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Review

Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas

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ABSTRACT

Anthropogenic contaminants reach the marine environment mostly directly from land-based sources, but there are cases in which they are emitted or re-mobilized in the marine environment itself. This paper reviews the literature, with a predominant focus on the European environment, to compile a list of contaminants potentially released into the sea from sea-based sources and provide an overview of their consideration under existing EU regulatory frameworks. The resulting list contains 276 substances and for some of them (22 antifouling biocides, 32 aquaculture medicinal products and 34 warfare agents) concentrations and toxicity data are additionally provided. The EU Marine Strategy Framework Directive Descriptor 8, together with the Water Framework Directive and the Regional Sea Conventions, provides the provisions against pollution of marine waters by chemical substances. This literature review should inform about the current state of knowledge regarding marine contaminant sources and provide support for setting-up of monitoring approaches, including hotspots screening.

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1. Introduction

* Corresponding author. *E-mail address:* victoria.tornero@jrc.ec.europa.eu (V. Tornero). Contamination caused by hazardous substances is a major environmental concern in European waters and consequently is addressed by a number of EU legislative measures and policies. The Water Framework

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Directive (WFD, 2000/60/EC) provides for measures against chemical pollution of surface waters. There are two components – the selection and regulation of substances of EU-wide concern (priority substances, PS) as a means to assess the chemical status of water bodies up to 12 nautical miles from the straightened coastline, and 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". In 2001 a first list of 33 PS was adopted (Decision 2455/2001) and in 2008 the Environmental Quality Standards (EQSs) for those substances and eight other pollutants already regulated at EU level were set in the Directive 2008/105/EC (or EQS Directive), which was amended by the Directive 2013/39/EU.

The Marine Strategy Framework Directive (MSFD, 2008/56/EC) aims to provide an integrative marine environment status assessment and considers both coastal and offshore environment, thus overlapping with WFD for some parts of the marine environment. The approach taken on contaminants under MSFD Descriptor 8 "Concentrations of contaminants are at levels not giving rise to pollution effects" should, therefore, be properly integrated and aligned with the work on identification and review of PS and EQS under the WFD. The identification of substances which are not listed as WFD PS or RBSP, but entail a significant risk to the marine environment is part of the MSFD provisions (Commission Decision 2010/477/EU).

It has been suggested that harmonization in MSFD Descriptor 8 implementation would be improved by compiling a list of contaminants which pose a risk to, or via, the marine environment (Tornero et al., 2015). This process has to take into consideration the relevant provisions of the WFD for territorial and/or coastal waters, but also the activities of the Regional Sea Conventions (RSCs), which cover EU marine regions or sub-regions: OSPAR (Convention for the Protection of the Marine Environment in the North-East Atlantic), HELCOM (Convention on the Protection of the Marine Environment in the Baltic Sea), Barcelona Convention (Convention for the Protection of Marine Environment and the Coastal Region of the Mediterranean), and Bucharest Convention (Convention for the Protection of the Black Sea).

This paper reviews the available literature to provide a list of chemical substances that have been, are being or might be released into the marine environment through sea-based human activities, with an overview of the policies and regulations in place for their management and control within the EU. This review should improve the knowledge regarding substances that might occur in the marine environment. However, it is important to note that the substances have been listed without considering their toxicological properties and/or marine concentrations, and therefore this paper does not provide a risk assessment. The resulting list might support the 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.

2. Approach

The information has been gathered through an extensive review of the existing literature, mainly peer-reviewed papers and books, but also reports, assessments and proposals from RSCs and research projects, conference proceedings, and other literature regarding the occurrence of contaminants in marine waters, and with a special focus on the European environment. The paper first compiles the relevant contaminants on the basis of the sea-based human activities potentially resulting in their release into the marine environment. Contaminants entering the marine environment through atmospheric transport are beyond the scope of this review. For selected groups of identified substances (biocides in ship antifouling paints, medicinal products in the marine aquaculture industry, and main constituents of warfare material dumped at sea), specific information on their concentrations and toxicity in the marine environment is also compiled. The gathered information is used to create a list of marine-relevant contaminants, which includes their chemical identity and major seabased sources. This list also gives information on the relevant international regulations/legislations and RSC monitoring programmes which deal with those substances, thus allowing the analysis of their coverage in European marine waters.

3. Sea-based activities resulting in the release of contaminants into the marine environment

3.1. Shipping

Maritime traffic on the world's oceans has increased dramatically over the past 20 years, thus increasing the risk of pollution caused by shipping (Tournadre, 2014). Although environmental regulations are strict, particularly under the MARPOL Convention (International Convention for the Prevention of Pollution from Ships), polluting substances continue to be discharged into the sea, often illegally (EMSA, 2012).

3.1.1. Accidental spillage

3.1.1.1. Chemical spills. Shipping is the most important mode of transport for a significant number of chemicals, referred to as Hazardous and Noxious Substances (HNS), and defined as any substance other than oil, which if introduced into the marine environment is 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).

It is estimated that about 2000 different chemicals used by man are regularly transported by sea, either in bulk or in packaged form, and the chemical seaborne trade is estimated to reach 215 million tonnes by 2015 (Purnell, 2009). According to the data compiled by the European Maritime Safety Agency (EMSA), incidents resulting in HNS release happen regularly in European waters (EMSA, 2007, 2008, 2009, 2010). The ecological hazards involved in these spills are less recognized and understood than those involving oil pollution (Neuparth et al., 2011). It seems logical to think that the most commonly transported chemicals are the ones most likely to be involved in one incident, so updated information about transported chemicals would be a first step to be prepared for and reduce the risk from possible incidents (Sheahan et al., 2015). However, putting together a comprehensive list of chemicals such as this is complicated due to the high number and diversity of HNS. Moreover, the data on the chemical transportation volumes in the EU is limited and decentralized, and the exact quantities of different chemicals transported and spilled are often not available and/or accessible (Posti and Häkkinen, 2012; EMSA, 2013a). Despite this, there are some studies that have gathered very valuable information. Cunha et al. (2015) collected information on the behavior, fate, weathering, and impact of HNS spilled at sea around the world and converted it into a database that can be accessed by the general public. In Europe, the HASREP project (Response to Harmful Substances spilled at sea) identified the top 100 chemicals being transported in and along European waters and found that the 15 bulk HNSs most handled were 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). These chemicals were mostly the same as those most transported/handled in the Baltic Sea according to the Chembaltic project (Risks of Maritime Transportation of Chemicals in Baltic Sea) (Posti and Häkkinen, 2012). According to the EMSA analysis of significant HNS incidents, the most released substances during 1978–2013 in European waters were styrene, sulphuric acid, benzene, and phosphoric acid. Other released substances include methyl-ketone, propane, phenols, isopropyl alcohol, acrylonitrile, acetone, and compounds of potassium, zinc, calcium, barium, lead, and sodium (EMSA, 2013a).

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