

NIOZ Royal Netherlands Institute for Sea Research

THE ISSUE OF NON-OIL SPILLS

hydrophobic and insoluble chemicals discharged into the marine environment and the effects on marine wildlife

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NIOZ is part of the Netherlands Organisation for Scientific Research (NWO)



NIOZ A mystery spill....

January 2007, Noord-Holland, The Netherlands

- Seabirds covered in a green, sticky mass
- An estimated 20-28 tonnes of material washed ashore
- A sinister aspect: fresh carcasses dissolved at a high rate
- The substance turned out to be a chemical mix, with high concentrations of sulphur, strontium, arsenic, copper, and traces of 4-tert-butylphenol (CAS 98-54-4) and 4-(1,1-dimethylpropyl)phenol (CAS 80-46-6)
- People working with the casualties suffered from a serious irritation of the upper respiratory tract
- No bird survived
- The source of the spill was never traced

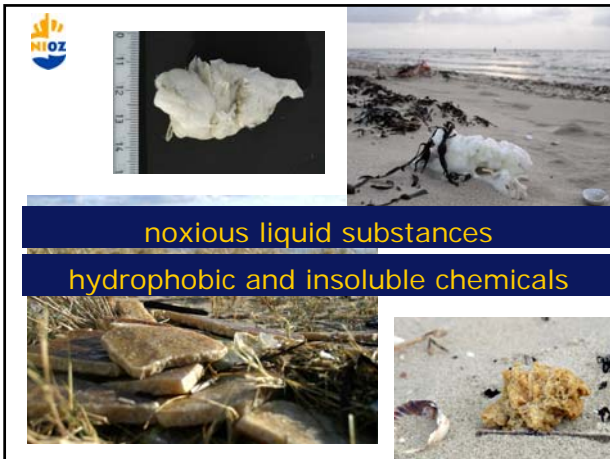
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NIOZ marine oil pollution




IFAW
Chronic oil pollution in Europe

From IFAW's 'Environmental Status Report' by the Royal Netherlands Institute for Sea Research




noxious liquid substances

hydrophobic and insoluble chemicals



International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL)




Annex II: Control of pollution by noxious liquid substances
 Entry into force: 6 April 1987
 (Revised Annex II enters into force 1 January 2007)

Annex II details the **discharge criteria** and measures for the control of pollution by **noxious liquid substances** carried in bulk.

Some 250 substances were evaluated and included in the list appended to the Convention. The discharge of their residues is allowed only to reception facilities until certain concentrations and conditions (which vary with the category of substances) are complied with.

In any case, **zero discharge** of residues containing noxious substances is permitted **within 12 miles of the nearest land** or within the Antarctic zone.

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Pollution categories under MARPOL Annex II (revised list)

Substances presenting

- A major hazard** **Category X**
- A hazard** **Category Y**
- A minor hazard** **Category Z**

to either marine resources or human health and, therefore,
 (x) justify the prohibition,
 (y) justify a limitation on the quality and quantity
 or (z) justify less stringent restrictions
 of the discharge into the marine environment

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Pollution categories under MARPOL Annex II (revised list)

Category OS → "other substances"

presenting **no harm** 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

Listed substances of least concern (OS) include slurries of clays, coal, glucose solution, hydrogenated starch hydrolysate, lecithin, molasses, non-noxious liquids, sorbitol solution, hydrolysed vegetable protein solution, and water

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THE REVISED GESAMP HAZARD EVALUATION PROCEDURE

Hazardous Rating	Aquatic environment			
	A. Bioaccumulation and Biodegradation		B. Aquatic Toxicity	
0	log Pow < 3	BCP	LD50 (mg/kg)	LD50 (mg/kg)
1	11-12	not recommended	100-1000	10-100
2	13-14	not recommended	10-100	1-10
3	15-16	not recommended	1-10	0.1-1
4	17-18	not recommended	0.1-1	0.01-0.1
5	19-20	not recommended	0.01-0.1	0.001-0.01

Hazardous Rating	Human health (Toxic Effects to Mammals)			
	C. Acute Mammalian Toxicity		D. Irritation, Corrosion & Long-term health effects	
0	LD50 (mg/kg)	LD50 (mg/kg)	LD50 (mg/kg)	LD50 (mg/kg)
1	1000-10000	100-1000	not irritating	not irritating
2	100-1000	10-100	irritating	irritating
3	10-100	1-10	severe irritation	severe irritation
4	1-10	0.1-1	corrosive	corrosive

Hazardous Rating	Interference with other uses of the sea	
	E.1. High BOD5 & turbidity	E.2. Interference with Coastal Activities
0	0	0
1	1	1
2	2	2
3	3	3

A. Bioaccumulation and Biodegradation


B. Aquatic Toxicity

C. Acute Mammalian Toxicity


D. Irritation, corrosion, and long-term health effects

E. Interference with other uses of the sea

GESAMP 2002. The Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships.
 IMO/FAO/UNESCO/IOC/WMO/WHO/IAEA/UN/EP, London, 2002.



CASE 1 Category X substance



Several cases involved spills of **nonylphenol** and **dodecylphenol**:

Example: a series of spills of Nonylphenol in winter 1988/89 (several thousands of seabirds affected)¹


Various other substances on the birds, including vegetable oils, ethylester and 2-hydroxy-1-(hydroxymethylethyl)hexadecanoic acid

¹Averbeck 1990, Zoun 1991, Zoun *et al.* 1991ab

Category X → substances presenting a major hazard, to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment

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CASE 2 Category Y substance




- Hundreds of seabirds affected, Wadden Sea
- Cause: a discharge of **linseed oil** (90%) a highly sticky substance and other unknown substances
- Hundreds of kilograms on beaches, more or less solidified
- The effect on birds was first immobilisation, hypothermia, exhaustion and starvation.
- A very low proportion of the birds received in rehab centres survived and could be released
- Cleaning these birds required unusually aggressive cleaning agents


Engelen K.A.M. 1987. Zeevogels op de Waddemilanden het slachtoffer van lijmachtige substantie. Sula 1(4): 112-113.

Category Y → substances presenting 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

CASE 3 Category Z substance



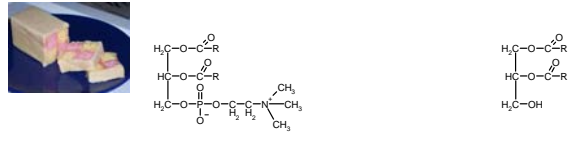
≥1100 seabirds affected by **Polyisobutylene (PIB; C₄H₈)_n** → a "non-toxic, non-aggressive substance", used to make chewing gum and cello tape



Camphuysen et al. 1999. Seabirds in the North Sea demobilised and killed by polyisobutylene (C₄H₈)_n. Mar. Poll. Bull. 38(12): 1171-1176.

Category Z → substances presenting 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

CASE 4 Category OS substance

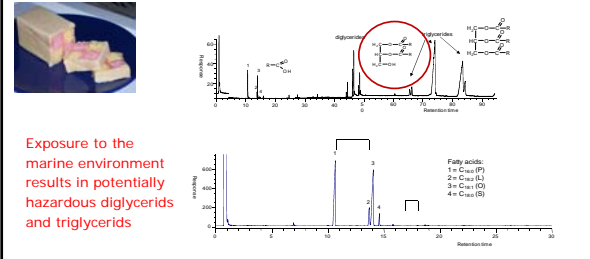


Lecithins (Cat. OS) → environmental exposure → diglycerides (Cat. Y)

Decomposition of Lecithin following environmental exposure

Category OS → "other substances (OS)" presenting **no harm** 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

CASE 4 Category OS substance



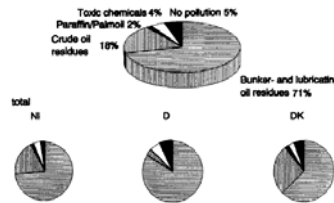
Exposure to the marine environment results in potentially hazardous diglycerides and triglycerides

Gas chromatogram of stomach content Northern Fulmar *Fulmarus glacialis* before and after hydrolysis

Category OS → "other substances (OS)" presenting **no harm** 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

Fuel oil – Crude oil - Vegetable oils - Chemicals

Dodecylphenol, detergents, alcohols, thiophenes, alkylated bis-phenols, phthalates (plasticizers), halogenated hydrocarbons (insecticides), alkylated aromatics



Dahlmann G., Timm D., Auerbeck C., Camphuysen C.J. & Skov H. 1994. Oiled seabirds - Comparative investigations on oiled seabirds and oiled beaches in the Netherlands, Denmark and Germany (1990-1993). Mar. Poll. Bull. 28: 305-310.

TABLE 6
Cases of pollution by non-toxic chemicals (legal discharges)

Date	Country	Substance	Impact
1990-92	D/NL/DK	Paraffin wax	11 different cases of pollution on different sampling sites
August 1991	D	Pulverem, Latgeog, Juis, Amrum	Paraffin wax (Petroleum)
September 1991	D	Friedrichskoog	Paraffin wax
December 1991	D	Sylt	Paraffin wax
November 1992	D	St. Peter	Paraffin wax
December 1992	D	Amrum	Paraffin wax
February/March 1993	NL	Northern part	Paraffin wax
February 1991	DK	Bornholm	Palm oil
November 1991	NL	Teut	Palm oil
April 1992	NL	Teut	Palm oil
November 1992	NL	Teut	Palm oil
July 1991	D	Föhr	Palm oil
May 1991	D	Helgoland	Palm oil
November 1992	D	Sylt	Palm oil
November 1992	DK	W-coast	C12-fatty-acid

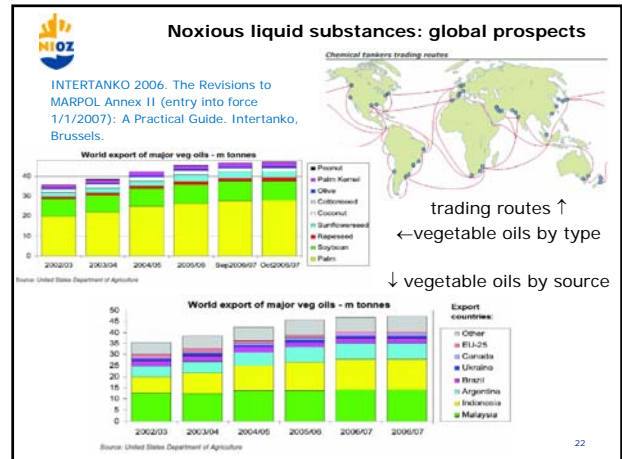
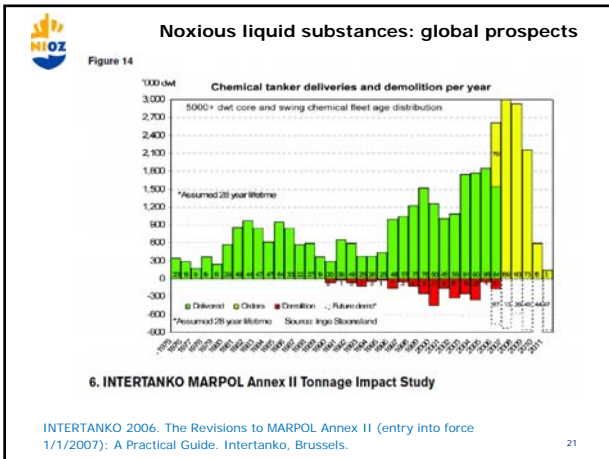
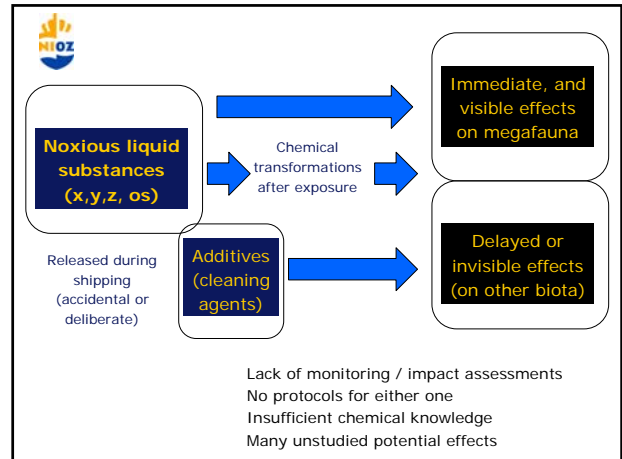
TABLE 7
Special cases of pollution by more or less toxic chemicals

Date	Country	Substance	Impact
February 1990	NL	Dodecylphenols + lubricating oil	Polluted birds
March 1990	DK	Bornholm	Polluted birds
November 1990	NL	Helgoland	Polluted birds
January 1991	DK	Juis	Polluted birds
February-March 1991	NL	Helgoland	Polluted birds
March 1991	DK	Baltic	Pollution
April 1991	DK	NW-coast	200 kg. Beaches heavily polluted
June 1991	D	Juis, Sylt	Several tons on the beaches
January-February 1992	DK	Bornholm, Sylt	Many polluted birds
April 1992	N	Ruga	Pollution
July 1991	DK	Bornholm	Pollution
	DK	NW-coast	Pollution

Effects of noxious liquid substances on wildlife

- A 1. **direct toxic effects** (after ingestion, inhalation, or skin contact)
2. **loss of waterproofing** and insulation → hypothermia, exhaustion
3. **mechanical defects** (locomotion)
- B 4. **weight loss, starvation** (e.g. when the digestive system or foraging capabilities are affected)
5. **disease** or impaired disease resistance (i.e. susceptibility to infectious disease)
6. **reduced immunologic function**
7. **pathological changes in tissue** (e.g. inflammation of gastrointestinal lining, malformations, atrophy or accumulation of fluids)
- C 8. **physiologic disruptions** (e.g. altered endocrine function, liver and kidney disorders, altered blood chemistry, blood disorders, impaired salt gland function, etc)
9. **reduced growth** and development
- D 10. **food chain effects** (through bioaccumulation)
11. **impaired reproduction**


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- Remaining issues**
1. Uncertainties about the origin, nature and chemical composition of substances spilled or their environmentally transformed products
 2. Uncertainties how to respond (for those involved in clean-up and response; including scientific investigations of the casualties)
 3. Absence of a monitoring protocol in which all details about cause and effects are logged, and
 4. Absence of a final publications reviewing all details and accumulated information in case of spills
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- Conclusions**
- Non-mineral oil pollutions currently more prominent than before (oil declines)
 - Case studies with each of the categories represented
 - Potential effects (environmental hazards) unclear
 - Note similarities with effects of mineral oil pollution caused by *visibility* of effects
 - Note delayed or hidden effects
 - Bias towards the effect on 'charismatic megafauna' due to *visibility* of effects
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 **Thank you**



A photograph of a dead bird, possibly a gull, lying on a surface. The bird's head is covered in a thick, dark, greenish-brown substance. A small white tag with handwritten text is attached to the bird's neck. A green question mark is drawn over the substance on the bird's head. In the bottom right corner of the photograph, there is a small cartoon illustration of a person in a yellow shirt looking at a laptop screen that displays a green skull and crossbones symbol. The text 'green substance' is written above the cartoon.

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