µg/L (Sanderson et al., 2008). | Log Kow = 1.93 BCF = 0.8 (Sanderson et al., 2007). | Predicted LC50 = 17 mg/L (fish); 8.5 mg/L (algae) (Sanderson et al., 2007). HC5 = 500 µg/L (fish community) (Sanderson et al., 2008). | | Not easily soluble in water and hydrolyzes slowly, but produces non-toxic and non-persistent degradation products (HELCOM, 2013a). |
| <i>Choking agents</i> | | | | | |
| Chlorine (Cl ₂) | | | | 10 µg/l (UK MAC-EQS, total residual oxidant) (SEPA, 2014). | Non persistent. |
| Phosgene <i>Carbonyl dichloride</i> | | Log Kow = -0.71 BCF = 3.1 (Sanderson et al., 2007). | Predicted LC50 = 989 mg/L (fish) (Sanderson et al., 2007). | | Hydrolyses quickly and degrades to non-hazardous compounds, posing no a large threat to the marine environment (Theobald, 2002). |
| Diphosgene | | Log Kow = 1.49 BCF = 2.8 (Sanderson et al., 2007). | Predicted LC50 = 88.7 mg/L (fish) (Sanderson et al., 2007). | | Potentially persistent (Sanderson et al., 2007). |

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| <i>Nerve agents</i> | | | | | |
| Cyclosarin <i>Cyclohexyl methylphosphonofluoridate</i> | | Log Kow = 1.6 BCF = 3.4 (Sanderson et al., 2007). | Predicted LC50 = 22.5 mg/L (fish); 2.7 mg/L (algae) (Sanderson et al., 2007). | | Potentially persistent (Sanderson et al., 2007). |
| Sarin <i>Isopropyl methylphosphonofluoridate</i> | | Log Kow = 0.3 BCF = 3.1 (Sanderson et al., 2007). | Predicted LC50 = 89.6 mg/L (fish); 10.3 mg/L (algae) (Sanderson et al., 2007). | | Able to accumulate in bivalve molluscs resistant to acetylcholinesterase (AChE) inhibition (Sanderson et al., 2007). |
| Soman <i>Pinacolyl methylphosphonofluoridate</i> | | Log Kow = 1.82 BCF = 4.68 (Sanderson et al., 2007). | Predicted LC50 = 23 mg/L (fish); 2.7 mg/L (algae) (Sanderson et al., 2007). | | Potentially persistent. Able to accumulate in bivalve molluscs resistant to AChE inhibition (Sanderson et al., 2007). |
| Tabun <i>N,N-dimethyl phosphoroamidocyanidate</i> | Not detected in sediments and porewater of the Bornholm dumpsite (Sanderson et al., 2012). | Log Kow = 0.29 BCF = 3.16 (Sanderson et al., 2007). | Predicted LC50 = 97.7 mg/L (fish); 11.3 mg/L (algae) (Sanderson et al., 2007). | | Soluble in water, it would be rapidly mixed with sea water and diluted, thus having a very short-term effect (OSPAR, 2010c). |
| VG <i>O,O-diethyl S-[2-(diethylamino)ethyl] phosphorothioate</i> | | Log Kow = 1.7 BCF = 4.1 (Sanderson et al., 2007). | Predicted LC50 = 27.8 mg/L (fish); 2.9 mg/L (algae) (Sanderson et al., 2007). | | Potentially persistent (Sanderson et al., 2007). |
| VM <i>S-[2-(diethylamino)ethyl] O-ethyl methylphosphonothioate</i> | | Log Kow = 1.23 BCF = 1.7 (Sanderson et al., 2007). | Predicted LC50 = 47 mg/L (fish); 5.5 mg/L (algae) (Sanderson et al., 2007). | | Potentially persistent (Sanderson et al., 2007). |
| VX <i>O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate</i> | | Log Kow = 2.09 BCF = 8.1 (Sanderson et al., 2007). | Predicted LC50 = 13.8 mg/L (fish); 2.3 mg/L (algae) (Sanderson et al., 2007). | | Potentially persistent. Hydrolysis products predicted to be 10 and 30 times more toxic towards aquatic species than the parent compound (Sanderson et al., 2007). |
| <i>Blood agents</i> | | | | | |
| Hydrogen cyanide (HCN) | | Log Kow = -0.69 BCF = 3.16 (Sanderson et al., 2007). | HC5 = 1 µg/L (fish community) (Sanderson et al., 2008). | 1 µg/l (UK AA-EQS); 5 µg/l (UK MAC-EQS) (SEPA, 2014). | Dissolves in the alkaline seawater as cyanide. While effects on the immediate environment are possible upon release, it is easily and quickly degraded and dissipates in the marine environment (HELCOM, 2013a). |
| <i>Additives</i> | | | | | |

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| Chlorobenzene | Up to 17.9 µg/kg ww in few sediment samples of the Bornholm dumpsite (Missiaen et al., 2010). | Log Kow = 2.64-2.84 (Missiaen et al., 2010). | HC5 = 100 µg/L (fish community) (Sander-son et al., 2008). | | Stable, highly resistant to hydrolysis and oxidation (Missiaen et al., 2010). |
| Conventional Munitions | | | | | |
| Nitroaromatic Explosives | | | | | |
| TNT 2,4,6-trinitrotoluene | Not detected (LOD < 5pg/µL) in fish samples from Adriatic dumpsites (REDCOD, 2006). | Log Kow = 1.6-2.7 (Pascoe et al., 2010). BCF = 0.31-9.71 (Lotufo et al., 2013). | <p><i>Algae:</i> EC50 = 0.61 mg/L (<i>Ulva fasciata</i>, germling growth).</p> <p><i>Invertebrates:</i> 4d LC50 = 0.98 mg/L (<i>Americamysis bahia</i>); 19.5 mg/L (<i>Mytilus galloprovincialis</i>, adult); 3.6 mg/L (<i>Leptocheirus plumulosus</i>); 7.6 mg/L (<i>Nitocra spinipes</i>); 4.5 (<i>Eohaustorius estuarius</i>); 8.2 mg/L (<i>Crassostrea gigas</i>, larvae). 7d LC50 = 5.6 mg/L (<i>Dinophilus gyrocolia-tus</i>).</p> <p>2d EC50 = 075 mg/L (<i>Mytilus galloprovincialis</i>, embryo development); 12 mg/L (<i>Arbacia punctulata</i>, embryo development). 4d EC50 = 55 mg/L (<i>Schizopera knabeni</i>, reproduction). 7d EC50 = 1.1 mg/L (<i>Dinophilus gyrocolia-tus</i>, reproduction). LOEC = 38 mg/Kg sediment (<i>Eohaustorius estuarius</i>); 228 mg/Kg sediment (<i>Leptocheirus</i></p> | 1.1-12.8 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | <p>By far mostly used, but there is paucity of data for the marine environment.</p> <p>Breaks down very slowly in water, but once dissolved it will decompose easily. Leakage to seawater significantly reduced when TNT is covered with fine-grained sediment (Ek et al., 2007).</p> <p>Acute toxicity values derived for marine organisms comparable to those derived for freshwater organisms (Lotufo et al., 2013). To date, no evidence of significant ecological effects, maybe because containers have not yet corroded (Beddington and Kinloch, 2005).</p> |

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| | | | <p><i>Plumulosus</i>); 508 mg/Kg sediment (<i>Ne-anthes arenaceodentata</i>)</p> <p><i>Fish</i>: 2d LC50 = 7.6 mg/L (<i>Sciaenops ocellatus</i>). 5d LC50 = 1.7 mg/L (<i>Cyprinodon variegatus</i>) (Lotufo et al., 2013).</p> | | |
| <p>Tetryl 2,4,6-trinitrophenylmethylnitramine</p> | | <p>Log Kow = 2.04. No BCF data for aquatic organisms, but potential for bioconcentration considered low (Lotufo et al., 2013).</p> | <p><i>Algae</i>: 4d EC50 = 0.20 mg/L (<i>Ulva fasciata</i>, germling growth). <i>Invertebrates</i>: 2d EC50 = 0.05 mg/L (<i>Arbacia punctulata</i>, embryro development). 7d EC50 = 0.01 mg/L (<i>Dinophilus gyrociliatus</i>, reproduction). 4d LC50 = 0.37 mg/L (<i>Americamysis bahia</i>). 7d LC50 = 0.03 mg/L (<i>Dinophilus gyrociliatus</i>, reproduction). LOEC = 4 mg/Kg (<i>Ampelisca abdita</i>, sandy sediment). <i>Fish</i>: 2d LC50 = 1.1 mg/L (<i>Sciaenops ocellatus</i>) (Lotufo et al., 2013).</p> | <p>0.6-6.1 mg/kg OC (SQB_{OC}) (Pascoe et al., 2010).</p> | <p>Photolysis and hydrolysis are major environmental transformation processes in aqueous media. Although no data for the bioaccumulation in marine or freshwater fish and invertebrates were found, the potential for bioconcentration in aquatic organisms is considered low (Lotufo et al., 2013). Low solubility in water, and a tendency to sorb to organic carbon (Briggs et al., 2016).</p> |
| Explosive D (Ammonium Picrate) | | No data. | | | Highly soluble in water, low tendency to partition from water to organic sediment (Briggs et al., 2016). |
| <p>Picric Acid 2,4,6-trinitrophenol</p> | | <p>Log Kow = 1.33. No BCF data for aquatic organisms, but potential for bi-</p> | <p><i>Algae</i>: 4d EC50 = 94 mg/L (<i>Ulva fasciata</i>, germling growth) (Lotufo et al., 2013).</p> | <p>340 mg/kg OC (SQB_{OC}) (Pascoe et al., 2010).</p> | <p>Degrades to many identifiable transformation products, e.g. 2,4-dinitrophenol and picramic acid, which are more toxic than</p> |

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| | | oconcentration considered low (Lotufo et al., 2013). | <p><i>Invertebrates:</i> NOEC = 9.2 mg/L (<i>Americamysis bahia</i>, juvenile survival) (Pascoe et al., 2010). 2d EC50 = 281 mg/L (<i>Arbacia punctulata</i>, embryo development). 4d EC50 = 60 mg/L (<i>Schizopera knabeni</i>, reproduction). 6d EC50 = 28 mg/L (<i>Crassostrea virginica</i>, shell deposition). 7d EC50 = 155 mg/L (<i>Dinophilus gyrociliatus</i>, reproduction). 4d LC50 = 13 mg/L (<i>Americamysis bahia</i>). 7d LC50 = 265 mg/L (<i>Dinophilus gyrociliatus</i>). LOEC = 162 mg/Kg (<i>Ampelisca abdita</i>, sandy sediment). <i>Fish:</i> 2d LC50 = 127 mg/L (<i>Sciaenops ocellatus</i>). 4d LC50 = 130 mg/L (<i>Cyprinodon variegatus</i>) (Lotufo et al., 2013).</p> | | the parent compound (Pascoe et al., 2010). Binds to sediment and resist hydrolysis, biodegradation and photolysis (Lotufo et al., 2013). |
| Nitramine Explosives | | | | | |
| HMX (High Melting Explosive) Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine | | Log Kow = 0.17 (Lotufo et al., 2013). | Concentrations at or near the solubility limit do not cause have significant lethal or sublethal effects in marine species (Lotufo et al., 2013). | 0.38-42.9 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | Resides on the water body floor as a solid with dissolution into the water column over time (Lotufo et al., 2013). In the laboratory, dissolution, transformation and absorption rates in close agreement in fresh and saline waters (Beddington and Kinloch, 2005). |

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| RDX (Royal Demolition Explosive) <i>Hexahydro-1,3,5-trinitro-1,3,5-triazine</i> | | Log Kow = 0.9. BCF = 0.7-1.7 (Lotufo et al., 2013). | <i>Algae:</i> 4d EC50 = 8.1 mg/L (<i>Ulva fasciata</i> , germling growth) (Lotufo et al., 2013). <i>Invertebrates:</i> 4d LC50 = 2.4 mg/L (<i>Citharichthys</i> <i>stigmaeus</i>). 7d EC50 = 26 mg/L (<i>Dinophilus gyrociliatus</i> , reproduction). <i>Fish:</i> 4d LC50 = 9.8 mg/L (<i>Cyprinodon variegatus</i>); 7.1 mg/L (<i>Menidia beryllina</i>) (Lotufo et al., 2013). | 1.2-7.8 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | In the laboratory, dissolution, transformation and absorption rates in close agreement in fresh and saline waters (Beddington and Kinloch, 2005). Expected to weakly sorb to solids when released to water. Degradation by hydrolysis at a slow rate (Briggs et al., 2016). |
| <i>Propellants/plasticizers/stabilizers</i> | | | | | |
| DEGDN <i>Diethylene glycol dinitrate</i> | | Log Kow = 0.98. No BCF data for aquatic organisms, but potential for bioconcentration considered low (Lotufo et al., 2013). | No marine toxicity data. LC50 values for freshwater organisms from 90.1-491 mg/L (Lotufo et al., 2013). | | Stable compound once dissolved in water (Lotufo et al., 2013). |
| Diphenylamine | | Log Kow = 3.42 (Pascoe et al., 2010). | No marine toxicity data. 48h EC50 = 1.2 mg/L (<i>Daphnia magna</i>) (Pascoe et al., 2010). | 280 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | |
| Nitrocellulose | | No data. | No marine toxicity data. In freshwater organisms, no acute toxicity at 1000 mg/L (Lotufo et al., 2013). | | Very recalcitrant to microbial degradation (Lotufo et al., 2013). |
| Nitroglycerin | | Log Kow = 1.62. No BCF data for aquatic organisms, but potential for bioconcentration considered low (Lotufo et al., 2013). | No marine toxicity data. LC50 = 0.7 mg/L and LOEC = 16 mg/L for freshwater organisms (Lotufo et al., 2013). | 127-581 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | |

| | | | | | |
|--|---|--|---|---|---|
| Nitroguanidine | | Log Kow = -0.89. No BCF data for aquatic organisms, but potential for bioconcentration considered low (Lotufo et al., 2013). | In water, no lethal effect to a marine copepod at 683 mg/L (Lotufo et al., 2013). | 35-6500 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | Negligible degradation (Lotufo et al., 2013). |
| PETN <i>Pentaerythrite tetranitrate</i> | | Log Kow = 1.61-3.71 (Pascoe et al., 2010; Lotufo et al., 2013). No BCF data for aquatic organisms, but potential for bioconcentration considered low (Lotufo et al., 2013). | In water, no lethal effect to a marine copepod at 32 mg/L (Lotufo et al., 2013). | 32533-152150 mg/kg OC (SQB _{OC}) (Pascoe et al., 2010). | Not prone to hydrolyze at ambient temperature and recalcitrant to microbial degradation (Lotufo et al., 2013). |
| <i>Incendiary devices</i> | | | | | |
| White phosphorus | Not found in sediments and biota samples from NE Ireland (Beaufort's Dyke explosives disposal site) (REDCOD, 2006). | Log Kow = 1.2 (HELCOM, 2013a). | | | Extremely poisonous to various organisms. Highly flammable, may spontaneously ignite on contact with air. Occurs as solid and can be washed up onto beaches, posing a risk for beach goers (HELCOM, 2013a). |

MEC: Measured environmental concentrations; PEC: Predicted environmental concentrations; dwt: dry weight; wwt: wet weight; LOD: Limit of detection.

Log Kow (log octanol/water partition coefficient) reflects the chemical's tendency to bioaccumulate in organisms.

BCF (Bioconcentration Factor) reflects the extent to which pollutants concentrate from water into aquatic organisms.

LC50 (Median lethal concentration); EC50 (Median effective concentration); LOEC (Lowest observed effect concentration); NOEC (No effect concentration); HC5 (Concentrations at which the acute toxicity LC50/EC50 is exceeded for 95% of species tested).

SQB (Sediment quality benchmark); OC (Organic carbon).

3.6 OFFSHORE RENEWABLE ENERGY GENERATION

The need to combat climate change, ocean acidification, and energy security, has led to the exploration and development of new and renewable sources of energy generation from the ocean. One of the major challenges to building and deploying offshore renewable energy structures (wind, wave and tidal energy devices) is to understand the potential effects of those devices on the marine environment. Main concerns are related to the increase of noise levels and risks of collisions with marine animals (Bailey et al., 2014). Pollution by chemicals might also be a problem due to the increased vessel traffic and associated potential spills or from disturbance of seabed sediments. Pollution risks do also exist during routine and maintenance operations, including leaching of chemicals from antifouling paints and accidental spills of hydraulic fluid or lubricant oil from operational devices (Bonar et al., 2015). Organic or metal pollutants associated with the infrastructure used for electrical signals, and metals associated with sacrificial anodes might be also released into the surrounding environment (Bejarano et al., 2013; California State Lands Commission, 2013; Copping et al., 2015). The main contaminants potentially discharged from marine renewable energy devices are showed in the table 8.

Table 8. Substances potentially released from marine renewable energy devices.

| | |
|---|---|
| Metals | Aluminum Copper Mercury Zinc |
| Booster biocides | Diuron Irgarol |
| Diesel fuel | BTEX PAHs (e.g. naphthalene) |
| Dielectric fluids | Silicone fluids (e.g. polydimethylsiloxane) Mineral oils (e.g. naphthenic oil) Vegetable oils (e.g. biodiesel, soybean oil, canola oil, corn oil, sunflower oil) Synthetic esters (e.g. MIDEL 7131, pentaerythritol) |
| Coolants, anti-freezer and sloshing damper | Ethylene glycol Propylene glycol |
| Electrolytes | Sulfuric acid |

3.7 SHIPWRECKS

Throughout history, the occurrence of severe weather, armed conflict or human error has left a legacy of thousands of sunken vessels across the oceans (Rogowska et al., 2010). Most sunken wrecks are deteriorating and their metal plates are corroding, hence threatening to release their contents into the sea. Main concerns are related to oil since a fully-fuelled vessel may carry thousands of tonnes of fuel. 25% of the potentially polluting wrecks worldwide are estimated to be in the North Atlantic Ocean and 4% in the Mediterranean. These wrecks are believed to contain nearly 43% of the total volume of oil trapped in sunken vessels (CoE, 2012). Yet shipwreck-related pollution risks are not limited to oil and may also come from other chemicals such as metals and metalloids (e.g. arsenic, cadmium, copper, chromium, lead, mercury, and zinc), PCBs, asbestos, biocides, PVC, and radioactive waste (Alcaro et al., 2007; Annibaldi et al., 2011; Landquist et al., 2013; Sprovieri et al., 2013).

The need for a common policy on the treatment and removal of wrecks has long been a topic of discussion under IMO. The Nairobi International Convention on the Removal of

Wrecks of 2007 (Nairobi Convention)⁵⁴ provides a harmonized legal framework for dealing with the issue of removal of wrecks that may affect adversely the safety of lives, goods and property at sea, as well as the marine environment.

3.8 SEABED MINING

The amount of minerals at the ocean floor is potentially enormous. Seabed mining is concerned with the retrieval of these minerals to ensure security of supply and fill a gap in the market where either recycling is not possible or adequate, or the burden on terrestrial mines is too great. By 2020, deep seabed mining could provide 5% of the world's minerals, including cobalt, copper and zinc and this could rise to 10% by 2030⁵⁵.

The regulations governing deep sea mining activities depend on whether they take place inside or outside the jurisdictional waters of a sovereign state. When operating within the Exclusive Economic Zone (EEZ) (up to 200 nautical miles from the territorial sea baseline) of a certain country, mining activities are subject to the country's internal legislation. However, when deep sea mining operations occur in the international seabed (the "Area" which is the seabed and ocean floor and subsoil thereof beyond the limits of national jurisdiction), the rules of the 1982 UNCLOS apply. Compliance with these rules is checked by the International Seabed Authority (ISA)⁵⁶, an intergovernmental body established under UNCLOS. Deep sea mining is not directly addressed in EU law and actually most of the EU legal instruments potentially relevant to this activity are concerned with environmental protection. Thus, the MSFD can constitute an important mechanism for regulating the environmental aspects of potential deep sea mining operations (EC, 2014).

The number of contracts granted by ISA to explore minerals on the seabed has increased greatly in latest years and commercial exploitation is planned to begin in the near future (Jaeckel, 2015). The main deep sea mineral deposits subject of commercial interest are seafloor massive sulphides, manganese nodules and cobalt-rich ferromanganese crusts. Certain types of rare earth elements have been also more recently found in high concentrations within seafloor muds in the southeast and equatorial Pacific Ocean at about 5000m water depths (EC, 2014).

Sea-floor massive sulphides form as a result of hydrothermal activity. Their composition is highly variable, and not all elements contained are of commercial interest. The commodities which are expected to be mined include copper and zinc, and valuable metals such as gold and silver. Other trace elements, such as bismuth, cadmium, gallium, germanium, antimony, tellurium, thallium, and indium, are normally present in low quantities, but can be significantly enriched in some deposits, especially those that form at volcanic arcs. With the exception of a few deposits that have been drilled through the Ocean Drilling Program or by commercial or scientific projects, little is known about the interiors of most SMS deposits (Hein and Petersen, 2013a; EC, 2014).

Manganese nodules are concretions of iron and manganese hydroxides and are most abundant in the abyssal areas of the ocean (4000-6500 m water depth). Manganese, or more accurately polymetallic, nodules contain significant concentrations of metals of high economic interest such as nickel, copper, cobalt, manganese. There are also traces of other valuable metals, such as molybdenum, rare-earth elements, and lithium (Hein and Petersen, 2013b).

Cobalt-rich ferromanganese crusts are formed by the precipitation of manganese and iron from cold seawater. Cobalt, the trace metal of greatest economic interest, can be up to 2

⁵⁴ <http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/Nairobi-International-Convention-on-the-Removal-of-Wrecks.aspx>

⁵⁵ http://ec.europa.eu/maritimeaffairs/policy/seabed_mining/index_en.htm

⁵⁶ International Seabed Authority (ISA). <https://www.isa.org.jm>

per cent. The crusts also contain the highest concentrations of the rare metal tellurium, which is used in the solar cell industry to produce thin-film photovoltaics. Little is known about the abundance of ferromanganese crusts in most areas of the global ocean (Hein and Petersen, 2013c).

Besides the potential for new mineral resources, seabed mining also raises serious environmental concerns. The physical activity of the mining machine, the movement of the unconsolidated sediment drape, and the dewatering process may generate contaminant plumes whose spatial distribution will depend on the mining activity and the strength of surface and bottom currents (Coffey, 2008; Clark and Smith, 2013). Accidental hydraulic fluid leaks, fuel and ore spills may also result in the release of chemicals into the marine environment (Hunter and Taylor, 2014). One of the main concerns is related to the release of metals (e.g. zinc, copper, cadmium, and mercury) (Boschen et al., 2013). Moreover, several chemicals used during ore processing can be also emitted into the aquatic environment. Process chemicals include flotation agents (e.g. xanthate salts and Lilaflot) and flocculants (e.g. polyacrylamide). These substances are considered to be very toxic to aquatic biota, but little is known about their effects on marine wildlife (Olsvik et al., 2015; Ramirez-Llodra et al., 2015). The MIDAS project⁵⁷, funded in 2013 under the European Commission's Framework 7 programme, aims at investigating the nature and scales of the potential environmental impacts of extracting mineral and energy resources from the deep sea environment, including the toxic chemicals that might be released and their effects. This kind of information is essential to develop sustainable guidelines and regulations for managing deep sea mining activities (Hunter and Taylor, 2014).

⁵⁷ MIDAS (Managing Impacts of Deep-sea resource exploitation). <http://www.eu-midas.net/>

4 RESULTS

The table 9 presents the list of chemical contaminants identified by Tornero and Hanke (*in press*) as potentially released into the marine environment from sea-based anthropogenic activities. It contains 276 substances with their Chemical Abstracts Service (CAS) identification number and major sea-based sources and separated into five main groups: metals/metalloids, organometallic compounds, inorganic compounds, organic compounds, and radionuclides. This table also provides an overview of the current legislative and regulatory frameworks and managerial activities dealing with these substances in European marine waters.

Furthermore, and in order to have a complete overview of the substances prioritized at European level, the table 10 provides a list of WFD PS and RSC priority contaminants for which no relevant sea-based sources have been identified.

Table 9. Sea-based sourced chemical contaminants and their consideration under relevant legislative/regulatory frameworks and RSCs in European marine waters (as published in Tornero and Hanke, *in press*).

| Substance | CAS number | Potential sea-based source | | | | | | | | Legislative/ regulatory framework | HELCOM | OSPAR | Barcelona Convention | Black Sea Commission |
|---------------------------|------------|----------------------------|-------------|-------------------------------|-----------------------------------|---------------|--------------------------------------|--------------------------|------------|---|--|---|--|-------------------------|
| | | Shipping | Mariculture | Offshore oil and gas industry | Offshore renewable energy devices | Seabed mining | Dredging/dumping of dredged material | Historical dumping sites | Shipwrecks | | | | | |
| Metals/Metalloids | | | | | | | | | | | | | | |
| Aluminum | 7429-90-5 | X | | | X | | | X | | | | | | BSIMAP (optional). |
| Arsenic | 7440-38-2 | X | X | X | | | X | | X | | Recommendation 36/2. | Agreement 2014-06. Agreement 14-05. | | |
| Barium | 7440-39-3 | | | X | | | | | | | Recommendation 18/2. | Agreement 14-05. | | |
| Cadmium and its compounds | 7440-43-9 | X | | X | | X | X | | X | WFD PS. WFD PHS. | Core indicators for hazardous substances. BSAP specific concern in the Baltic Sea. Recommendation 36/2. Recommendation 18/2. | Chemical for Priority Action (part A). Monitoring under CEMP. Agreement 2014-06. Agreement 14-05. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |

| | | | | | | | | | | | | | | |
|---------------------------|-----------|---|---|---|---|---|---|---|---|--|--|---|--|---------------------|
| Chromium | 7440-47-3 | X | | X | | | X | | X | | Recommendation 36/2. Recommendation 18/2. | Agreement 2014-06. Agreement 14-05. | | BSIMAP (optional). |
| Cobalt | 7440-48-4 | | X | | | | | | | | | | | BSIMAP (optional). |
| Copper | 7440-50-8 | X | X | X | X | X | X | X | X | BPD (existing active substance, dossier under review). | Recommendation 36/2. Recommendation 18/2. | Agreement 2014-06. PARCOM Recommendation 94/6. Agreement 14-05. | | BSIMAP (mandatory). |
| Iron | 7439-89-6 | X | X | X | | | | X | | | | Agreement 14-05. | | BSIMAP (optional). |
| Lead and its compounds | 7439-92-1 | X | | X | | | X | X | X | WFD PS. | Core indicators for hazardous substances. Recommendation 36/2. Recommendation 18/2. | Chemical for Priority Action (part A). Monitoring under CEMP. Agreement 2014-06. Agreement 14-05. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |
| Magnesium | 7439-95-4 | | X | | | | | | | | | | | |
| Manganese | 7439-96-5 | X | X | X | | | | | | | | | | BSIMAP (optional). |
| Mercury and its compounds | 7439-97-6 | | | X | | X | X | | X | WFD PS. WFD PHS. | Core indicators for hazardous substances. BSAP specific concern in the Baltic Sea. Recommendation 36/2. Recommendation 18/2. | Chemical for Priority Action (part A). Monitoring under CEMP. Agreement 2014-06. Agreement 14-05. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |
| Molybdenum | 7439-98-7 | | | X | | | | | | | | | | |
| Nickel and its compounds | 7440-02-0 | X | | X | | | X | X | | WFD PS. | Recommendation 36/2. | Agreement 2014-06. Agreement 14-05. | | BSIMAP (optional). |
| Selenium | 7782-49-2 | | X | | | | | | | | | | | |
| Tin | 7440-31-5 | | | | | | | X | | | | | | |
| Tungsten | 7440-33-7 | | | | | | | X | | | | | | |
| Vanadium | 7440-62-2 | X | | X | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|--|------------|---|---|---|---|---|---|---|---|--|---|--|--|--------------------|
| Zinc | 7440-66-6 | X | X | X | X | X | X | X | X | | Recommendation 36/2. | Agreement 2014-06. PARCOM Recommendation 94/6. Agreement 14-05. | | BSIMAP (optional). |
| Organometallic compounds | | | | | | | | | | | | | | |
| Copper pyrrhione | 14915-37-8 | X | X | | | | | | | BPD (existing active substance, dossier under review). | | | | |
| Dibutyltin (DBT) | 1002-53-5 | X | | | | | | | X | WFD PS | | | | |
| Monobutyltin (MBT) | 78763-54-9 | X | | | | | | | X | WFD PS | | | | |
| TPBP (KH101) (tri-phenylborane pyridine) | 971-66-4 | X | | | | | | | | BPD (not identified as biocidal product). | | | | |
| Tributyl phosphate | 126-73-8 | | | X | | | | | | | | | | |
| Tributyltin compounds (tributyltin-cation) | 36643-28-4 | X | | | | | | X | X | WFD PS. WFD PHS: tributyltin-cation. BPD (globally banned). | Core indicators for hazardous substances. BSAP specific concern in the Baltic Sea. Recommendation 36/2. | Chemical for Priority Action (part A): organic tin compounds. Monitoring under CEMP. | | |
| Triphenyl tin (TPHT) | 668-34-8 | | | | | | | X | | | | Substance of Possible Concern (section B). Agreement 2014-06. | | |
| Zinc pyrrhione | 13463-41-7 | X | X | | | | | | | BPD (notified substance, dossier submitted, and pending approval). | | | | |
| Zineb | 12122-67-7 | X | X | | | | | | | BPD (approved as active substance for product type 21). | | | | |
| Ziram | 137-30-4 | X | | | | | | | | BPD (non-inclusion into Annex I or Ia; not allowed in formulations placed on | | | | |

| | | | | | | | | | | | | | | |
|--|------------|---|---|---|--|--|--|---|--|--|--------------------|-----------------------------|--|--|
| | | | | | | | | | | the market since 2008). | | | | |
| Inorganic compounds | | | | | | | | | | | | | | |
| Copper (I) oxide (Cu ₂ O) | 1317-39-1 | | X | | | | | | | | | | | |
| Ammonia | 7664-41-7 | X | | | | | | | | | | | | |
| Ammonium bisulfite | 10192-30-0 | | | X | | | | | | | | Agreement 2013-06. | | |
| Barite (barium sulfate) | 13462-86-7 | | | X | | | | | | | | Agreement 2013-06. | | |
| Basic zinc carbonate | 5970-47-8 | | | X | | | | | | | | | | |
| Bentonite (sodium montmorillonite) | 1302-78-9 | | | X | | | | | | | | Agreement 2013-06. | | |
| Calcite (calcium carbonate, limestone) | 471-34-1 | | | X | | | | | | | | Agreement 2013-06. | | |
| Chlorine (Cl ₂) | 7782-50-5 | | | | | | | X | | CWC (agent banned in warfare). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Chromium trioxide | 1333-82-0 | X | | | | | | | | BPD (not applicable as product type 21). | | | | |
| Copper thiocyanate | 1111-67-7 | X | | | | | | | | BPD (existing active substance, dossier under review). | | | | |
| Hematite (diiron trioxide) | 1309-37-1 | | | X | | | | | | | | Agreement 2013-06. | | |
| Hydrogen peroxide | 7722-84-1 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Ilmenite (iron titanium oxide) | 12168-52-4 | | | X | | | | | | | | Agreement 2013-06. | | |
| Iodophoros | 25655-41-8 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Lime (calcium oxide) | 1305-78-8 | | | X | | | | | | | | Agreement 2013-06. | | |
| Phosphoric acid | 7664-38-2 | X | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|------------|---|---|---|---|--|--|---|--|---|---|----------------------------------|--|--|
| Potassium chloride (mu- riate of potash) | 7447-40-7 | | | X | | | | | | | | Agreement 2013-06. | | |
| Sodium hydroxide (caustic soda) | 1310-73-2 | X | | X | | | | | | | | | | |
| Sulfuric acid | 7664-93-9 | X | | | X | | | | | | | | | |
| Titanium dioxide | 13463-67-7 | | | | | | | X | | Titanium Dioxide Directives. | | PARCOM Recom- mendation 84/1. | | |
| Trichloroarsine | 7784-34-1 | | | | | | | X | | CWC (schedule 2). | HELCOM SUB- MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- cally consid- ered in the Dumping Protocol. | |
| Triiron tetraoxide | 1317-61-9 | | | X | | | | | | | | Agreement 2013-06. | | |
| White phosphorus | 12185-10-3 | | | | | | | X | | CCWC. | HELCOM SUB- MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- cally consid- ered in the Dumping Protocol. | |
| Zinc oxide | 1314-13-2 | | | X | | | | | | | | | | |
| Organic compounds | | | | | | | | | | | | | | |
| 1-dodecanol | 112-53-8 | X | | | | | | | | | | | | |
| 1-nonanol (nonyl alco- hol) | 143-08-8 | X | | | | | | | | | | | | |
| 2-butoxyethanol | 111-76-2 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Disper- sants Inven- tory). | | | | |
| 2,6-ditert-butyl-4- methylphenol (bu- tylated hydroxytoluene) | 128-37-0 | | X | | | | | | | Recommended for the first WFD Watch List. Reg. 1881/2003, an- nex I. | | | | |
| 2-imidazoline | 504-75-6 | | | X | | | | | | | | | | |
| Acenaphtene | 83-32-9 | | | X | | | | | | | Core indicators for hazardous substances. | Agreement 14- 05. | | |

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|-------------------------------------|----------------|---|---|---|--|--|---|---|---|---|---|--|--|--|
| Acenaphthylene | 208-96-8 | | | X | | | | | | | Core indicators for hazardous substances. | Agreement 14-05. | | |
| Acetic acid | 55896-93-0 | X | | X | | | | | | | | Agreement 14-05. Agreement 2013-06. | | |
| Acrylonitrile | 107-13-1 | X | | | | | | | | | | | | |
| Adamsite | 578-94-9 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Alkyl (C5-C8, C9) benzenes | Not applicable | X | | | | | | | | | | | | |
| Alkylacrylate sulfonate derivatives | Not applicable | | | X | | | | | | | | | | |
| Aluminum stearate | 7047-84-9 | | | X | | | | | | | | | | |
| Amides | Not applicable | | | X | | | | | | | | | | |
| Amines | Not applicable | | | X | | | | | | | | | | |
| Ammonium picrate | 131-74-8 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Amoxicillin | 26787-78-0 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Aniline | 62-53-3 | X | | | | | | | | | | | | |
| Anthracene | 120-12-7 | | | X | | | X | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. | | |
| Asbestos | 1332-21-4 | | | | | | | | X | | | | | |

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|----------------------|------------|---|---|---|---|--|---|---|--|--|--|--|--|--|
| Astaxanthin | 472-61-7 | | X | | | | | | | Reg. 1881/2003, annex I (authorized additive). | | | | |
| Azamethiphos | 35575-96-3 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Benz(a)anthracene | 56-55-3 | | | X | | | X | | | | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. Agreement 14-05. | | |
| Benzene | 71-43-2 | X | | X | X | | | X | | WFD PS. | | Agreement 14-05. | | |
| Benzo(a)pyrene | 50-32-8 | | | | | | X | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. Agreement 14-05. | | |
| Benzo(b)fluoranthene | 205-99-2 | | | X | | | | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. | Agreement 14-05. | | |
| Benzo(g,h,i)perylene | 191-24-2 | | | X | | | X | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. Agreement 14-05. | | |
| Benzo(k)fluoranthene | 205-99-2 | | | X | | | | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. | Agreement 14-05. | | |
| Benzocaine | 94-09-7 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Benzoic acid | 65-85-0 | | | X | | | | | | | | | | |
| Biodiesel (B100) | 67784-80-9 | | | | X | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|----------------|---|---|---|---|--|--|---|--|--|---|---|--|--|
| Bis(2-ethylhexyl) adipate | 103-23-1 | X | | | | | | | | | | | | |
| Brominated diphenylethers | Not applicable | | X | | | | | | | WFD PS. WFD PHS: tetra, penta, hexa, heptabromodiphenylether. | Core indicators for hazardous substances: PBDE 28, 47, 99, 100, 153 and 154. BSAP specific concern in the Baltic Sea: penta, octa, and decabromodiphenylether. | Chemical for Priority Action (part C): 2,4,6-bromophenyl 1-2(2,3-dibromo-2-methylpropyl). Monitoring under CEMP. | | |
| Bronopol | 52-51-7 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Butyl Acrylate (all isomers) | 141-32-2 | X | | | | | | | | | | | | |
| Butylated hydroxyanisole | 25013-16-5 | | X | | | | | | | Reg. 1881/2003, annex I. | | Substance of Possible Concern (section B). | | |
| Butyric acid | 107-92-6 | | | X | | | | | | | | Agreement 14-05. | | |
| Canola oil | 120962-03-0 | X | | | X | | | | | | | | | |
| Canthaxanthin | 514-78-3 | | X | | | | | | | Reg. 1881/2003, annex I. | | | | |
| Capsaicin | 404-86-4 | X | | | | | | X | | BPD (proposed candidate as biocide). CWC (agent banned in warfare). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Carbon tetrachloride (tetrachloromethane) | 56-23-5 | | | | | | | X | | WFD other pollutants. | | | | |
| Carboxymethyl cellulose | 9000-11-7 | | | X | | | | | | | | | | |

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|---------------------|------------|---|---|---|---|--|---|---|--|--|--|--|--|--|--|
| Chloramphenicol | 56-75-7 | | X | | | | | | | Com. 37/2010 (prohibited substance). | Reg. (pro-substance). | | | | |
| Chlorobenzene | 108-90-7 | | | | | | | X | | | | | | | |
| Chlorothalonil | 1897-45-6 | X | X | | | | | | | BPD (non-inclusion into Annex I or Ia; not allowed in formulations placed on the market since 2008). | | | | | |
| Chrysene | 218-01-9 | | | X | | | X | | | | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. Agreement 14-05. | | | |
| Clark I | 712-48-1 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | | |
| Clark II | 23525-22-6 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | | |
| Corn oil | 8001-30-7 | X | | | X | | | | | | | | | | |
| Cybutryne (irgarol) | 28159-98-0 | X | X | | X | | | | | WFD PS. BPD (existing active substance, dossier under review). | | | | | |
| Cyclohexane | 110-82-7 | X | | | | | | | | | | | | | |
| Cyclopentadiene | 542-92-7 | X | | | | | | | | | | | | | |
| Cyclosarin | 329-99-7 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- | | |

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| | | | | | | | | | | | | | cally consid- ered in the Dumping Protocol. | |
| Cypermethrin | 52315-07-8 | | X | | | | | | | WFD PS: isomer mixture of cy- permethrin, al- pha-cyperme- thrin, beta-cy- permethrin, theta-cyperme- thrin, and zeta- cypermethrin. Com. Reg. 37/2010 (al- lowed sub- stance, MRL es- tablished). | | PARCOM Recom- mendation 94/6. | | |
| DCOIT (sea-Nine 211) | 64359-81-5 | X | X | | | | | | | BPD (existing active sub- stance, dossier under review). | | | | |
| DDTs | Not applica- ble | | X | | | | X | | | WFD other pollu- tants. | | Agreement 2014-06: orga- nochlorine pesti- cides. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |
| Decanoic acid | 334-48-5 | X | | | | | | | | | | | | |
| DEGDN | 693-21-0 | | | | | | | X | | CWC. | HELCOM SUB- MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- cally consid- ered in the Dumping Protocol. | |
| Deltamethrin | 52918-63-5 | | X | | | | | | | Com. Reg. 37/2010 (al- lowed sub- stance, MRL es- tablished). | | PARCOM Recom- mendation 94/6. | | |
| Dibenzo(a,h)anthracene | 53-70-3 | | | X | | | | | | | Core indicators for hazardous substances. | Substance of Possible Concern (section A). Agreement 14- 05. | | |

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| Dibenzothiophene | 132-65-0 | | | X | | | | | | | | Substance of Possible Concern (section A). Agreement 14-05. | | |
| Dichlofluanid | 1085-98-9 | X | X | | | | | | | BPD (existing active substance, dossier under review). | | | | |
| Dichlorvos | 62-73-7 | | X | | | | | | | WFD PS. | | | | |
| Diesel fuel | 68476-29-9 | | | X | X | | | | | | | | | |
| Diethylhexylphthalate (DEHP) | 117-81-7 | X | | | | | | | | WFD PS. WFD PHS. | | Chemical for Priority Action (part A). Agreement 2014-06: characterization of phthalates may be necessary. | | |
| Diflubenzuron | 35367-38-5 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Dimethylamine | 124-40-3 | | | X | | | | | | | | | | |
| Dimethylphenols | Not applicable | | | X | | | | | | | | | | |
| Dioxins and dioxin-like compounds (sum of PCDD+PCDF+PCB-DL) | Not applicable | | X | | | | X | | | WFD PS. WFD PHS: 2,3,7,8-TCDD, 1,2,3,7,8-PCDD, 1,2,3,4,7,8- HCDD, 1,2,3,6,7,8- HCDD, 1,2,3,7,8,9- HCDD, 1,2,3,4,6,7,8- HCDD, 1,2,3,4,6,7,8,9- OCDD, 2,3,7,8- TCDF, 1,2,3,7,8- PCDF, 2,3,4,7,8- PCDF, 1,2,3,4,7,8- | Core indicators for hazardous substances: PCBs 28, 52, 101, 118, 138, 153, and 180; WHO-TEQ of dioxins, furans +dl-PCBs. BSAP specific concern in the Baltic Sea. Recommendation 36/2: PCB 28, 52, 101, 118, 138, 153, and 180. | Chemical for Priority Action (part A): PCBs, PCDDs, PCDFs. Pre-CEMP. Agreement 2014-06: PCB 28, 52, 101, 138, 153, and 180. Characterization of PCDDs /PCDFs may be necessary. | | |

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| | | | | | | | | | | HCDF, 1,2,3,6,7,8- HCDF, 1,2,3,7,8,9- HCDF, 2,3,4,6,7,8- HCDF, 1,2,3,4,6,7,8- HCDF, 1,2,3,4,7,8,9- HCDF, 1,2,3,4,6,7,8,9- OCDF, 3,3',4,4'- TCB, and PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189. | | | | |
| Diphenylamine | 122-39-4 | | | | | | | X | | CWC. | HELCOM SUB- MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- cally consid- ered in the Dumping Protocol. | |
| Diphosgene | 503-38-8 | | | | | | | X | | CWC. | HELCOM SUB- MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifi- cally consid- ered in the Dumping Protocol. | |
| Di-propylene glycol butyl ether | 29911-28-2 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Disper- sants Inven- tory). | | | | |
| Di-propylene glycol monomethyl ether | 34590-94-8 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants | | | | |

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| | | | | | | | | | | (EMSA Dispersants Inventory). | | | | |
| Distillates (petroleum), hydrotreated light (SP 250) | 64742-47-8 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | Substance of Possible Concern (section B). | | |
| Diuron | 330-54-1 | X | X | | X | | | | | WFD PS. BPD (non-inclusion into Annex I or Ia; not allowed in formulations placed on the market since 2008). | | | | |
| Enamectin benzoate | 155569-91-8 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Enrofloxacin | 93106-60-6 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Erythromycin | 114-07-8 | | X | | | | | | | Recommended for the first WFD Watch List. Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Ethoxyquin | 91-53-2 | | X | | | | | | | Reg. 1881/2003, annex I. | | | | |
| Ethylbenzene | 100-41-4 | X | | X | X | | | | | | | Agreement 14-05. | | |
| Ethylene glycol (glycol) | 107-21-1 | X | | X | X | | | | | National rules and regulations for usage of oil spill dispersants | | Agreement 2013-06. | | |

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| | | | | | | | | | | (EMSA Dispersants Inventory). | | | | |
| Fatty acids, fish-oil, ethoxylated | 103991-30-6 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | | | |
| Florfenicol | 73231-34-2 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Flumequine | 42835-25-6 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Fluoranthene | 206-44-0 | | | X | | | X | | | WFD PS. | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. | | |
| Fluorene | 86-73-7 | | | X | | | | | | | Core indicators for hazardous substances. | Agreement 14-05. | | |
| Folpet | 133-07-3 | X | | | | | | | | BPD (non-inclusion into Annex I or Ia; not allowed in formulations placed on the market since 2008). | | | | |
| Formalin | 50-00-0 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Formic acid | 64-18-6 | | | X | | | | | | | | Agreement 14-05. Agreement 2013-06. | | |

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| Glutaraldehyde (pentane-1,5-dial) | 111-30-8 | | | X | | | | | | | | | | | |
| Glycerin (glycerol) | 56-81-5 | | | X | | | | | | | | | Agreement 2013-06. | | |
| Graphite | 7782-42-5 | | | X | | | | | | | | | Agreement 2013-06. | | |
| Heptane (all isomers) | 142-82-5 | X | | | | | | | | | | | | | |
| Hexachlorobenzene (HCB) | 118-74-1 | | X | | | | | | | WFD PS. WFD PHS. | | | Substance of Possible Concern (section B). | UNEP/MAP MED POL monitoring programme. | |
| Hexane (all isomers) | 110-54-3 | X | | | | | | | | | | | | | |
| Hexanoic acid | 142-62-1 | | | X | | | | | | | | | | | |
| HMX | 2691-41-0 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Hydrogen cyanide | 74-90-8 | | | | | | | X | | CWC (schedule 3). | HELCOM SUB-MERGED. | | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Hydroxyethyl cellulose | 9004-62-0 | | | X | | | | | | | | | Agreement 2013-06. | | |
| Indeno(1,2,3-cd)pyrene | 193-39-5 | | | X | | | X | | | WFD PS. WFD PHS. | Core indicators for hazardous substances. Recommendation 36/2. | | Agreement 2014-06. Agreement 14-05. | | |
| Isobutyric acid | 79-31-2 | | | X | | | | | | | | | Agreement 14-05. | | |
| Isononanol | 27458-94-2 | X | | | | | | | | | | | | | |
| Isovaleric acid | 503-74-2 | | | X | | | | | | | | | Agreement 14-05. | | |
| Ivermectin | 70288-86-7 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not established for fish). | | | | | |

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| Kathon (mixture of 5-chloro-2 methyl-4-iso-thiazolin-3-one and 2-methyl-4-isothiazolin-3-one) | 55965-84-9 | | | X | | | | | | | | | | |
| Lewisite | 541-25-3 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Lignite | 129521-66-0 | | | X | | | | | | | | Agreement 2013-06. | | |
| Lignosulfonate | 8062-15-5 | | | X | | | | | | | | | | |
| Lilaflot (a mixture of N-(3-(tridecyloxy)propyl)-1,3-propane diamine and N-(3-(tridecyloxy)propyl)-1,3-propane diamine acetate) | 22023-23-0 19073-42-8 | | | | | X | | | | | | | | |
| Malachite green | 569-64-2 | | X | | | | | | | Com. Reg. 37/2010 (not authorized substance). | | | | |
| Malonic acid | 141-82-2 | | | X | | | | | | | | | | |
| Maneb | 12427-38-2 | X | | | | | | | | BPD (not identified as biocidal product). | | | | |
| MB554 (mixture of 4-(2-nitrobutyl) morpholine and 4,4-(2-ethyl-2-nitrotrimethylene) dimorpholine) | 2224-44-4 1854-23-5 | | | X | | | | | | | | | | |
| Medetomidine | 86347-14-0 | X | | | | | | | | BPD (new substance, dossier submitted for approval as product type 21). | | | | |
| Metacaine | 886-86-2 | | X | | | | | | | | | | | |
| Methanol | 67-56-1 | X | | X | | | | | | | | Agreement 2013-06. | | |

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| Methyl tert-butyl ether (MTBE) | 1634-04-4 | X | | | | | | | | | | | | |
| Methylphenols (cresols) | 1319-77-3 | X | | X | | | | | | | | | | |
| MIDEL 7131 (synthetic ester) | 68424-31-7 | | | | X | | | | | | | | | |
| Nalidixic acid | 389-08-2 | | X | | | | | | | | | | | |
| Naphtha (petroleum), hydrotreated light | 64742-49-0 | | | | X | | | | | | | | | |
| Naphthalene | 91-20-3 | | | X | X | | | | | WFD PS. | Core indicators for hazardous substances. | Agreement 14-05. | | |
| Naphthenic acid | 1338-24-5 | | | X | | | | | | | | Agreement 14-05. | | |
| Nitrobenzene | 98-95-3 | X | | | | | | | | | | | | |
| Nitrocellulose | 9004-70-0 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Nitrogen mustard | 55-86-7 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Nitroglycerin | 55-63-0 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Nitroguanidine | 556-88-7 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Nonane (all isomers) | 111-84-2 | X | | | | | | | | | | | | |
| Nonylphenols | Not applicable | X | | X | | | | | | WFD PS. WFD PHS: | BSAP specific concern in the | Chemical for Priority Action (part | | |

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| | | | | | | | | | | nonylphenol, including isomers 4-nonylphenol and 4-nonylphenol (branched). | Baltic Sea: nonylphenols/ethoxylates. | A): nonylphenols/ethoxylates and related substances. Agreement 14-05. | | |
| Octane (all isomers) | 111-65-9 | X | | | | | | | | | | | | |
| Octylphenols | Not applicable | X | | X | | | | | | WFD PS: octylphenol, including isomer 4-(1,1',3,3'-tetramethylbutyl)-phenol. | BSAP specific concern in the Baltic Sea (octylphenol/ethoxylates). | Chemical for Priority Action (part A). Agreement 14-05. | | |
| Organophosphorus pesticides | Not applicable | | | | | | X | | | | | Agreement 2014-06: characterization may be necessary. | | |
| Orthophosphate | 14265-44-2 | | | X | | | | | | | | | | |
| Oxalic acid | 144-62-7 | | | X | | | | | | | | | | |
| Oxolinic acid | 14698-29-4 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Oxytetracycline | 79-57-2 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Palm oil | 68440-15-3 | X | | | | | | | | | | | | |
| Pentaerythritol | 115-77-5 | | | | X | | | | | | | | | |
| Perchloroethylene (tetrachloroethylene) | 127-18-4 | X | | | | | | | | | | | | |
| Perfluorooctane sulfonic acid and its derivatives (PFOS) | 1763-23-1 | | | | | | X | | | WFD PS. WFD PHS. | Core indicators for hazardous substances: perfluorooctane sulfonate. BSAP specific concern in the Baltic Sea: perfluorooctane sulfonate and perfluorooctanoic acid. | Chemical for Priority Action (part A). Pre-CEMP. | | |

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| PETN | 78-11-5 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Phenanthrene | 85-01-8 | | | X | | | X | | | | Core indicators for hazardous substances. Recommendation 36/2. | Agreement 2014-06. Agreement 14-05. | | |
| Phenol | 108-95-2 | X | | X | | | | | | | | Agreement 14-05. | | BSIMAP (optional). |
| Phenoxyethanol | 122-99-6 | | X | | | | | | | | | PARCOM Recommendation 94/6. | | |
| Phenyldichloroarsine | 696-28-6 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Phosgene | 75-44-5 | | | | | | | X | | CWC (schedule 3). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Picric acid | 88-89-1 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Piromidic acid | 19562-30-2 | | X | | | | | X | | | | | | |
| Polyacrylamide | 9003-05-8 | | | X | | X | | | | | | | | |
| Polyaromatic hydrocarbons (PAHs) | Not applicable | X | X | X | X | | X | | X | WFD PS. | Core indicators for hazardous substances: US EPA 16 PAHs/selected metabolites. | Chemical for Priority Action (part A). CEMP: monitoring of parent PAHs. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |

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| | | | | | | | | | | | Recommendation 36/2: ΣPAH16 and/or ΣPAH9 as a subgroup of ΣPAH16. Recommendation 18/2: total hydrocarbon content. | Pre-CEMP: alkylated PAHs. Agreement 2014-06. | | |
| Polychlorinated biphenyls (PCBs) | Not applicable | | X | | | | X | | X | | | Chemical for Priority Action (part A). Monitoring under CEMP. Agreement 2014-06: PCB characterization may be necessary. | UNEP/MAP MED POL monitoring programme. | BSIMAP (mandatory). |
| Polydimethylsiloxane (PDMS) | 63148-62-9 | | | X | X | | | | | | | | | |
| Polyethylene oxide | 25322-68-3 | | | X | | | | | | | | | | |
| Polyvinyl chloride (PVC) | 9002-86-2 | | | | | | | | X | | | | | |
| Propionic acid | 79-09-4 | | | X | | | | | | | | Agreement 14-05ef. | | |
| Propylene glycol (1,2-propanediol) | 57-55-6 | X | | X | X | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | | | |
| Propylene oxide (methyloxirane) | 75-56-9 | X | | | | | | | | | | | | |
| Pyrene | 129-00-0 | | | X | | | X | | | | Core indicators for hazardous substances. Recommendation 36/2. | Substance of Possible Concern (section A). Agreement 2014-06. Agreement 14-05. | | |
| Quaternary ammonium compounds | 12001-31-9 | | | X | | | | | | | | | | |
| Quinaldine | 91-63-4 | | X | | | | | | | | | | | |

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| RDX | 121-82-4 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Sarafloxacin | 98105-99-8 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Sarin | 107-44-8 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Sodium di-iso-octyl sulphosuccinate (DOSS) | 577-11-7 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | | | |
| Soman | 96-64-0 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Sorbitan, mono-(9Z)-9-octadecenoate | 1338-43-8 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | | | |
| Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives | 9005-65-6 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants | | | | |

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| | | | | | | | | | | (EMSA Dispersants Inventory). | | | | |
| Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives | 9005-70-3 | X | | X | | | | | | National rules and regulations for usage of oil spill dispersants (EMSA Dispersants Inventory). | | | | |
| Soybean oil | 8001-22-7 | X | | | X | | | | | | | | | |
| Styrene monomer | 100-42-5 | X | | | | | | | | | | | | |
| Sulfadiazine | 68-35-9 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Sulfamethoxazole | 723-46-6 | | X | | | | | | | | | | | |
| Sulfathiazole | 72-14-0 | | X | | | | | | | | | | | |
| Sulfonated salts of asphalt (gilsonite) | 8052-42-4 | | | X | | | | | | | | | | |
| Sulfur mustard | 505-60-2 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Sunflower oil | 8001-21-6 | X | | | X | | | | | | | | | |
| Tabun | 77-81-6 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Tannins | 1401-55-4 | | | X | | | | | | | | | | |
| TCMS pyridine (Densil 100) | 13108-52-6 | X | X | | | | | | | BPD (not identified as biocidal product). | | | | |
| TCMTB (Busan) | 21564-17-0 | X | | | | | | | | BPD (not identified as biocidal product). | | | | |

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| Tear gas | 532-27-4 | | | | | | | X | | CWC (agent banned in warfare). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Teflubenzuron | 83121-18-0 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Tetrachloro-ethylene | 127-18-4 | X | | | | | | | | WFD other pollutants. | | | | |
| Tetryl | 479-45-8 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Thiram | 137-26-8 | X | | | | | | | | BPD (not applicable as product type 21). | | | | |
| TNT | 118-96-7 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Toluene | 108-88-3 | X | | X | X | | | | | | | Agreement 14-05. | | |
| Tolylfluanid | 731-27-1 | X | | | | | | | | BPD (existing substance, dossier under review). | | | | |
| Tralopyril (Econea) | 122454-29-9 | X | | | | | | | | BPD (new substance, dossier submitted for approval as product type 21). | | | | |

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|--------------------------------------|-----------|---|---|---|--|--|--|---|--|--|--------------------|--|--|--|
| Tricaine methane sulphonate (MS-222) | 886-86-2 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). | | PARCOM Recommendation 94/6. | | |
| Trichlorfon | 52-68-6 | | X | | | | | | | | | | | |
| Trichloroethylene | 79-01-6 | X | | | | | | | | WFD other pollutants. | | | | |
| Trifluralin | 1582-09-8 | | X | | | | | | | WFD PS. WFD PHS. | | Chemical for Priority Action (Part A). | | |
| Trimethoprim | 738-70-5 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL established). | | PARCOM Recommendation 94/6. | | |
| Triphenylarsine | 603-32-7 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Valeric acid (pentanoic acid) | 109-52-4 | | | X | | | | | | | | Agreement 14-05. | | |
| VG | 78-53-5 | | | | | | | X | | CWC (schedule 2). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Vitamin C (L-ascorbic acid) | 50-81-7 | | X | | | | | | | Reg. 1881/2003, annex I. | | Agreement 2013-06. | | |
| Vitamin E (α-tocopherol) | 59-02-9 | | X | | | | | | | Com. Reg. 37/2010 (allowed substance, MRL not required). Reg. 1881/2003, annex I. | | | | |

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| VM | 21770-86-5 | | | | | | | X | | CWC. | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| VX | 50782-69-9 | | | | | | | X | | CWC (schedule 1). | HELCOM SUB-MERGED. | Recommendation 2010/20. | Obsolete ordnance not specifically considered in the Dumping Protocol. | |
| Xanthate salts | Not applicable | | | | | X | | | | | | | | |
| Xylene | 1330-20-7 | X | | X | X | | | | | | | Agreement 14-05. | | |
| Radionuclides | | | | | | | | | | | | | | |
| 241Am | | | | | | | | X | | | | Recommendation 26/3 (voluntary). | | |
| 14C | | | | | | | | X | | | | | | |
| 58Co | | | | | | | | X | | | | | | |
| 60Co | | | | | | | | X | | | | | | |
| 134Cs | | | | | | | | X | | | | Recommendation 26/3 (obligatory). | | |
| 137Cs | | | | | | | | X | | EURATOM Treaty (Art. 36). | Core indicators for hazardous substances. Recommendation 26/3 (obligatory). | | | BSIMAP (optional). |
| 55Fe | | | | | | | | X | | | | | | |
| 3H | | | | | | | | X | | | | Recommendation 26/3 (voluntary). | Agreement 2013-11. | |
| 131I | | | | X | | | | | | | | Agreement 2013-11. | | |
| 224Ra | | | | X | | | | | | | | | | |
| 226Ra | | | | X | | | | | | | | Agreement 2013-11. | | |
| 228Ra | | | | X | | | | | | | | Agreement 2013-11. | | |
| 210Pb | | | | X | | | | | | | | Agreement 2013-11. | | |

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|-----------|--|--|--|---|--|--|--|---|--|---------------------------|----------------------------------|--------------------|--|--------------------|
| 210Po | | | | X | | | | | | | Recommendation 26/3 (voluntary). | | | |
| 238Pu | | | | | | | | X | | | | | | |
| 239,240Pu | | | | | | | | X | | | Recommendation 26/3 (voluntary). | | | |
| 90Sr | | | | | | | | X | | EURATOM Treaty (Art. 36). | Recommendation 26/3 (voluntary). | | | BSIMAP (optional). |
| 228Th | | | | X | | | | | | | | Agreement 2013-11. | | |
| 238U | | | | X | | | | | | | | | | |

WFD PS: Water Framework Directive Priority Substance; PHS: Water Framework Directive Priority Hazardous Substance (status as at Directive 2013/39/EU of 12 August 2013).

WFD Other Pollutants: Pollutants included in the Annex II of Directive 2013/39/EU and for which a European standard applies, but not in the priority substances list.

WFD Watch list: New mechanism to support the identification of priority substances for regulation under WFD. A restricted number of substances or group of substances (up to 10) are to be included in a dynamic Watch List, remaining there for limited time (Carvalho et al., 2015).

BPD: EU Biocide Regulation (528/2012 and amendment 334/2014): All biocidal products require an authorization before they can be placed on the market, and the active substances contained in that biocidal product must be previously approved. Hence, a list of active substances agreed for inclusion in biocidal products are listed in Annexes I and IA and classified under 22 different biocidal product types, including antifouling agents (product type 21).

Regulation (EC) No 1831/2003: European Union legislation on feed additives.

CWC: Chemical Weapons Convention:

- Schedule 1 substances are chemicals which can either be used as toxic chemical weapons themselves or used in the manufacture of chemical weapons but which have as little or no use for purposes not prohibited under this Convention.
- Schedule 2 substances are chemicals which can either be used as toxic chemical weapons themselves or used in the manufacture of chemical weapons but which are not produced in large commercial quantities for purposes not prohibited under this Convention.
- Schedule 3 substances are chemicals which can either be used as toxic chemical weapons themselves or used in the manufacture of chemical weapons but which also may be produced in large commercial quantities for purposes not prohibited under this Convention.

CCWC: Convention on Certain Conventional Weapons, Protocol III on Incendiary Weapons.

Com. Reg. 37/2010: Commission Regulation (EU) No 37/2010 of 22 December 2009 on pharmacologically active substances and their classification regarding maximum residue limits in foodstuffs of animal origin.

EMSA Dispersants Inventory: This inventory contains information for each Member State regarding the national rules and regulations for usage of oil spill dispersants as an at-sea oil spill response method. The inventory is updated in regular intervals (latest in EMSA, 2014).

Titanium Dioxide Directives (Council Directive 78/176/EEC, 82/883/EEC, 92/112/EEC): Community legislation to prevent and progressively reduce pollution caused by waste from the titanium dioxide industry with a view to the elimination of such pollution.

HELCOM SUBMERGED: HELCOM expert group on environmental risks of hazardous submerged objects (assessment period agreed for 2015-2017). The terms of reference of this group include also sea dumped chemical munitions.

HELCOM core indicators: Core indicators for hazardous substances as concluded in the final report of the HELCOM CORESET project (HELCOM, 2013b).

BSAP specific concern in the Baltic Sea: Hazardous substances of the Baltic Sea Action Plan to follow the reaching of the ecological objectives under the strategic goal of hazardous substances (HELCOM, 2007).

HELCOM Recommendation 18/2: HELCOM guidelines for the environmental performance of offshore activities HELCOM Recommendation 18/2 adopted 12 March 1997. <http://www.helcom.fi/Recommendations/Rec%2018-2.pdf>.

HELCOM Recommendation 36/2: HELCOM Guidelines for Management of Dredged Material at Sea, adopted by HELCOM 36-2015 on 4 March 2015. <http://www.helcom.fi/Lists/Publications/HELCOM%20Guidelines%20for%20Management%20of%20Dredged%20Material%20at%20Sea.pdf>.

HELCOM Recommendation 26/3: HELCOM guidelines for regular monitoring programme of radioactive substances. <http://helcom.fi/Lists/Publications/Guidelines%20for%20Monitoring%20of%20Radioactive%20Substances.pdf>.

OSPAR List of Chemicals for Priority Action:

- Part A: Chemicals where a background document has been or is being prepared.

- Part B: Chemicals where no background document is being prepared because they are intermediates in closed systems.
- Part C: Chemicals where no background document is being prepared because there is no current production or use interest.

OSPAR List of Substances of Possible Concern:

- Section A: substances which warrant further work by OSPAR because they do not meet the criteria for Sections B-D and substances for which, for the time being, information is insufficient to group them in Sections B-D.
- Section B: substances which are of concern for OSPAR but which are adequately addressed by EC initiatives or other international forums.
- Section C: substances which are not produced and/or used in the OSPAR catchment or are used in sufficiently contained systems making a threat to the marine environment unlikely.
- Section D: substances which appear not to be "hazardous substances" in the meaning of the Hazardous Substances Strategy but where the evidence is not conclusive.

CEMP: OSPAR Coordinated Environmental Monitoring programme (concentrations and effects in the marine environment).

OSPAR Recommendation 2010/20: OSPAR framework for reporting encounters with conventional and chemical munitions in the OSPAR Maritime Area (from 1 January 2011).

OSPAR Agreement 2014-06: OSPAR guidelines for the Management of Dredged Material at Sea, including its chemical characterization.

PARCOM Recommendation 94/6: Best Environmental Practice (BEP) for the Reduction of Inputs of Potentially Toxic Chemicals from Aquaculture Use (implementation reporting on this recommendation ceased in 2006, but that if there were significant developments in the aquaculture industry in the future, the need for implementation reporting should be revisited) (OSPAR, 2006).

PARCOM Recommendation 84/1 on pollution by titanium dioxide wastes.

OSPAR Agreement 14-05: OSPAR list of potentially harmful substances typically analyzed to characterize produced water samples from the offshore industry.

OSPAR Agreement 2013-06: OSPAR list of substances used and discharged offshore which do not normally need to be strongly regulated as the OSPAR Commission considers them to pose little or no risk to the environment (PLONOR).

OSPAR Agreement 2013-11: Reporting procedures to be used for annual reporting of data on discharges from the non-nuclear sector, as required by the OSPAR Radioactive Substances Strategy. www.ospar.org/work-areas/rsc/non-nuclear-discharges.

UNEP/MAP MED POL Monitoring programme (Annex IX Contaminants): Indicators Monitoring Fact Sheets on Ecological Objective 9: Contaminants (UNEP/MAP, 2015).

UNEP/MAP Dumping protocol: Protocol for the Prevention of Pollution in the Mediterranean Sea by Dumping from Ships and Aircraft.

BSIMAP: Black Sea Integrated Monitoring and Assessment Programme. www.blacksea-commission.org/_bsimap.asp.

EURATOM Treaty (Art. 36): Commission recommendation of 8 June 2000 on the application of Article 36 of the Euratom Treaty concerning the monitoring of the levels of radioactivity in the environment for the purpose of assessing the exposure of the population as a whole. <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32000H0473&from=EN>.

Table 10. Chemical contaminants prioritized under different European frameworks for which no significant sea-based sources have been identified.

| Substance | CAS number | EC WFD | HELCOM | OSPAR | Barcelona Convention | Black Sea Commission |
|--|--------------------------------|---|--|--|---|----------------------|
| Acetamiprid | 135410-20-7 160430-64-8 | Recommended for the first WFD Watch List. | | | | |
| Aclonifen | 74070-46-5 | PS. | | | | |
| Alachlor | 15972-60-8 | PS. | | | | |
| 17-alpha-ethinylestradiol (EE2) | 57-63-3 | Recommended for the first WFD Watch List. | Core indicators for hazardous substances. | Substance of Possible Concern (section A). | | |
| Atrazine | 1912-24-9 | PS. | | Substance of Possible Concern (section B). | | |
| Azithromycin | 83905-01-5 | Recommended for the first WFD Watch List. | | | | |
| BifenoX | 42576-02-3 | PS. | | | | |
| Chlorfenvinphos | 470-90-6 | PS. | | | | |
| Chloroalkanes, C10-13 | 85535-84-8 | PS. PHS. | BSAP specific concern in the Baltic Sea: short-chain chlorinated paraffins (SCCP or chloroalkanes, C10-13) and medium-chain chlorinated paraffins (MCCP or chloroalkanes, C14-17). | Substance of Possible Concern (section A). Chemical for Priority Action (part A): short chained chlorinated paraffins (SCCP). | | |
| Chlorpyrifos | 2921-88-2 | PS. | | Substance of Possible Concern (section B). | | |
| Clarithromycin | 81103-11-9 | Recommended for the first WFD Watch List. | | | | |
| Clothianidin | 210880-92-5 | Recommended for the first WFD Watch List. | | | | |
| Clotrimazole | 23593-75-1 | | | Chemical for Priority Action (part A). | | |
| Cyclodiene pesticides: Aldrin Dieldrin Endrin | 309-00-2 60-57-1 72-20-8 | WFD other pollutants. | | Chemical for Priority Action (part C): isodrin. | UNEP/MAP MED POL monitoring programme: aldrin and dieldrin. | |

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|--|-----------------------|---|---|--|--|--|
| Isodrin | 465-73-6 | | | Substance of Possible Concern (section B): Aldrin, dieldrin, endrin | | |
| 1,5,9 cyclododecatriene | 4904-61-4 | | | Chemical for Priority Action (part B). | | |
| Dibutylphthalate (DBP) | 84-74-2 | | | Chemical for Priority Action (part A). Agreement 2014-06e: characterization of phthalates may be necessary. | | |
| 1,2-dichloroethane | 107-06-2 | PS. | | | | |
| Dichloromethane | 75-09-2 | PS. | | | | |
| Diclofenac | 15307-79-6 | Recommended for the first WFD Watch List. | Core indicators for hazardous substances. | | | |
| Dicofol | 115-32-2 | PS. PHS. | | Chemical for Priority Action (part A). | | |
| 4-(dimethylbutylamino)diphenylamin (6PPD) | 793-24-8 | | | Chemical for Priority Action (part A). | | |
| Diosgenin | 512-04-9 | | | Chemical for Priority Action (part C). | | |
| Endosulfan | 115-29-7 | PS. PHS. | BSAP specific concern in the Baltic Sea. | Chemical for Priority Action (part A). | | |
| 17 β -estradiol (17 β -oestradiol, E2) | 50-28-2 | Recommended for the first WFD Watch List. | | Substance of Possible Concern (section A). | | |
| 2-ethylhexyl 4-methoxycinnamate | 5466-77-3 | Recommended for the first WFD Watch List. | | | | |
| Ethyl O-(p-nitrophenyl) phenyl phosphonothionate (EPN) | 2104-64-5 | | | Chemical for Priority Action (part C). | | |
| Flucythrinate | 70124-77-5 | | | Chemical for Priority Action (part A). | | |
| Heptachlor and heptachlor epoxide | 76-44-8/ 1024-57-3 | PS. PHS. | | Substance of Possible Concern (section B): heptachlor. | | |

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|-------------------------------------|----------------------------|--|---|--|---|---------------------|
| | | | | Substance of Possible Concern (section C): heptachlor epoxide. | | |
| Heptachloronorbornene | 28680-45-7 | | | Chemical for Priority Action (part C). | | |
| Hexabromocyclododecanes (HBCDD) | Not applicable | PS. PHS: 1,3,5,7,9,11-hexabromocyclododecane, 1,2,5,6,9,10-hexabromocyclododecane, α -hexabromocyclododecane, β -hexabromocyclododecane, and γ -hexabromocyclododecane. | Core indicators for hazardous substances. BSAP specific concern in the Baltic Sea. | Chemical for Priority Action (part B): cyclododecane. | | |
| Hexachlorobutadiene | 87-68-3 | PS. PHS. | | Substance of Possible Concern (section B). | | |
| Hexachlorocyclohexane isomers (HCH) | 608-73-1 | PS. PHS. | | Chemical for Priority Action (part A). | UNEP/MAP MED POL monitoring programme: γ HCH, lindane. | BSIMAP (mandatory). |
| Imidacloprid | 105827-78-9 138261-41-3 | Recommended for the first WFD Watch List. | | | | |
| Isoproturon | 34123-59-6 | PS. | | | | |
| Methiocarb | 2032-65-7 | Recommended for the first WFD Watch List. | | | | |
| Methoxychlor | 72-43-5 | | | Chemical for Priority Action (part A). | | |
| Musk xylene | 81-15-2 | | | Chemical for Priority Action (part A). | | |
| Neodecanoic acid, ethenyl ester | 51000-52-3 | | | Chemical for Priority Action (part A). | | |

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|--|-------------|---|--|--|--|--|
| Oxadiazon | 19666-30-9 | Recommended for the first WFD Watch List. | | | | |
| Pentabromoethylbenzene | 85-22-3 | | | Chemical for Priority Action (part C). | | |
| Pentachloroanisole | 1825-21-4 | | | Chemical for Priority Action (part C). | | |
| Pentachlorobenzene | 608-93-5 | PS. PHS. | | Substance of Possible Concern (section B). | | |
| Pentachlorophenol (PCP) | 87-86-5 | PS. | | Chemical for Priority Action (part A). | | |
| Polychlorinated naphthalenes | | | | Chemical for Priority Action (part C): trichloronaphthalene, tetrachloronaphthalene, pentachloronaphthalene, hexachloronaphthalene, heptachloronaphthalene, octachloronaphthalene, naphthalene, chloro derivs. | | |
| 2-propenoic acid, (pentabromo)methyl ester | 59447-55-1 | | | Chemical for Priority Action (part C). | | |
| Quinoxifen | 124495-18-7 | PS. PHS. | | | | |
| Simazine | 122-34-9 | PS. | | | | |
| Terbutryn | 886-50-0 | | | | | |
| Tetrabromobisphenol A (TBBP-A) | 79-94-7 | | | Chemical for Priority Action (part A). | | |
| Tetrasul | 2227-13-6 | | | Chemical for Priority Action (part C). | | |
| Thiacloprid | 111988-49-9 | Recommended for the first WFD Watch List. | | | | |
| Thiamethoxam | 153719-23-4 | Recommended for the first WFD Watch List. | | | | |

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| Tri-allate | 2303-17-5 | Recommended for the first WFD Watch List. | | Substance of Possible Concern (section B). | | |
| Trichlorobenzenes | 12002-48-1 | PS. | | Chemical for Priority Action (part A): 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene. | | |
| Trichloromethane (chloroform) | 67-66-3 | PS. | | | | |
| 2,4,6-tri-tert-butylphenol | 732-26-3 | | | Chemical for Priority Action (part A). | | |
| 3,3'-(ureylenedimethylene)bis(3,5,5-trimethylcyclohexyl) diisocyanate | 55525-54-7 | | | Chemical for Priority Action (part C). | | |

5 CONCLUSIONS

This report assesses and compiles relevant data and information to provide an extensive list of chemical substances that have been, are being or might be released into the marine environment from sea-based anthropogenic sources. The list also provides an overview of the policies and frameworks for the management and regulation of the identified substances within the EU. Such a list may represent a valuable starting point to approach the management of marine chemical pollution and contribute to the setting-up of monitoring strategies, including hotspots screening. As already stated by Tornero and Hanke (*in press*), the level of harmonization with regard to the contaminants considered by different frameworks across Europe can be considered rather low. Only four WFD PS (PAHs, cadmium, mercury, and lead) are also prioritized in the four European RSC, while other contaminants are tackled by the different frameworks in a different way. Nevertheless, a number of other European or international legislations and regulations as well as recommendations, agreements and programmes at national or regional level, deal direct or indirectly with most substances or group of substances in the list, although approximately one-third of them seem not to be currently tackled by any framework.

It is important to keep in mind that this compilation cannot be regarded as a risk assessment. All substances in the list are likely to occur in the marine environment, but this does not imply that all of them are hazardous or released into the sea at harmful concentrations. This review has not taken into account these characteristics to compile the final list of contaminants, yet it has evidenced either a lack of information on many of these crucial aspects or the difficulty to access it (as seen in the tables 5, 6, and 7).

The information provided here can help identify where efforts are needed to access and mobilize additional data as well as help understand which marine pollutants are currently considered at European and/or regional level or might need further control and/or monitoring actions.

A close collaboration across the shared basins is needed in order to improve resource efficiency and take the cross-basin nature of contaminant issues into account (Perseus policy brief, 2015). International campaigns, involving institutions from RSCs countries and expert laboratories may be a way forward to have a more complete assessment of chemical contamination in marine waters. While previously it may not have been possible to consider a large number of contaminants in monitoring programs, the current development of new instrumental analytical methodologies will support the challenging analysis of multiple compounds⁵⁸.

⁵⁸ Non-target screening of organic chemicals for a comprehensive environmental risk assessment. <http://www.nontarget2016>

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List of abbreviations and definitions

AA: Annual average

ACE project: Assessment of Antifouling Agents in Coastal Environments

ARCOPOL: Atlantic Region-Coastal Pollution Response

RAMOCS: Implementation of risk assessment methodologies for oil and chemical spills in the European marine environment

Barcelona Convention: Convention for the Protection of Marine Environment and the Coastal Region of the Mediterranean

BCF: Bioconcentration Factor, which reflects the extent to which pollutants concentrate from water into aquatic organisms

BDP: Biocides Directive

BSAP: Baltic Sea Action Plan

BSIMAP: Black Sea Integrated Monitoring and Assessment Programme

BTEX: Benzene-toluene-ethylbenzene-xylene

Bucharest Convention: Convention on the Protection of the Black Sea against Pollution

CAS: Chemical Abstracts Service

CCWC: Convention on Certain Conventional Weapons

CEMP: OSPAR Coordinated Environmental Monitoring Programme

CHEMSEA: Chemical Munitions, Search and Assessment

COW: Crude Oil Washing

CWA: Chemical Warfare Agents

CWC: Chemical Weapons Convention

Dwt: dry weight

EC10: Effective Concentration of a toxic substance at 10% inhibition

EC50: Median effective concentration

ECHA: European Chemicals Agency

EEZ: Exclusive Economic Zone

EMSA: European Maritime Safety Agency

EQS: Environmental Quality Standards

ERL: Environmental Risk Limit

GES: Good Environmental Status

HCBs: Hexachlorobenzenes

HELCOM MUNI: HELCOM expert group to update and review the existing information on dumped chemical munitions in the Baltic Sea

HELCOM SUBMERGED: HELCOM expert group on environmental risks of hazardous submerged objects

HELCOM: Convention on the Protection of the Marine Environment in the Baltic Sea

HNS: Hazardous and Noxious Substances

IAEA; International Atomic Energy Agency

IC50: Half maximal inhibitory concentration

IMO: International Maritime Organization

ISA: International Seabed Authority

LC50: Median lethal concentration

LD50: Median lethal dose

LOD: Limit of detection

LOEC: Lowest observed effect concentration

Log Kow: log octanol/water partition coefficient, which reflects the chemical's tendency to bioaccumulate in organisms

MAC: Maximum allowable concentration

MARPOL: International Convention for the Prevention of Pollution from Ships

MEC: Measured environmental concentrations

MERCW: Modeling of Environmental Risks related to sea-dumped Chemical Weapons

MRL: Maximum Residue Level, which is defined as the maximum concentration of residue resulting from the use of a veterinary medicinal product that may be accepted to be legally permitted or recognized as acceptable on a food

MSFD: Marine Strategy Framework Directive

NOEC: No effect concentration

OSPAR: Convention for the protection of the marine environment of the North-East Atlantic

PAH: Polycyclic aromatic hydrocarbons

PBDEs: Polybrominated diphenyl ethers

PCBs: Polychlorinated biphenyls

PCDDs: Polychlorinated dibenzodioxins

PCDFs: Polychlorinated dibenzofurans

PEC: Predicted environmental concentrations

PHS: Priority Hazardous Substance

PLONOR: Substances considered by OSPAR to pose little or no risk to the environment

PNEC: Predicted no-effect concentration

PS: Priority Substance

RBSP: River Basin Specific Pollutants

RED COD: Research on Environmental Damage caused by Chemical Ordnance Dumped at sea

RSC: Regional Sea Convention

SEPA EQS: Operational water and sediment Quality Standards applied by the Scottish Environmental Protection Agency for regulating the use of chemicals in aquaculture

SEPA: Scottish Environmental Protection Agency

SOLAS: International Convention for the Safety of Life at Sea

SQG: Sediment quality guidelines

UNCLOS: United Nations Convention on the Law of the Sea

USEPA: United States Environmental Protection Agency

TBT: Organotin tributyltin

VOCs: Volatile Organic Compounds

WFD Other Pollutants: Pollutants included in the Annex II of Directive 2013/39/EU and for which a European standard applies, but not in the priority substances list

WFD Watch list: New mechanism is to support the identification of priority substances for regulation under WFD

WFD: Water Framework Directive

Wwt: wet weight

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