

# CHLOROFORM

E.U. Classification:



UN n°: 1888

MARPOL Classification: Y

SEBC Classification: SD



Cedre

# CHLOROFORM

*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 and financial support from the French Navy.

## **Warning**

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

The information contained in this guide is the result of research and experimentation conducted by *Cedre*. *Cedre* cannot be held responsible for the consequences resulting from the use of this information.

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## Purpose of this guide

As part of the research funded by ARKEMA, *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) has 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 having occurred in the

Channel and in a river. 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)  
Tel.: + 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 chloroform

A

## Definition (INRS 2006, INERIS 2005)

Chloroform, a molecule of natural origin, is a colourless, volatile liquid. It can be obtained by direct chlorination of methane. Its ethereal odour can be detected from 85 ppm. Its solubility in freshwater is low (0.8% in weight at 20°C), however it is miscible with most organic solvents such as fats, oils and resins. It is a noxious, irritating, non-flammable and non-explosive substance. The fumes generated by its decomposition are however toxic. In the environment, 90% of chloroform emissions are natural.

## Use (INRS 2006, INERIS 2005)

Chloroform is mainly used (around 75%) to produce chlorofluoromethane (HCFC-22) which is used as a refrigerant. In the pharmaceutical industry, it is used to extract antibiotics, hormones, nicotine, quinine and vitamins. Essential oils and alkaloids can also be extracted with chloroform. In the plastics industry, chloroform acts as a solvent and purifying agent.

## Risks

### - Toxicity

Chloroform is harmful if inhaled or swallowed.

### - Fire

Chloroform is considered non-flammable.

### - Decomposition

The fumes generated by the decomposition of chloroform during a fire are toxic.

## Behaviour in the environment

(INERIS 2005)

Chloroform readily evaporates from the ground or hard surfaces. It is also very mobile in soil, however it does not tend to accumulate in the upper layers. It can however reach and contaminate groundwater by leaching.

When spilt in water, chloroform will rapidly sink due to its density (1.48). Although classed as non-evaporating, dissolved chloroform tends to evaporate upon contact with air, or in agitated, shallow waters.

Chloroform is not a bioaccumulable substance.

# 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**
- Transportation, handling, storage \_\_\_\_\_ **B9**

B

## First aid information

(ARKEMA SDS, 2006; INRS, 2006)

**Immediately remove all soiled or spotted clothes, including shoes.**

### Intoxication by inhalation

- Remove the victim from the polluted area after having taken all the necessary precautions.
- If the victim is unconscious, place them in the recovery position.
- If the victim has stopped breathing, begin assisted respiration.
- Transfer to hospital.

### Skin contact

- Remove contaminated clothing.
- Immediately rinse the skin with plenty of water for 15 minutes.
- Consult a doctor if skin lesions appear or in the case of extended or prolonged contamination.

### Eye contact

- Immediately rinse the eyes with plenty of water for 15 minutes.
- Consult an ophthalmologist if symptoms appear (pain, redness or impaired sight).

### Intoxication by ingestion

- Do not induce vomiting.
- If the victim is conscious, rinse the mouth and lips with plenty of water.
- If the victim is unconscious, place them in the recovery position.
- If the victim has stopped breathing, begin assisted respiration.
- Transfer to hospital.

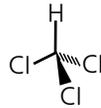
**Where necessary, contact the nearest poison control centre (cf. page 4).**

## ID card

# Chloroform

Gross formula:  $\text{CHCl}_3$

Semi-developed formula:



### Synonyms and trade names

Trichloromethane, Haloform, Chloroform, Formyl trichloride, Methane trichloride, Methenyl trichloride, Methyl trichloride, Trichloroform, Freon 20, Refrigerant R20, Formylchlorid, HCC 20.

Hazardous compounds to be listed on label: chloroform

Shipping name: chloroform

### Classification (EC regulation n° 1272/2008)

Oral: Acute toxicity, 4, H302.

Inhalation: Acute toxicity, 4, H332.

Skin irritation, 2, H315.

Eye irritation, 2, H319.

Carcinogenicity, 2, H351.

Reproductive toxicity, 2, H361d.

Oral: Specific target organ toxicity - repeated exposure, 2, H373

Inhalation: Specific target organ toxicity - repeated exposure, 2, Liver, Kidney, H373

Specific target organ toxicity - single exposure, 3, Central nervous system, H336

### Classification (Directive 67/548/EEC)

Xn: R20/22 R48/20/22

Xi: R36/38

Carc. Cat. 3; R 40

Repro. Cat. 3; R63

R67

CAS n°: 67-66-3

EC n° (EINECS): 200-663-8

INDEX N°: 602-006-00-4

### Classification for transportation

UN n°: 1888

Class: 6.1

B2

## Physical data

**Conversion factor (in air)**  
1 ppm = 5 mg/m<sup>3</sup>, 1 mg/m<sup>3</sup> = 0.2 ppm, 1 atm = 1.013×10<sup>5</sup> Pa

B3

Physical state	Colourless liquid
Chemical family	Halogenated Aliphatic Hydrocarbon (CSST, 2006)
Group	Volatile Halogenated Compounds (IFREMER, 2005)
Molecular mass	119.38 (INERIS 2005, ARKEMA 2007, CSST 2006, IPCS 1994)
Relative vapour density (air = 1)	4.12 (INRS 2006)
Relative density (water=1) (g.cm <sup>3</sup> ) D <sup>20</sup> <sub>4</sub> (air = 20°C)	1.48 (CSST 2006, IPCS 1994)
Vapour pressure/tension	21.3 kPa at 20°C (INRS 2006)
Solubility in seawater	No data available
Solubility in fresh water	8.7 g.L <sup>-1</sup> at 20°C (0.82 %) (Reach 2010)
Evaporation rate (ether = 1)	1.79 (CSST 2009)
Evaporation index (diethyl ether = 1)	2.5 (INRS 2006)
Olfactory threshold	85 ppm (INERIS 2005, INRS 2006)
Henry's law constant	299 at 20°C
log Kow (octanol-water partition coefficient)	1.97 (IPCS 1994)
Surface tension	27 mN/m (ARKEMA 2010)
Partition coefficient (water/oil) If less than 1: substance liable to be absorbed by the skin	0.011 at 20°C (CSST 2009)
Boiling point	61°C at 1013 hPa (ARKEMA 2010)

## Flammability data

### Explosive limits

Non-flammable, explosive substance

### Flash point

No flash point in the trial conditions (ARKEMA 2007)

### Auto-ignition point

> 1000°C (IPCS 1994)

Heat of combustion: 373 kJ.mol<sup>-1</sup> (IPCS 1994)

### Dangerous products of decomposition (CSST 2009)

In normal conditions of use, chloroform is a stable substance.

When exposed to natural light for long periods, with or without the presence of air, it breaks down slowly.

Chloroform breaks down into different products:

- Photochemical degradation (due to light) in the presence of oxygen produces phosgene, hydrogen chloride and chlorine.
- Degradation in the dark in the presence of oxygen produces hydrogen chloride, chlorine and carbonyl dichloride (phosgene).
- Thermal degradation produces hydrogen chloride and phosgene.

B4

## Toxicological data

### Acute human toxicity (INRS, 2006)

- Intoxication by ingestion and inhalation: coma (more or less profound) which occurs rapidly and can be associated with breathing and heart trouble (respiratory depression, cardiovascular collapse). Within 24 hours after ingestion, effects on the liver and kidneys can be observed.
- By skin contact: light irritation.
- By eye contact: severe eye irritation if exposed to chloroform vapours and contact with the liquid.

### Chronic human toxicity

(INRS 2006, INERIS 2005)

- Abnormal consumption of products containing chloroform may affect the Central Nervous System (CNS) and the Peripheral Nervous System (PNS) as well as the hepatic system.
- Professional chronic exposure to chloroform vapours can result in the appearance of neurological problems, irritation and sometimes hepato-renal anomalies.
- Prolonged contact with the product can cause dermatitis.

### Threshold toxicological values

#### Occupational exposure values

(INRS 2006)

COUNTRY	MEV (8 hour weighted average)	
	ppm	mg.m <sup>-3</sup>
EU	2	10
US (TLV-TWA)	10	49
Germany (MAK values)	0.5	2.5
France	2	10

COUNTRY	ELV (15 min)	
	ppm	mg.m <sup>-3</sup>
EU	-	-
US	50	240
Germany (MAK values)	2	10
France	50	250

### Risk management values for the population

(US EPA, 2007)

- Immediately Dangerous to Life or Health concentration (IDLH)

IDLH: 500 ppm

- Emergency Planning Response Guidelines (EPRG)

ERPGs -1: NA (Not Appropriate)

ERPGs -2: 50 ppm

ERPGs -3: 5,000 ppm

- Emergency Exposure Guidance Level (EEGL)

EEGL (1 h): 100 ppm

EEGL (24 h): 30 ppm

### Specific effects

#### Effects on reproduction

Chloroform can cross the placental barrier. Studies conducted on rats and mice indicate embryotoxic effects (increase in foetal resorption, delayed development) (INRS 2006).

#### Mutagenic effects

Most *in vivo* and *in vitro* studies have proven negative. Available data indicates that chloroform and its metabolites do not appear able to interact directly with DNA and do not show genotoxic activity (AFSSET 2009).

#### Carcinogenic effects:

- Assessment by RSST: suspected carcinogenic effect
- Assessment by IARC: the agent is possibly carcinogenic to humans (group 2B)
- Assessment by ACGIH: confirmed animal carcinogen with unknown relevance to humans (group 3A)

## Ecotoxicological data

### Acute ecotoxicity (INERIS 2005, ECB 2000, ARKEMA 2007)

Alga ( <i>Chlamydomonas reinhardtii</i> )	EC <sub>50</sub> (72 h)	= 13.3 mg/L (fresh water)
Invertebrate ( <i>Daphnia magna</i> )	LC <sub>50</sub> (48 h)	= 79 mg/L (fresh water)
	NOEC	= 13 mg/L (fresh water)
Oyster ( <i>Crassostrea gigas</i> , embryos)	EC <sub>50</sub> (48 h)	= 152 mg/L (seawater)
Fish ( <i>Micropterus salmoides</i> )	LC <sub>50</sub> (96 h)	= 51 mg/L (fresh water)
Fish ( <i>Oncorhynchus mykiss</i> )	LC <sub>50</sub> (96 h)	= 18 mg/L (fresh water)
Fish ( <i>Limanda limanda</i> )	LC <sub>50</sub>	= 28 mg/L (seawater)

**PNEC** (Predicted No Effect Concentration) PNEC fresh water: 146 µg.L<sup>-1</sup> (extrapolation factor of 10)  
(IFREMER 2005, INERIS 2005).

## Persistence in the environment

### Abiotic degradation

No information.

### Biotic degradation

In aerobic environments, chloroform is not biodegradable. However, in anaerobic environments (without oxygen), chloroform is degraded.

Experimentally observed half-lives range from 2 to 37 days in methanogenic sediments. A reasonable value of 15 days can be taken.

### Abiotic degradation

Hydrolysis is not a relevant mechanism for the degradation of chloroform. In the atmosphere, where chloroform is preferentially partitioned according to its properties, the available data gives an average half-life of 70 days.

### Bioaccumulation

Chloroform is not a persistent, bioaccumulable or toxic substance (PBT), nor very persistent and very bioaccumulable (vPvB).

B7

# Classification

## ESIS classification

- Hazards: R/S (Risk and Safety)

SEBC classification: SD (sinks and dissolves)

MARPOL classification: Y

E.U. Classification:

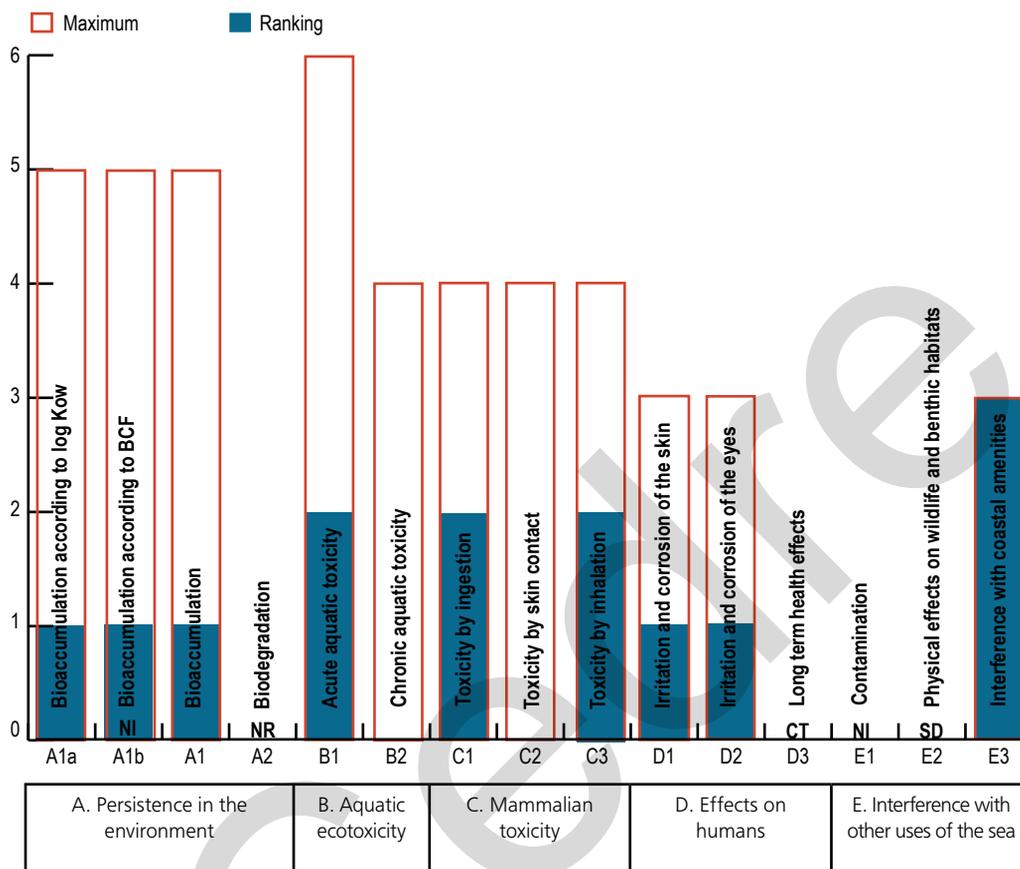


B8

## Risk phrases

R20/22	Harmful by inhalation and if swallowed
R36/38	Irritating to eyes and skin
R40	Limited evidence of a carcinogenic effect
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R63	Possible risk of harm to the unborn child
R67	Vapours may cause drowsiness and dizziness
H302	Harmful if swallowed
H315	Causes skin irritation
H319	Causes serious eye irritation
H332	Harmful if inhaled
H336	May cause drowsiness or dizziness
H351	Suspected of causing cancer
H361d	Suspected of damaging the unborn child
H373	May cause damage to organs through prolonged or repeated exposure

## GESAMP classification of chloroform



A1a: Very slight potential to bioaccumulate in aquatic organisms

A1b: Very slight potential to bioaccumulate in aquatic organisms

A1: Very slightly bioaccumulable

A2: **NR**: Not Readily biodegradable

B1: Slight acute aquatic toxicity

B2: Negligible chronic aquatic toxicity

C1: Moderate toxicity when ingested by mammals

C2: Negligible toxicity by skin contact with mammals

C3: Moderate toxicity when inhaled by mammals

D1: Mildly irritating or corrosive to the skin

D2: Mildly irritating to the eyes

D3: **C**: Carcinogen

**T**: Target organ systemic toxicity (following single or repeated exposure, the substance produces changes to the function or morphology of an organ, the biochemistry or haematology of an organism)

E1: **NI**: No Information

E2: **SD**: Sinks and Dissolves

E3: Highly objectionable, closure of amenity

# Transportation, handling, storage

## Transportation

(ARKEMA 2007)

Identification n° (UN): 1888

### Land transport:

#### RID (rail) /ADR (road)

Shipping name: CHLOROFORM

Hazard identification n°: 60

Classification code: T1

Class: 6.1

Packaging group: III

Danger labels: 6.1

### Transportation via inland waterways:

#### ADN/ADNR

Classification code: T1

Class: 6.1

Packaging group: III

Danger labels: 8

### Maritime transport: IMDG

Shipping name: CHLOROFORM

Class: 6.1

Packaging group: III

Marine pollutant (MP): NO

Danger labels: 6.1

### Air transport: IATA

Shipping name: CHLOROFORM

Class: 6.1

Packaging group: III

Danger labels: 6.1

## Handling (ARKEMA 2007, CSST 2006, INRS 2006)

- Regular or frequent handling of chloroform requires eye baths and safety showers in compliance with standards in force. They should be positioned near workstations.

- If, when handling the product, there is insufficient ventilation, the user must be equipped with appropriate respiratory protection.

- Avoid direct contact with chloroform. To do so, gloves, safety goggles and protective clothing will be made available to personnel and regularly maintained.

- Avoid contact with the skin and eyes.

- Wash hands, face, forearms and neck upon exit from restricted areas.

- Do not eat, drink or smoke in the work area.

- Shower and put on clean clothes at the end of the day to prevent cross contamination by contact with civilian clothing.

- Prevent the formation of vapours and/or spray.

- Keep away from incompatible substances during handling.

- Keep away from all flames or hot metal surfaces during handling.

- Periodically conduct atmospheric controls.

- Inform the personnel of the risks the product may present in the event of a spill (training exercises).

- Never conduct operations on or in tanks containing or having contained chloroform without taking the necessary precautions.

- Waste should be stored in closed, watertight metal containers.

- Never directly pour water polluted with chloroform down the drain.

- In the event of a major leak or spill, recover the product using an absorbent material. If the quantities are too large, evacuate the personnel and ensure that only trained personnel equipped with protective equipment are involved in response.

- In the event of a minor leak or spill, contain the leak if this can be done without danger. Absorb or cover with earth, sand or any

other non-combustible substance. Store in watertight containers.

- Finally, chloroform should be disposed of either by the company or in a specialised centre in compliance with the conditions authorised by regulations.

### **Storage** (ARKEMA 2007, CSST 2006, INRS 2006)

- Store the product in a cool, dark, well ventilated place, away from incompatible products, in an opaque container.
- Protect against light.
- Recommended packaging materials: iron, tinned iron.
- Packaging materials to be avoided: light metals and alloys in the presence of humidity, these materials are also to be avoided for all elements of the installation that may be in contact with the product.
- The storage room should have an impermeable floor, forming a retention tank able, in the event of a leak or spill, to contain the product and prevent it from spreading throughout the premises.
- Recipients containing the product should have a watertight seal and be clearly labelled. If the product is shared between various storage containers, each container must be labelled.

### **Incompatible products** (CSST 2009)

Violent reactions with strong bases, strong oxidants, ketones, alkali metals, reactive metals, acetone, disilane, magnesium or dinitrogen tetroxide.

Violent reactions of chloroform with acetone and methanol as well as in the presence of hydroxides (sodium, potassium or calcium hydroxide).

Violent reactions, even causing explosion in some cases, with strong oxidants, lithium, sodium, potassium, aluminium (powdered), magnesium (powdered), fluorine and solid potassium tert-butoxide.

In the presence of methanol, chloroform reacts violently with sodium methylate.

# Results of accident scenarios

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



## Reminder of properties

### Transportation

Chloroform is transported in bulk or in containers, by sea.

### Vapour density and tension

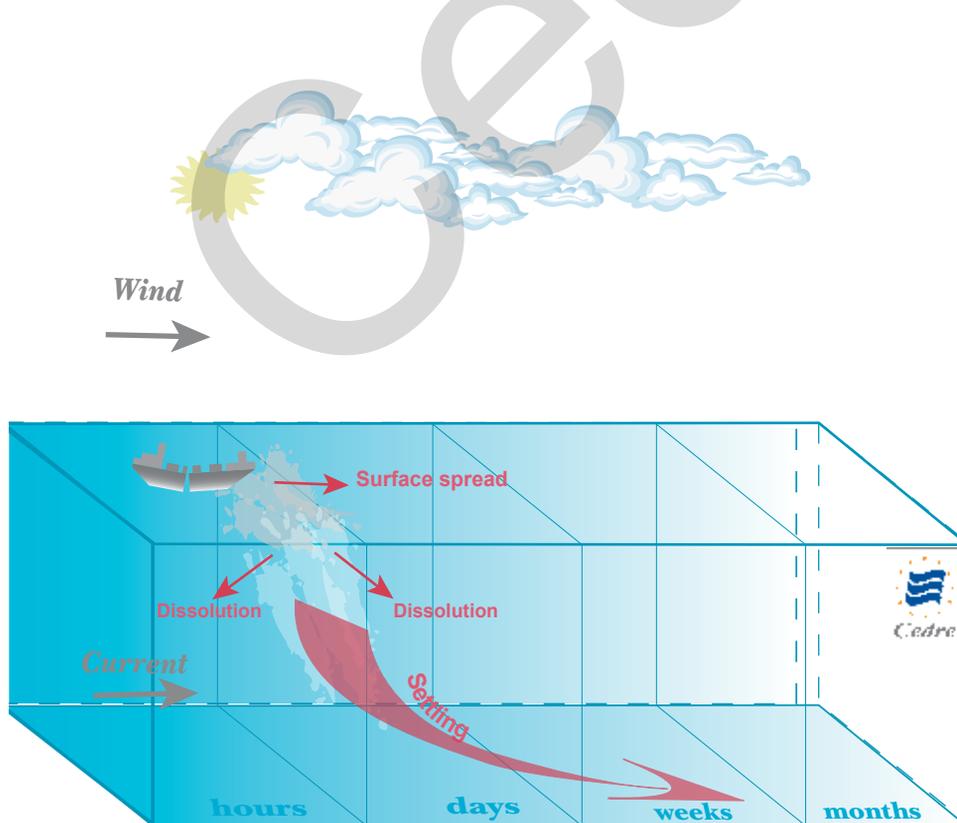
- Relative density: 1.48 at 20°C
- Vapour density: 4.12
- Vapour tension: 21.3 kPa at 20°C

### Solubility

Chloroform is slightly soluble in water (solubility in fresh water = 8.2 g.L<sup>-1</sup> at 20°C). Its solubility, density and vapour pressure mean that this product is classed SD (sinks and dissolves) according to the SEBC classification.

### Behaviour when spilt in the aquatic environment

At the spill location, chloroform sinks and dissolves in water. A small part will however evaporate according to the spill and environmental conditions.



Behaviour of chloroform spilt in water

# Accident scenarios

## Use of scenarios

The following accident scenarios were produced using the chemical spill model CHEMMAP available at *Cedre*. This software is used to model the behaviour of a product over time, as well as its movement in the water mass and atmosphere.

The six scenarios defined are used to estimate the evolution of chloroform in the water mass, on the bottom and in the atmosphere. A real spill will necessarily differ from the chosen scenarios. However, the scenarios provided will give initial insight into the risks encountered, before the results of models using the actual parameters of the given situation are available.

The results presented aim to answer the questions raised by responders and crisis managers:

- What distances should be taken for shipping exclusion zones or population containment zones? In most cases, this will be determined by the areas in which the concentration of chloroform is equal to the IDLH, i.e. 500 ppm in the atmosphere for 30 minutes or more.
- In which areas will the atmospheric concentrations allow the presence of workers for 8 hours (i.e. 2 ppm, equal to the MEV)?
- At what distance from the spill location will atmospheric concentrations be lower than the olfactory threshold?
- In which areas should fishing be banned and then monitored? These areas are those where PEC/PNEC ratio > 1 in the water mass.

C2

### WARNING

In reality, concentrations of the chemical (in the atmosphere and the water mass) are not homogeneous. It forms "bubbles" in which the concentration of the product is greater than that recorded in the surrounding areas. These "bubbles" may therefore be present at distances greater than those indicated in the summary table on p 27. Concentrations may reach the IDLH toxic values, however their time-frame is limited and in all cases less than 30 minutes. The same goes for the olfactory threshold which can occasionally be reached downwind at distances of up to 25 km from the spill location.

## Selected parameters

Shipping accidents in the Channel	
<p>SCENARIO 1</p> <ul style="list-style-type: none"> <li>Large breach: instantaneous spill (500 t in 20 min)*</li> <li>Wind: 2 m/s</li> <li>Surface spill</li> <li>Channel currents**</li> <li>Air and water temperature: 10°C</li> </ul>	<p>SCENARIO 2</p> <ul style="list-style-type: none"> <li>Large breach: instantaneous spill (500 t in 20 min)*</li> <li>Wind: 10 m/s</li> <li>Surface spill</li> <li>Channel currents**</li> <li>Air and water temperature: 10°C</li> </ul>
<p>SCENARIO 3</p> <ul style="list-style-type: none"> <li>Small breach: slow release (500 t in 5 h)*</li> <li>Wind: 2 m/s</li> <li>Surface spill</li> <li>Channel currents**</li> <li>Air and water temperature: 10°C</li> </ul>	<p>SCENARIO 4</p> <ul style="list-style-type: none"> <li>Small breach: slow release (500 t in 5 h)*</li> <li>Wind: 10 m/s</li> <li>Surface spill</li> <li>Channel currents**</li> <li>Air and water temperature: 10°C</li> </ul>
River accident	Wreck in the Channel
<p>SCENARIO 5</p> <ul style="list-style-type: none"> <li>Small breach: slow release (500 t in 5 h)*</li> <li>Wind: 2 m/s</li> <li>Surface spill</li> <li>Current: 0.4 m/s</li> <li>Air and water temperature: 15°C</li> </ul>	<p>SCENARIO 6</p> <ul style="list-style-type: none"> <li>Small breach: very slow release (500 t in 24 h)</li> <li>Wind: 2 m/s</li> <li>Spill 70 m below the surface</li> <li>Channel currents**</li> <li>Air and water temperature: 15°C</li> </ul>

\* Based on a leak of the chemical from a breach located one metre below the surface.

\*\* Currents: Channel currents with a tidal coefficient of 80, 30 nautical miles north-west of La Hague.

## Scenarios 1 to 4: spills at sea

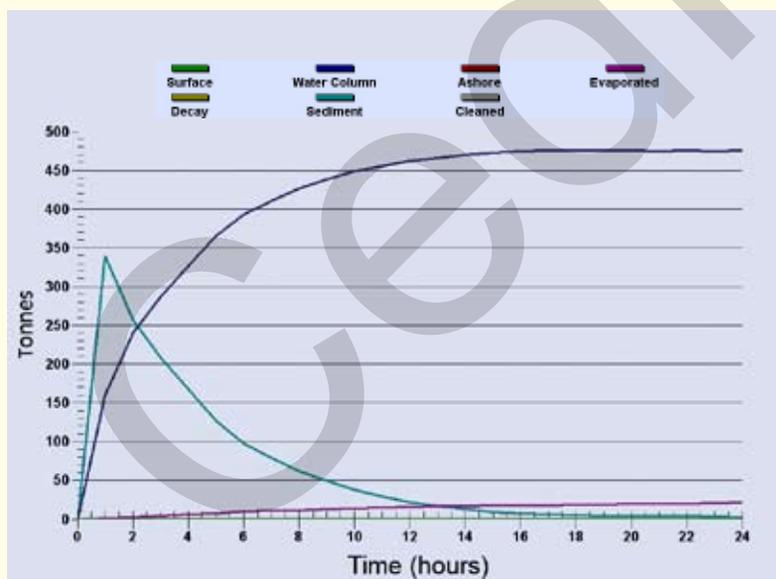
### General behaviour of the chemical spilt in seawater

A large part of the chloroform will dissolve in the water while the chemical sinks due to its density. Evaporation will be low, and will be generated by the dissolved chloroform, which will evaporate more readily with greater surface agitation. In shallow waters, evaporation will occur for longer due to exchanges between the dissolved chloroform and the atmosphere.

After 24 hours, less than 5% of the mass of chloroform released in the environment will have evaporated. The rest sinks and dissolves (Graph 1). After 48 hours, less than 10% of the mass of chloroform released in the environment will have evaporated.

The spill at sea occurs: 50° North - 003° West - NW winds.

### Scenarios 1 and 2: 500 tonnes spilt instantaneously (20 minutes) with wind speeds of 2 m/s and 10 m/s.



Graph 1: mass distribution for an instantaneous spill of 500 tonnes

The IDLH is never reached (500 ppm in the atmosphere for 30 min).

The MEV (2 ppm for 8 h) will never be reached with a wind speed of 2 m/s. With a wind speed of 10 m/s, the MEV is reached over a distance of 20 km in a SE direction.

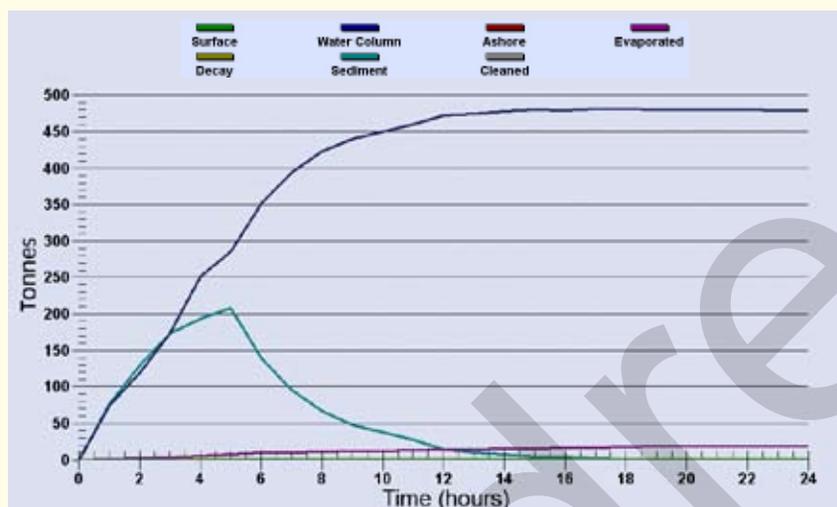
The TLV-TWA (10 ppm for 8 hours) is never reached with a wind speed of 2 m/s. With a wind speed of 10 m/s, the area concerned is 2 km wide by 5 km long, SE of the spill location.

Protective equipment (cartridge masks and SCBA) should be within reach.

The olfactory threshold (85 ppm) may be detected more or less fleetingly, up to a distance of 22 km downwind and up to 36 hours after the spill, with a wind speed of 10 m/s.

The 48 hour fishing ban area represents an ellipse 18 km long by 0.5 km wide, centred on the spill location and angled at 70°-250°.

### Scenarios 3 and 4: 500 tonnes of chloroform spilt in 5 hours with wind speeds of 2 and 10 m/s



Graph 2: mass distribution for a spill of 500 tonnes of chloroform over 5 hours

The overall behaviour of the chloroform is identical to that during the instantaneous spill, except that for the 5 hours during which the chemical is released, the curves are flattened. The atmospheric quantity of chloroform remains low (3 to 4 % in 24 hours).

Due to the 5 hour duration of the spill and tidal currents, the contaminated water mass will be greater than for an instantaneous spill.

- The IDLH value is never reached.
- The MEV will be reached over 3 km in a NE-SW direction, with a wind speed of 2 m/s. This distance is 5.5 km SSW of the spill location with a wind speed of 10 m/s.
- TLV-TWA. An area 1.5 km by 1.2 km (in the direction SW-NE) centred at the spill point with a permanent concentration of 10 ppm in the atmosphere for a duration of 8 hours. However, protective equipment (cartridge masks and SCBA) should be within reach.
- The olfactory threshold (85 ppm) can be detected very locally up to a distance of 24 km (SE and downwind of the accident) and up to 36 hours after the accident.
- The 48 hour fishing ban area represents an ellipse 18 km long by 1.2 km wide, centred on the spill location and angled at 70° - 250°.

## Scenario 5: river accident

A single river scenario with a single atmospheric condition (low wind: 2 m/s) was simulated by the model. The spill location on the Rhone was located 20 km upstream of the river mouth. In rivers, the input parameters are very different to those at sea: currents, bathymetry, particles in suspension, salinity, temperature...

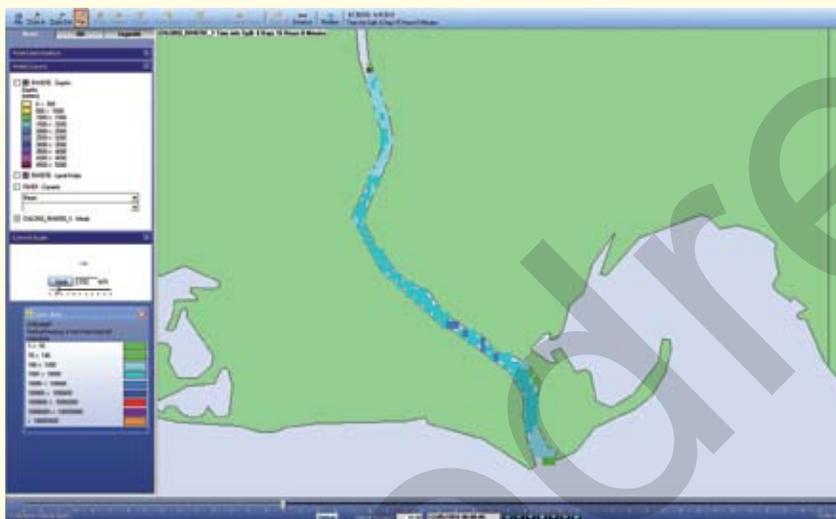


Figure 1: Aerial view of a spill of 500 tonnes over 5 hours in a river, 15 hours after the beginning of the spill

- In the water mass, concentrations greater than or equal to the PNEC cover the entire length of the river from the spill location to the sea, i.e. a distance of 20 km, 16 hours after the beginning of the spill.
- The IDLH value is never reached.
- The MEV (2 ppm for 8 h) is reached up to 34 km SSE of the spill. The plume is 10 km wide (Northerly wind, 2 m/s).
- The TLV-TWA will reach a distance of 15 km SSE of the spill.
- The olfactory threshold (85 ppm) can be detected over a distance of 4 km south of the spill.

## Scenario 6: wreck in the Channel

In this spill scenario, the vessel has sunk in waters 70 m deep and its cargo is slowly leaking.

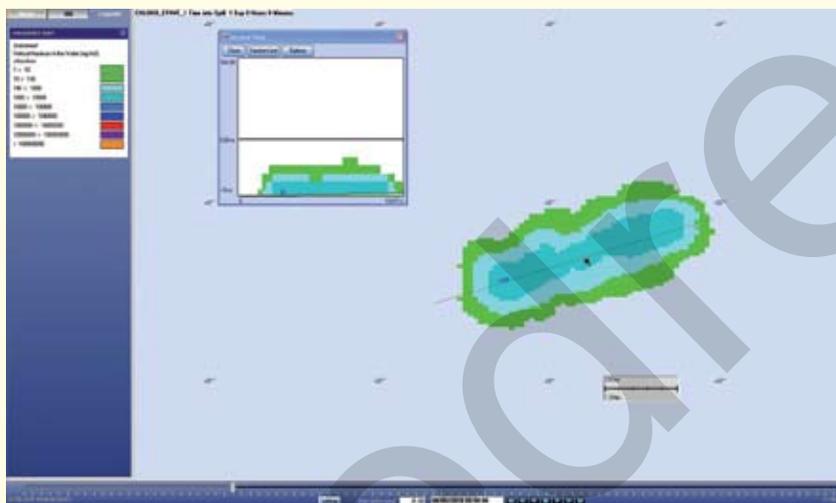


Figure 2: chloroform leak from a wreck.

Aerial view of the bottom and cross-section in insert. The dark blue and light blue colours show where PEC/PNEC >1. The affected areas stretches over a distance of 20 km in a SW-NE direction and is 7 km wide.

As chloroform sinks, maximum concentrations of the substance in the water mass are observed towards the bottom of the water column; it therefore tends to stay in the depths. According to model predictions, chloroform only reaches the layers closest to the surface in very small quantities and only after 48 hours. The maximum area covered by the product in the water mass at concentrations greater than or equal to the PNEC is 20 km by 7 km. The chemical's atmospheric concentration is nil throughout the simulation, as it never reaches the atmosphere.

- The IDLH is never reached.
- The TLV-TWA is never reached.
- The olfactory threshold is never reached.
- The fishing ban area stretches 20 km SW-NE centred around the spill area and is 7 km wide.

Scenario results summary table

Quantity spilt	Wind	Limit values	Results: Maximum distances travelled	Protection*	
500 t instantaneous spill (20 min) at sea	2 m/s	IDLH (500 ppm)	IDLH never reached		
		MEV (2 ppm)	MEV never reached		
		TLV-TWA (10 ppm)	TWA never reached	B	
		Olfactory threshold (85 ppm)	21 km ESE of the spill location, T + 48 hours**	B	
		PEC/PNEC ( $\geq 1$ )	18 km by 0.5 km SE T + 74 hours**		
		Maximum concentration in the water mass	20 mg/L T + 2 hours		
	10 m/s	IDLH (500 ppm)	IDLH never reached		
		MEV (2 ppm)	20 km in the direction SE-NW		
		TLV-TWA (10 ppm)	2 km by 5 km SE	B	
		Olfactory threshold (85 ppm)	22 km SE of the spill location, T + 36 hours**	B	
		PEC/PNEC ( $\geq 1$ )	18 km by 0.5 km T + 36 hours**		
		Maximum concentration in the water mass	21.5 mg/L T + 2 hours		
500 t over 5 h (100 t/h) at sea	2 m/s	IDLH (500 ppm)	IDLH never reached		
		MEV (2 ppm)	3 km in the direction NE-SW		
		TLV-TWA (10 ppm)	1.5 km by 1.2 km	B	
		Olfactory threshold (85 ppm)	Up to 24 km SE of the spill	B	
		PEC/PNEC ( $\geq 1$ )	18 km by 1.5 km E of the spill T + 38 hours		
	10 m/s	Maximum concentration in the water mass	14.6 mg/l T + 5 hours**		
		IDLH (500 ppm)	IDLH never reached		
		TLV-TWA (10 ppm)	1.5 km by 1.2 km	B	
		Olfactory threshold (85 ppm)	Up to 24 km ESE of the spill	B	
		PEC/PNEC ( $\geq 1$ )	18 km by 1.5 km E T + 38 hours**		
Maximum concentration in the water mass		14.7 mg/L T + 5 hours			
	500 t over 5 h in a river	2 m/s	IDLH (500 ppm)	IDHL never reached	
			TLV-TWA (10 ppm)	15 km SSE of the spill	B
			Olfactory threshold (85 ppm)	4 km south of the spill T + 68 hours**	B
			PEC/PNEC ( $\geq 1$ )	5 km T + 63 hours**	
Maximum concentration in the water mass			170 mg/L T + 5 hours**		

\* Protection B: wear a cartridge mask as a precaution or have SCBA within reach.

\*\*Time required to reach maximum distance.

## Consumption scenarios

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

# Spill response

- Examples of spills ————— **D1**
- Response recommendations ————— **D2**
- Response techniques ————— **D3**
- Choosing Personal Protective Equipment (PPE) ————— **D4**
- Measuring devices and waste treatment ————— **D5**

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## Examples of spills

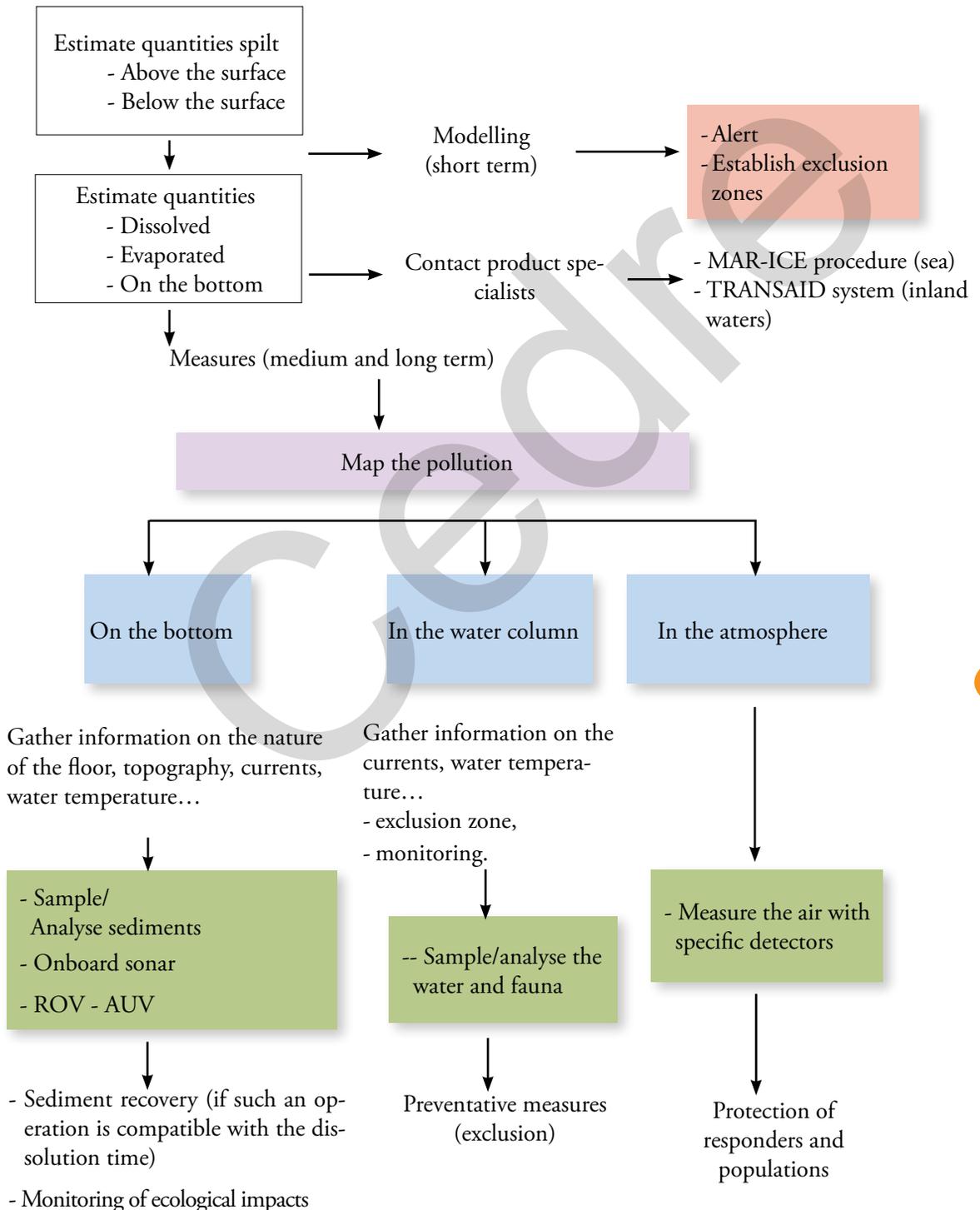
To the best of our knowledge, no spills of chloroform have occurred at sea.

In inland waters, an accident is known to have occurred in Brazil in 1983. A truck hit a storage site, generating a spill of 500 m<sup>3</sup> of chloroform, 1,2-dichloroethane and 1,1,2-trichloroethane into a river. All three of these chemicals are denser than water.

After 5 days of pumping operations in the depths of the river, close to the spill location, 20 m<sup>3</sup> of products were recovered. The contaminated silt was removed by dredging. Two drains were dug to recover the products sitting on the river bed.

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## Response recommendations



### Is response possible? (ERICARD, 2009)

The environmental conditions and circumstances of the accident will determine to what extent response on the vessel and in the environment is possible, timely and justified.

Among the parameters to be taken into consideration we find:

- Environmental parameters
  - Sea state: swell, wind sea, current, spray...
  - Wind: force, direction, forecast, atmospheric stability...
  - Situation (position) of the vessel: traffic separation scheme, sheltered area, near residential areas...
  - Depth, type and slope of bottom...
  - Turbulence (agitation) in the environment, stratification...
- Incident-related parameters
  - Diameter of the breach
  - Location of the breach: on deck (container), below the water line or not
  - Volume of the affected tank

### Emergency measures in the event of a leak or spill

Stop the leak if possible.

Although it sinks rapidly, chloroform spilt in water will partially dissolve. Due to agitation, the contaminated water, in contact with the atmosphere, will release part of the dissolved chloroform into the air. Responders should therefore be equipped to protect their upper respiratory tract.

Establish an exclusion zone, which will vary according to the volume of chloroform involved and the atmospheric stability. In stable atmospheres, we remember that the olfactory threshold (85 ppm) will be detected over 22 km from the spill location (500 tonnes spilt in 20 min). See scenarios p. 23.

Tow the vessel to a sheltered area to assess its condition and make it safe before beginning to tow it to a port equipped to receive the chemical when pumped out.

If the ship's condition or the distance prevents it from being towed to an equipped port, ship-to-ship transfer in the refuge area must be considered. This type of transfer will also be conducted in the case of grounding.

### Emergency measures in the case of a tank or container on fire

Chloroform is non-flammable. However, in the event of fire, the smoke and gas emitted by chloroform during its thermal degradation contain substances that are highly toxic for humans (hydrogen chloride gas, phosgene). Move away and fight the fire from response vessels located upwind of the vessel in difficulty.

## Response techniques

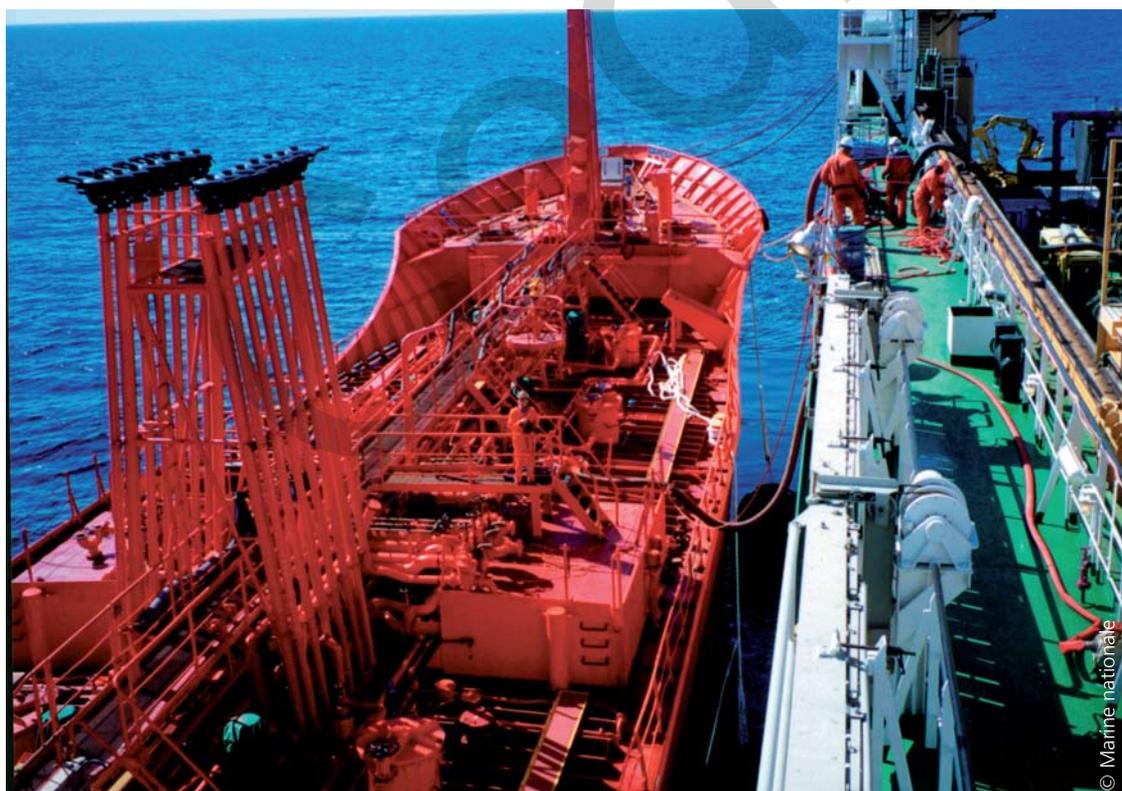
### Transshipment

The contents of tanks are rarely transferred between ships in the open sea (or exceptional conditions would be required, both in terms of the sea and weather conditions and the socio-political circumstances surrounding the accident).

Ship-to-ship transfer should preferably be conducted in a sheltered area, by specialised companies working by the book and in safety conditions in compliance with European criteria.

### Spill response

In most cases, no response operations can be conducted on the chemical once it has been spilled in water, except in waters less than a few dozen metres deep (port area). Dredging is not an emergency measure, but where considered necessary, the decision must be made as quickly as possible, as the product will dissolve in a few days in strong currents.



Transshipment of the cargo of the *levoli Sun* onto the chemical tanker *Angela*

D3

# Choosing Personal Protective Equipment (PPE)

Ensure maximum protection in the case of high or unknown concentrations of chloroform.

## Choosing breathing apparatus

It is recommended that responders use self-contained breathing apparatus with full face protection by a positive pressure mask.

A cartridge mask suitable for chloroform and with full facial protection is possible where the concentration in air is known and the time in the contaminated environment is compatible with the cartridge's lifetime.

## Choosing protective clothing

In addition to mucous membranes, responders' skin must be fully protected. Protective clothing made of fluoroelastomer presents good resistance to chloroform, as does poly-vinyl alcohol.

Protective items made of natural latex, vinyl (PVC) or neoprene are not recommended.

Nitrile may be used against splashes only (moderate resistance).

## Recommendations for use in an emergency

Protective equipment should be used by trained personnel. All use by untrained persons may have dangerous consequences for the user in particular when using a face mask.



PPE for short periods of exposure or low concentrations

## Measuring devices and waste treatment

### Methods of detection and determination in air (INRS, 2006) and water

Chloroform is detected after adsorption onto activated carbon then desorption with carbon disulphide. The measurement is then conducted by gas phase chromatography and detection by flame ionisation or electron capture. A field PID (Photo Ionisation Detection) or FID (Flame Ionisation Detection) may be used after calibration. DRAEGER and GASTECH colorimetric indicator tubes covering different scales of concentration are simple to use in the field. In water, the Stir Bar Sorptive Extraction (SBSE) method can be used for preference over liquid-liquid extraction which requires large sample volumes.

### Waste treatment

Waste should be transported to and processed by hazardous waste treatment centres. Small quantities of polluted water (rivers) can be treated locally by activated carbon treatment units.



Detection of vapours by photo-ionisation (top) and with an indicator tube (bottom)

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# Further information

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

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# Glossary

## Auto-ignition point

Minimal temperature at which vapours ignite spontaneously.

## 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).

## Effective concentration 50 (EC<sub>50</sub>)

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.

## Henry's law constant

Value indicating a substance's volatility.

## 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.

## Leaching

Process in which a liquid infiltrates into the ground, possibly reaching groundwater.

## 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 (LC<sub>50</sub>)

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.

## 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.

## Occupational Exposure Limit Value

Concentration in the atmosphere which should not be exceeded to protect workers' health.

## Olfactory threshold

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

## Personal protective equipment (PPE)

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 appara-

tus/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.

#### **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.

#### **Predicted No Effect Concentration (PNEC)**

Predicated concentration at which a substance will have no effect on the environment.

#### **Surface tension**

A constant that expresses the force owing to molecular interaction exerted at the surface of a liquid when it comes into contact with another surface (liquid or solid) and that affects surface dispersion.

#### **Threshold Limit Value (TLV)**

Average limit value (weighted as a function of time) that people can be exposed to regularly at work 8 hours a day, 5 days a week without experiencing noxious effects. This value was defined and determined by ACGIH.

TLV-STEL: Mean weighted 15 minutes concentration that must never be exceeded at any time during the day.

TLV-TWA: Mean weighted values for an 8 hour period per day and 40 hours a week.

TLV-ceiling: Ceiling values never to be exceeded not even for an instant.

#### **Vapour pressure or tension**

Partial pressure of gas molecules in a state of equilibrium with the liquid phase for a given temperature.

## Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American International Health Alliance
CAS	Chemical Abstracts Service
CEDRE	Centre of Documentation, Research and Experimentation on Accidental Water Pollution
CSST	Commission de la Santé et de la Sécurité du Travail
EC	Effective Concentration
ECB	European Chemicals Bureau
EINECS	European INventory of Existing Chemical Substances
ELV	Exposure Limit Value
ESIS	European chemical Substances Information System
GESAMP	Group of Experts on Scientific Aspects of Marine Environmental Protection
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IATA	International Air Transport Association
IDLH	Immediately Dangerous to Life or Health concentrations
INERIS	Institut National de l'Environnement Industriel et des RISques
INRS	Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles
IPCS	International Programme on Chemical Safety
LC	Lethal Concentration
MEV	Mean Exposure Value
NOEC	No Observed Effect Concentration
OELV	Occupational Exposure Limit Value
PNEC	Predicted No Effect Concentration
PPE	Personal Protective Equipment
ppm	parts per million
RSST	Règlement sur la Santé et la Sécurité du Travail
SCBA	Self Contained Breathing Apparatus
SDS	Safety Data Sheet
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
TLV-TWA	Threshold Limit Values - Time Weighted Average
US EPA	United States Environmental Protection Agency
VPvB	Very Persistent very Bioaccumulable

## Useful websites

**CEDRE (Centre of Documentation, Research and Experimentation on Accidental Water Pollution)**, [online],

Available at <http://www.cedre.fr>

**CEFIC (European Chemical Industry Council)**, [online],

Available at <http://www.ericards.net>

**CSST (Commission de la Santé et de la Sécurité au Travail)**, [online],

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

**ECB (European Chemical Bureau)**, [online],

Available at <http://ecb.jrc.it>

**HSDB (Hazardous Substances Data Bank)**, [online],

Available at <http://toxnet.nlm.nih.gov>

**ICSC (International Chemical Safety Cards)**, [online],

Available at <http://www.cdc.gov/niosh/ipcs/french.html>

**INRS (Institut National de Recherche et de Sécurité)**, [online],

Available at <http://www.inrs.fr>

**NIOSH (National Institute for Occupational Safety and Health)**, [online],

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## **ANNEX**

Classification of noxious liquid substances  
transported in bulk

## ANNEX: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES TRANSPORTED IN BULK

### Dangerous goods

Regulations governing the carriage in bulk of hazardous liquid substances (MARPOL Annex II) provide valuable indications on the hazards that such substances can produce during transportation.

Noxious liquid substances are divided into 4 categories (X, Y, Z and OS) starting with the most dangerous substances (MARPOL X) and ending with the least dangerous ones (MARPOL OS).

The MARPOL classification system is based on risk assessment profiles for chemicals transported in bulk by sea, as defined by a GESAMP working group (Joint Group of Experts on the Scientific Aspects of Marine Protection).

### Revised Annex II of MARPOL classification (IMO, 2005)

This revision, adopted in October 2004, includes a new classification of the dangers of noxious liquid substances transported by sea in bulk and entered into force on 1st 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.

**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.