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

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ABSTRACT

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).

by case basis. Only validated or otherwise reliable Quantitative Structure Activity Relationships were used. We mean by validated and reliable QSAR, those relationships based on scientific data obtained experimentally in compliance to OECD Principles of Good Laboratory Practice for that chemical group in question (GESAMP, 2014). The results obtained through the models were analysed by the authors, and observed how they congruently correspond to the expected values, as a function of the variables known experimentally, and by comparing one compound to others, and to other compounds not under the scope of the paper, but with a similar chemistry. Whenever possible, the values of environmental conditions commonly observed in the open sea conditions (depth, wind speed, currents) were entered in the model, as it was the case of the Water Volatilization model used to determine the volatilization half-life of the compounds.

The information collected was inserted into a MySQL (v.5) database. It is possible to use queries to search by name of the HNS and behaviour at sea. The database is hosted at CIIMAR's (Interdisciplinary Centre of Marine and Environmental Research) servers and is available worldwide on our website (http://www.ciimar.up.pt/hns/substances.php) programmed in HTML with PHP scripting. The database can also be accessed directly from the Arcopol Platform website.

2.2.1. Physicochemical properties

Most of the physicochemical properties values (physical state, behaviour, relative molecular mass, density, vapour pressure, water solubility, dynamic viscosity, melting point and boiling point) were collected from the literature and online databases. Some volatilization half-life values were also estimated by the Water Volatilization model of EPI Suite. The model is based upon an adaptation of the recommended method by Thomas (1990). Since the model was developed for lakes, estimates of volatilization half-lives were performed adjusting lake environmental properties to values that may be observed in open sea: depth was set to 100 m, water current to 0.25 m s^{-1} and wind velocity to 10 m s^{-1}. These values were also defined to cover a wide range of possible scenarios because it is known that many incidents of greatest concern occur in shallower inshore waters.

Fugacity and persistence values were determined using the Level III fugacity model (EPI suite) whose methodology and programming approach were developed by Mackay and co-workers (Mackay, 1991; Mackay et al., 1996a, 1996b). The default values entered in the model were as follow: the environmental emission rates entered were 0 kg/h for air, 1000 kg/h for water and 0 kg/h for soil. The half-life factors entered in the model were 1 for water and 9 for sediment.

2.2.2. Physicochemical degradation and biodegradation

Atmospheric oxidation and ozone reaction, the two parameters selected to define physicochemical degradation, were estimated by Atmospheric Oxidation Program (AOPWIN) at EPI suite. Detailed information on model used can be found in Atkinson and Carter (1984).

The biodegradation rate was collected in GESAMP (2014) and analysed taking into account the GESAMP criteria (GESAMP, 2002).

Values of aerobic biodegradation probability were obtained using the MITI (Ministry of International Trade and Industry) model derived through non-linear regression based on Tunkel et al. (2000).

Biowin 3 and 4 models were used to estimate the time required for "complete" primary and ultimate biodegradation. These models are based upon a survey of 17 biodegradation experts conducted by EPA, in which the experts were asked to evaluate 200 compounds in terms of the time required to achieve ultimate and primary biodegradation in a typical or "evaluative" aquatic environment (Boethling et al., 1994). In a second survey, each expert rated the ultimate and primary biodegradation of each compound on a scale of 1 to 5 (see Table 8 in the supplementary material). Ratings are only semi-quantitative and are not half-lives. Model domain, accuracy and validation are further discussed in Boethling et al. (1994).

Hydrocarbon biodegradation half-life was predicted with BioHCwin model specifically developed for the biodegradation half-life prediction of petroleum hydrocarbons. The methodology used is described in Howard et al. (2005).

Biowin7 model was used to estimate the probability of fast biodegradation under methanogenic anaerobic conditions; specifically, under the conditions of the "serum bottle" anaerobic biodegradation screening test. A fast degradation is defined as predicted probability >0.5. Model domain, accuracy and validation are explained thoroughly by Meylan et al. (2007).

2.2.3. Bioaccumulation/biotransformation

Values of biotransformation half-life, octanol/water partition coefficient (log Kow), and adsorption coefficient (log Koc) were collected from the literature. The bioaccumulation rates were collected in GESAMP (2014) and analysed taking into account the GESAMP's rating scheme (GESAMP, 2002). On the other hand, the BCF values were estimated with a BSFBAF model (EPI Suite). More information on the model can be found in Meylan et al. (1999).

2.2.4. Acute and chronic toxicity to aquatic organisms and mammalian/human health effects

Acute and chronic aquatic toxicity values and mammalian/human health effects (acute: oral, percutaneous, inhalation, skin irritation/corrosion and eye irritation/corrosion toxicity scores; chronic: mutagenicity, reprotoxicity, sensitizing, aspiration hazard, target organ systemic toxicity, lung injury, neurotoxicity and immunotoxicity) were obtained from GESAMP's hazard list (GESAMP, 2014) and analysed according to their rating schemes (GESAMP, 2002).

Toxicity score for humans was initially screened based upon the acute toxicity, with particular emphasis on inhalation exposure, as this is considered the major route for widespread exposure of the public. Severity score (Harold et al., 2014) was estimated as a measure of acute human health effects. It was calculated as the product of the scores for toxicity (GESAMP list, 2014) and behaviour characteristics (SEBC, 1991).

IARC (International Agency for Research on Cancer) classification was used to score carcinogenic effects, although the scale was reversed and adapted to a score scheme similar to GESAMP's, also with 5 levels.

3. Results

3.1. Physicochemical properties

The physicochemical properties of the 24 HNS studied are presented in Table 2. All the priority HNS selected are in the liquid state at 14 °C and at normal ambient pressure, with the exception of 1-dodecanol and decanoic acid which are in the solid state under such conditions.

The water solubility values shown (Table 2) refer to freshwater, since values for saltwater are not ready available for most of the HNS. The temperature considered was 20 °C.

The viscosity values presented in this study (Table 2) were measured at 20 °C.

In relation to fugacity and persistence determined, most of the compounds studied tend to be present in the water compartment at much higher concentration than in the others compartments (air, soil and sediment), when the compound is emitted directly in the water (Table 2). An exception is nonylphenol, a persistent floater, which tends to exist in water and sediments in similar proportions. Other floaters (pentylbenzene, cyclohexylbenzene and di-2-ethylhexyl adipate) also tend to be present in the sediment to a considerable extent. As expected, the evaporator benzene tends to be present at high concentration in the air compartment under steady state conditions.

Table 2
Physicochemical properties of the 24 priority HNS studied.

HNS name	Behaviour (GESAMP, 2014)[a,b]	Relative molecular mass[b]	Density (kg/L)[b]	Vapour pressure (kPa)[b]	Water solubility (mg/L)[b]	Dynamic viscosity (mPa s)[b,c]	Melting point (°C)[b]	Boiling point (°C)[b]	Volatilization half-life (days)[d]	Fugacity (%)[d,e]				Persistence (days)[d]
										Air	Water	Soil	Sediment	
Benzene	E	78.1	0.88	12.64	1790	0.60	5.5	80.1	23.3	15.10	84.10	0.04	0.76	11.9
Cyclohexane	E	84.2	0.78	12.92	55	0.89	6.6	80.7	23.9	7.57	91.70	0.00	0.69	8.4
Hexane	E	86.2	0.65	20.13	10	0.30	−95.3	68.7	24.2	8.99	90.05	0.00	0.54	6.8
Toluene	E	92.1	0.86	3.79	526	0.56	−94.9	110.6	25.2	8.26	90.60	0.03	0.97	8.6
Heptane	E	100.2	0.68	6.13	3	0.39	−90.6	98.5	26.8	7.78	91.40	0.00	0.80	6.7
Styrene	FE	104.2	0.91	0.85	310	0.70	−31.0	145.0	27.1	1.01	97.20	0.01	1.74	8.2
m-Xylene	FE	106.2	0.87	1.11	161	0.62	−47.8	139.1	27.0	3.13	95.40	0.01	1.48	8.2
1-Nonene	FE	126.2	0.74	0.72	1.12	0.64	−81.3	146.9	58.1	1.78	95.50	0.00	2.75	8.1
Octane	FE	114.2	0.70	1.88	1	0.51	−56.8	125.7	27.8	6.82	92.00	0.00	1.21	6.7
Aniline	FD	93.1	1.02	0.09	36,000	3.85	−6.0	184.2	707.4	0.01	99.50	0.01	0.47	14.2
Pentylbenzene	F	148.2	0.86	0.06	3	1.49	−75.0	205.4	4.8	5.70	86.80	0.04	7.46	8.9
Cyclohexylbenzene	F	160.3	0.94	0.00	5	2.38	7.3	240.1	5.2	3.66	83.20	0.07	13.10	9.8
Nonylphenol	Fp	220.4	0.95	0.00	7	–	42.0	295.0	1966.0	0.00	48.80	0.08	51.20	26.8
Isononanol	Fp	144.3	0.82	0.00	460	13.20	−75.0	208.5	73.1	0.74	98.80	0.05	0.42	12.8
1-Nonanol	Fp	144.3	0.83	0.00	140	14.30	−5.0	213.3	86.6	0.58	99.00	0.03	0.41	9.1
Di-2-ethylhexyl adipate	Fp	370.6	0.92	0.00	1	13.70	−67.8	417.0	6384.0	0.00	91.70	0.01	8.31	10.4
1-Dodecanol	Fp	186.3	0.83	0.00	4	–	24.0	259.0	123.4	0.34	97.90	0.05	1.67	13.6
Decanoic acid	Fp	172.3	0.89	0.00	62	–	31.9	268.7	1476.0	0.03	99.40	0.03	0.49	9.6
Butyl acrylate	FED	128.2	0.89	0.73	2000	0.90	−64.6	145.0	5.1	3.05	96.60	0.02	0.29	7.3
Nitrobenzene	SD	123.1	1.20	0.03	2090	2.03	5.7	210.8	94.9	1.97	96.80	0.23	1.01	13.7
m-Cresol	SD	108.1	1.03	0.01	22,700	12.90	11.8	202.2	1762.0	0.00	98.70	0.01	1.29	14.4
Tetrachloroethylene	S	165.8	1.62	2.47	206	0.89	−22.3	121.3	33.7	19.00	80.50	0.01	0.54	13.1
Trichloroethene	SD	131.4	1.46	9.20	1280	0.55	−84.7	87.2	30.0	12.90	86.70	0.01	0.42	11.4
Acrylonitrile	DE	53.1	0.80	14.53	74,500	0.34	−83.5	77.3	26.5	3.99	95.70	0.05	0.21	11.4

[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.

[b] Values collected from the literature and public databases e.g. PubChem.

[c] "–" corresponds to values not found in the literature or in available databases.

[d] Values estimated with models of the EPI suite™.

[e] In the present study, only emissions in water were considered.

3.2. Physicochemical degradation and biodegradation

Values of physicochemical degradation (atmospheric oxidation) and biodegradation obtained for the priority HNS studied are presented in Table 3. Only 6 of the 24 priority HNS react with ozone: styrene (0.5 days), 1-nonene (1 day), butyl acrylate (6.5 days), acrylonitrile (131 days), trichloroethene (2239 days) and tetrachloroethylene (15,660 days).

3.3. Bioaccumulation/biotransformation

Values of biotransformation half-life, octanol/water partition coefficient (log Kow), bioconcentration factor (BCF), bioaccumulation rate (GESAMP, 2014) and adsorption coefficient (log Koc) for the 24 HNS considered are presented in Table 4. According to Chiou (2002), tissue BCFs > 1000 (e.g. octane) are considered high, under 250 (e.g. acrylonitrile) low, while from 250 to 1000 (e.g. pentylbenzene) are classified as moderate.

3.4. Acute and chronic toxicity to aquatic organisms and mammalian/human health effects

Acute and chronic aquatic toxicity values and mammalian/human health effects for the priority HNS studied were collected in Tables 5 and 6.

4. Discussion

4.1. Physicochemical properties

An important point to refer regarding physicochemical parameter is that the temperature considered for water solubility (20 °C) does not correspond to the real average seawater temperature in the Atlantic area, nor that of many worldwide locations with high HNS traffic, although it is a reasonable temperature for comparison of relative values of the various HNS. It is a normal temperature commonly used as a standard for testing and documentation of chemical and physical processes used by the US National Institute of Standards and Technology (NIST), and most parameters were measured at these established normal temperature. Therefore, it is also essential to obtain estimated and experimental values at real temperatures for the parameters analysed. Some adjustments must be done for modelling real situations since it is known that most spills occur in extreme adverse sea conditions e.g. during the winter at temperate zones or under tropical storms. Accordingly, the effect of temperature on e.g. the solubility, viscosity, density, vapour pressure of the 24 HNS should be modelled in order to get values closer to field situations. It is known that the temperature influences the physicochemical parameters of chemicals. For instance, acrylonitrile density decreases with increasing temperature while its solubility and vapour pressure increase (INEOS, 2007). Thus, it should be taken in consideration that the physicochemical properties often derived at a standard temperature of 20 °C, may affect estimations, for example, in situations in which seawater temperature is low (e.g. 5 °C) as it is the case of sub-Arctic or sub-Antarctic waters. Some chemicals may indeed change state from liquid to solid, modifying their behaviour and the strategy to monitor, detect and recover it from water. This is the case of *m*-cresol, cyclohexane, benzene, nitrobenzene and cyclohexylbenzene, whose melting temperature follows between 5 and 20 °C. Salinity is another parameter that often should be tuned, given that some available measurements were performed in freshwater and derived for seawater. Many values were obtained in a scenario assuming low depth, still water, no wind or turbulence on the air above, which often does not simulate closely the conditions of marine spills. Differences observed between the volatilization half-life values collected from the literature

Table 3
Results of physicochemical degradation (atmospheric oxidation) and biodegradation obtained for the priority HNS studied.

		Biodegradation					
HNS name	Atmospheric oxidation (h)[a]	Biodegradation rate (GESAMP, 2014)[b,c]	Aerobic biodegradation probability[a]	Primary aerobic biodegradation half-life[a,d]	Ultimate aerobic biodegradation half-life[a,d]	Hydrocarbon biodegradation half-life (days)[a,e]	Anaerobic biodegradation probability[a]
Benzene	65.8	R	0.73	3.39 (days-weeks)	2.44 (weeks-months)	4.5	0.00
Cyclohexane	15.1	NR	0.82	3.73 (days-weeks)	3.01 (weeks)	55.4	0.12
Hexane	23.5	R	0.86	3.99 (days)	3.31 (days-weeks)	4.7	0.46
Toluene	24.6	R	0.68	3.65 (days-weeks)	2.94 (weeks)	4.5	0.21
Heptane	18.7	R	0.86	3.97 (days)	3.28 (days-weeks)	5.5	0.49
Styrene	4.6	R	0.55	3.70 (days-weeks)	2.99 (weeks)	3.9	0.35
m-Xylene	9.5	NR	0.64	3.56 (days-weeks)	2.81 (weeks)	4.4	0.29
1-Nonene	3.7	–	0.37	3.93 (days)	3.10 (weeks)	5.9	0.37
Octane	15.5	R	0.86	4.22 (days)	3.54 (days-weeks)	6.4	0.20
Aniline	1.2	R	0.31	3.61 (days-weeks)	2.88 (weeks)	–	0.30
Pentylbenzene	12.7	NR	0.51	3.84 (days)	3.12 (weeks)	7.9	0.14
Cyclohexylbenzene	8.8	–	0.49	3.55 (days-weeks)	2.79 (weeks)	46.2	0.10
Nonylphenol	2.5	NR	0.51	3.77 (days)	2.99 (weeks)	–	0.20
Isononanol	9.2	NR	0.87	3.77 (days)	3.04 (weeks)	–	0.80
1-Nonanol	9.2	NR	0.94	4.04 (days)	3.34 (days-weeks)	–	0.78
Di-2-ethylhexyl adipate	5.1	R	0.93	4.31 (hours-days)	3.26 (days-weeks)	–	0.26
1-Dodecanol	7.1	R	0.95	3.98 (days)	3.25 (weeks)	–	0.86
Decanoic acid	11.5	R	0.90	4.25 (hours-days)	3.48 (days-weeks)	–	0.83
Butyl acrylate	9.3	R	0.93	4.16 (days)	3.35 (days-weeks)	–	0.47
Nitrobenzene	526.7	R	0.06	3.57 (days-weeks)	2.78 (weeks)	–	0.36
m-Cresol	1.5	R	0.66	3.66 (days-weeks)	2.94 (weeks)	–	0.16
Tetrachloroethylene	599.8	NR	0.01	3.21 (weeks)	2.14 (months)	–	0.78
Trichloroethene	154.5	NR	0.04	3.36 (days-weeks)	2.39 (weeks-month)	–	0.72
Acrylonitrile	30.5	NR	0.79	3.71 (days-weeks)	3.00 (weeks)	–	0.62

[a] Values estimated with models of the EPI suite™.
[b] Results obtained from the literature.
[c] GESAMP criteria consider substances to be "readily biodegradable" (R) if, in 28-day biodegradation studies, the following levels of degradation are achieved: in tests based upon dissolved organic carbon (DOC) die-away: ≥70%; or in tests based upon oxygen depletion or carbon dioxide generation: ≥60% of the theoretical maxima; or where only COD and BOD5 data are available, the ratio of BOD$_5$/COD ≥0.5; or where other convincing scientific evidence is available to demonstrate that the substance can be degraded (biotically and/or abiotically) in the aquatic environment to a level of >70% within a 28-day period. Otherwise they are "not readily biodegradable" (NR) (GESAMP, 2002). No result was found for cyclohexylbenzene and 1-nonene.
[d] See Table 8 in the supplementary material for more information on the rating reported by Boethling et al. (1994).
[e] "–" corresponds to values not found.

Table 4
Results of bioaccumulation/biotransformation obtained for the priority HNS studied.

	Bioaccumulation/biotransformation				
HNS name	Biotransformation half-life (days)[a]	Partition coefficient (log Kow)[a]	BCF[b]	Bioaccumulation rate (GESAMP, 2014)[c]	Adsorption coefficient (log Koc)[a]
Benzene	1.54	2.13	14.8	1	1.92
Cyclohexane	0.76	3.44	70.0	3	2.57
Hexane	1.15	3.90	307.1	3	2.75
Toluene	0.29	2.73	37.8	2	2.27
Heptane	1.92	4.66	681.8	4	3.21
Styrene	0.50	2.95	64.6	3	2.95
m-Xylene	0.99	3.20	119.2	3	2.53
1-Nonene	2.77	5.15	1843	4	4.47
Octane	2.92	5.18	1086.0	5	3.57
Aniline	0.03	0.90	1.6	0	1.62
Pentylbenzene	1.21	4.90	473.5	4	3.84
Cyclohexylbenzene	1.07	4.81	416.8	–	3.94
Nonylphenol	1.33	5.76	221.0	4	4.43
Isononanol	0.36	3.50	103.3	3	2.11
1-Nonanol	0.46	3.77	148.1	3	2.22
Di-2-ethylhexyl adipate	0.31	8.10	5.6	2	4.92
1-Dodecanol	1.11	5.13	441.5	2	3.17
Decanoic acid	1.35	4.09	394.8	4	2.20
Butyl acrylate	0.06	2.36	10.8	2	1.86
Nitrobenzene	0.10	1.85	6.4	1	2.15
m-Cresol	0.11	1.96	7.7	2	2.33
Tetrachloroethylene	3.36	3.40	46.0	2	2.46
Trichloroethene	1.12	2.42	23.7	2	1.94
Acrylonitrile	0.07	0.25	1.0	2	1.19

[a] Values collected from the literature and public databases e.g. PubChem.
[b] Values estimated with one model of the EPI suite™.
[c] See Table 9 in the supplementary material for more information on GESAMP classification. No result was found for cyclohexylbenzene.

Table 5
Results of aquatic toxicity (GESAMP rate), acute and chronic mammalian/human health effects obtained for the priority HNS studied.

	Aquatic toxicity (GESAMP, 2014)		Acute mammalian/human health effects (scores)							Chronic mammalian/human health effects (scores)
HNS name	Acute toxicity[a]	Chronic toxicity[b]	Oral toxicity (GESAMP, 2014)[c]	Percutaneous toxicity (GESAMP, 2014)[c]	Inhalation toxicity (GESAMP, 2014)[c]	Skin irritation/corrosion toxicity (GESAMP, 2014)[d]	Eye irritation/corrosion toxicity (GESAMP, 2014)[e]	Toxicity	Severity	Carcinogenicity (IARC)[f]
Benzene	2	–	1	0	0	2	2	0	0	4
Cyclohexane	3	–	0	0	1	0	1	0	0	–
Hexane	4	–	0	0	0	2	2	0	0	–
Toluene	3	0	0	0	0	2	2	0	0	1
Heptane	4	–	0	0	0	1	1	0	0	–
Styrene	3	–	1	0	2	2	2	2	14	2
m-Xylene	3	0	0	0	0	2	2	0	0	1
1-Nonene	3	–	0	0	0	1	1	0	0	–
Octane	4	–	0	0	0	0	0	0	0	–
Aniline	3	2	2	2	3	1	3	5	15	1
Pentylbenzene	4	–	0	0	2	2	1	2	8	–
Cyclohexylbenzene	–	–	–	–	–	–	–	–	–	–
Nonylphenol	5	3	1	0	3	3	3	7	28	–
Isononanol	3	1	0	0	2	2	2	2	8	–
1-Nonanol	3	1	0	0	2	2	2	2	8	–
Di-2-ethylhexyl adipate	4	2	0	0	0	1	1	0	0	1
1-Dodecanol	4	1	0	0	1	1	1	0	0	–
Decanoic acid	4	1	0	0	2	2	2	2	8	–
Butyl acrylate	3	–	1	1	1	2	2	0	0	1
Nitrobenzene	3	4	2	2	2	1	1	2	3	1
m-Cresol	3	0	2	2	4	3	3	8	12	2
Tetrachloroethylene	3	2	0	0	0	2	1	0	0	3
Trichloroethene	3	–	0	0	0	2	2	0	0	3
Acrylonitrile	3	0	2	3	3	2	2	3	15	2

"–" corresponds to values not found/available. Cyclohexylbenzene is not present on GESAMP's list.

[a] See Table 10 in the supplementary material for more information on GESAMP classification.

[b] Chronic toxicity values only exist on GESAMP list for a limited number of compounds. See Table 11 in the supplementary material for more information on GESAMP classification.

[c] See Table 12 in the supplementary material for more information on GESAMP classification.

[d] 0 - no irritating at all; 1 - mildly irritating; 2 - irritating; 3 - severely irritant or corrosive to the skin (GESAMP, 2002).

[e] 0 - no irritating at all; 1 - mildly irritating; 2 - irritating to the eye; 3 - severely irritant with irreversible corneal injury (GESAMP, 2002).

[f] See Table 13 in the supplementary material for more information on IARC classification.

(data not shown) and those estimated with the Water Volatilization model of EPI suite (Table 2) may be explained by the above mentioned facts. Hence, the behaviour of priority HNS should be measured in laboratory, under controlled conditions that would resemble those in nature, in order to obtain sound data for models that would allow better forecast of HNS spill plumes behaviour (Cunha et al., 2015; Aprin et al., 2014a,b).

4.2. Fate, behaviour and weathering of the main groups of HNS

The potential of a spilled HNS to cause ecological damage to the marine environment partly depends on its behaviour in seawater, determined by the physicochemical characteristics. The short term behaviour (t0) is modulated by climatic and ocean conditions determining the long term behaviour (Δt) (weathering) of the substance (Alcaro et al., 2007). Moreover, HNS behaviour models shall also take into account the seawater properties (temperature, salinity, and density), the weather (e.g. wind, light) and ocean conditions, and the time (Δt) factor (Cunha et al. 2015). Sea conditions in the affected zone such as turbulence, surface and deep currents, presence of thermoclines and haloclines, are of major importance because they affect the chemical distribution through the water column and/or its loss at the water surface. In addition to HNS's behaviour, parameters such as bioaccumulation and biomagnification determine the compartments of the food web affected.

Dissolver compounds readily solubilise in seawater and the steady state concentration will reflect the amount released, solubility, volume of water, dispersion, currents and wind velocity as mentioned by Harold et al. (2011). Most evidences seem to indicate that the environmental impact of dissolvers is localized in time and space (Cunha et al., 2015). They have a high acute toxicity risk as they disperse easily and become bioavailable for aquatic organisms, at all levels of water column (Neuparth et al., 2011). In sensitive ecosystems and shallower waters, the direct and indirect reactivation of toxic metals and persistent

Table 6
Results of chronic mammalian/human health effects obtained for the priority HNS studied.

Chemicals considered to cause: (GESAMP, 2014)							
Mutagenicity	Reprotoxicity	Sensitizing	Aspiration hazard	Target organ systemic toxicity	Lung injury	Neurotoxicity	Immunotoxicity
Benzene	Toluene	Aniline	Toluene	Benzene	None	Toluene	None
Acrylonitrile	Nitrobenzene	Acrylonitrile	1-Nonene	Aniline		Hexane	
Trichloroethene Styrene	Di-2-ethylexyl adipate	Butyl acrylate	Octane Butyl acrylate	Nitrobenzene			
			Hexane				
			Heptane				

organic chemicals adsorbed in the sediments, causing longer-term effects, has to be considered (Cunha et al., 2015). On the other hand, if there is turbulence and currents that disperse the dissolver, the potential for chronic toxicity is low, since concentrations are more rapidly reduced below a threshold of effect. Dissolvers are most likely to affect pelagic fish and demersal fish, plankton, marine mammals, benthic organisms and also other organisms that inhabit the water column (Alcaro et al., 2007; Bonn Agreement, 2015). Some plumes of dissolved chemicals may, in theory, be oxidized, neutralized, flocculated, or reduced by the application of other chemicals. Acrylonitrile is an example of a HNS that was analysed in the present work and which dissolves in water (>5%). However, one must keep in mind that acrylonitrile also evaporates quickly (14.5 kPa).

An evaporator (e.g. benzene, cyclohexane) is likely to contaminate air, may form a toxic cloud or plume and will impact wildlife (e.g. seabirds) and humans, principally through inhalation exposure (Harold et al., 2011). The vapour cloud formed by evaporators behaves in the same way as that of a gas (EMSA, 2007). Evaporators tend to dissipate with the current and the wind as they evaporate, and the concentration of these pollutants tends to zero in the aquatic environment after some time (Bonn Agreement, 2015). In the case of *Samho Brother* incident (West Pacific Ocean, 2005), where the ship capsized and sunk 70 m deep, no benzene (highly toxic to flora and fauna) was detected later, neither in the air, water or in the shore. As the exposure time is frequently short for these substances, only acute effects are likely and only in the case of substances with a high toxicity. Hence, evaporators usually represent a low threat to the marine environment except if they also dissolve in water (dissolvers evaporators – e.g. Acrylonitrile) as reported by Neuparth et al. (2011). For example, the *Anna Broere* which sank in the Netherlands in 1988 released 200 t of acrylonitrile (DE) in the liquid state. Acrylonitrile is toxic, flammable and explosive, giving off toxic fumes in case of fire. The tonnes of acrylonitrile that leaked out quickly dispersed into the sea and caused damage to the marine biota but with significantly less impact than anticipated presumably because a large quantity evaporated and hence was no longer bioavailable for aquatic organisms (Cunha et al., 2015).

Floaters (e.g. pentylbenzene, cyclohexylbenzene) tend to drift with the wind, which generally blows faster than currents, and thus they spread quickly over the water surface. They pose a higher potential risk to neritic and intertidal zones that typically have a high biodiversity (Bonn Agreement, 2015). In the latter case, hard and soft sediments are affected in beaches and shores (Alcaro et al., 2007). In the open ocean, floaters create a barrier on the surface for oxygen to dissolve, contaminating marine mammals when they come up for breathing and seabirds seeking food or resting. Neuston and pleuston organisms are much affected. Further problems with floaters arise when a spill occurs in or reaches shallow waters or when it happens in the breeding season of birds and mammals (Bonn Agreement, 2015). On tide pools and still water, floating chemicals prevent exchange and mixing of oxygen and CO_2 causing anoxic conditions. Therefore, the main hazards (e.g. fire) associated with the group of floaters are due to their natural spreading on the surface, which affects the aquatic environment (Bonn Agreement, 2015), as referred above. Floaters have also the potential of dermal exposure for humans (Harold et al., 2011).

The tanker *Ievoli Sun* which sank at the English Channel in 2000 released 1000 t of styrene. This is an example of an incident involving a floating substance which slowly evaporates (0.85 kPa), but does not dissolve (<0.1%) (FE). The entire cargo of styrene, a synthetic chemical considered as a marine pollutant, toxic, relatively insoluble (310 mg/L) and with a lower density than seawater (specific gravity 0.91 vs. 1.04), was pumped out. Styrene was detected in the gills and tissues of crabs in the vicinity of the wreck. Initial visual surface observation showed slick and styrene vapours were detected at a nearby Island (Alderney). Additionally, high intensity currents resulted in significant dilution or spreading of styrene in seawater. The possibility of chronic effects was considered to be minimal due to the behaviour of styrene following release from the vessel (Cunha et al., 2015).

Other spill incident at the sea involving styrene (*Chung Mu N°1*, China, 1995) can be found in the online database elaborated by CIIMAR. The authors mentioned that styrene is a reactive product (exothermic polymerization), irritant and flammable, with impact on the environment (tainting of edible organisms, i.e. causes a change in the organoleptic characteristics of the flesh of fish and shellfish) (Cunha et al., 2015).

Sinkers (e.g. tetrachloroethylene) are not readily soluble being lipophilic and denser than seawater (Harold et al., 2011). Solid and liquid sinkers fall to sediments and affect mostly benthic fish and other benthos communities and also other organisms that feed on the bottom (e.g. predators of benthic organisms) (Bonn agreement, 2015). They mix with the sediments and tend to be retained for a long time depending on the solubility and physical state. Low solubility solids tend to remain for very long time, while liquids, if not insoluble, are more prone to disperse. At seabed, liquids spread and create a physical barrier that prevents oxygen exchange, covering the habitat for a time that depends on solubility, turbulence and currents. Sinking solids may clog the sediment surface for very long periods if insoluble and for less time if they dissolve. However, if they dissolve (sinkers dissolvers), they are more bioavailable for the food chain. In the case of being toxic, the time they persist before dispersing and/or dissolving determines their acute or chronic toxicity.

Dissolvers and sinkers (e.g. nitrobenzene, tetrachloroethylene) are the substances that might cause the highest potential ecological impacts on the marine environment after a spill as they will disperse easily, and hence may be bioavailable for aquatic organisms, both in the water column and the sediments (Neuparth et al. 2011). On the other hand, regarding human health, the revised GESAMP hazard evaluation procedure (GESAMP, 2002) states that the principal mode of human exposure after spillage is expected to be through vapours. Therefore, the human exposure is likely to occur predominantly from air-borne contamination and consequently inhalation exposure. From the human health perspective, the chemicals of priority concern are those that have some capacity for evaporation (e.g. toluene, benzene) and which may induce a health effect (Harold et al., 2011, 2014).

4.3. Final remarks

This study compiles data and uses mathematical models to estimate key parameters that are essential to predict the fate, behaviour and weathering of 24 priority HNS from the Top 100 harmful substances handled in bulk in the EU Atlantic ports (HASREP, 2005). The data produced here are made available for general public use and specialized stakeholders involved in HNS spills preparedness and response, on an online database (http://www.ciimar.up.pt/hns/substances.php), that also includes (eco)toxicological data. This sort of tool has been identified as a key instrument to improve the preparedness and response to accidental marine spill. These data are expected to be used to develop more accurate HNS modelling tools and consequently to improve the predictions related to the HNS plumes behaviour and potential hazards to the marine environment and associated resources such as fisheries, recreational areas, etc. Additionally, much of the data obtained in the present study will assist laboratory experiments at the pilot level involving the priority HNS analysed in order to simulate and also understand their behaviours at sea (e.g. behaviour and weathering assays in simulation tanks). Lack of data for the priority HNS measured under real and controlled laboratory conditions is highlighted. These studies will set the foundations for improving modelling tools for forecasting and for supporting and following the initial stages of response operations. Others parameters analysed are more related to the effect on the biota and indicate possible impacts to be assessed by monitoring programs. The data may be very useful from an ecotoxicological stand point as it will allow better estimations of the risks to the ecosystem and the drawing of monitoring strategies for the priority HNS.

The dataset developed has the merit of assembling a brief and concise profile of the different priority HNS and aims to be a tool to assist relevant bodies in planning, preparedness and response to accidental HNS spills (e.g. in the upgrading of HNS pollutant responses protocols and/or waste management protocols, in the development of pilot, and training exercises, booming/contention protection plans as well as guidelines for volunteers, maritime professionals and local authorities), focusing on the environmental and public health impacts. This information is, therefore, essential to help in the decision-making process at the operational level. Policy makers and legislators may also benefit from the concise and synthetic information provided. In a near future, it is expected that the dataset evolve in order to contain information on other top 100 harmful substances handled in bulk in the EU Atlantic, beyond the 24 selected based on a former prioritization exercise performed by Neuparth et al. (2011).

Online resources

- Chemicals Screening Information Datasheets (SIDS) for high volume chemicals (UNEP)
- Hazardous and Noxious Substances Spill Incidents – www.ciimar.up.pt/hns
- ChemSpider database, Advancing Chemical Sciences, Royal Society of Chemistry (RSC)
- Distributed Structure-Searchable Toxicity (DSSTox) Database Network (EPA)
- Ecological Categorization Results from the Canadian Domestic Substance List (OECD)
- ECOTOX Database (Environmental Protection Agency – EPA, US)
- Environmental Fate Data Base (EFDB) from Syracuse Research Corporation (SRC)
- ESIS: European chemical Substances Information System (EC)
- European INventory of Existing Commercial chemical Substances (EINECS)
- Fiches Toxicologiques from Institut National de Recherche et de Securité (INRS), France
- Hazardous Substances Data Bank (HSDB) of TOXNET, National Library of Medicine (NLM)
- Interactive PhysProp Database from Syracuse Research Corporation (SRC)
- International Chemical Safety Cards (ICSC) database from Int. Labour Org. (ILO/UN)
- MSDSonline, online library of Safety Data Sheets
- National Toxicology Program (NTP), database search application, US
- Toxic Substance Control Act Test Submission Database (TSCATS) from EPA and SRC

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2016.06.090.

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