ARCOPOL

Identify chemicals that pose major environmental risk

Activity 6

Task 6.2.1

ARCOPOL

The Atlantic Regions' Coastal Pollution Response

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Context of the task

The document has been produced as part of Task 6.2, Environmental damage assessment, and is the first step towards drafting standardised monitoring procedures for evaluating environmental damage and restoration following an HNS spill. The report aims to draw up a list of priority HNS that potentially pose a major risk to the marine environments in the European Atlantic waters and collate marine toxicological data for each identified substance. The work is based on a review of scientific literature, HNS incidents and validated chemical databases.

1. Selection of the priority Hazardous Noxious Substances (HNS) that pose major risk to marine environment

During the last twenty years, there has been a considerable increase in the transportation and handling of Hazardous Noxious Substances (HNS) around the Atlantic waters and therefore the risk of incidents and pollution is a growing problem. Despite the extensive transport of HNS at sea, there is current lack of knowledge of the effects of many of them on the marine biota (most of the ecotoxicological data available are for fresh water organisms). The understanding of the threat and consequences of maritime HNS spills are not as well known as oil spills. Whereas most oils float on the sea surface and are immiscible with water, HNS chemicals exhibit a wider range of behaviours (sinking, floating, gassing, evaporating, and dissolution) and toxicity to marine organisms. Thus, there is a clear need to evaluate the potential ecological hazards of HNS spills, and collect more detail information on the impact in marine organisms.

1.1 METHODOLOGY

Due to the great diversity of HNS that are transported over sea it is difficult to assess the potential effects of every chemical substance on the marine environment. Therefore, the purpose of this task is to identify the major HNS of concern (HNS which are largely transported in EU Atlantic waters and which pose a major risk to the marine environment in case of a spill), in order to assess the potential environmental damage after a HNS spill. The identification of the priority HNS is established by reviewing information reported in past EU projects, international scientific literature, chemical databases etc.

The criteria for the selection of priority HNS are as follow:

1. HNS transport frequency – identification of the most transported HNS by Sea in EU Atlantic waters;

2. Alerts and incidents - review of the major shipping incidents involving the carriage of HNS in European waters;

3. Physical behaviour of the substances released– Following a discharge into the aquatic environments, HNS substances may behave differently depending on their physical properties. It is important to understand this behaviour, not only to facilitate the evaluation of the possible impacts but also to adequate to adequate the response operation.

4. Chemical toxicity to marine organisms – In order to identify the priority HNS, it is necessary to consider their toxicity to the aquatic organisms. Spills can cause acute and chronic effects on organisms; also many of HNS can bioaccumulate within the tissues of biota and or be persistent in the environment. To evaluate these criteria we will be making use of the Hazard profile of Chemical Substances Carried by Ships done by the GESAMP working group (IMO 2001; GESAMP 2008) the reviewed Annex II of MARPOL classification (INTERTANKO 2006) and validated chemical databases. Based on available ecotoxicity data, only HNS harmful to the marine biota will be selected.

1.2 - RESULTS

1.2.1- **HNS transport frequency**

A desktop study was carried out to identify the most transported HNS by sea in EU Atlantic waters. This review analyses the information available in the European project HASREP (AMRIE, 2005) which lists the most common HNS handled in the main EU Atlantic ports.

Table 1 - Top 100 HNS handled in the EU Atlantic ports

Nº	SUBSTANCE	QUANTITY (Ton)
1	Palm oil and other vegetable oils	3.614.476
2	Methanol	1.909.733
3	Benzene and mixtures >10% benzene	1.424.325
4	Anhydrous Ammonia	1.024.842
5	Methyl tert-butyl ether	1.006.963
6	Sodium hydroxide solution	811.064
7	Styrene monomer	809.418
8	Xylenes	749.066
9	Phenol	694.788
10	Phosphoric acid	612.955
11	Ethanol (Ethyl alcohol)	576.049
12	Sulphuric acid	483.242
13	Acetone	433.592
14	Cyclohexane	376.608
15	Acetic acid	367.873
16	Toluene	331.235
17	Nonene (all isomers)	309.280
18	Ethylene glycol	307.973
19	Aniline	292.983
20	Ethylene	292.328
21	Fatty acid methyl ester C10-C16	245.261
22	2-Ethylhexanol	220.619
23	Vinyl chloride	216.560
24	Propylene oxide	201.418
25	Acrylonitrile	197.348
26	Isobutane	167.433
27	Nitrobenzene	147.159
28	Ethyl acetate	141.767
29	Palm and other vegetable fatty acids	136.962
30	Ethylbenzene	129.404
31	Butanol (Butyl alcohol)	125.098
32	Formaldehyde solutions (45% or less)	121.684
33	Isopropanol	119.978
34	Adiponitrile	115.899
35	Methyl methacrylate	110.708
36	Vinyl acetate	108.306
37	Isononanol	107.952
38	Diisononyl phthalate	100.425
39	n-Alkanes (C10+)	100.162
40	Methyl ethyl ketone	99.818
41	Butadiene	97.675
42	Sulphur (molten)	95.468
43	Alkyl (C5-C8, C9) benzenes	94.249
44	Cyclohexanone, Cyclohexanol mixture	87.259

45	Propylene glycol mono methyl ether	81.544
46	Calcium lignosulphonate solutions	81.134
47	Ethylene dichloride	79.545
48	Nonylphenol poly(4-12)ethoxylates	75.802
49	Fatty alcohol	74.880
50	Propylene glycol	68.600
51	Methyl diphenil isocianate	67.674
52	Molasses	63.867
53	Octane (all isomers)	62.924
54	1-Nonanol (Nonil alcohol)	56.050
55	Potasium hidroxide	54.844
56	Methylene chloride	54.036
57	Butyl acrylate (all isomers)	52.718
58	Ethylene glycol methyl butyl ether	51.731
59	Isobutanol	49.422
60	Tetrahydrofuran	48.018
61	Formic acid	44.751
62	Chloroform	44.555
63	Fish oil	41.448
64	Butyl acetate (all isomers)	38.688
65	Di(2-ethylhexyl) adipate	35.685
66	Polyisobutenamine in aliphatic(C10-C14) solvent	28.150
67	Dodecane acid	27.670
68	Methyl isobutyl ketone	26.511
69	2,2,4-Trimethyl-1,3-pentanediol- 1-isobutyrate	25.342
70	Acrylic acid	24.525
71	Propionic acid	24.331
72	2-Ethylhexyl acrylate	22.818
73	Trichloroethylene	21.817
74	Hexane (all isomers)	20.169
75	Dimethylformamide	18.064
76	2-Ethylhexanoic acid	17.492
77	Diethylene glycol	17.171
78	Epichlorohydrin	16.875
79	Alkanes (C6-C9)	16.026
80	Ethyl tert-butyl ether	14.704
81	Propylene glycol mono methyl ether acetate	13.300
82	Dodecylbenzene	12.253
83	Acetone cyanohydrin	12.099
84	Diethanolamine	12.090
85	Heptane (all isomers)	10.801
86	1 Dodecanol	10.704
87	Isoprene	9.854
88	Hexamethylenediamine (molten)	9.453
89	2-Methyl-1,3-propanediol	8.850
90	Olefins (C13+, all isomers)	8.807
91	Octanol (all isomers)	8.586

92	Norm-propanol n-propyl alcohol	8.243
93	Tetrachloromethane	7.736
94	Ethylhexanoic acid	6.550
95	2-Hydroxy-4(methylthio)butanoic acid	6.489
96	Cresols (all isomers)	6.458
97	Decanoic acid	5.331
98	Methyl acrylate	5.215
99	Perchloroethylene	4.516
100	Butyl methacrylate	3.800

The values presented in the Table 1 were established from the quantities (tonnes) loaded/unloaded per year in EU Atlantic ports as an average for the years 2002, 2003 and 2004 (AMRIE, 2005).

1.2.2) Alert and incidents

Several sources of information were reviewed to assemble the data on shipping incidents concerning HNS in European waters such as IMO (2002), Cedre spill guide, Cedre (2009) and HELCOM (2003).

Some of the incidents were well documented, whilst 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 on what could better mitigate the consequences next time. The purpose of this review is to identify the risk of accidental pollution by evaluating the potential environmental impact of the past HNS spills incidents. The incidents will be briefly described in annex 1 and a summary list with 18 incidents classified according to the products transported/spilled, the HNS impact to the marine environment and their behaviour after being spilled at sea are presented in table 2.

Table 2: Summary of the HNS incidents at EU waters.

Ship name	Accident date	Country	HNS Transp/spilled	MARPOL Classification a)	GESAMP Classification a)			Physical behavior	Traffic Ranking
					Bioaccumulation	Biodegradation	Acute Toxicity		
Canon	1987	UK	Xylene	Y	3	NR	3	FE	8
			Butanol	Z	0	R	0	D	31
			Butyl acrylate	Y	2	R	3	FED	57
			Cyclohexanone	Y	1	R	2	FED	44
			Sodium	-	-	-	-	-	-
			Anilin oil	Y	0		3	FD	-
			Diphenyl-methan	-	-		-	-	-
			o-cresol	Y	2	R	3	SD	96
			Dibutyl phtalate	-	-		-	-	-
			Phosphoric acid	Z	0	Inorg.	1	D	10
			Phthalic anhydride	Y	1	R	2	S	-
Anna broere	1988	The Netherlands	Acrylonitrile	Y	2	NR	3	DE	25
			Dodecyl benzene	Y	0	NR	0	F	82
Alessan-dro primo	1991	Italy	Acrylonitrile	Y	2	NR	3	F	25
			Ethylene dichloride	Y	1	NR	2	SD	47
Kimya	1991	UK	Sunflower oil	Y	0	R	0	Fp	1
Grape One	1993	UK	Xylene	Y	3	NR	3	FE	8
Weisshorn	1994	Spain	Rice	-	-	-	-	-	-
Fenes	1996	France	Wheat	-	-	-	-	-	-
Allegra	1997	UK	Palm oil	Y	0	R	0	Fp	1
Albion II	1997	France	Calcium carbide	-	-	-	-	-	-
			Iodine	-	-	-		-	-
			Camphor	-	-	-		-	-
			Ammonia anhydrous	Y	0	R	3	DE	4
Junior M	1999	France	Ammonium Nitrate	Z	0	R	3	D	-
Ievoli Sun	2000	UK	Styrene	Y	3	R	3	FE	7
			Methyl hepthyl ketone	-	3	R	3	FED	-
			Isopropyl alcohol	-	0	R	0	D	-

Ballu	2001	Spain	sulphuric acid	Y	0	Inorg.	2	D	12
Lykes liberator	2002	France	aluminium	-	-	-	-	-	-
			diethyl iodide	-	-	-		-	-
			diethyl zinc	-	-	-	-		-
			Toluene	Y	2	R	3	FE	16
Bow Eagle	2002	France, Channel	ethyl acetate	Z	0	R	1	DE	28
			methyl-ethyl-ketone	Z	0	R	1	DE	40
			cyclohexane	Y	3	NR	3	E	14
			toluene	Y	2	R	3	FE	16
			benzene	Y	1	R	2	E	3
			ethanol	Z	0	R	0	Fp	11
			soya	-	-	-	-	-	-
			sunflower oil	Y	0	r	0	Fp	1
			vegetable oil	Y	0	r	0	Fp	1
Jambo	2003	UK	Zinc Sulphide	-	-	-	-	-	-
Ece	2006	France	Phosphoric acid	Z	0	Inor	1	D	10
Rokia Delmas	2006	Isle of Ré, France	Cocoa beans	-	-	-	-	-	-
MSC Napoli	2007	UK	Several dangerous chemicals						

a) Note: see table 3 and 4 for GESAMP and MARPOL classification

1.2.3) Physical behaviour of the substances released

Chemicals which are spilled into the sea behave in different ways depending on their physical properties and environmental conditions. The European Behaviour Classification System has been elaborated in order to classify chemicals according to their physical behaviours when spilled into the sea. The main principle of the system is a characterisation of spilled loose chemicals as evaporators, floaters, dissolvers and sinkers. From this basic characterisation and from other details regarding physical properties, the chemicals are classified in the following 12 Property Groups according to their behaviour in contact with sea-water:

- Gas (G),
- Gas/dissolver (GD)
- Evaporator (E)
- Evaporator/dissolver (ED)
- Floater (F)
- Floater/evaporator (FE)

- Floater/evaporator/dissolver (FED)
- Floater/dissolver (FD)
- Dissolver (D)
- Dissolver/evaporator (DE)
- Sinker (S)
- Sinker/dissolver (SD)

The behaviour classification of the most transported HNS in EU Atlantic waters are presented in Table 5.

The European Behaviour Classification system for evaluating the short-term behaviour of chemical spilled at sea was used to help the selection of priority HNS based on their physical properties. Dissolvers and sinkers are the substances with higher potential ecological costs for marine environments after a spill as they will disperse easily, and hence be bioavailable for aquatic organisms. Marine mammals, species of fish, invertebrates and other organisms that inhabit the water column or in sediments are all at risk from dissolver and sinker HNS. The hazards associated with the group of floaters are due to natural dispersion in the water column affecting the aquatic environment; floaters drift with the wind or current and can reach sensitive areas along the coast. Moreover, further problems arise when a spill occurs in shallow waters or when a spill happens in the breeding season for birds and mammals. The main hazards produced by Gas and evaporators is air toxicity, usually they represent a low threat to the marine environment except if they dissolve in the water. Considering the likely impact on the marine environment produced by the dissolvers floaters, and sinkers, the priority HNS list will cover mainly these behaviour categories.

1.2.4- Chemical toxicity to marine organisms

The procedure to select priority HNS after a spill should consider chemicals that have a combination of harmful characteristics to marine organisms. These include toxicity in combination with bioaccumulation and persistence potential.

- **Toxicity** is an inherent property of a chemical. In order to rate the hazard posed by chemical substances to aquatic organisms, the most common solution is still the use of acute toxicity test data, because in most of the cases chronic ecotoxicological data is not available.

- **Bioaccumulation** in aquatic organisms is a general term describing the complex process by which chemical substances are taken up into the body through all exposure routes (water, food and sediment) i.e. bioconcentration. The bioconcentration factor, BCF, is usually used as an indicator for bioconcentration in conjugation with the *n*-octanol/water partition coefficient, log Kow.
- **Persistence**: Knowledge of the rate at which HNS substances degrade in the aquatic environment is of great importance in determining their impact and minimising biological effects. The persistence of a substance reflects the potential for long-term exposure of organisms, but also the potential for the substance to be widely distributed in the environment. The available information on biodegradability of HNS is dominated by data on "ready biodegradability". There are a wide range of tests, based on O2 consumption, CO2 evolution or dissolved organic carbon removal, that are designed to select rapidly biodegrading substances.

HNS that combine properties of toxicity, potential to bioaccumulate and persistence represent the highest hazard to marine environment after a spill. In this report we have applied the revised hazard evaluation procedures elaborated by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (IMO 2001; GESAMP 2008) to numerically classify the 100 most transported HNS in EU Atlantic waters defined at section 1. The GESAMP Bioaccumulation, Biodegradation and Toxicity criteria (GESAMP 2002) will be used as a tool for assessing the danger posed by the 100 HNS and selecting the priority HNS. In addition, the Revised Annex II of MARPOL classification will also be considered in the HNS prioritisation.

1.2.4a) Evaluation of the 100 most transported HNS in EU Atlantic waters according to GESAMP and MARPOL classification

The GESAMP hazardous evaluation procedure for Biodegradation, Bioaccumulation and toxicity are summarised in Table 3:

Table 3: Bioaccumulation, Biodegradation and Toxicity GESAMP guidelines to categorization of HNS (in GESAMP 2002)

Numerical Rating	Bioaccumulation			Bio-degradation	Toxicity			
					Acute Toxicity		Chronic Toxicity	
	Description	Criteria for log Pow	Criteria for BCF		LC/EC/50 (mg/l)	Description	NOEC (mg/l)	Description
0	No potential to bioaccumulate	≤ 1 or >ca.7	No measurable	R: readily biodegradable NR: not readily biodegradable Inorg.: Inorganic	> 1000	No toxic	> 1	Negligible
1	Very low potential to bioaccumulate	≥ 1 - < 2	≥ 1 - < 10		100-1000	Practically no toxic	*> 0.1 ≤ 1*	low
2	Low potential to bioaccumulate	≥ 2 - < 3	≥ 10 - < 100		10-100	slightly toxic	*> 0.01 ≤ 0.1*	Moderate
3	Moderate potential to bioaccumulate	≥ 3 - < 4	≥ 100 - < 500		1-10	Moderately toxic	*> 0.001≤ 0.01*	High
4	High potential to bioaccumulate	≥ 4 - < 5	≥ 500 - < 4000		0.01 - 1	highly toxic	*≤ 0.001*	Very High
5	Very high potential to bioaccumulate	≥5 -< ca. 7	≥ 4000		< 0.01	extremely toxic		

The revised Annex II of MARPOL classification defined for pollution categories of noxious liquid substances are rated by their potential impact on the environment. The categories are Category X - major hazard; Category Y - hazard; Category Z - minor hazard; and Category OS – "other substances" with no risk as described in the table 4:

Table 4: MARPOL classification to ~~to~~ categorization of HNS

Category X	Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present **a major hazard to either marine resources or human health** and, therefore, justify the prohibition of the discharge into the marine environment
Category Y	Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present **a hazard to either marine resources or human health** or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment

Category Z	Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present **a minor hazard to either marine resources or human health** and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment
Other substances	substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present **no harm to marine resources, human health,** amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning of deballasting operations. The discharge of bilge or ballast water or other residues or mixtures containing these substances are not subject to any requirements of MARPOL Annex II

According to the GESAMP and MARPOL criteria, the table 5 presents the classification of the 100 most transported HNS in EU Atlantic waters.

Table 5 - GESAMP, MARPOL and Behaviour classification of the most transported HNS in Atlantic waters

HNS	GESAMP Class.				Marpol Class.	Physical Behaviour SEBC code	Previous Incident	Traffic Rank
	Bio accumulation	Bio degradation	Acute T.	Chronic T.				
Palm oil + other vegetable oils	0	R	0	-	Y	F	Kimya, Allegra, Bow Eagle	1
Methanol	0	R	0	0	Y	FD		2
Benzene+mixtures > 10% benzene	1	R	2	-	Y	E	Bow Eagle	3
Anhydrous Ammonia	0	R	3	2	Y	DE	Albion II	4
Methyl ter-butyl ether	1	NR	1	0	Z	ED		5
Sodium hydroxide solution	0	Inorg.	2	-	Y	D		6
Styrene monomer	3	R	3	-	Y	FE	Ievoli Sun	7
Xylenes	3	NR	3	0	Y	FE	Cason, Gape one	8
Phenol	2	R	3	0	Y	S		9
Phosphoric acid	0	Inorg.	1	-	Z	D	Cason, Ece	10
Ethanol (Ethyl alcohol)	0	R	0	-	Z	D	Bow Eagle	11
Sulphuric acid	0	Inorg	2	-	Y	D	Ballu	12
Acetone	0	R	0	0	Z	DE		13
Cyclohexane	3	NR	3	-	Y	E	Bow Eagle	14
Acetic acid	0	R	1	-	Z	D		15
Toluene	2	R	3	0	Y	FE	Lykes Liberator, Bow Eagle	16
Nonene (all isomers)	4	-	3	-	Y	FE		17
Ethylene glycol	0	R	0	0	Y	D		18
Aniline	0	R	3	2	Y	FD		19
Ethylene	-	-	-	-	-	-		20
Fatty acid methyl ester C10-C16	0	R	2	-	Y	Fp		21
2-Ethylhexanol	0	-	2	-	-	E		22
Vinyl chloride	0	-	-	-	Y	E		23
Propylene oxide	0	R	2	-	Y	DE		24
Acrylonitrile	2	NR	3	0	Y	DE	Anna Broere,	25

							Alessandro Primo	
Isobutane	-	-	-	-	-	-		26
Nitrobenzene	1	R	3	-	Y	SD		27
Ethyl acetate	0	R	1	0	Z	DE	Bow Eagle	28
Palm and other vegetable fatty acids	0	R	0	-	Y	Fp		29
Ethylbenzene	2	R	3	1	Y	FE		30
Butanol (Butyl alcohol)	0	R	0	-	Y	D	Cason	31
Formaldehyde solutions	0	R	2	-	Y	D		32
Isopropanol	0	R	0	0	Z	D		33
Adiponitrile	0	R	1	-	Y	FD		34
Methyl methacrylate	1	R	2	-	Y	ED		35
Vinyl acetate	0	R	2	-	Y	ED		36
Isononanol	3	-	3	1	Y	Fp		37
Diisononyl phthalate	0	R	0	0	-	Fp		38
n-Alkanes (C10+)	5	R	0	-	Y	F		39
Methyl ethyl ketone	0	R	1	0	Z	DE	Bow Eagle	40
Butadiene	-	-	-		-	-		41
Sulphur (molten)	0	Inorg.	0	-	Z	S		42
Alkyl (C5-C8, C9) benzenes	4	NR	4	-	Y	F		43
Cyclohexanone, Cyclohexanol mixtures	1	R	2	0	Y	FED	Cason	44
Propylene glycol mono methyl ether	0	-	1	-	-	-		45
Calcium lingo-sulphonate solutions	0	NR	0	-	Z	D		46
Ethylene dichloride	1	NR	2	0	Y	SD	Alessandro Primo	47
Nonylphenol poly(4-12) ethoxylates	4	NR	3	1	Y	D		48
Fatty alcohol	0	-	3	-	-	-		49

Propylene glycol	0	NR	1	-	Z	D		50
Methyl diphenil isocianate	-	-	-	-	-	-		51
Molasses	0	R	0	-	Z	D		52
Octane (all isomers)	5	R	4	-	X	FE		53
1-Nononol (Nonyl alcohol)	3	NR	3	1	Y	Fp		54
Potassium hydroxide	0	Inorg.	2	-	Y	D		55
Methylene chloride	-	-	-	-	Z	-		56
Butyl acrylate (all isomers)	2	R	3	-	Y	FED	Cason	57
Ethylene glycol methyl butyl ether	1	-	1	-	Z	D		58
Isobutanol	0	R	1	0	Z	D		59
Tetrahydrofuran	0	R	0	0	Z	DE		60
Formic acid	0	R	2	-	Y	D		61
Chloroform	1	NR	2	0	Y	SD		62
Fish oil	0	R	0	-	Y	Fp		63
Butyl acetate	1	R	2	-	Y	FED		64
Di(2-ethylhexyl) adipate	2	R	4	2	Y	Fp		65
Polyisobutenaine in aliphatic (C10-C14)solvent	0	NR	2	-	Y	FDE		66
Dodecane acid	-	-	-	-	Y	Fp		67
Methyl isobutyl ketone	0	R	1	0	Y	FDE		68
2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate	3	-	2	-	Y	-		69
Acrylic acid	0	R	4	-	Y	D		70
Propionic acid	0	R	2	-	Y	D		71
2-Ethylhexyl acrylate	3	R	2	-	Y	F		72
Trichloro-ethylene	2	NR	3	-	Y	SD		73
Hexane (all isomers)	3	R	4	-	Y	E		74
dimethylformamie	0	R	1	0	Y	D		75
2-ethylhexanoic	2	R	2	-	Y	FD		76

acid								
Diethylene glycol	0	R	0	0	-	D		77
Epichlorohydrin	0	R	3	1	Y	D		78
Alkanes (C6-C9)	5	R	4	-	Y	FE		79
Ethyl tert-butyl ether	1	-	2	-	Y	E		80
Propylene glycol mono methyl ether acetate	0	NR	1	-	Z	D		81
Dodecylbenzene	0	NR	0	-	Y	F	Anna Broere	82
Acetone cyanohydrin	0	R	4	-	Y	D		83
diethanolamine	0	R	1	0	Y	D		84
Heptane (all isomers)	4	R	4	-	Y	D		85
1-Dodecanol	5	R	4	-	-	Fp		86
Isoprene	2	NR	2	-	Y	E		87
Hexamethylene-diamine (molten)	0	R	2	-	Y	D		88
2-methyl-1,3-propanediol	0	NR	0	0	Z	D		89
Olefins (C13+, all isomers)	5	NR	0	-	Y	Fp		90
Octanol (all isomers)	3	R	2	0	Y	Fp		91
Norm-propanol n-propyl alcohol	-	-	-	-	Y	-		92
Tetra-chloromethane	3	NR	2	0	-	-		93
Ethylhexanoic acid	2	R	2	-	Y	FD		94
2-Hydroxy-4(methylthio) butanoic acid	1	R	1	-	Z	D		95
Cresols (all isomers)	2	R	3	0	Y	SD	Cason	96
Decanoic acid	4	R	4	1	X	Fp		97
Methyl acrylate	0	R	3	-	Y	D		98
Perchloro-ethylene	2	NR	3	2	Y	S		99
Butyl methacrylate	2	NR	1	-	Y	FE		100

Some of the HNS highlighted in table 5 will not be considered in the selection process because their GESAMP classification for bioaccumulation, biodegradation and toxicity is not available.

1.2.4b) Proposal for criteria and cut-off values for prioritisation process

The following criteria have been selected to prioritise HNS for ecotoxicological risk:

- GESAMP hazard evaluation:
  - Bioaccumulation rank of **at least 2** (low potential to bioaccumulate)
  - Biodegradation of "**Not Readily biodegradable**"
  - Acute toxicity rank of **at least 3** (moderate acute toxic) **and/or** Chronic toxicity rank of **at least 2** (moderate chronic toxic)

  OR:
  - Bioaccumulation rank of at **least 3**
  - Biodegradation of "**Readily biodegradable**"
  - Acute toxicity rank of **at least 4 and/or** Chronic toxicity rank of **at least 2**

  OR:
  - 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

- Revised annex II of MARPOL classification, we have selected HNS with the **X** ("posing a major hazard") or the **Y** ("posing a hazard") category.

According to this proposal, the most transported HNS in EU Atlantic waters must have potential to bioaccumulate, be persistent and toxic, and also to pose a risk based on the Marpol classification. The criterion taking part of previous incidents was also considered if the HNS is harmful to aquatic organisms.

HNS that have a long term carcinogenic impact in mammalians will also be considered for integration in the list of priority HNS.

The list of the priority HNS selected are given in table 6.

Table 6- priority list of HNS in EU Atlantic waters

HNS	GESAMP Class.				Marpol Class.	Observa-tions	Previous Incident	Physical Behavior SEBC code	Traffic Rank
	Bio Accumu-lation	Bio Degra-dation	Acute T.	Chronic T.					
Benzene + mixtures >10%	1	R	2	-	Y	Mammalian Carcinogen	Bow Eagle	E	3
Anhydrous Ammonia	0	R	3	2	Y		Albion II	DE	4
Styrene monomer	3	R	3	-	Y		Ievoli Sun	FE	8
Xylenes	3	NR	3	0	Y		Cason	FE	7
Cyclohexane	3	NR	3	-	Y		Bow Eagle	E	14
Toluene	2	R	3	0	Y		Lykes Liberator, Bow Eagle	FE	16
Nonene (all isomers)	4	-	3	-	Y		-	FE	17
Aniline	0	R	3	2	Y		-	FD	19
Acrylonitrile	2	NR	3	0	Y		Anna Broere, A. Primo	DE	25
Nitrobenzene	1	R	3	-	Y	Mammalian Carcinogen	-	SD	27
Isononanol	3	NR	3	1	Y		-	Fp	37
Alkyl (C5-C8, C9) benzenes	4	NR	4	-	Y		-	F	43
Nonylphenol poly(4-12) ethoxylates	4	NR	3	1	Y		-	D	48
Octane (all isomers)	5	R	4	-	X		-	FE	53
1-Nonanol (Nonyl alcohol)	3	NR	3	1	Y		-	Fp	54
Butyl acrylate (all isomers)	2	R	3	-	Y		Cason	FED	57
Di (2-ethylhexyl) adipate	2	R	4	2	Y		-	Fp	65
Trichloro-ethylene	2	NR	3	-	Y		-	SD	73
Hexane (all isomers)	3	R	4	-	Y		-	E	74
Heptane (all isomers)	4	R	4	-	Y		-	D	85

1-Dodecanol	**5**	**R**	**4**	**-**	**-**		**-**	**Fp**	**86**
Cresols (all isomers)	**2**	**R**	**3**	**0**	**Y**		**Cason**	**SD**	**96**
Decanoic acid	**4**	**R**	**4**	**1**	**X**		**-**	**Fp**	**97**
Perchloroethylene	**2**	**NR**	**3**	**2**	**Y**		**-**	**S**	**99**

1.3- CONCLUSIONS

The proposed list of priority HNS for Atlantic European waters contains 24 chemicals: Benzene, Ammonium, Styrene, Xylenes, Cyclohexane, Toluene, Nonene, Aniline, Acrylonitrile, Nitrobenzene, Isononanol, Alkyl (C5-C8, C9) benzenes, Nonylphenol poly(4-12) ethoxylates, Octane, 1-Nonanol, Butyl acrylate, Di (2-ethylhexyl) adipate, Trichloroethylene, Hexane, Heptane, 1-Dodecanol, Cresol, Decanoic acid, and Perchloroethylene. The selection of these compounds was based mostly on the environmental hazard by the use of a combination of criteria, i.e., persistency, toxicity and bioaccumulation, but also in the sea traffic extension, incidents occurred and HNS physical behaviour.

The prioritisation procedure and list will need to be continuously updated and reviewed as more data becomes available on chemical toxicity.

2. Marine toxicological datasheet for the selected HNS that pose major environmental risk

The main objective of this sub-task was to gather relevant information concerning the potential effects of the 24 selected HNS chemicals on marine biota. For this purpose we have created a datasheet with the information obtained in scientific literature and in validated reports available online (eg. Inchem, ecotox database, toxline etc). This datasheet was divided into different sections:

- General information which contain the name of the chemical, CAS nº and chemical formula
- Marine Toxicity data with the information available for acute and chronic toxicity in marine species representative of different taxonomic groups. If no data is found for acute or chronic toxicity in marine organisms, freshwater organisms' data is presented (if available).
- Summary of the GESAMP classification

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Annex 1 – Brief description of past HNS incidents occurred in European waters

The most relevant HNS incidents occurred in European waters will be briefly described below including the scene of the incident; HNS involved; the identification of the related risks and response actions taken.

CASON, 1987 - Spain

Incident: The ship caught on fire, a tug tried to salvage Cason, but adverse weather and the fire on board stopped the operation, and Cason went aground 100 m from the shore on the Galician "Death Coast".

HNS involved / quantity of HNS spilled: The ship carried several different types of chemicals: xylene, butanol, butyl acrylate, cyclohexanone, sodium, anilin oil, diphenyl-methan, o-cresol, dibutyl phthalate, phosphoric acid, phthalic anhydride. The total of HNS spilled was 1.100 tonnes.

Risks: The fire started in one of the 11 containers with 126 tons of sodium. All the HNS transported were toxic to the environment and harmful to human health and some explosively reactive with water.

Response: European assistance and IMO expertise were mobilized for identification of the cargo, initially unknown. Plans to unload hazardous substances from the ship were hampered by bad weather conditions and fire on board. Part of the cargo loaded on the deck was unloaded, but then a series of explosions shook the vessel. The operation necessitated 3 months work, with monitoring of water and air contamination. Following the explosion, 15.000 people were evacuated from the surrounding area overnight with buses. Great difficulties were encountered in evaluating risks involved without proper information on the cargo. A delay occurred in transporting intervention equipment to the site.

ANNA BROERE, 1988 – The Netherlands

Incident: On May 27, 1988, the carrier Anna Broere, on her way from Rotterdam to England, collided with the Swedish container ship Atlantic Compass. Atlantic

Compass could continue its journey towards Antwerp while Anna Broere was severely damaged and sank in the shallow water.

HNS involved / quantity of HNS spilled: The Anna Broere was transporting 547 tonnes of acrylonitrile and 500 tonnes of dodecyl benzene

Risk Acrylonitrile is a flammable liquid, toxic to both human and marine life, in seawater, it dissolves and evaporates. dodecyl benzene is not regarded as a marine pollutant.

Response: An exclusion zone with a radius of 10 km and a height of 300 m was therefore set up. Dutch authorities started an operation in order to recover the acrylonitrile with the help of a large floating crane and about half of the acrylonitrile was recovered. The other half had leaked out and rather quickly dispersed into the sea. During the operation the concentrations of acrylonitrile in air and water was continuously monitored. Because of hard weather the operation was delayed several times. The operation lasted a total of 73 days.It can be discussed however if the calculated impacts on the environment would have been that severe. The 200 tonnes of acrylonitrile that leaked out did cause damage to the marine biota, but with significantly less impact than anticipated.

KIMYA, 1991 - UK

Incident: On 6 January 1991**,** the cargo tanker Kimya was sailing in a heavy storm in the Irish Sea when she stranded off the south of the Isle of Anglesey (Wales). The hull of the Kimya was upturned and she drifted ashore. In February, the vessel was refloated. The wreck was eventually anchored to the seabed.

HNS involved / quantity of HNS spilled: 1500 t of sunflower oil spilled.

Risks: Sunflower and other vegetable oils are usually considered little dangerous and non-toxic products as it is a consumable goods however, they may become hazardous to marine life, even when spilled in small amounts in water, by the following ways:

(1) Smothering – most of the vegetable oils are less dense than water and would float on the surface when spilled. This would reduce the oxygen exchange across the air-water interface and allow conditions of oxygen depletion and therefore pelagic and

benthonic animals will be affected. It is also possible that these oils adhere to the oxygen exchange organs of animals (ie gills) reducing their effectiveness.

(2) Direct toxicity – vegetable oils may have a direct toxicity for animals or cause subletal effects such as lower growth rate (Salgado, 1995).

(3) Polymerization: Sunflower and other oils polymerize with time and lead to a formation of an impermeable cap over the sediment surface. This reduces the rate of oxygen diffusion into the sediments which leads to the loss of many species.

Response: Environmental monitoring confirmed some impact on intertidal populations. Gulls and other seabirds were observed diving on the wreck site and significant mussel mortality was observed in the intertidal zone near the incident. Scientific tests were carried out, revealing that molecules of sunflower oil had polymerised with wave action. Once on the beaches, the oil and sand formed an impermeable aggregate, under which shoreline species were prisoners. This seriously affected biodiversity. Mussels died by suffocation within 2 weeks after being in contact with the sunflower oil. Laboratory testing showed that their internal shell lost its nacre lining and that their external shell became chalky with the oil. Almost 6 years later, concrete-like aggregates of sand remained on the beaches.

ALESSANDRO PRIMO, 1991 - Italy

Incident: On February 1, 1991, the chemical carrier Alessandro Primo sank in the Adriatic Sea 16 miles off the coast of Italy. The water depth of the incident was 110 m**.** and. The vessel was lying on her starboard side with a rupture in an acrylonitrile pipe.

HNS involved / quantity of HNS spilled: aboard the ship was a cargo of 550 tonnes of acrylonitrile and 3000 tonnes of ethylene dichloride

Risk: Acrylonitrile is a flammable liquid, toxic to both human and marine life, in seawater, it dissolves and evaporates. Ethylene dichloride is oily liquid, flammable and toxic, upon contact with seawater it dissolves.

Response: An exclusion zone of ten mile radius was set up around the wreck. During the following days water samples were taken around the wreck at various depths. Four days after the incident a trace of acrylonitrile was found 500 m from the wrecks position. It was considered to be impossible to recover the entire ship which had been severely damaged when hitting the bottom. Three companies specialised in the area was hired to recover the cargo which threatened to pollute the area. The first step was to block the leaking of acrylonitrile and this was done by February 21. By the beginning of April the recovery operations started. All of the remaining cargo was taken care of, although most acrylonitrile had leaked out before the recovery operation started. The incident was complicated due to the great depth and very dangerous chemicals. The environmental impact of the incident was very small, especially regarding that two very pollutant chemicals were involved.

GRAPE ONE, 1993- UK

Incident: Error while ballasting ship caused shipwreck with 3 041 t of Xylene on board.
HNS involved / quantity of HNS spilled: 3 041 tonnes of Xylene.
Risks: Moderate pollutant, very flammable.
Response: Crew evacuated and winched to safety. Ship stranded and shipwrecked with cargo in the Channel. No further response was implemented and how much of the cargo was spilled remains unknown.

WEISSHORN, 1994 – Spain
Incident: On 27 February 1994, the container ship the Weisshorn was waiting for a space in the port of Sevilla off the Guadalquivir estuary (Andalusia) when it met with severe weather conditions. The anchor gave way and the ship was thrown onto rocks, heavily damaging the hull. The ship could not be moved from its position. It was left spilling its cargo and was dismantled over time by winter storms
HNS involved / quantity of HNS spilled: 6,200 tonnes of rice
Risk: Possibility of organic pollution by rotting rice. The rice fermented and gave off breakdown products liable to affect the environment.
Response: No response is known

FENES, 1996 – France
Incident: the Fenes Grounded in the marine reserve Lavezzi islands (Bonifacio, Corsica).

HNS involved / quantity of HNS spilled: Loss of 2 600 t of wheat

Risk: Wheat fermentation, with production of gaseous fermentation products (H2S) capable of intoxicating intervention personnel and generating local acidity, which is damaging to sessile benthos.

Response: the rotting cargo was dumped over the sea bed (15-20 m), where it formed a coat of up to 2m. It was recognised as a pollutant, to be removed. It was pumped onto a barge and dumped in the high sea at a low density. The ship remains were collected and removed during an eight month operation.

ALLEGRA, 1997 – English Channel, UK

Incident: On 1 October 1997, in the Channel, just off the coast of Guernsey, the Liberian tanker the Allegra was involved in a collision and 900 tonnes of palm oil spilled. Following the accident, the spilled oil quickly solidified to form a slick 800 by 400 metres. This then spread over an area of 20 km by 4 km. The slick came ashore in 5 to 50 cm diameter margarine-like balls in the Channel Islands and on the Cotentin Peninsula (Normandy, France).

HNS involved / quantity of HNS spilled: the tanker was transporting 15,000 tonnes of palm oil and 900 tonnes were spilled.

Risk: see Kimya incident

Response: Slick drift was monitored by French Customs and MPCU remote sensing aircraft using airborne SLAR (Sideways Looking Airborne Radar) systems. These methods enabled the pilots to locate and track the slick for the two days following the accident. a technique commonly employed for oil slick tracking. The palm oil slick was assessed as not being a risk to the marine environment, but had an adverse impact upon recreational areas and bathing beaches. After the spill, small scale testing was conducted at the Cedre in a bid to simulate the Allegra spill. The oil solidified almost instantaneously into very small particles, which subsequently aggregated into balls of 5 to 10 cm in diameter. Testing showed that the oil dispersed naturally in the water column. Operations to recover oil residues on the coast was conducted and 12 tonnes were picked up.

ALBION II, 1997 – North Atlantic Sea, Bay of Biscay, France

Incident: The cargo vessel Albion II broke in two and sank silently off the Bay of Biscay in waters 120 m deep.

HNS involved: calcium carbide, iodine, camphor, ammonia anhydrous

Risks: The vessel was carrying 10 dangerous substances, according to the IMO code, plus 1 100 t of propulsion fuel (IFO180).With regard to the chemicals, the presence of calcium carbide (114 tonnes packaged in 500 barrels of 50 kg and 800 barrels of 100 kg) meant a risk of explosion. This product spontaneously reacts with water to produce acetylene, a flammable gas (10 kg of calcium carbide gives off 3 to 4 m^3 of acetylene). Ecological impact has not been determined.

Response: No response known

JUNIOR M, 1999 – France

Incident: The Egyptian cargo boat Junior M, transporting 6,900 tonnes of ammonium nitrate in bulk, had a water leakage in one of its three holds.

HNS involved / quantity of HNS spilled: Ammonium Nitrate, 700 tones spilled.

Risk: Ammonium nitrate is an agricultural fertilizer compound, soluble in water, highly explosive when heated. As a fertilizer, it may promote eutrophication in waterways.

Response: The Junior M was diverted towards Brest's harbour. The reception operation of the Junior M was built around a safety area, where its holds could be flooded if fire started. As the water leakage in one of the holds in the bow could not be sealed, nearly 50 m^3 of water, which dissolved more and more the remaining ammonium nitrate, was pumped from the vessel. After an ecological assessment comparing land and sea disposal options, the decision was made to dump the nitrate solution in the open sea.

IEVOLI SUN, 2000 - English Channel, UK

Incident: The Italian chemical product tanker Ievoli Sun, en route from Southampton to Genoa, began taking water in bad weather and was abandoned in the west of Guernsey in the English Channel. The Ievoli Sun was taken in tow to Cherbourg overnight. The vessel subsequently sank at around 11 miles to the northwest of Alderney in 70 m depth of water.

HNS involved / quantity of HNS spilled: The vessel carried a mixed cargo of chemicals, comprising 4000 tonnes of styrene (vinylbenzene) and 1000 tonnes each of methyl hepthyl ketone (2-butanone; MEK) and isopropyl alcohol (2-propanol; IPA); and bunkers of 180 tonnes of intermediate fuel oil IFO180 and 53 tonnes of gasoil. More than 1000 tonnes of styrene spilled.

Risk: Both isopropyl alcohol and methyl ethyl ketone are volatile solvents which are fully miscible with water and would be rapidly dispersed and diluted within the water column following release. Styrene, a synthetic chemical is also volatile, but it is almost insoluble in water and has a lower density than seawater (specific gravity 0.909 vs. 1.035). Following release from the vessel on the seabed, this chemical would therefore rise rapidly to the sea surface, from where it would rapidly evaporate. In a pure state styrene will spontaneously polymerise. All of these three chemicals are of low to moderate toxicity to aquatic life and are not persistent. They also have a very low bioaccumulation potential in marine animals, and would be rapidly depurated once exposure ceased. Styrene can contaminate fish and shellfish and is classed by GESAMP as a possible carcinogen.

Response: A pollution control response was coordinated by the French with assistance from the UK.s MCA. Scientists from both countries agreed that the methyl ethyl ketone and the isopropyl alcohol posed no threat to the environment and would dissipate immediately on contact with water; however the presence of styrene did pose a threat to the environment and would require careful monitoring. The marine diesel oil and intermediate fuel oil onboard also posed a risk of pollution. More than 1000 tonnes of styrene are believed to have been lost to sea during the incident, resulting in an aerial plume of vapour which crossed Alderney and episodic contamination of air and water in the immediate vicinity of the wreck site. Analysis of edible tissues using coupled gas chromatography/mass spectrometry, performed soon after the incident, demonstrated low-level styrene contamination of crabs recovered from pots laid very close to the wreck site prior to the incident. These concentrations posed no risks to human consumers, and no fishery controls were implemented. The possibility of chronic effects was considered to be minimal, due to the behavior of styrene following release from the vessel.

Monitoring in air and water around the wreck site was undertaken after the incident. Styrene was detected in both air and water samples periodically, and on at least one occasion (9 November) operations in the area were suspended due to the high concentrations measured. During the next week intermittent styrene pollution could be detected in waters around the wreck site.

The salvage operation began in April 2001. The plan involved removal of the intermediate fuel oil and the styrene cargo and the controlled slow release to the water column of the methyl ethyl ketone and the isopropyl alcohol. The release of the two solvent chemicals showed no evidence of environmental impact. The styrene and the fuel were successful removed with the help of a remote operated offloading system.

BALU, 2001 – Spain

Incident: Chemical tanker the Balu, transporting 8,000 tonnes of sulphuric acid, sank in a storm in the Bay of Biscay at a depth estimated between 4,600 and 4,800 metres.

HNS involved / quantity of HNS spilled: sulphuric acid - 8,000 tonnes spilled.

Risks - Sulphuric acid is denser than water (d = 1.84), and therefore the acid would sink and is diluted in water. At the depth concerned, sea bed populations are low in biomass by unit of surface, not diversified and are not the subject of any exploitation. So, there would be no risk for fishing and the environmental impact can be considered temporary and localized. The risk presented by sulphuric acid for the environment is due to hydronium ions (pH effect). The effect of sulphuric acid therefore depends on the buffering capacity of the aquatic ecosystem. A pH of less than 5.5 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution and in seawater by a buffering effect, but marine organisms generally cannot endure significant variations in pH.

Response: No response known.

LYKES LIBERATOR, 2002 - off the coast of Finistère

Incident: Saturday, 2 February 2002: the container ship Lykes Liberator, sailing from Bremerhaven (Germany) to Charleston (USA) with 3000 containers on board reports the loss of 60 containers in rough sea, 120 nautical miles west of the island of Sein. One of the containers holds products classified as dangerous. It is a 40-feet open container (i.e. a simple metal structure, without roof or sides).

HNS involved/ quantity of HNS spilled: The dangerous chemicals were catalysts used in synthetic rubber, cosmetics and the pharmaceutical industry: aluminium diethyl iodide and toluene diethyl zinc.

Risk: Both products react when in contact with water (heat release), ignite spontaneously when in contact with air, and are known to cause serious burns.

Response: The Préfecture Maritime have required a risk assessment of the impact on human health and the environment, should the tanks strand on the shore. The information sent by the ship on the content of the drifting tanks was vague. The reference given was that of a class of chemical catalysts, aluminium alkyds, not that of a particular product. The risk to human health is roughly assessed (risk of explosion) but not the risk for the environment. Six days after, a tank was located close to the Ushant Traffic Separation Scheme. The Préfecture Maritime decided to launch recovery operations the following day. A tug was sent on site to mark out the tank's position. The support ship the Alcyon took them in tow towards Brest's harbour where they were delivered to Albermale Co's security administrator the next day. There were neither victims nor pollution, but a heavy emergency response workload in harsh conditions was necessary to ensure effective protection of men and the environment.

BOW EAGLE, 2002 – Channel, France

Incident: On Monday 26 August 2002, the chemical tanker Bow Eagle, en route from Brazil to Rotterdam, collided with a trawler in the middle of the night, in the Channel.

HNS involved / quantity of HNS spilled: loss of 200 tonnes of ethyl acetate, but the ship also transported methyl-ethyl-ketone, cyclohexane, toluene, benzene, ethanol, lecithin of soya, sunflower oil and vegetable oil.

Risk: The ship transported 510 t of lecithin of soya, 1652 t of sunflower oil, 1 050 t of methyl-ethyl-ketone, 4 750 t of cyclohexane, 3 108 t of toluene, 500 t of vegetable oil, 2 100 t of ethyl acetate, 4 725 t of benzene , 5 250 t of ethanol. 200 t of ethyl acetate leaked from the tanker before the chemical could be transferred to another tank. Luckily, there was no significant pollution.

Response: The breach was sealed.

JAMBO, 2003 – North Coast of Scotland

Incident: Bulk carrier the *Jambo*, on passage from Dublin to Odda in Norway, grounded on rocks on the on the north coast of Scotland on 29 June 2003. The vessel was carrying 3,300 tonnes of zinc concentrate (sphalerite), a zinc sulphide mineral and traces of other metals such as lead, cadmium and arsenic

HNS involved / quantity of HNS spilled: Zinc Sulphide – 1,100 tonnes spilled

Risks: zinc sulphide has low solubility in sea water, is of low toxicity and has a low potential to accumulate up the food chain.

Response: Following the sinking of the vessel, the Secretary of State's Representative for Marine Salvage and Intervention (SOSREP) took control of the salvage operation. By 7 July most of the fuel oil on board had been successfully recovered and salvage operations commenced to recover the cargo. This operation proved difficult due to the nature of the cargo, which was very heavy and in a fine powder form. During September, the vessel slipped into deeper water and capsized, making access to the cargo for recovery impossible. The estimated recovery of cargo was 1,500 tonnes. At this point salvage operations ceased and Scottish Environment Protection Agency (SEPA) undertook a monitoring programme covering the water column and the seabed sediments. In summary the monitoring progamme reports show that:

- Measured levels of zinc in the water column were mostly very low. Elevations of zinc in deep waters may occur if more material is disturbed but such events are expected to be localized and transient.

-Toxic impacts of zinc to water column animals are therefore considered very unlikely

-Measured levels of zinc in sediments are low except in the immediate vicinity of wreck (ca100 metres radius)

-Toxic and smothering impacts to benthic (seabed) animals are therefore expected to be similarly localized.

-There is currently no evidence to suggest that the discharged cargo from the *Jambo* has resulted in persistent elevated levels of zinc cadmium or arsenic in scallop and crab tissues.

- It is concluded that eating shellfish from the area around the *Jambo* incident does not raise any food safety concerns for consumers.

(*In* Final Report of the Jambo Environment Group to the Secretary of State's Representative, 2004).

ECE, 2006 - France

Incident: On the night of 30 to 31 January 2006, the Maltese bulk carrier transporting 26,000 tonnes of phosphates collided with the chemical tanker the Ece en route from Casablanca in Morocco to Ghent in Belgium. The accident occurred in a zone located 90 km west of Cherbourg, near the Casquet Traffic Separation Scheme in international waters. The Ece, transporting 10,000 tonnes of phosphoric acid, developed a leak and a significant list.

Chemicals involved / quantity spilled: The Ece was transporting 10,000 tonnes of phosphoric acid.

Risk: The phosphoric acid is a corrosive product, irritating the skin and eyes. It is toxic if ingested, inhaled or in contact with the skin. In the aquatic environment it sinks and gradually dissolves to produce H^+ (hydrogen) and PO_4^{3-} (phosphate) ions by exothermic reaction. It is an inorganic, non bioaccumulable substance. Its toxicity is therefore mainly linked to the acidification of the local environment where the spill occurs (decrease in pH) and to the presence of impurities.

Response: The Préfecture Maritime for the English Channel and the North Sea (Premar-Manche) carried out a pollution risk analysis, with the support of the French Navy anti-pollution centre (CEPPOL) and Cedre. In addition to the cargo, there were 70 tonnes of propulsion fuel (IFO 180), 20 tonnes of marine diesel and 20 tonnes of lubricating oil onboard the Ece. The assessment teams did not note any pollution, and boarded the two damaged ships. When the assessment had been completed, the vessel was taken in tow by the tug the Abeille Liberté bound for the port of Le Havre. In the course of towing, the Ece sank 70 m deep 50 nautical miles west of the point of The Hague.

ROKIA DELMAS, 2006 - Isle of Ré, France

Incident: On 24 October 2006, the container ship the Rokia Delmas, suffering from total engine failure, was driven ashore by a storm on the south coast of the Ile de Ré, French Atlantic coast and hit a rocky outcrop, 1 nautical mile south of the coast.

Chemicals involved / quantity spilled: The Rokia Delmas was transporting 300 containers of cocoa beans, wood, 500 tonnes of heavy fuel oil (IFO 380) and 50 tonnes of marine diesel.

Risks: The vessel was mainly transporting cocoa beans, wood and more than 500 t of IFO 380 and 50 t of marine diesel. The cocoa beans could rot if spilled and generate organic pollution in a major oyster farming area.

Response: As a precautionary measure, the Polmar Land Plan for Charente Maritime was activated. An oil spill response vessel was sent to the site. On 30 October, 430 m^3 of fuel was pumped out of the tanks. Oyster beds were protected by booms. The main concern then turned to the 300 containers of cocoa beans onboard the vessel. Upon request from the Préfecture Maritime, Cedre set up a series of experiments to determine the behaviour of cocoa beans, in the event the containers fell into the water. By the third day of immersion, a great abundance of suspended matter and turbidity was observed in the water. Over time, an increasing proportion of beans sank and a white oily film on the surface indicated the release of lipids. Monitoring of the gaseous release showed the generation of hydrogen sulphide by the fermentation of cocoa beans in seawater. During a 15 month operation, the ship cargo was removed, the wreck was cut into five pieces and the pieces were removed.

MSC NAPOLI, 2007 – South Devon Coast, UK

Incident: On January 20, 2007, the 53,000 tonne container ship *MSC Napoli,* in heavy weather, developed structural damage in the form of hull cracks visible from the engine room through which water entered and flooded the stern section. Originally, the plan was to tow the vessel to Portland where her fuel and cargo could be offloaded, but further serious structural damage sustained en route necessitated the decision by the Secretary of States Representative (SOSREP) to beach her in Lyme Bay on the south coast of England.

Chemicals involved / quantity spilled: The ship carried more than 1,600 tonnes of chemical products classified by the International Maritime Organisation (IMO) as dangerous goods (e.g. bisphenol A, epichlorohydrin-epoxy resin, alkylphenols, isophoronediamine nonylphenol, propaquizafop, profenofos, carbendazim, hexamethylindanopyran, and dibutyltinoxide, as well as organic solvents, acids, and corrosive materials). In addition, 3,780 tonnes of heavy fuel oil (IFO 380) and 45 tonnes of diesel oil.

Risks: Among the chemicals on board of greatest potential hazard were a number of pesticides (including an organophosphate) and herbicides.

Response: A salvage operation was begun with the aim of removing the oil and cargo from the ship. A number of bodies (Defra, Marine and Fisheries Agency, Environment Agency, Cefas, Health Protection Agency, Natural England, Devon and Dorset Councils, the International Tanker Owners Pollution Federation) assisted the Maritime and Coastguard Agency in devising an appropriate response. As a quantity of oil and approximately 100 containers had been lost during and immediately following the grounding of the *MSC Napoli*, it was also decided to design and implement a monitoring programme in Lyme Bay in order to assess any environmental impact and to protect the human food chain.

Six weeks post-incident, once the fuel oil had been removed and the initial concerns receded, the focus of the environmental group turned to the hazard posed by the mix of chemicals remaining on board in the containers. To provide an integrated assessment of the range of contaminants in the containers, a bioassay approach was used. The bioassay approach was applied to the direct toxicity assessment of water sampled from the seven flooded holds and engine room of the vessel. The 'hold water' was considered to represent a solution that integrated the full range of chemical components being released from the cargo and would provide biological effects data that could be used to assess toxicological impact if there were a substantial release of hold contents into the surrounding water. Two established and internationally accepted bioassays were used. The first was with the marine harpacticoid copepod, *Tisbe battagliai*, a 48 h acute toxicity test conducted in 12 well cell plates. The second method was a 72 h growth inhibition test conducted in a 96-well microplates using the marine diatom, *Skeletonema costatum.* Alongside the toxicity testing, hold and engine room water samples were analysed for target chemicals using coupled gas chromatography–mass spectrometry. The results of the bioassays showed that after day 55 post-incident, the water from the holds or engine room did not show any significant levels of acute toxicity to the copepod. However, in contrast, on several occasions from several holds demonstrable levels of algal growth inhibition were apparent up to and including day 93 post-incident. From day 103 post-incident the samples removed from the vessel showed no acutely toxic effects for either species. The concomitant chemical analysis showed the detection of a wide range of chemical compounds: phthalates, dibutyl tin compounds, xylene, sulphur, tetrachloroethylene and dimethyl sulphide.

(*In* Kirby et al, 2008; Cefas Lowestoft, 2008)