

DIMETHYL DISULPHIDE

EU classification:

F: Highly flammable



Xn: Harmful



N: Dangerous for the environment



UN n°: 2381

MARPOL classification: Y

SEBC classification: S (sinks)



Cedre

DIMETHYL DISULPHIDE

PRACTICAL GUIDE

INFORMATION

DECISION-MAKING

RESPONSE

This document was drafted by *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) with financial support and technical guidance from ARKEMA as well as financial support from the French Navy.

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The information contained within this guide is a result of *Cedre's* research and experience. *Cedre* cannot be held responsible for the consequences resulting from the use of this information.

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Warning

Certain data, regulations, values and norms may be liable to change subsequent to publication. We recommend that you check them.

Purpose of this guide

As part of the research funded, ARKEMA and *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) have produced a series of response guides for chemical hazards. They can be used to assist in emergency response in the event of an incident involving a vessel carrying hazardous substances which may cause water pollution.

These guides are updates of the 61 "mini response guides" published by *Cedre* in the early 1990s.

These guides are designed to allow rapid access to the necessary initial information (see chapter entitled "First line emergency data"), in addition to providing relevant bibliographical sources to obtain further information.

They also contain the results of scenarios relating to incidents which have occurred in

the Channel, the Mediterranean, in ports and in rivers. These scenarios are only intended to provide response authorities with indications of what to do in an emergency. Each real incident should be analysed individually and the response authorities should not underestimate the importance of taking in-situ measurements (air, water, sediment and marine fauna) in order to determine exclusion areas.

These guides are intended primarily for specialists who know about the techniques to use in the event of an emergency in addition to the relevant operational response measures. The main concern is to mitigate the consequences of a spill, however we cannot afford to overlook responder safety and human toxicology.

To contact the duty engineer at *Cedre* (24/7)
Please call: + 33 (0)2 98 33 10 10

National toxicology surveillance system in the event of a major toxicological threat.

In France, a hotline is manned around the clock by Division 7 of the General Department of Health (SD7/DGS).

During opening hours please call:
Tel.: + 33 (0)1 40 56 47 95
Fax: + 33 (0)1 40 56 50 56

Outside normal working hours please call the relevant authority.

Poison Control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: + 33 (0)2 41 48 21 21
Bordeaux (Hôpital Pellegrin-Tripode) Tel.: + 33 (0)5 56 96 40 80
Grenoble (Hôpital Albert Michallon) Tel.: + 33 (0)4 76 76 56 46
Lille (Centre Hospitalier Universitaire) Tel.: + 33 (0)8 25 81 28 22
Lyon (Hôpital Edouard Herriot) Tel.: + 33 (0)4 72 11 69 11
Marseille (Hôpital Salvator) Tel.: + 33 (0)4 91 75 25 25
Nancy (Hôpital Central) Tel.: + 33 (0)3 83 32 36 36
Paris (Hôpital Fernand Widal) Tel.: + 33 (0)1 40 05 48 48
Reims (Hôpital Maison Blanche) Tel.: + 33 (0)3 26 78 48 21
Rennes (Hôpital de Pontchaillou) Tel.: + 33 (0)2 99 59 22 22
Rouen (Hôpital Charles Nicolle) Tel.: + 33 (0)2 35 88 44 00
Strasbourg (Hôpitaux Universitaires) Tel.: + 33 (0)3 88 37 37 37
Toulouse (Hôpital de Purpan) Tel.: + 33 (0)5 61 77 74 47

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What you need to know about dimethyl disulphide

A

Definition

Dimethyl disulphide (DMDS) is a pale yellow liquid with a strong, pungent odour. It is a highly flammable, volatile organic compound (with a flash point of 15°C). It is harmful for humans and dangerous for the environment. The olfactory threshold is very low, around 0.01 ppm.

Uses

Dimethyl disulphide is used in oil refining as a sulphiding agent, in petrochemicals for decoking operations and in metallurgy for its anticorrosion properties.

Its great efficiency as a nematocide makes dimethyl disulphide a potential substitute for methyl bromide in agriculture. It is also used as a chemical intermediate in the manufacture of pesticides.

Risks

- Toxicity:

Dimethyl disulphide is harmful if inhaled or swallowed.

- Fire:

Dimethyl disulphide is a readily flammable compound whose fumes are irritating and toxic.

The substance breaks down at 390°C into flammable and toxic products (sulphur oxides, carbon monoxide, carbon dioxide, hydrogen sulphide, methyl mercaptan and dimethyl sulphide).

- Explosion:

Vapours can form explosive mixtures with air. The vapours are heavier than air and can accumulate in depressions in the ground.

Heating containers also leads to a risk of explosion.

See conversion factors (p. 10)

Behaviour in the environment

Dimethyl disulphide is slightly soluble (1 to 2 g/L) in water, however this part dissolves rapidly.

When spilt on a calm water body, because of its surface tension, dimethyl disulphide will tend to remain at the surface and evaporate before sinking. It will accumulate on the bottom while dissolving slightly. This product is very stable over time.

When spilt in agitated water, although the product sinks and accumulates on the bottom, the surface movement causes evaporation. The greater the agitation and the shallower the water column, the greater the evaporation will be.

When spilt on land, dimethyl disulphide will be broken down by photolysis and by volatilisation.

The vapours are heavier than air and can spread out at ground level.

According to its Kow and BCF values, dimethyl disulphide is not bioaccumulable.

When dissolved in water, DMDS is stable and will not break down within two months.

First line emergency data

- First aid information _____ **B1**
- ID card _____ **B2**
- Physical data _____ **B3**
- Flammability data _____ **B4**
- Toxicological data _____ **B5**
- Ecotoxicological data _____ **B6**
- Persistence in the environment _____ **B7**
- Classification _____ **B8**
- Particular risks _____ **B9**
- Transportation, handling, storage _____ **B10**

B

First aid information

(ARKEMA SDS, 2005; IPCS INCHEM, 2004; CEFIC, 2005; HSDB, 2006)

Immediately remove all soiled or spotted clothes with suitable gloves.

Intoxication by inhalation

- Move the victim into the open air and lie them down.
- Apply artificial respiration if necessary.
- Place the victim under medical supervision.
- Transfer to hospital in the event of complications (loss of consciousness, suffocation).

Contact with the skin

- Do not attempt to remove clothing if it is stuck to the skin.
- Immediately wash thoroughly with soap and water.
- Consult a doctor in the event of adverse effects (irritation, redness, burns).

Contact with the eyes

- Immediately rinse with plenty of water for 15 minutes, removing contact lenses if easily possible.
- Transfer to hospital if the feelings of irritation, pain, swelling, watering eyes or photophobia persist.

Intoxication by ingestion

- Rinse the mouth out with water.
- Do not attempt to induce vomiting if the victim is unconscious.
- Transfer to hospital.

Where necessary, contact the nearest poison control centre (cf. page 4).

B1

ID card¹

Dimethyl disulphide

Gross formula: $C_2 H_6 S_2$

Semi-developed formula: $CH_3-S-S-CH_3$

Synonyms

DMDS; Dimethyl disulfide; 2,3-Dithiobutane; 2,3-Dithiabutane; Methyl disulphide; Methyl disulfide; Methyl dithiomethane; Dimethyl disulfane.

EU Classification

F: Highly flammable

Xn: Harmful

N: Dangerous for the environment

R11: Highly flammable.

R20/22: Harmful by inhalation and if swallowed.

R36: Irritating to eyes.

R51/53: Toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment.

S16: Keep away from sources of ignition. No smoking.

S28: After contact with skin, wash immediately with plenty of water.

S61: Avoid release to the environment. Refer to special instructions/safety data sheet.

CAS n°: 624-92-0

EC n° (EINECS): 210-871-0

Classification for transportation

UN n°: 2381

Class: 3

B2

¹ Additional data and sources in annex 1

Physical data

Conversion factors:

1 ppm = 3.853 mg/m³

1 mg/m³ = 0.260 ppm

1 atm = 1.013×10⁵ Pa

B3

Melting point	- 84.7°C <small>DIPPR, 2006</small>
Boiling point	109.8°C <small>DIPPR, 2006</small>
Critical temperature	333°C <small>YAWS, 1999</small>
Relative density (water = 1)	1.063 at 20°C <small>ARKEMA SDS, 2004</small>
Relative vapour density (air = 1)	3.25 <small>ARKEMA SDS, 2004</small>
Solubility in seawater	1 g/L <small>CEDRE, 2007</small>
Solubility in fresh water	2 g/L <small>CEDRE, 2007</small>
Vapour pressure/tension	29 hPa (mbar) at 20°C <small>DIPPR, 2006</small> 38 hPa (mbar) at 25°C
Viscosity at 20°C	0.62 mPa.s <small>DIPPR, 2006</small>
Olfactory threshold	0.01 ppm <small>ARKEMA SDS, 2004</small>
Henry's law constant	122.5 Pa.m ³ /mole at 20°C (0.001225 atm.m ³ /mole) <small>ARKEMA SDS, 2004</small>
Molecular mass	94.2 g/mol <small>ARKEMA SDS, 2004</small>
Evaporation rate	no data available
Surface tension	33.94 mN/m at 20°C <small>CEDRE, 2007</small>

Flammability data

Explosive limits by volume (% in air) ARKEMA SDS, 2004

Lower limit: 1.1 % or 11,000 ppm

Upper limit: 16 % or 160,000 ppm

Regression speed: no data available

Flash point ARKEMA SDS, 2004

closed cup: 15°C (ASTM D 93)

Self-ignition point ARKEMA SDS, 2004

300°C

Decomposition temperature ARKEMA SDS, 2004

390°C

Dangerous products of decomposition

ARKEMA SDS, 2004; CSST, 1994; ICSC, 2005

Irritating, toxic fumes.

Thermal decomposition into flammable, **toxic** products: hydrogen sulphide, sulphur oxides, carbon monoxide, carbon dioxide.

Thermal decomposition into flammable, **harmful** products: methylmercaptan, dimethyl sulphide (DMS).

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Toxicological data

Acute human toxicity

(CANUTEC, 2000; ICSC, 2005; ARKEMA SDS, 2004; HSDB, 2006)

The effects caused by exposure to DMDS (inhalation, ingestion or contact with the skin) may be deferred.

- By ingestion: headaches, nausea, dizziness, drowsiness.
- By contact with the skin: irritation, redness.
- By contact with the eyes: ocular irritation.
- By inhalation: headaches, nausea, dizziness, drowsiness. Dimethyl disulphide has an irritating effect on the respiratory tract. The inhalation of decomposition fumes can cause bronchospasms, pneumonia and pulmonary oedema.

Chronic human toxicity

(HSDB, 2006)

Repeated or prolonged exposure to the skin can cause dermatitis.

Disorders of the iron metabolism have been observed in workers exposed to dimethyl disulphide and other sulphur compounds.

Alkyl disulphides can cause haemolytic anaemia.

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Threshold toxicological values

Occupational exposure values

no data available

Risk management values for the population

(US DEPARTMENT OF ENERGY'S CHEMICAL SAFETY PROGRAM, 2005)

TEEL 0: $0.0013 \text{ mg/m}^3 = 0.0035 \text{ ppm}$

TEEL 1: $0.03853 \text{ mg/m}^3 = 0.01 \text{ ppm}$

TEEL 2: $192.65 \text{ mg/m}^3 = 50 \text{ ppm}$

TEEL 3: $963.25 \text{ mg/m}^3 = 250 \text{ ppm}$

Specific effects

(ARKEMA SDS, 2004; ONTARIO MINISTRY OF THE ENVIRONMENT, 2005)

Genotoxic effects: the *in vitro* and *in vivo* results do not cause the product to be considered as genotoxic.

Effects on reproduction: absence of congenital malformations in animals.

Carcinogenic effects: no data available.

Ecotoxicological data

Acute ecotoxicity (ARKEMA SDS, 2004)

Crustacean (<i>Daphnia</i> sp.)	EC ₅₀ (48 h) = 7 mg/L (fresh water) (OECD 202)
Crustacean (<i>Americamysis bahia</i>)	LC ₅₀ (96 h) = 5.0 mg/L (seawater) (OECD 201)
Fish (<i>Salmo gairdneri</i>)	LC ₅₀ (120 h) = 1.75 mg/L (fresh water)
Fish (<i>Cyprinodon variegatus</i>)	LC ₅₀ (96 h) = 5.6 mg/L (seawater)
Algae (<i>Pseudokirchneriella subcapitata</i>)	LC ₅₀ (72 h) = 11 mg/L (fresh water) (OECD 201)

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Chronic ecotoxicity (ARKEMA SDS, 2004)

Algae (<i>Pseudokirchneriella subcapitata</i>)	NOEC (72 h) = 10.43 mg/L (OECD 201)
--	-------------------------------------

PNEC (Predicted No-Effect Concentration): According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated PNEC_{water} is 1.75 µg/L. A safety factor of 1,000 is applied to the lowest value of the three trophic levels.

Persistence in the environment

(ONTARIO MINISTRY OF THE ENVIRONMENT, 2005)

Volatilisation

In the air, dimethyl disulphide is present in the form of vapours in the atmosphere, due to its vapour pressure (38 hPa at 25°C). On land, its Henry's law constant (1.22×10^{-3} atm.m³/mole) means that it rapidly evaporates.

In water, although part of the dimethyl disulphide spilt will sink, another part may evaporate. The evaporation half-life for a river scenario is 3 hours and for a lake scenario is 4 days.

Photolysis

In air, dimethyl disulphide present in the form of vapours is broken down by hydroxyl radicals (half-life = 3.5 days), nitrate radicals (half-life = several hours) and atomic oxygen (half-life = 6.2 days). Liquid dimethyl disulphide is also broken down by hydroxyl radicals (half-life = 4 hours), direct photolysis (half-life = 3.2 to 4.6 hours in full sun) and by nitrate

radicals (half-life = 1.1 hours). On the ground or the water surface, dimethyl disulphide may be present in the form of vapours or liquid. It is therefore broken down by photolysis in a few hours.

Mobility

Due to its Koc, dimethyl disulphide is mobile in soil and can be adsorbed by soil or sediments. In water, dimethyl disulphide is slightly soluble (1 to 2 g/L) and tends to sink. It is not adsorbed by matter in suspension nor by sediments.

Bioaccumulation

According to its Kow and BCF values, dimethyl disulphide is not bioaccumulable.

Organic carbon/water partition coefficient: $\log K_{oc} = 2.34$

ARKEMA SDS, 2004

Octanol/water partition coefficient: $\log K_{ow} = 1.77$

ARKEMA SDS, 2004

Bioconcentration factor: $BCF = 13$

HSDB, 2004

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Classification

Classification (IMO, 2004)

- Hazards: S/P (safety/pollution risk)
- Ship type: 2
- Tank type: 2G (integral gravity tank)
- Tank vents: open
- Controlled venting: no
- Electrical equipment:
class i: T3
class i': II A
class i''': no (flash point < 60°C)
- Gauging: R (restricted gauging)
- Vapour detection: F-T (flammable and toxic vapours)
- Fire protection: B: ordinary foam, comprising all the foams that do not resist alcohol,

in particular fluoroprotein foams and those that form an aqueous film (AFFF).

- Materials of construction: no particular instruction
- Respiratory and eye protection: no protection required

SEBC classification: S (sinks)

MARPOL classification: Y

B8

EU classification:



F: Highly flammable



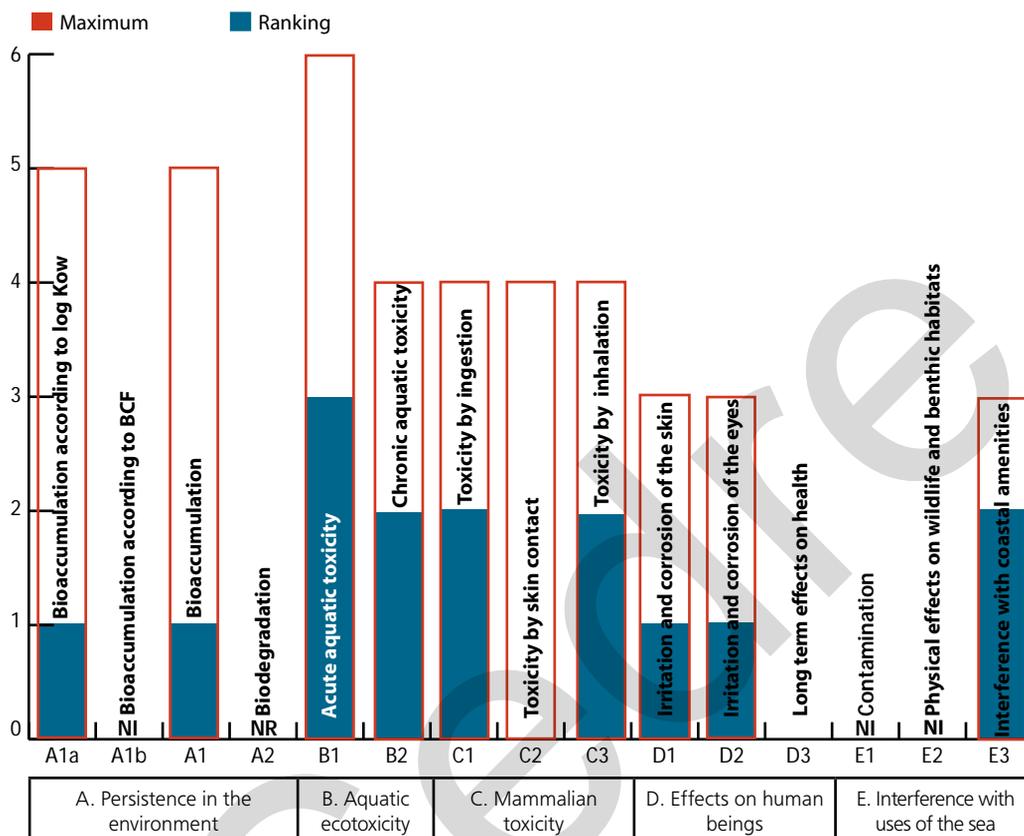
Xn: Harmful



N: Dangerous for the environment

R11	Highly flammable.
R20/22	Harmful by inhalation and if swallowed.
R36	Irritating to eyes.
R51/53	Toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment.
S16	Keep away from sources of ignition. No smoking.
S28	After contact with skin, wash immediately with plenty of water.
S61	Avoid release to the environment. Refer to special instructions/safety data sheet.
210-871-0	E.C. n° (EINECS)

GESAMP classification of dimethyl disulphide: (GESAMP, 2006)



A1a: very slight potential to bioaccumulate in aquatic organisms

A1b: **NI**: no information

A1: very slight potential to bioaccumulate in aquatic organisms

A2: **NR**: not readily biodegradable

B1: moderate acute aquatic toxicity

B2: moderate chronic aquatic toxicity

C1: moderate toxicity when ingested by mammals

C2: negligible toxicity through skin contact with mammals

C3: moderate toxicity through inhalation by mammals

D1: moderately irritating to the skin

D2: moderately irritating to the eyes

D3: no long term effects

E1: **NI**: no information

E2: **NI**: no information

E3: moderately objectionable, possible closure of amenities.

Particular risks

Polymerisation

N/A

Danger (IPCS INCHEM, 2004; CEFIC, 2005; CANUTEC, 2000)

Heating or combustion of the product gives off toxic, irritating fumes including sulphur oxides.

Dimethyl disulphide can form explosive air/vapour mixtures.

When a receptacle containing DMDS is heated, there is an increase in pressure leading to a risk of the container bursting and a possibility of a fireball (BLEVE).

The vapours are invisible and heavier than air. They spread out across the ground and can infiltrate sewer systems and basements.

The vapours can spread as far as a source of ignition and cause flashback to the source of the leak.

Stability and reactivity (ARKEMA SDS, 2004; CSST, 1994)

Safety precautions: keep away from heat and sources of ignition. Do not overheat, in order to prevent thermal decomposition.

Substances to be avoided: violent reactions with powerful oxidants (hydrogen peroxide, nitric acid, hypochlorites), strong bases and strong reducing agents.

Dangerous decompositions products at temperatures of over 390°C:

- thermal decomposition into flammable, **toxic** products: hydrogen sulphide, sulphur oxides, carbon monoxide
- thermal decomposition into flammable, **harmful** products: methylmercaptan, dimethyl sulphide (DMS).

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Transportation, handling, storage

Transportation

Identification n° (UN): 2381

Land transportation:

RID (rail) /ADR (road)

Danger n°: 33

Classification code: F1

Class: 3

Packaging group: II

Label(s): 3

Transportation via inland waterways:

ADN/ADNR

Danger n°: 33

Classification code: F1

Class: 3

Packaging group: II

Label(s): 3

Maritime transport: IMDG

Class: 3

Packaging group: II

Marine pollutant (MP): No

Label(s): 3

Air freight: IATA

Class: 3

Packaging group: II

Label(s): 3

Handling (ARKEMA SDS, 2004)

- Provide appropriate exhaust ventilation for machinery.
- Provide showers and eye washers.
- Provide self-contained breathing apparatus nearby.
- Ventilate empty vats and tanks well before entering.
- Keep away from flames.
- Eliminate all sources of sparks or ignition. Do not smoke.
- Take precautionary measures against static discharges.
- Open drums carefully as contents may be under pressure.

Storage (ARKEMA SDS, 2004)

- Store in tightly closed containers in a cool, well ventilated area.
- Store away from heat and ignition sources.
- Provide a retention tank.
- Ensure the floor is impermeable.
- Provide fireproof electrical equipment and ensure that it is earthed.

Incompatible products

Powerful oxidants (hydrogen peroxide, nitric acid, hypochlorites), strong bases and strong reducing agents.

Recommended packaging materials

Stainless steel drums or stainless steel inner lining. Joints: polyethylene, rislan.

Packaging materials to be avoided

Rubber, plastics.

Results of accident scenarios

- Reminder of properties ————— C1
- Accident scenarios ————— C2
- Consumption scenarios ————— C3



Reminder of properties

Transportation

Dimethyl disulphide is transported in tanks in liquid form.

Vapour density and tension

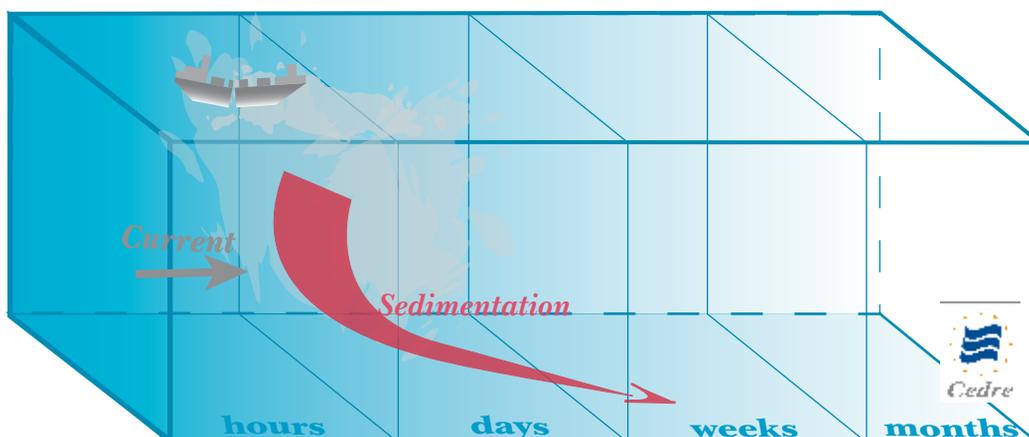
- Relative density: 1.063 at 20°C
- Vapour density: 3.25
- Vapour tension: 29 hPa (mbar) at 20°C

Solubility

Dimethyl disulphide is slightly soluble in water (1 g/L in seawater to 2 g/L in fresh water).

Behaviour in the environment

When spilt in water, dimethyl disulphide will sink and settle on the bottom, according to its SEBC classification. Surface agitation will lead to evaporation. The greater the agitation and the shallower the water column, the greater the evaporation will be. DMDS is pale yellow in colour, not very viscous and not very visible on the bottom.



Behaviour of dimethyl disulphide when spilt at sea

Accident scenarios

The scenarios defined here are simply designed to give an indication of the possible behaviour of DMDS. In the event of a real spill, the results of simulations will naturally be different from those given here. The CHEMMAP behaviour model, the emergency response model employed by Cedre, was used for these simulations. Other more sophisticated models exist, but require response times which are incompatible with an emergency situation.

Three DMDS spill scenarios will be presented below, with different spill rates:

- Channel scenario: 100 tonnes/hour of dimethyl disulphide, spilt continuously over 5 hours
- Port scenario: 1 tonne/hour of dimethyl disulphide, spilt continuously over 5 hours
- River scenario: 20 tonnes of dimethyl disulphide spilt instantaneously.

The scenarios

Channel scenario

- Location 50°N, 3°W
- Air and water temperature: 10°C
- Channel currents
- Wind speed: 3 m/s (NW)
- Spill depth: 1 m
- Model time step: 15 min
- Duration of spill: 5 hours

River scenario

- Depth of river: 4 to 5 m
- Width of river: 150 m
- Air and water temperature: 15°C
- Wind speed: 3 m/s (NW)
- Current speed: 0.72 m/s
- Spill depth: 1 m
- Model time step: 15 min
- Duration of spill: instantaneous

Port scenario

- Location: Port of Cherbourg 49°39N; 1°36W
- Air and water temperature: 10°C
- Slow current
- Wind speed: 3 m/s (NW)
- Spill depth: 1 m
- Model time step: 15 min
- Duration of spill: 5 hours

The case of a wreck

A wreck is lying on the seabed 100 metres below the surface not far from an inhabited coastline.

The decision-making process must take into account several factors:

- the actual solubility of the chemical in the prevailing conditions
- the spill rate and droplet diameter
- the currents
- the accessibility of the tanks.

If the wreck is leaking:

- take measurements in the water column and the sediment
- plug the holes as a temporary measure.

If the wreck is not leaking (or no longer leaking):

- where possible, begin recovery operations (MARPOL Y product).

Modelling

CHEMMAP software was used to model hypothetical spillages of dimethyl disulphide in the aquatic environment.

This is a chemical spill model designed by ASA (Applied Science Associates, Inc - USA) which predicts the movement and fate of the spilled product in fresh and sea water. This model

indicates both the movement of the product on the water surface and its distribution in the environment (evaporation, dissolution in the water column...).

The time step used for the calculations is 15 minutes.

Example of results obtained after a spill of dimethyl disulphide



Figure 1

Location of the hypothetical spill in the Channel

 Spill location



Figure 2

View of the part settled on the bottom

Example of a cross-section obtained from figure 2

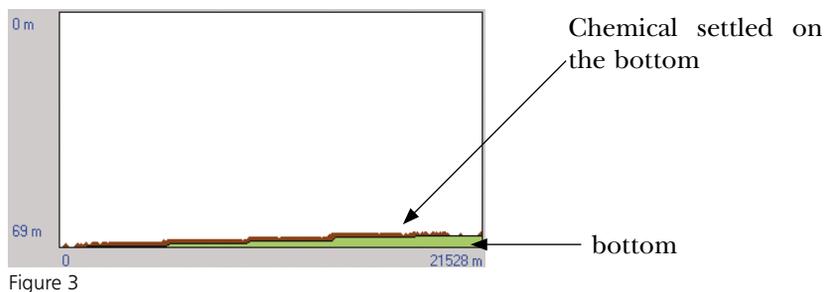
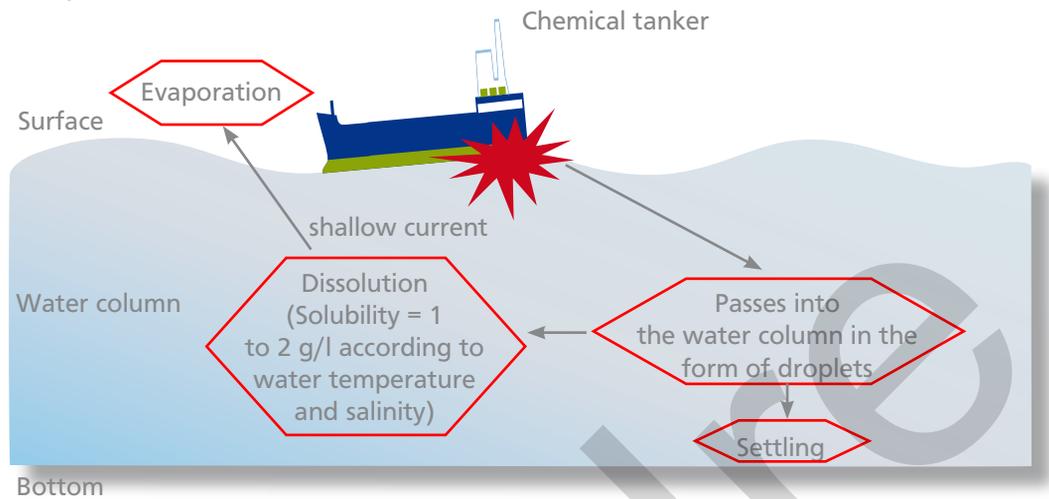


Figure 3

Diagram of a dimethyl disulphide spill (breach in hull 1 m below water surface)

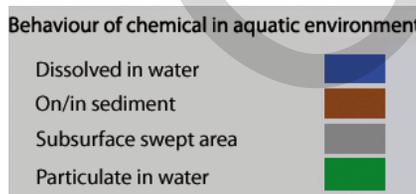


Key used in this guide:

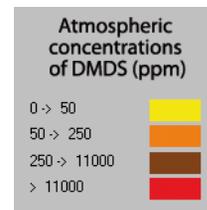
- for the graphs



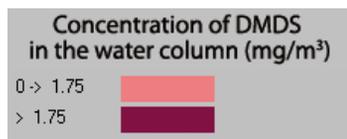
- for the behaviour of dimethyl disulphide



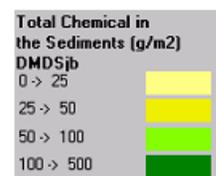
- for atmospheric concentrations of dimethyl disulphide



- for concentrations of dimethyl disulphide in the water column

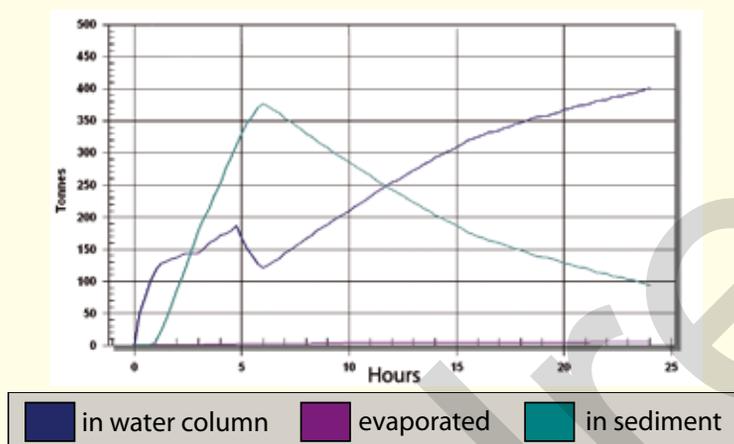


- for quantities of dimethyl disulphide on the bottom



Results of the Channel scenario

Continuous spill of 500 tonnes of dimethyl disulphide over 5 hours (spill rate of 100 t/h) in the open sea with a NW 3 m/s wind. The spill occurs 1 metre below the surface.



Graph 1

By the end of the spill (after 5 hours), the results of modelling show that the dimethyl disulphide is distributed as follows: 65% is on the seafloor and 35% in the water column, both in the form of particles and dissolved in the water. After 24 hours, 80% of the dimethyl disulphide is found in the water column, while 20% remains on the bottom. Little of the chemical evaporates.

Behaviour of 100 t/h of dimethyl disulphide spilt over 5 hours, 24 hours after the spill, with a NW 3 m/s wind.

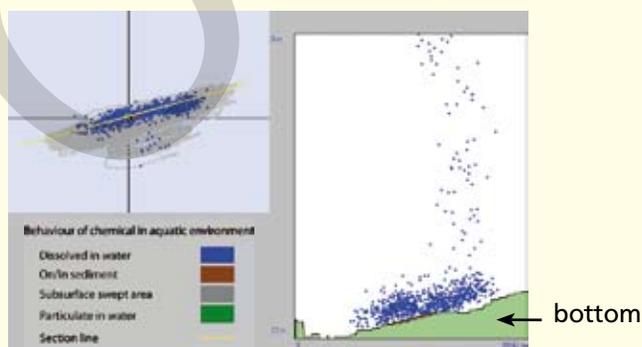


Figure 4

24 hours after the spill, the dimethyl disulphide, under the influence of the currents, affects the whole of the depth of the water column and spreads 19 nautical miles east-west and 6.5 nautical miles north-south.

Part of the chemical (around 20%) settles on the seafloor.

**Concentrations of dimethyl disulphide obtained in the water:
The toxicity threshold is the $PNEC_{\text{water}} = 1.75 \mu\text{g/L}$ (1.75 mg/m^3).**

Dimethyl disulphide is present in the water column in the form of droplets up to 6 hours after the spill. A maximum concentration of 10^9 mg/m^3 can be observed from the beginning of the spill, near the initial spill location.

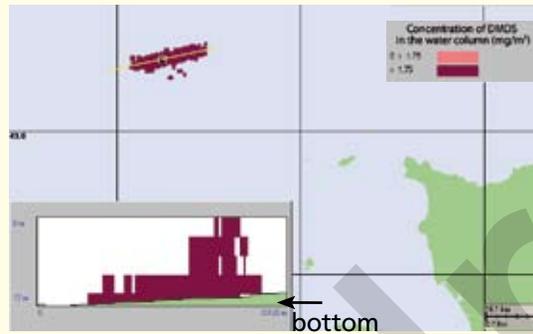


Figure 5

24 hours after the spill, the concentrations of dimethyl disulphide in the water column exceed the $PNEC_{\text{water}}$ over a distance of around 30 km and affect the entire depth of the water column.

Surface area affected by dimethyl disulphide settled on the seafloor:



Figure 6

5 hours after the spill, the concentrations of dimethyl disulphide on the seafloor can reach a maximum of 50 g/m^2 up to around 10 km on each side of the spill location.

The case of a wreck

A wreck lying in waters 71 m deep around 25 nautical miles from an inhabited coastline begins to leak. The leak leads to the continuous release of 1,000 tonnes of dimethyl disulphide over 5 hours from the tanks of the wreck (spill rate of 200 t/h).

By the end of the spill (after 5 hours), around 20% of the chemical is found in the water column, while 80% is settled on the seafloor. The dimethyl disulphide then dissolves slowly and contaminates the water column over a depth of 40 m from the seafloor upwards. After 24 hours, 80% of the dimethyl disulphide is found in the water column, while 20% remains on the bottom. The surface area affected spreads 19 nautical miles east-west and 4 nautical miles north-south. The dimethyl disulphide deposited on the seafloor covers a surface area with a diameter of 1 nautical mile.

Concentrations of dimethyl disulphide obtained in the water:

The toxicity threshold is the $PNEC_{\text{water}} = 1.75 \mu\text{g/L}$ (1.75 mg/m^3).

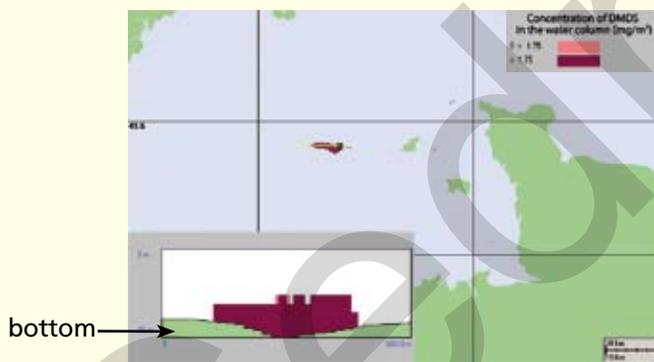


Figure 7

24 hours after the spill, the concentrations of dimethyl disulphide are greater than the $PNEC_{\text{water}}$ over a distance of around 25 km east-west. Only the lower part of the water column is affected, over a depth of around 40 m.

Surface area affected by dimethyl disulphide settled on the seafloor:

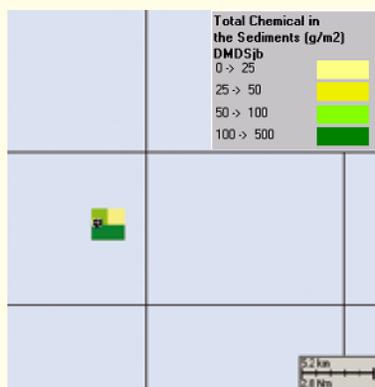


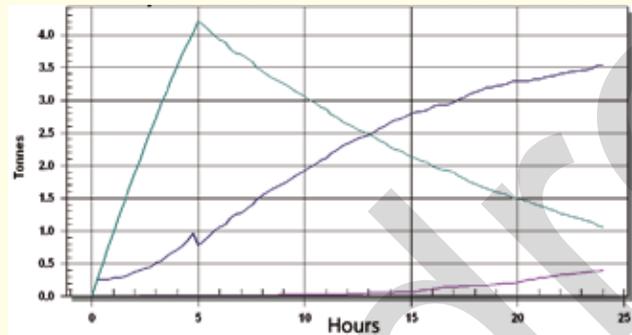
Figure 8

5 hours after the spill, the concentrations of dimethyl disulphide on the seafloor can reach values of over 100 g/m^2 up to about 2.5 km around the spill location.

Results of the port scenario

Continuous spill of 5 tonnes of dimethyl disulphide over 5 hours (spill rate of 1 t/h), in shallow waters (3 m), with a slow current and a NW 3 m/s wind. The spill occurs 1 m below the surface.

Behaviour of dimethyl disulphide



Graph 2



By the end of the spill (after 5 hours), the results of modelling show that the dimethyl disulphide is distributed as follows: 85 % is on the bottom and 15 % in the water column, both in the form of particles and dissolved in the water. After 24 hours, 70 % of the dimethyl disulphide is found in the water column, while 20% remains on the bottom and 10% has evaporated.

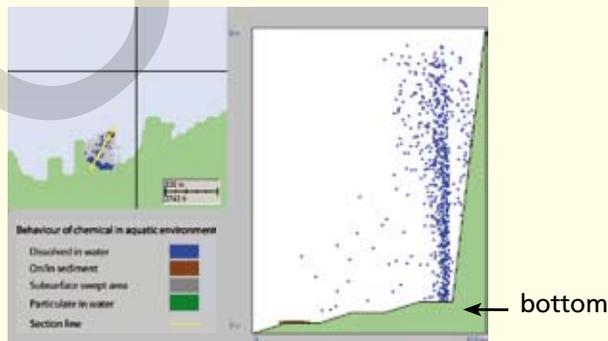


Figure 9

24 hours after the spill, the dimethyl disulphide covers a surface area of 2,500 m² and affects the entire depth of the water column. Part of the chemical (around 20%) settles on the bottom.

Atmospheric concentrations of dimethyl disulphide:

The thresholds used are: TEEL 2 = 50 ppm; TEEL 3 = 250 ppm; LEL = 11,000 ppm

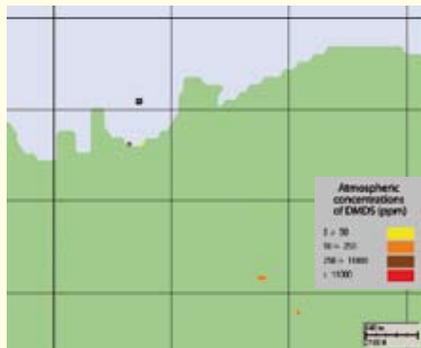


Figure 10

Around 15 hours after the spill, the atmospheric concentrations of dimethyl disulphide can reach 250 ppm (TEEL 3) up to 3 km downwind of the spill location. Concentrations equal to and greater than the lower explosive limit (11,000 ppm) are liable to be reached up to 24 hours after the spill and up to 500 m around the spill location.

Concentrations of dimethyl disulphide obtained in the water:

The toxicity threshold is the $PNEC_{\text{water}} = 1.75 \mu\text{g/L}$ (1.75 mg/m^3).

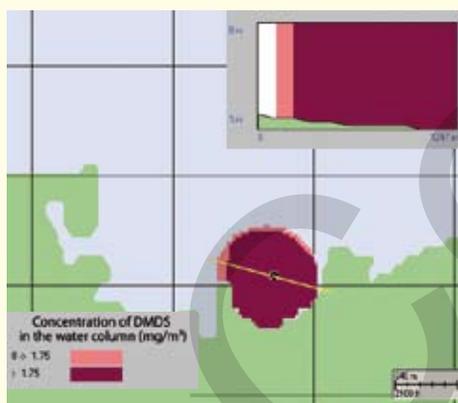


Figure 11

24 hours after the spill, the concentrations of dimethyl disulphide in the water column exceed the $PNEC_{\text{water}}$ over a distance of about 1,200 m around the spill location. The entire depth of the water column is affected.

Surface area affected by dimethyl disulphide settled on the bottom:

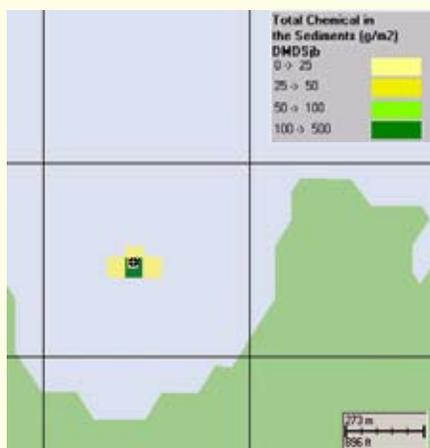


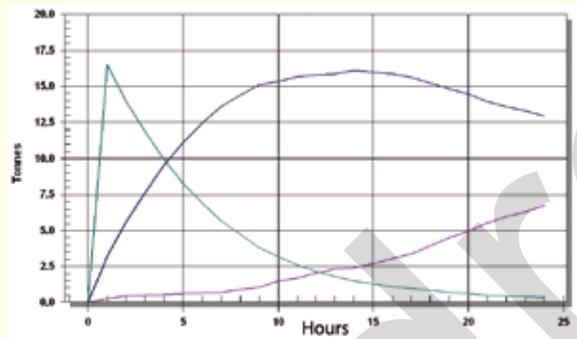
Figure 12

24 hours after the spill, the concentrations of dimethyl disulphide settled on the bottom reach values greater than 100 g/m^2 . The distance affected is about 180 m around the spill location.

Results of the river scenario

Instantaneous spill of 20 tonnes of dimethyl disulphide in a river (fresh water), with a 3 m/s NW wind and a 0.72 m/s current. The spill occurs 1 metre below the surface.

Behaviour of dimethyl disulphide



Graph 3



After an hour, 80% of the dimethyl disulphide is settled on the riverbed. After 24 hours, 60% of the dimethyl disulphide is found in the water column, while 37% is in the atmosphere and 3% remains on the riverbed.

Behaviour over 24 hours of dimethyl disulphide spilt in the river with a 0.72 m/s current and a 3 m/s NW wind.

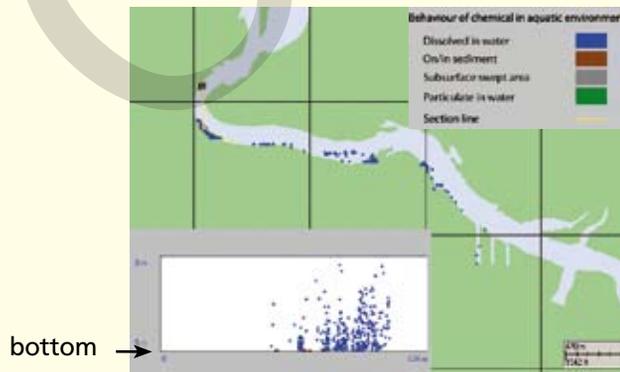


Figure 13

5 hours after the spill, the dimethyl disulphide, under the influence of the current, affects the whole of the depth of the water column and spreads over a distance of 3 km downstream of the spill location. Part of the chemical (around 40%) is settled on the riverbed, 5 m below the spill location.

Concentrations of dimethyl disulphide obtained in the water:
The toxicity threshold is the $PNEC_{\text{water}} = 1.75 \mu\text{g/L}$ (1.75 mg/m^3).

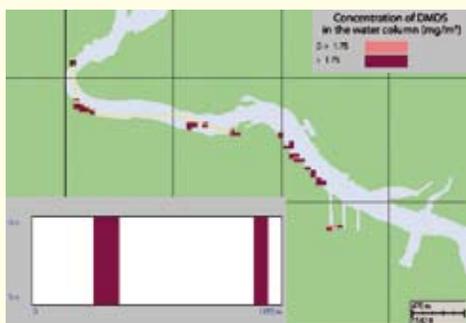


Figure 14

24 hours after the spill, the concentrations of dimethyl disulphide in the water column exceed the $PNEC_{\text{water}}$ over a distance of around 3 km and affect the entire depth of the water column.

Surface area affected by dimethyl disulphide settled on the riverbed:



Figure 15

5 hours after the spill, the concentrations of dimethyl disulphide on the riverbed may reach values greater than 100 g/m^2 .

In the case of a slower current (0.12 m/s):

The dimethyl disulphide is distributed in the same way: after an hour, 80% of the DMDS is settled on the riverbed. After 24 hours, 60% of the dimethyl disulphide is found in the water column, while 37% is in the atmosphere and 3% remains on the riverbed. The surface area affected spreads 600 m downstream of the spill location. The concentrations of DMDS in the water column are greater than the $PNEC_{\text{water}}$ after 24 hours and the chemical affects the entire depth of the water column, i.e. 5 m.

Consumption scenarios

Due to the very low tendency of dimethyl disulphide to bioaccumulate along the trophic chain, it is unlikely that this chemical will exist in sufficiently large quantities to have an impact on humans who consume contaminated fish or seafood.

Cedre

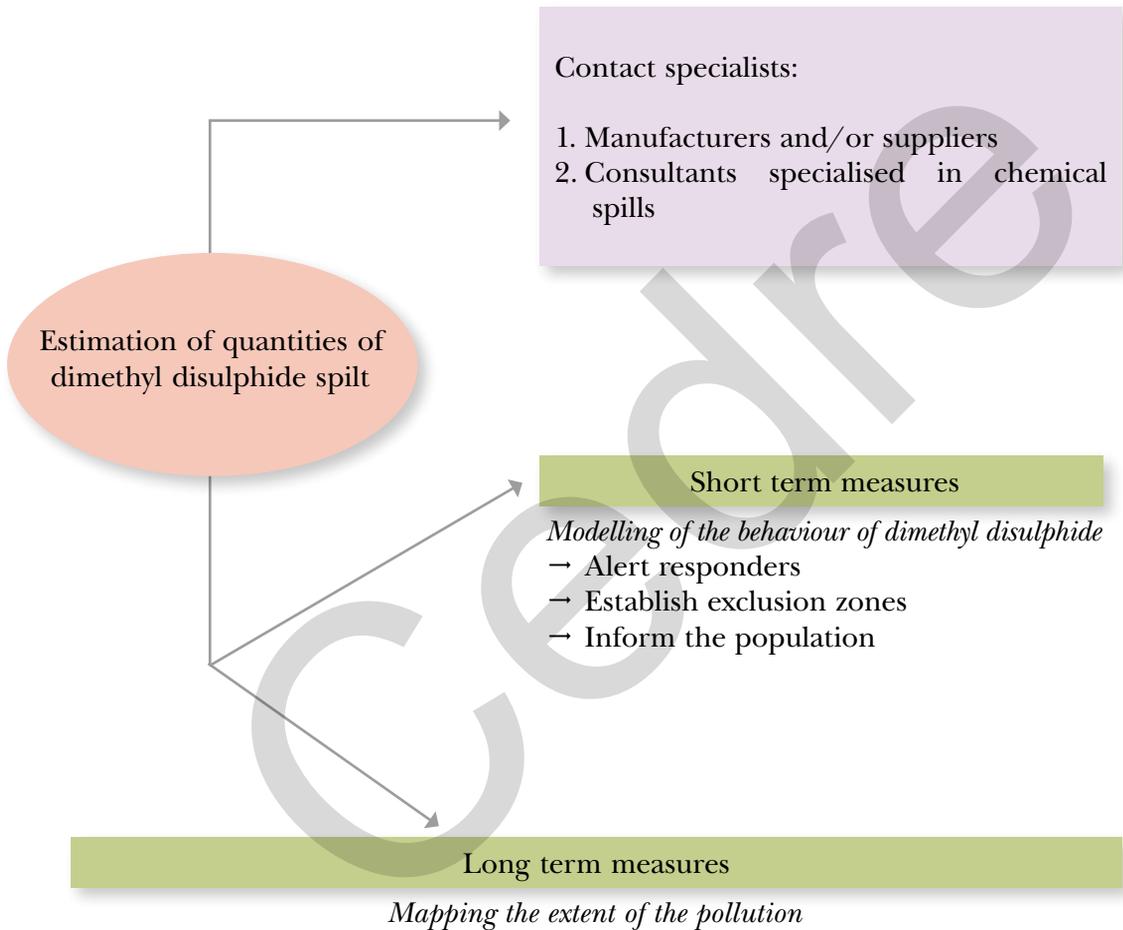
Response

- Response recommendations ————— **D1**
- Response techniques ————— **D2**
- Choosing Personal Protective Equipment (PPE) ————— **D3**
- Measuring devices and waste treatment ————— **D4**

Cedre

Response recommendations

Diagram showing response action in the event of a spill on water



In the sediments

Gather information on the type of sediments, the currents, topography...

- Sample/test the sediments
- Monitor the ecological impact
- Set up exclusion zones (fishing, water intakes)

In the water column

Gather information on the type of currents, the water temperature...

- Sample/test the water
- Set up exclusion zones (fishing, water intakes)

In the atmosphere

- Measure atmospheric concentrations
- Reduce evaporation
- Protect responders and the surrounding population

Is response possible? (CEFIC, 2005; CANUTEC, 2000)

Response may be envisaged if the following precautions are taken:

- Approach the accident area from upwind (wind behind you), equipped with the personal protective equipment (PPE) described in the "Personal Protective Equipment" chapter, explosimeters and dimethyl disulphide atmospheric measuring equipment: portable detection apparatus is presented in the chapter on "Measuring devices and waste treatment".
- Avoid all sources of ignition, sparks and heating, and only use fireproof equipment.
- Closed environments must be ventilated before entering and depressions in the ground should be avoided.

Emergency response in the event of fire (CEFIC, 2005; ARKEMA SDS, 2004; CANUTEC, 2000; GUIDE DES SAPEURS POMPIERS GENEVOIS, 2003)

If the fire is too far on, evacuate within a minimum radius of 800 m and leave the fire to burn. Otherwise, intervention may be considered if the following precautions are taken:

In the event of a minor fire

- The recommended fire extinguishing agents are: dry chemical powder, carbon dioxide, water spray and alcohol-resistant foam.

In the event of a major fire

- Remove containers of dimethyl disulphide from the area on fire if doing so is not dangerous. Otherwise, cool the containers by spraying with water to prevent them from bursting or corroding. Continue this operation for a long time after the fire has been extinguished.
- Provide specific detectors for hydrogen sulphide, sulphur oxides, methylmercaptan and dimethyl sulphide.
- Knock down vapours with water spray.

- The recommended fire extinguishing agents are: alcohol-resistant foam and water spray.
- Use remote-controlled hoses or water canons in order to fight the fire from as far away as possible.

Emergency measures in the event of a leak or spill (CEFIC, 2005; ARKEMA SDS, 2004; FICHE RÉFLEXE D'INTERVENTION ANTIPOLLUTION « PRODUITS DANS LA COLONNE D'EAU ET SUR LE FOND : LIQUIDES SOLUBLES ET COULANTS » - CEDRE 2004; CANUTEC, 2001)

- Ban access to the spill area within a minimum radius of 50 to 100 m and prohibit the use of polluted waters.
- Stop or reduce the leak if doing so does not constitute a risk.
- Do not smoke, remove all sources of ignition.
- Dyke the area and absorb the liquid using earth, sand or other similar non-combustible materials or cover with foam.
- Alert all downstream installations so that they may close any water intakes.
- Avoid contact with the skin and eyes and do not inhale vapours.
- Monitor the explosive limits and atmospheric and aquatic toxicity (chapter on "Measuring devices and waste treatment").
- Pump into an inert backup tank using fireproof equipment.
- Prevent the chemical from entering confined areas (basements, sewers...).

Response techniques

Response

(FICHE RÉFLEXE D'INTERVENTION ANTIPOLLUTION « PRODUITS DANS LA COLONNE D'EAU ET SUR LE FOND : LIQUIDES SOLUBLES ET COULANTS - FICHE ANTIPOLLUTION « STRATEGIES ET MOYENS » N°5 « DÉTECTION, MODÉLISATION ET REPÉRAGE », N°6 « CONFINEMENT ET RÉCUPÉRATION SUR LE SOL, N°8 « RÉCUPÉRATION DANS LA COLONNE D'EAU, N°11 « CONFINEMENT ET RÉCUPÉRATION SUR LE FOND » – CEDRE 2004 - FICHE GUIDE N°3 : « LUTTE EN MILIEU AQUATIQUE ».)

On land

Before conducting any response actions, the atmospheric concentrations must be tested and checked against the explosive limits.

Vapours can be contained by a water curtain, by water shields, or by covering the slick with a layer of foam.

It is essential to intervene as rapidly as possible in order to prevent any polluted water from reaching the sewer system or a waterway, by containing the spill with dams made of earth, sand or other materials or by deflecting it towards an impermeable surface.

The chemical slick can be absorbed using non-combustible sorbents.

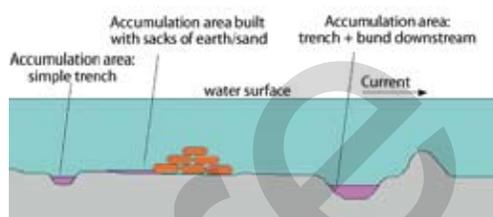
In inland waters and on water bodies

Before any response actions, the atmospheric concentrations must also be tested and checked against the explosive limits. The slick should also be covered with a layer of foam to reduce its evaporation. The concentration of the chemical in the water mass should be monitored and the vapour cloud and area of settled chemical can be modelled (the models can be confirmed by taking measurements).

As dimethyl disulphide sinks, it may be necessary to mark the spill location with moored buoys and predict its possible movement if there is a current by modelling and by testing the water and sediments.

Once the chemical has been spilt, it gradually sinks; it is therefore possible to create a retention area for the product on the bottom a few hours after the spill by building a dyke (sacks of earth/sand) or digging a trench. Different recovery systems can then be considered, involving dredging or pumping.

Given the chemical's tendency to dissolve, intervention must be carried out rapidly (a few hours after the spill).



Building accumulation areas on a riverbed.

At sea

It is also essential to locate and mark the spill location (using a buoy attached to an anchor or mooring post).

The chemical may be recovered from the seafloor by mechanical dredging or by suction if the following conditions are all fulfilled:

- response to dimethyl disulphide settled on the seafloor (a few hours after the spill)
- area of shallow water
- response equipment available nearby (port areas).

Transshipment

- Dimethyl disulphide must be unloaded from tanks with extreme caution. Accumulations of static electricity can cause the vapours to ignite.
- Lightering can be carried out by pumping or by discharge using an inert gas (nitrogen or combustion gas). The pressure exerted on the tank should never exceed the working pressure at which the safety valve is set to open.
- The equipment used must be fireproof and sparkproof.
- Never enter the tank.

D2

Choosing Personal Protective Equipment (PPE)

Ensure maximum protection in the case of high concentrations of the product.

Choosing breathing apparatus

(ARKEMA SDS, 2004; FINGAS, M., 2000)

Wear a filter respirator outside of the area of toxicity and in the open air if:

- the concentration of dimethyl disulphide is less than 0.5% in volume
- the concentration of oxygen is greater than 17% in volume.

This apparatus is fitted with a filter which protects against gases and vapours of organic compounds (filter A) and a filter which protects against inorganic, acidic gases and vapours in case of fire (filter B). The full-face mask provides maximum protection.

Wear SCBA (Self-Contained Breathing Apparatus) if:

- the concentrations of dimethyl disulphide are unknown or high
- the oxygen concentration is, or is liable to become, less than 17% in volume.

Pressure demand and positive pressure, compressed air, open circuit (if the exhaled air is released into the atmosphere), self-contained breathing apparatus have a protection factor of around 10,000.

Choosing protective clothing

(ARKEMA SDS, 2004)

Wear a chemical splash suit. It is also recommended that responders wear protective gloves made of nitrile with a coating thickness of 0.75 mm.

Recommendations for use in the event of a spill

(INRS, 2003)

Self-contained breathing apparatus (SCBA) provides the best protection as it supplies air from an uncontaminated source. The user is independent of the surrounding atmosphere. Certain facial characteristics such as a facial hair (even two day stubble), side-burns, scars, skin eruptions or glasses may prevent the mask from being water tight. Special frames exist for ordinary corrective glasses. However contact lenses can now be used, as new contact lenses allow for gas exchange and thus do not dry out or stick to the eyeball. Mask adjustment tests are recommended for new users and regular tests for other users in order to ensure optimal protection.

Measures to take after using PPE in a spill situation

(CEFIC, 2005)

- Wash down contaminated clothing and breathing apparatus with water/detergent before removing the face mask and protective suit.
- Recover decontamination effluents in drums which comply with the storage conditions outlined in the chapter on "Transportation, handling, storage".

Measuring devices and waste treatment

Air sampling methods:

- pumping dimethyl disulphide vapours into a collection bag or sample tube: the pump must have a teflon or stainless steel diaphragm.

Measuring devices (DRIRE, 2004; GAUDRY A. *et al.* IN CHEMOSPHERE, 1981)

Examples of <u>specific</u> measuring devices for sulphur products	Products detected	Measuring scale	Resolution
MiniWarn® (Dräger Safety): gas and vapour monitor equipped with up to 4 sensors for simultaneous detection.			
DrägerSensor XS EC Odorant (n° 6809200)	Dimethyl disulphide Methylmercaptan Dimethyl sulphide (Gases produced by thermal decomposition)	0 - 40 ppm 0 - 40 ppm 0 - 40 ppm	+/-0.5 ppm
DrägerSensor XS R H2S (n° 6810260)	Hydrogen sulphide (Gas produced by thermal decomposition)	0 - 100 ppm	+/-1 ppm
DrägerSensor XS R CO (n°6810258)	Carbon monoxide (Gas produced by thermal decomposition)	0 - 2000 ppm	+/-1 ppm
<u>Non-specific</u> measuring devices	Products detected	Sensitivity	Resolution
SIRIUS® (MSA GALLET): photoionisation detector which can also be configured with up to 4 additional sensors for simultaneous detection.	Total Volatile Organic Compounds (VOC)	0 - 9900 ppb 0 - 200 ppm 200 - 2000 ppm	+/- 100 ppb +/- 0.1 ppm +/- 1 ppm
	Carbon monoxide Hydrogen sulphide (Gases produced by thermal decomposition)	0 - 500 ppm 0 - 200 ppm	+/- 1 ppm +/- 1 ppm
ppbRAE Plus® (RAESystems): photoionisation detector for monitoring VOCs in the air	Total Volatile Organic Compounds (VOC)	0 - 9999 ppb 10 - 99.9 ppb 100 - 2000 ppm	+/- 1 ppb +/- 0.1 ppm +/- 1 ppm

Laboratory testing

Emissions of sulphur compounds such as dimethyl disulphide can be detected in the atmosphere and in water by gas phase chromatography through detection by flame photometry or mass spectrometry.

Main European manufacturers of dimethyl disulphide

ARKEMA

D4

Further information

- Glossary ————— E1
- Acronyms ————— E2
- Useful websites ————— E3
- Bibliography ————— E4

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Glossary

Acceptable Daily Dose (ADD)

For humans this dose is the quantity of a substance that can be ingested by an organism per day for its entire lifetime without presenting a health hazard for the organism in question.

Acute Exposure Guideline Levels (AEGs)

Defined by the National Research Council's Committee on Toxicology (USA), AEGs are three levels above which the general population may experience certain effects. These three AEGs are given for five exposure times: 10, 30 min, 1, 4 and 8 hours.

AEGL 1: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non sensory effects. However, the effects are transient and reversible when exposure ceases.

AEGL 2: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Adsorption

Elevation of the concentration of a substance dissolved at the interface of a condensed phase and a liquid phase under the influence of surface forces. Adsorption can also occur at the interface of a condensed phase and a gas phase.

Aerosol

A mass of particles, solids or liquids in suspension in a gaseous environment.

Bioaccumulation

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor increases all the time).

Bioamplification

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

Bioconcentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in the lifetime of the organism.

Bioconcentration factor (BCF)

Ratio of the chemical concentration in the exposed organism (minus the concentration in a control organism) to that in surrounding water.

Biotransformation

Biological transformation of substances in a living organism via enzymatic processes.

Boiling Liquid Expanding Vapour Explosion (BLEVE)

A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has burst.

Boiling point (measured at a pressure of 1 atmosphere)

Temperature at which a liquid begins to boil. More specifically, when the temperature at which saturating vapour pressure of a liquid is equal to standard atmospheric pressure (1,013.25 hPa). The boiling point measured depends on atmospheric pressure.

Buffering capacity

Capacity of a solution to absorb a certain quantity of acid or base without causing a significant variation in pH. In the marine environment, the buffering capacity is due to the dihydrogenocarbonate/carbonate balance.

Combustion rate

Rate at which an object subjected to fire will burn entirely.

Critical point

Point at which the temperature and pressure at which the intensive properties of a liquid and vapour (density, calorific value...) are equal. It represents the highest temperature (critical temperature) and pressure (critical pressure) at which a gas phase and a liquid phase of a given compound can coexist.

Critical pressure

Maximum pressure for which the distinction can be made between a gas and a liquid.

Critical temperature

Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

Daily exposure dose

Dose (internal or external) of a substance in an organism compared to the weight of the individual and the number of days of exposure (in the case of a non carcinogenic substance) and the number of days lived by the organism (for a carcinogenic substance).

Decomposition products

Products stemming from chemical or thermal disintegration of a substance.

Diffusion coefficient in air (and in water)

A constant that describes the movement of a substance in the gas phase (or liquid phase) in response to a concentration differential in the gas phase (or liquid phase).

Effective concentration 50 (EC₅₀)

Concentration causing a given effect (mortality, growth inhibition...) for 50% of the population under consideration during a given period of time.

Emergency Response Planning Guidelines (ERPG)

The American International Health Alliance (AIHA) set three maximum concentrations in 1988 below which a category of effects is not expected for an exposure duration of one hour, in a bid to protect the general public.

ERPG1: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly identifiable odour.

ERPG2: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to protect themselves.

ERPG3: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

Exposure limit value (ELV)

Ceiling exposure value measured for a maximum duration of 15 minutes.

Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately

when in contact with a flame.

Foam

The foam layer absorbs most of the vapours, physically eliminates vapours and isolates the chemical from sunlight and ambient air which reduces the amount of heat and subsequent vaporisation.

Henry's law constant

Value indicating a substance's volatility (see graph on p. 41)

Immediately Dangerous to Life or Health (IDLH)

Level below which a worker can escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere, without respiratory protection and without impairing his ability to escape.

Irreversible effect threshold (IET)

Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

Lethal effect threshold (LET)

Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

Lower Explosive Limit (LEL)

Minimum airborne concentration above which vapours ignite.

Lowest Observed Effect Concentration (LOEC)

Lowest concentration at which an effect is observed.

Marine pollutant

Substance, object or matter likely to cause serious damage to the marine environment when spilled.

Maximum Allowable Relief Valve Setting (MARVS)

Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

Mean exposure value (MEV)

Value that has been measured or estimated for a work station lasting 8 hours and is intended to protect workers from long term effects. MEV can be exceeded for very short periods providing the ELV value (should there be one) is not exceeded.

Median lethal concentration (LC₅₀)

Concentration of a substance deduced statistically that should, during or after exposure and for a given period of time, cause the death of 50% of the animals exposed during a given time period.

Melting point

Temperature at which solid and liquid state coexist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

Minimum Risk Level (MRL)

This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic noxious effect on health for a specific exposure duration.

Miscible

Matter that mixes readily with water

Nautical Mile

1 nautical mile is the equivalent of 1,852 metres and corresponds to one minute of latitude.

N-octanol/water partition coefficient (Kow)

Ratio of the equilibrium concentrations of a substance dissolved in a two phase system made up of two solvents that virtually do not mix.

No Observed Effect Concentration (NOEC)

Concentration of a substance measured during chronic toxicity tests for which no effect is observed, meaning that the substance presents no chronic toxicity below this concentration.

No Observed Effect Level (NOEL)

The highest dose of a substance that causes no distinct changes as compared with those observed in control animals.

Olfactory threshold

Minimum air or waterborne concentration to which the human nose is sensitive.

Partition coefficient for organic carbon and water (Koc) (for organic substances)

Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

Photo-oxidation

Oxidation of a chemical compound caused by exposure to light energy.

Polymerisation

This term describes the chemical reaction generally associated with the production of plastics. Fundamentally, the individual molecules of a chemical (liquid or gas) react together to form a long chain. These chains can be used for many applications.

Protective equipment

This refers to the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).

Level A: an SCBA (self contained breathing apparatus/respirator) and fully air and chemical-tight suit (that resists permeation).

Level B: an SCBA and a suit that protects against liquid spray (splash proof).

Level C: a full face mask or goggles and a suit that protects responders against chemicals (splash proof).

Level D: overalls without a respirator.

Rate of evaporation or volatility (ether = 1)

The rate of evaporation expresses the number of times that a product takes to evaporate as compared with a control substance of an equal volume (ether for instance). This rate varies with the nature of the product and the temperature.

Regression speed

Speed at which a burning liquid slick reduces in thickness. For a given liquid, this speed is constant regardless of the slick surface (slick diameter greater than 2 metres). Regression speed allows the total duration of a fire to be estimated if no attempt is made to extinguish it.

e.g. a 1,000 mm thick slick, where the regression speed is 10 mm/minute
duration of fire = 1000/10 = 100 minutes.

Relative density

Ratio of the mass of a substance to that of water for a liquid or to that of air for a gas.

Relative vapour density

Weight of a volume of vapour or pure gas (without air) compared to that of an equal volume of dry air at the same temperature and pressure.

A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When the vapour density is higher than 1, vapour is heavier than air and will tend to stay near ground level and spread.

Self-ignition temperature

Minimal temperature at which vapours ignite spontaneously.

Solubility

Quantity of a substance dissolved in water. It will depend on salinity and temperature.

Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ADD	Acceptable Daily Dose
ADNR	European Agreement concerning International Carriage of Dangerous Goods on the Rhine river
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
AEGLs	Acute Exposure Guideline Levels
AFFF	Aqueous Film-Forming Foam
AFSSA	French National Agency for Food Safety
AIHA	American International Health Alliance
ALOHA	Areal Locations of Hazardous Atmospheres
ATSDR	Agency for Toxic Substances and Disease Registry
AUV	Autonomous Underwater Vehicle
BCF	Bio Concentration Factor
BLEVE	Boiling Liquid Expanding Vapour Explosion
BOD	Biochemical Oxygen Demand
CAS	Chemical Abstracts Service
CEA	French Atomic Energy Commission
CEDRE	Centre of Documentation, Research and Experimentation on Accidental Water Pollution
CEFIC	European Chemical Industry Council
CHRIS	Chemical Hazards Response Information System
COD	Chemical Oxygen Demand
CSST	French Occupational Health and Safety Commission
CSTEE	French Scientific Committee on Toxicity, Ecotoxicity and the Environment
DDASS	French Departmental Health and Social Action Directorate
DDE	French Departmental Equipment Directorate
DMDS	Dimethyl disulphide
DRASS	French Regional Department of Health and Social Affairs
DRIRE	French Regional Directorates for Industry, Research and Environment
EC	Effective Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EFMA	European Fertilizer Manufacturers Association
EINECS	European Inventory of Existing Chemical Substances
ELV	Exposure Limit Value
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
ETC	Environmental Technology Centre
FID	Flame Ionisation Detector
GPC	Gas Phase Chromatography
HSDB	Hazardous Substances Data Bank
IATA	International Air Transport Association
IBC	International Bulk chemical Code
ICSC	International Chemical Safety Cards
IDLH	Immediately Dangerous to Life or Health
IFREMER	French Research Institute for Exploitation of the Sea
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
INCHEM	International Chemical industries, Inc.
INERIS	French National Institute for Industrial Environment and Risks
INRS	French National Research and Safety Institute for occupational risk prevention

IPCS	International Programme on Chemical Safety
IPSN	French Institute for Nuclear Safety and Protection
IUCLID	International Uniform Chemical Information Database
LC	Lethal Concentration
LEL	Lower Explosive Limit
LET	Lethal Effect Threshold
LLDPE	Linear Low Density PolyEthylene
LOEC	Lowest Observed Effect Concentration
MARPOL	Marine Pollution
MARVS	Maximum Allowable Relief Valve Setting
MCA	Maritime and Coastguard Agency
MEV	Mean Exposure Value
MFAG	Medical First Aid Guide
MP	Marine Pollutant
MRL	Minimum Risk Level
MUC	Maximum Use Concentration
NIOSH	National Institute for Occupational Safety and Health
NM	Nautical mile
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
PEC	Predicted Effect Concentration
PID	Photo Ionisation Detector
PNEC	Predicted No-Effect Concentration
ppb	Parts per billion
PPE	Personal Protective Equipment
ppm	Parts per million
PTBC	Para-tertiary-butylcatechol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
ROV	Remoted Operated Vehicle
SCBA	Self-Contained Breathing Apparatus
SDS	Safety Data Sheet (or MSDS, Material Safety Data Sheet)
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
SIDS	Screening Information Data Set
SIW	Special Industrial Waste
TEEL	Temporary Exposure Limits
TGD	Technical Guidance Document
TLV-ceiling	Threshold Limit Values – Ceiling
TLV-STEL	Threshold Limit Values – Short Term Exposure Limit
TLV-TWA	Threshold Limit Values – Time Weighted Average
TNO	Netherlands Organisation for Applied Scientific Research
TRANSAID	Agreement between UIC (French Chemical Industry Association) & the French Government
TROCS	Transport of Chemical Substances - database created by REMPEC
UEL	Upper Explosive Limit
UIISC	French Unit of Instruction and Intervention on Civil Security
US EPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion
VCM	Vinyl chloride monomer
VHF	Very High Frequency
v/v	Volume to volume
WHO	World Health Organisation

Useful websites

AFSSA (French National Agency for Food Safety) (French only)

<http://www.afssa.fr>

ARKEMA

<http://www.arkema.com>

ATSDR (Agency for Toxic Substances and Disease Registry)

<http://www.atsdr.cdc.gov/>

Bonn Agreement

<http://www.bonnagreement.org>

CEFIC (European Chemical Industry Council)

<http://www.ericards.net>

Chemfinder

<http://chemfinder.cambridgesoft.com>

CHRIS (Chemical Hazards Response Information System)

<http://www.chrismanual.com>

CSST (Occupational Health and Safety Commission)

<http://www.reptox.csst.qc.ca>

ETC (Environmental Technology Centre, Canada)

http://www.etc-cte.ec.gc.ca/etchome_e.html

European Chemicals Bureau

<http://ecb.jrc.it>

ICSC (International Chemical Safety Cards)

<http://www.cdc.gov/niosh/ipcs/ipcard.html>

INERIS (French National Institute for Industrial Environment and Risks)

<http://www.ineris.fr>

INRS (French National Research and Safety Institute for Occupational Risk Prevention)

<http://en.inrs.fr/>

IPCS (International Programme on Chemical Safety)

<http://www.inchem.org/>

NIOSH (US National Institute for Occupational Safety and Health)

<http://www.cdc.gov/niosh/idlh/intridl4.html>

NOAA (US National Oceanic and Atmospheric Administration), historical incident search page

<http://www.noaa.gov/ocean.html>

TROCS, REMPEC database (Regional marine pollution emergency response centre for the Mediterranean Sea) on transportation of chemicals

<http://www.rempec.org/databases.asp?lang=en>

UIC (French Chemical Industry Association)

<http://www.uic.fr/index-us.htm>

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ANNEXES

Annex 1: summary and additional physical and toxicological data

Annex 2: fax format data card

Annex 3: classification of noxious liquid substances

ANNEX 1: SUMMARY AND ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification

CAS n°: 624-92-0
EC n° (EINECS): 210-871-0
UN n°: 2381
Class: 3

Physical data

Conversion factor

1 ppm = 3.853 mg/m³
1 mg/m³ = 0.260 ppm
1 atm = 1.013×10⁵ Pa

Physical state at 20°C

Appearance: liquid
Colour: pale yellow
Odour: strong and pungent

Molecular mass

94.2 g/mol

Volumic mass

1,063 kg/m³ at 20°C

Density

Relative density (water = 1): 1.063 at 20°C
Relative density of the gas (air = 1): 3.25

Solubility

in seawater: 1 g/L
in fresh water: 2 g/L
in other compounds: soluble in diethyl ether, alcohols and hydrocarbons

Vapour pressure/tension

29 hPa (mbar) at 20°C
38 hPa (mbar) at 25°C

Key temperatures

Boiling point: 109.8°C
Melting point: - 84.7°C
Flash point (in closed cup ASTM D 93): 15°C
Self-ignition point: 300°C
Critical temperature: 333°C
Decomposition temperature: 390°C

Flammability

LEL = 1.1% or 11,000 ppm
UEL = 16% or 160,000 ppm

Other properties

Viscosity at 20°C: 0.62 mPa.s
Henry's law constant: 122.5 Pa.m³/mole at 20°C
(0.001225 atm.m³/mole)

Olfactory threshold

0.01 ppm

ARKEMA SDS, 2004

ARKEMA SDS, 2004

ARKEMA SDS, 2004

ARKEMA SDS, 2004

CEDRE, 2007

CEDRE, 2007

ARKEMA SDS, 2004

DIPPR, 2006

DIPPR, 2006

DIPPR, 2006

ARKEMA SDS, 2004

ARKEMA SDS, 2004

YAWS, 1999

ARKEMA SDS, 2004

ARKEMA SDS, 2004

ARKEMA SDS, 2004

DIPPR, 2006

ARKEMA SDS, 2004

ARKEMA SDS, 2004

Toxicological data

Threshold toxicological values

Risk management values for the population

TEEL 0: 0.0013 mg/m³ = 0.0035 ppm

TEEL 1: 0.03853 mg/m³ = 0.01 ppm

TEEL 2: 192.65 mg/m³ = 50 ppm

TEEL 3: 963.25 mg/m³ = 250 ppm

General toxicity

Acute human toxicity

The effects caused by exposure to DMDS (inhalation, ingestion or contact with the skin) may be deferred.

- By ingestion: headaches, nausea, dizziness, drowsiness.
- By contact with the skin: irritation, redness.
- By contact with the eyes: ocular irritation.
- By inhalation: headaches, nausea, dizziness, drowsiness. Dimethyl disulphide has an irritating effect on the respiratory tract.
The inhalation of decomposition fumes can cause bronchospasms, pneumonia and pulmonary oedema.

Chronic human toxicity

Repeated or prolonged exposure to the skin can cause dermatitis.

Disorders of the iron metabolism have been observed in workers exposed to dimethyl disulphide and other sulphur compounds.

Alkyl disulphides can cause haemolytic anaemia.

Specific effects

Genotoxic effects: the *in vitro* and *in vivo* results do not cause the product to be considered as genotoxic.

Effects on reproduction: absence of congenital malformations in animals.

Carcinogenic effects: no data available.

Acute ecotoxicity

Crustacean (*Daphnia sp.*)

EC₅₀ (48 h) = 7 mg/L (fresh water) (OECD 202)

Crustacean (*Americamysis bahia*)

LC₅₀ (96 h) = 5 mg/L (seawater)

Fish (*Salmo gairdneri*)

LC₅₀ (120 h) = 1.75 mg/L (fresh water)

Fish (*Cyprinodon variegatus*)

LC₅₀ (96 h) = 5.6 mg/L (seawater)

Algae (*Pseudokirchneriella subcapitata*)

LC₅₀ (72 h) = 11 mg/L (fresh water) (OECD 201)

Chronic ecotoxicity

Algae (*Pseudokirchneriella subcapitata*)

NOEC (72 h) = 10.43 mg/L (OECD 201)

PNEC (Predicted No-Effect Concentration): According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated PNEC_{water} is 1.75 µg/L. A safety factor of 1,000 is applied to the lowest value of the three trophic levels.

ANNEX 2: FAX FORMAT DATA CARD

Dimethyl disulphide		CAS n°: 624-92-0
DMDS; Dimethyl disulfide; 2,3-Dithiobutane;	$\text{CH}_3\text{-S-S-CH}_3$	EC n° (EINECS): 210-871-0
2,3-Dithiabutane; Methyl disulphide; Methyl disulfide;		UN n°: 2381
Methyl dithiomethane; Dimethyl disulfane.		Class: 3

First aid information	
Immediately remove all soiled or spotted clothes.	
<p>Intoxication by inhalation: Move the victim into the open air and lie them down; Apply artificial respiration if necessary; Place under medical supervision; Transfer to hospital in the event of complications (loss of consciousness, suffocation).</p> <p>Contact with the skin: Do not attempt to remove clothing if it is stuck to the skin; Immediately wash thoroughly with soap and water; Consult a doctor in the event of adverse effects (irritation, redness, burns).</p>	<p>Contact with the eyes: Immediately rinse with plenty of water for 15 minutes, removing contact lenses if easily possible; Transfer to hospital if the feelings of irritation, pain, swelling, watering eyes or photophobia persist.</p> <p>Intoxication by ingestion: Rinse the mouth out with water; Do not attempt to induce vomiting if the victim is unconscious; Transfer to hospital.</p>
Where necessary, contact the nearest poison control centre.	

Physicochemical data	
	Conversion factors: 1 ppm = 3.853 mg/m ³ 1 mg/m ³ = 0.260 ppm 1 atm = 1.013×10 ⁵ Pa
Melting point	- 84.7°C
Boiling point	109.8°C
Critical temperature	333°C
Relative density (water = 1)	1.063 at 20°C
Relative vapour density (air = 1)	3.25
Solubility in seawater	1 g/L
Solubility in fresh water	2 g/L
Vapour pressure/tension	29 hPa (mbar) at 20°C 38 hPa (mbar) at 25°C
Viscosity at 20°C	0.62 mPa.s
Olfactory threshold	0.01 ppm
Henry's law constant	122.5 Pa.m ³ /mole at 20°C (0.001225 atm.m ³ /mole)
Molecular mass	94.2 g/mol
Evaporation rate	no data available
Surface tension	33.94 mN/m at 20°C

EU classification:	
 F: Highly flammable	<p>R11: Highly flammable. R20/22: Harmful by inhalation and if swallowed. R36: Irritating to eyes. R51/53: Toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment. S16: Keep away from sources of ignition. No smoking. S28: After contact with skin, wash immediately with plenty of water. S61: Avoid release to the environment. Refer to special instructions/safety data sheet.</p>
 Xn: Harmful	
 N: Dangerous for the environment	

Toxicological data

Threshold toxicological values

TEEL 0: 0.0013 mg/m³ = 0.0035 ppm
TEEL 1: 0.03853 mg/m³ = 0.01 ppm
TEEL 2: 192.65 mg/m³ = 50 ppm
TEEL 3: 963.25 mg/m³ = 250 ppm

Specific effects

Genotoxic effects: the *in vitro* and *in vivo* results do not cause the product to be considered as genotoxic.
Effects on reproduction: absence of congenital malformations in animals.
Carcinogenic effects: no data available.

Acute human toxicity

The effects caused by exposure to DMDS (inhalation, ingestion or contact with the skin) may be deferred.

- By ingestion: headaches, nausea, dizziness, drowsiness.
 - By contact with the skin: irritation, redness.
 - By contact with the eyes: ocular irritation.
 - By inhalation: headaches, nausea, dizziness, drowsiness. Dimethyl disulphide has an irritating effect on the respiratory tract.
- The inhalation of decomposition fumes can cause bronchospasms, pneumonia and pulmonary oedema.

Chronic human toxicity

Repeated or prolonged exposure to the skin can cause dermatitis.
Disorders of the iron metabolism have been observed in workers exposed to dimethyl disulphide and other sulphur compounds.
Alkyl disulphides can cause haemolytic anaemia.

Ecotoxicological data

Acute ecotoxicity

Crustacean (*Daphnia sp.*)
EC₅₀ (48 h) = 7 mg/L (fresh water)
Crustacean (*Americamysis bahia*)
LC₅₀ (96 h) = 5 mg/L (seawater)
Fish (*Salmo gairdneri*)
LC₅₀ (120 h) = 1.75 mg/L (fresh water)
Fish (*Cyprinodon variegatus*)
LC₅₀ (96 h) = 5.6 mg/L (seawater)
Algae (*Pseudokirchneriella subcapitata*)
LC₅₀ (72 h) = 11 mg/L (fresh water)

Chronic ecotoxicity

Algae (*Pseudokirchneriella subcapitata*)
NOEC (72 h) = 10.43 mg/L
PNEC (Predicted No-Effect Concentration): According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated PNEC_{water} is 1.75 µg/L. A safety factor of 1,000 is applied to the lowest value of the three trophic levels

Persistence in the environment

Volatilisation

In the air, dimethyl disulphide is present in the form of vapours in the atmosphere, due to its vapour pressure (38 hPa at 25°C). On land, its Henry's law constant (1.22x10⁻³ atm.m³/mole) means that it rapidly evaporates. In water, although part of the dimethyl disulphide spilt will sink, another part may evaporate. The evaporation half-life for a river scenario is 3 hours and for a lake scenario is 4 days.

Photolysis

In air, dimethyl disulphide present in the form of vapours is broken down by hydroxyl radicals (half-life = 3.5 days), nitrate radicals (half-life = several hours) and atomic oxygen (half-life = 6.2 days). Liquid dimethyl disulphide is also broken down by hydroxyl radicals (half-life = 4 hours), direct photolysis (half-life = 3.2 to 4.6 hours in full sun) and by nitrate radicals (half-life = 1.1 hours). On the ground or the water surface, dimethyl disulphide may be present in the form of vapours or liquid. It is therefore broken down by photolysis in a few hours.

Mobility

Due to its Koc, dimethyl disulphide is mobile in soil and can be adsorbed by soil or sediments. In water, dimethyl disulphide is slightly soluble (1 to 2 g/L) and tends to sink. It is not adsorbed by matter in suspension nor by sediments.

Bioaccumulation

According to its Kow and BCF values, dimethyl disulphide is not bioaccumulable.

Organic carbon/water partition coefficient: log Koc = 2.34

Octanol/water partition coefficient: log Kow = 1.77

Bioconcentration factor: BCF = 13

SEBC classification: S (sinks)

MARPOL classification: Classification as of 1st January 2007: Y (definition in annex 3).

Particular risks

Danger

Heating or combustion of the product gives off toxic, irritating fumes including sulphur oxides.

Dimethyl disulphide can form explosive air/vapour mixtures.

When a receptacle containing DMDS is heated, there is an increase in pressure leading to a risk of the container bursting and a possibility of a fireball (BLEVE).

The vapours are invisible and heavier than air.

They spread out across the ground and can infiltrate sewer systems and basements.

The vapours can spread as far as a source of ignition and cause flashback to the source of the leak.

Stability and reactivity

Safety precautions: keep away from heat and sources of ignition. Do not overheat in order to prevent thermal decomposition.

Substances to be avoided: violent reactions with powerful oxidants (hydrogen peroxide, nitric acid, hypochlorites), strong bases and strong reducing agents.

Dangerous decompositions products at temperatures of over 390°C:

- thermal decomposition into flammable, **toxic** products: hydrogen sulphide, sulphur oxides, carbon monoxide.
- thermal decomposition into flammable, **harmful** products: methylmercaptan, dimethyl sulphide.

Transportation

Identification n° (UN): 2381

Land transportation:

RID (rail) / ADR (road)

Danger n°: 33

Classification code: F1

Class: 3

Packaging group: II

Label(s): 3

Transportation via inland waterways:

ADN/ADNR

Danger n°: 33

Classification code: F1

Class: 3

Packaging group: II

Label(s): 3

Maritime transport: IMDG

Class: 3

Packaging group: II

Marine pollutant (MP): No

Label(s): 3

Air freight: IATA

Class: 3

Packaging group: II

Label(s): 3

Handling

- Provide appropriate exhaust ventilation for machinery.
- Provide showers and eye washers.
- Provide self-contained breathing apparatus nearby.
- Ventilate empty vats and tanks well before entering.
- Keep away from flames.
- Eliminate all sources of sparks or ignition. Do not smoke.
- Take precautionary measures against static discharges.
- Open drums carefully as contents may be under pressure.

Storage

- Store in tightly closed containers in a cool, well ventilated area.
- Store away from heat and ignition sources.
- Provide a retention tank.
- Ensure the floor is impermeable.
- Provide fireproof electrical equipment and ensure that it is earthed.

Incompatible products

Powerful oxidants (hydrogen peroxide, nitric acid, hypochlorites), strong bases and strong reducing agents.

Recommended packaging materials

Stainless steel drums or stainless steel inner lining. Joints: polyethylene, rilsan.

Packaging materials to be avoided:

Rubber, plastics.

October 2007

ANNEX 3: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Revised MARPOL Annex II (IMO, 2005)

The revised Annex II Regulations for the control of pollution by noxious liquid substances in bulk was adopted in October 2004. It includes a new four-category categorization system for noxious and liquid substances. The revised annex entered into force on 1 January 2007.

The new categories are:

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; and

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 or deballasting operations.

The revision of this annex is based on the modification of other classifications such as the GESAMP classification and led to consequential amendments to the IBC Code.