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Viewpoint

Hazardous and Noxious Substances (HNS) in the marine environment: Prioritizing HNS that pose major risk in a European context

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ABSTRACT

Increases in the maritime transportation of Hazardous and Noxious Substances (HNS), alongside the need for an effective response to HNS spills have led environmental managers and the scientific community to focus attention on HNS spill preparedness and responsiveness. In the context of the ARCOPOL project, a weight-of-evidence approach was developed aimed at prioritizing HNS that pose major environmental risks to European waters. This approach takes into consideration the occurrence probability of HNS spills in European Atlantic waters and the severity of exposure associated with their physico-chemical properties and toxicity to marine organisms. Additionally, a screening analysis of the toxicological information available for the prioritization of HNS was performed. Here we discuss the need for a prioritization methodology to select HNS that are likely to cause severe marine environmental effects as an essential step towards the establishment of a more effective preparedness and response to HNS incidents.

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1. Introduction

A large volume of chemicals is currently produced and, for a significant number of these, shipping is the most important mode of transport in terms of volume [\(French McCay et al., 2006; Mamaca](#page-7-0) [et al., 2009; Purnell, 2009\)](#page-7-0). The constant growth in the volume of chemicals that are transported by sea increases the risk of accidental spillage and the severity of their impacts depending on several variables such as the substances hazardous properties. These groups of chemicals have been collectively termed Hazardous and Noxious Substance (HNS) that are 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\)](#page-7-0).

The growth in the maritime transportation of HNS, together with the need for an effective response to HNS spills have led authorities, environmental managers and the scientific community to focus on HNS spills preparedness and responses to them. The OPRC-HNS Protocol (The Protocol on Preparedness, Response and Co-operation to Pollution Incidents by Hazardous and Noxious Substances), adopted by [IMO \(2000\)](#page-7-0), entered into force in 2007 and has been, at the time of writing, ratified by 25 countries (12 EU/EFTA countries), representing 36.1% of the global tonnage. Even though the probability of an HNS incident is considered small due to high safety standards, it does exist as recent shipping incidents

involving HNS have shown. The Ievoli Sun, which sank in the English Channel in 2000, released 1000 tonnes of styrene. More recently, in 2007, the MSC Napoli, which carried >1600 tonnes of chemical products classified by IMO as dangerous goods, raised awareness of the potential ecological hazard of HNS spills [\(Law](#page-7-0) [et al., 2003; Kirby et al., 2008](#page-7-0)).

An understanding of the ecological hazards involved in HNS spills is less well recognized than those involving oil pollution. Whereas most oils float on the sea and are immiscible with water, HNS chemicals exhibit a wider range of behaviours (i.e. sinking, floating, gassing, evaporating, and dissolution) and toxicities to marine organisms [\(CEFAS, 2009\)](#page-7-0). There is a current paucity of knowledge about the effects of HNS on marine biota and the scarce available ecotoxicological HNS data result mostly from experiments conducted with freshwater organisms ([Mamaca et al., 2005; Purnell,](#page-7-0) [2009](#page-7-0)), making it difficult to predict the effects on marine organisms and to prepare contingency plans for these substances.

In order to respond to incidents involving HNS, the systematic classification of scientific ecotoxicological data for marine organisms should be a priority issue. Due to the high number and diversity of HNS transported by sea, it is, in practice, unrealistic to consider a full scientific ecotoxicological data survey for all such chemicals. Hence, the prioritization of HNS that are most likely to pose severe hazards to marine organisms is needed.

The present study develops a weight-of-evidence approach based on a set of key risk criteria that include (i) the volumes of HNS transported in European Atlantic waters; (ii) reported HNS incidents in European waters; (iii) HNS physico-chemical properties and (iv) their toxicities to marine organisms. The study further aimed at drawing up a list of priority HNS that are likely to

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pose a major risk to the marine environment if spilled in European Atlantic waters. The study also sought to collate the marine toxicological data available for each priority HNS. This approach is essential if we are to improve our knowledge about the significance of chemical spills to the marine environment and represents a step towards defining strategic risk information for the establishment of a more effective preparedness and response capability to HNS incidents.

2. Prioritization procedure: approach and methodology

The threat caused by different HNS chemicals depends on several variables, for example, their intrinsic characteristics (i.e. physico-chemical and toxicological properties) and the volumes transported by sea. The effective response to a HNS spill incident should consider the HNS impact on the marine environment, which requires an ecotoxicological dataset for representative marine organisms. Producing such a dataset for all HNS is a difficult task due to the large numbers and the particular properties of compounds transported in European waters. Hence, a more realistic approach consists of the selection and prioritization of HNS chemicals that are likely to pose the most severe risks to the marine environment if spilled. The prioritization procedure represents a weight-of-evidence approach based on the following key risk criteria: (i) HNS volumes transported in European Atlantic waters; (ii) reported HNS incidents in European waters; (iii) HNS physico-chemical properties and (iv) toxicity to marine organisms.

Table 1

Summary of the HNS incidents at EU waters.

^a See [Table 2](#page-2-0) for more information on GESAMP classification.

b D: dissolver; S: sinker F: floater; E: evaporator, DE dissolver/evaporator; SD: sinker/dissolver; FD: floater/dissolver; FE: floater/evaporator; FED: floater/evaporator/ dissolver.

^c According to the list of the 100 HNS most transported in European Atlantic waters elaborated by [HASREP \(2005\)](#page-7-0).

By using these four key risk criteria, this weight-of-evidence approach takes into consideration the probability (i.e. likelihood) of a spill in European Atlantic waters and the severity of exposure associated with the physico-chemical properties and toxicity of the HNS to marine life. The methodology developed in the present study will provide a tool to assist relevant bodies when developing contingency plans dealing with accidental HNS spills.

2.1. HNS volumes transported in European waters

The probability of occurrence of a spill in European Atlantic waters is assumed to be dependent on both the tonnage and frequency of HNS transported by sea. A European-funded project monitored the tonnage of chemicals transported in either bulk or packaged form and identified a list of 100 HNS chemicals most transported in European Atlantic waters [\(HASREP, 2005\)](#page-7-0). This list of chemicals most transported by sea in terms of tonnage was used as a starting point for the prioritization procedure. At present, the paucity of information available on shipping frequencies limits the ability of including this within this risk assessment.

2.2. Reported HNS incidents in European waters

Several sources of information were reviewed to assemble the data on HNS shipping incidents in European waters such as [IMO](#page-7-0) [\(2002\), Cedre spill guide, Mamaca et al. \(2009\) and HELCOM](#page-7-0) [\(2003\)](#page-7-0). Some of the incidents were well documented, whereas most have not been appropriately reviewed. Past incidents are not only essential references of what happened some time ago, they are also, when properly reported upon, first hand sources of information on what may happen again and what could better mitigate subsequent and resulting consequences. Eighteen of the most important incidents that have occurred recently in European waters were selected for closer examination. For each one of the 18 incidents, information based on the HNS transported/spilled, impacts on the marine environment, HNS physico-chemical properties and traffic ranking were compiled ([Table 1](#page-1-0)).

2.3. HNS physico-chemical properties

HNS spilled into the sea may behave differently depending on their physico-chemical properties and local marine environmental conditions. The European Behaviour Classification System [\(Bonn](#page-6-0) [Agreement, 1994\)](#page-6-0) has been developed in order to classify chemicals according to their physico-chemical behaviours when spilled into the sea. The main principle of the system is the characterization of spilled loose chemicals as: (i) gases (G) : (ii) evaporators (E) : (iii) floaters (F) ; (iv) dissolvers (D) ; (v) sinkers (S) and (vi) the various combinations of these, that is: (vii) gases/dissolvers (GD); (viii) evaporators/dissolvers (ED); (ix) floaters/evaporators (FE); (x) floaters/evaporators/dissolvers (FED); (xi) floaters/dissolvers (FD); (xii) dissolvers/evaporators (DE) and (xiii) sinkers/dissolvers (SD). The European Behaviour Classification system for evaluating the short-term behaviours of chemicals spilled at sea was indirectly used in the selection of priority HNS. Dissolvers and sinkers have the highest potential ecological impacts on the marine environment after spillage as they will disperse easily and are, hence, bioavailable for aquatic organisms, both in the water column and the sediments. Unlike dissolvers and sinkers, floaters drift with the wind and/or currents and can reach sensitive areas along the coast impacting mainly marine mammals, birds and benthic life forms. The main hazards produced by gases and evaporators are air toxicity and usually represent a low threat to the marine environment except if they also dissolve in water. Considering the likely impact on the marine environment produced by dissolvers, floaters, and sinkers, the priority HNS list will cover mainly these behaviour categories.

2.4. Toxicity to marine organisms

The procedure to identify priority HNS to the marine environment should consider chemicals that have a combination of harmful characteristics to marine organisms. These include moderate to high toxicity in combination with bioaccumulation, persistence potential and/or long term carcinogenic effects.

- Toxicity. In order to rate the hazard posed by chemicals to aquatic organisms, the most common solution is still the use of acute toxicity test data. However, both acute and chronic ecotoxicological data should be taken into account in the selection of priority HNS if both LC50 and NOEC/LOEC are available.
- Bioaccumulation. The bio-concentration factor, BCF, is usually used as an indicator for bioaccumulation in conjugation with the *n*-octanol/water partition coefficient and $log K_{ow}$ ([Höfer,](#page-7-0) [1999](#page-7-0)).
- Persistence. The available information on persistence of HNS in the marine environment is dominated by data on ''ready biodegradability". There are a wide range of tests, based on $O₂$

Table 2

Bioaccumulation, biodegradation and toxicity GESAMP guidelines for the categorization of HNS (adapted from [GESAMP \(2002\)\)](#page-7-0).

consumption, $CO₂$ evolution or dissolved organic carbon removal, that are designed to select rapidly biodegrading substances [\(Höfer, 1999\)](#page-7-0).

- Carcinogenic effects. Whilst information available concerning HNS carcinogenic effects for marine organisms is scarce, carcinogens possess the potential for irreversible effects in them. For this reason, the carcinogenic impact on mammals, for which a large set of information is available, will be considered in the selection of priority HNS.

HNS that combine properties of moderate to high toxicity, bioaccumulation potential, persistence and/or long term carcinogenic effects represent the highest levels of hazard to the marine environment after a spill. In the present work, the revised hazard evaluation procedures elaborated by GESAMP – the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection – ([GESAMP, 2002; IMO, 2008\)](#page-7-0) was applied to numerically score the 100 most transported HNS in EU Atlantic waters defined in Section [2.1](#page-2-0) above. The GESAMP bioaccumulation, biodegradation, toxicity and carcinogenic effects criteria ([GESAMP, 2002](#page-7-0)) will be used as a tool for assessing the risk posed by the 100 HNS and selecting the priority HNS [\(Table 2\)](#page-2-0).

3. Cut-off values for the prioritization process

In order to priorities HNS that pose the major risk for the marine environment, we propose the use of a cut-off values approach considering the 100 most transported HNS in EU Atlantic waters. Those compounds falling into one of the following categories were considered a priority:

(1)

- Bioaccumulation rank of at least 2 (low potential to bioaccumulate).
- Biodegradation of ''Not Readily biodegradable".
- Acute toxicity rank of at least 3 (moderately toxic) and/or chronic toxicity rank of at least 2 (moderately toxic).

(2)

- Bioaccumulation rank of at least 3 (moderate potential to bioaccumulate).
- Biodegradation of ''Readily biodegradable".
- Acute toxicity rank of at least 4 (highly toxic) and/or chronic toxicity rank of at least 2.

(3)

- Bioaccumulation rank of at least 2.
- Biodegradation of ''Readily biodegradable".
- Acute toxicity rank of at least 3 and/or chronic toxicity rank of at least 2.
- Involved in previous incidents.

Also HNS that have long term carcinogenic impacts on mammals were considered for integration into the list of priority HNS.

Based on this approach, the list of priority selected HNS is given in Table 3.

Table 3

Priority list of HNS in EU Atlantic waters.

^a R: readily biodegradable; NR: not readily biodegradable.

b C: carcinogenic; NC: no carcinogenic or no data available.

^c D: dissolver; S: sinker F: floater; E: evaporator, DE dissolver/evaporator; SD: sinker/dissolver; FD: floater/dissolver; FE: FED: floater/evaporator; floater/evaporator/ dissolver.

^d According to the list of the 100 HNS most transported in European Atlantic waters elaborated by [HASREP \(2005\)](#page-7-0).

Table 4

Acute and chronic toxicity of the priority HNS to aquatic organisms^{[a,b](#page-6-0)}.

(continued on next page)

Table 4 (continued)

Table 4 (continued)

NR: not reported.

b LC50: median effective lethal concentration; LOEC: lowest observed effect concentration; NOEC: no observed effect concentration; MATC: maximum acceptable toxicant concentration.

Alkyl (C5–C8, C9) benzenes.

4. Review of acute and chronic toxicological data for the priority HNS in European Atlantic waters

The main objective of this review was to gather toxicological information available for the 23 priority HNS, selected in Section [3](#page-3-0) of this study. For this, a dataset was created with acute and chronic toxicity data for marine species representative of different taxonomic groups, mainly crustaceans and fish [\(Table 4\)](#page-4-0). If no data were available for acute or chronic toxicity in marine organisms, data available for freshwater organisms is provided. The major sources of information, here referred to, were peer-reviewed literature and technical reports obtained using on-line databases. Standard terms used included: median effective (lethal) concentration E(L)C50, lowest observed effect concentration (LOEC), no observed effect concentration (NOEC) and Maximum Acceptable Toxicant Concentration (MATC). This dataset has the merit of assembling a brief and concise profile of the different priority HNS that can assist relevant bodies to predict HNS adverse effects in the marine environment.

As pointed out in [Table 4](#page-4-0), marine chronic toxicity data is lacking for most of the priority HNS, and for some of them – nonene, alkyl (C5–C8, C9) benzenes, butyl acrylate, di(2-ethylhexyl)adipate, heptane and cresol – only freshwater acute toxicity data are available. Therefore, studies to gather toxicological data for these priority HNS on the marine biota should be undertaken.

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