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# Fate, behaviour and weathering of priority HNS in the marine environment: An online tool

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A R T I C L E I N F O

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A B S T R A C T

Literature data and data obtained with modelling tools were compiled to derive the physicochemical behaviour of 24 priority Hazardous and Noxious Substances (HNS), as a proxy to improve environmental, public health and political issues in relation to HNS spills. Parameters that rule the HNS behaviour in water and those that determine their distribution and persistence in the environment, such as fugacity, physicochemical degradation, biodegradation, bioaccumulation/biotransformation and aquatic toxicity, were selected. Data systematized and produced in the frame of the Arcopol Platform project was made available through a public database (http://www.ciimar.up.pt/hns/substances.php). This tool is expected to assist stakeholders involved in HNS spills preparedness and response, policy makers and legislators, as well as to contribute to a current picture of the scientific knowledge on the fate, behaviour, weathering and toxicity of priority HNS, being essential to support future improvements in maritime safety and coastal pollution response before, during and after spill incidents.



## 1. Introduction

World maritime transport of Hazardous and Noxious Substances (HNS) has increased significantly in the last few decades, including transportation to, from and within European waters, due to the continuous development of the chemical industry, the need to supply raw materials to this industry and transport high volumes of products from the industries to the customers (HASREP, 2005; EMSA, 2007). The constant growth in the volume of chemicals that are transported by sea increases the risk of accidental spills (Sole et al., 2008a,b).

HNS are defined as any substance other than oil, which if introduced into the marine environment are likely to harm living resources and other marine life, create hazards to human health, damage amenities and/or interfere with other legitimate uses of the sea (IMO, 2000). The severity of the impact depends on the properties of the hazardous substances (e.g. physicochemical and toxicological properties), among other variables (Neuparth et al., 2011; Cunha et al., 2014, 2015).

The increase of HNS maritime transport, the serious threat posed by shipping-related accidental spills and consequently the need for an effective and safe response to HNS spills, have led environmental managers, international and national authorities, and the scientific community to focus their attention on responsiveness and preparedness to HNS spills. As a result, the Protocol on Preparedness, Response and Co-operation to Pollution Incidents by HNS (OPRC-HNS Protocol), aiming at improving the response to major HNS incidents, was adopted by the International Maritime Organization (IMO, 2000) and entered into force in 2007. Despite this protocol, much remains to be done concerning preparedness and response to HNS spills (Neuparth et al., 2012). According to IMO (2009), only 3 of the 12 EU members that ratified the OPRC–HNS protocol reported to have specialized capacity to respond to HNS spills.

Although the probability of shipping incidents involving HNS to occur is considered low, because of the high safety standards, it does in fact exist (Neuparth et al., 2011). The tanker *Anna Broere* which sank in the Netherlands in 1988 released 200 t of acrylonitrile, and the *Ievoli Sun* which sank in the English Channel in 2000 released 1000 t of styrene (Neuparth et al., 2011, 2013). Later (in 2007), the *MSC Napoli* - towed to Lyme Bay, Devon (UK), which carried >1600 t of chemical products (e.g. nonylphenol) classified by IMO as dangerous goods, raised awareness of the potential ecological risk of HNS spills (Neuparth et al., 2011). Several other large shipping incidents caused immediate and potential long-term adverse effects on marine habitats and ecosystems (Neuparth et al., 2012; Cunha et al., 2015). Information on HNS incidents has been compiled in an online database hosted at www.ciimar.up.pt/hns.

It is well recognized that attempts to better understand the risk of HNS spills in a meaningful way is not a simple issue considering the

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lack of reliable information available (Neuparth et al., 2013). Moreover, an understanding of the potential ecological hazards and risks involved in HNS spills is less well recognized and understood than those involving oil pollution. While most oils are immiscible with seawater and float on the sea surface, HNS chemicals are considered a threat because exhibit a wider range of behaviours once released into the environmental compartments and toxicities to marine organisms (Neuparth et al., 2011). In fact, the HNS that have bioaccumulation potential, moderate to high toxicity, properties of persistence and/or long term carcinogenic effects represent the highest hazard to the marine environment after a spill (Neuparth et al., 2011).

The behaviour of HNS spilled into the sea depends on their physicochemical properties (e.g. volatility, density and solubility) and local marine environmental conditions (GESAMP, 2002; EMSA, 2007; Bonn Agreement, 2015). The European Behaviour Classification System (Bonn Agreement, 2015) has been developed in order to classify chemicals according to their physicochemical behaviours when spilled into the sea. The main principle of the system is the characterization of spilled chemicals as: gases (G), evaporators (E), floaters (F), dissolvers (D), sinkers (S) and the various combinations of these (GD, ED, FE, FED, FD, DE and SD) (EMSA, 2007; Bonn Agreement, 2015). Classifying the chemicals into different subcategories leads to a need for a relatively low number of generally applicable response options in a spill event (Bonn Agreement, 2015).

Therefore, values of solubility, density and vapour pressure allow to determine the behaviour of groups of chemicals, and the range of these values for each group can be found at EMSA (2007). For example, sinkers (S) comprises all products which are denser than seawater and that are not soluble (solubility <0.1%). On the other hand, FED are floating substances which slowly evaporate (0.3–3 kPa) and also dissolve (0.1–5%). FED will completely disappear in time. Based on information on the short-term behaviour of the spilled compound, it is possible to define a detection and monitoring plan well adapted to the geographical location, particular sea and atmospheric conditions, hydrodynamics, and characteristics of the water column and sea bottom compartments (Cedre, 2009).

The selection of the appropriate response to an HNS incident requires detailed knowledge on the physicochemical and toxicological properties of the substance involved (Cedre, 2009). The need to deepen knowledge on several aspects related to preparedness and response to HNS spills has been emphasised (Cunha et al., 2015). Even though advances in HNS modelling tools have been achieved (Aprin et al., 2014a,b), one of the major gaps identified is the limited knowledge on HNS behaviour at sea in real conditions; this gap should be approached through experiments in the laboratory and at the pilot level involving priority HNS. Also, data on the hazards of HNS for humans and marine life are essential for the decision-making process and selection of an appropriate response. The importance of evaluating the physicochemical and toxicological properties of a contaminant for remediating environments affected by chemical incidents has recently been addressed (Wyke et al., 2014). For this reason, the fate, behaviour and weathering of priority HNS in seawater and shoreline environments were addressed in the present work, focusing on the environmental and public health impacts. To this end, the information available (e.g. physicochemical and toxicological data) in the literature and online databases for 24 priority HNS, initially selected from the HASREP (2005) list of the 100 HNS most transported in European Atlantic waters, was gathered and made available online for public use. However, given that for several priority HNS only limited information was available, mathematical tools were used to derive the physicochemical behaviour. This prioritization is essential because in practice it is unrealistic to consider a full scientific ecotoxicological data survey for all chemicals due to their high number, diversity, and consequently their particular properties (Neuparth et al., 2011). Nonetheless, in a near future, this database will evolve to incorporate more priority HNS, beyond the 24 selected presently, as well as more detailed (eco)toxicological endpoints as they become available.

## 2. Material and methods

### 2.1. Priority HNS

The HNS selected were identified by their name, CAS-RN number, behaviour in seawater (GESAMP, 2014) and traffic ranking (HASREP, 2005) (Table 1). Information on previous spill incidents occurred at the sea worldwide involving these priority HNS can be found in another online database (http://www.ciimar.up.pt/hns/incidents.php) elaborated by CIIMAR (Cunha et al., 2015).

### 2.2. Parameters analysed

Parameters analysed were chosen based on their contribution to characterise the 24 priority HNS in terms of fate, behaviour and weathering in water. They were various physicochemical properties and parameters related to bioaccumulation and biotransformation potential, acute and chronic toxicity to aquatic organisms, mammalian and human health. The values for the parameters were searched in the bibliography (e.g. GESAMP, 2014) and in several online databases (see the references section) and compiled. Those values not available from experimental measurements were estimated using the Estimation Programs Interface (EPI) Suite™, developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC).

The Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) preferably uses appropriate experimental data. The available information is considered as a whole by the experts and ratings are given on the basis of the total weight of evidence, in order to evaluate the hazard of the substances. However, where experimental data on bioaccumulation or acute aquatic toxicity are not available, generally accepted estimation techniques may be applied on a case

**Table 1**
Priority HNS selected and their CAS-RN number, behaviour and traffic ranking.

| HNS selected | CAS-RN number | Behaviour in seawater[a] | Traffic ranking[b] |
|---|---|---|---|
| Tetrachloroethylene | 127-18-4 | S | 99 |
| Decanoic acid | 334-48-5 | Fp | 97 |
| *m*-Cresol | 108-39-4 | SD | 96 |
| 1-Dodecanol | 112-53-8 | Fp | 86 |
| Heptane | 142-82-5 | E | 85 |
| Hexane | 110-54-3 | E | 74 |
| Trichloroethene | 79-01-6 | SD | 73 |
| Di (2-ethylhexyl) adipate | 103-23-1 | Fp | 65 |
| Butyl acrylate | 141-32-2 | FED | 57 |
| 1-Nonanol | 143-08-8 | Fp | 54 |
| Octane | 111-65-9 | FE | 53 |
| Nonylphenol | 104-40-5 | Fp | –* |
| Cyclohexylbenzene | 827-52-1 | F | 43 |
| Pentylbenzene | 538-68-1 | F | 43 |
| Isononanol | 27458-94-2 | Fp | 37 |
| Nitrobenzene | 98-95-3 | SD | 27 |
| Acrylonitrile | 107-13-1 | DE | 25 |
| Aniline | 62-53-3 | FD | 19 |
| 1-Nonene | 124-11-8 | FE | 17** |
| Toluene | 108-88-3 | E | 16 |
| Cyclohexane | 110-82-7 | E | 14 |
| *m*-Xylene | 108-38-3 | FE | 8 |
| Styrene | 100-42-5 | FE | 7 |
| Benzene | 71-43-2 | E | 3 |

*Traffic ranking = 48 for the dissolver Nonylphenol poly(4–12)ethoxylates (one of the 100 harmful HNS most transported in European Atlantic waters according to HASREP (2005)); ** traffic ranking for Nonene (all isomers).

[a] D: dissolver; E: evaporator; F: floater; S: sinker; DE: dissolver/evaporator; FD: floater/dissolver; FE: floater/evaporator; FED: floater/evaporator/dissolver; Fp: persistent floater; SD: sinker/dissolver (according to GESAMP (2014)).

[b] According to HASREP (2005).