

# STABILISED METHYL METHACRYLATE

EU classification:

F: Highly  
flammable



Xi: Irritant



UN n°: 1247

MARPOL classification: Y

SEBC classification: ED (evaporates/dissolves)





# STABILISED METHYL METHACRYLATE

*PRACTICAL GUIDE*

*INFORMATION*

*DECISION-MAKING*

*RESPONSE*

This document was drafted by *Cedre* (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.

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

Published in French: October 2008

English translation: November 2008

Translated by AlbaTraduction.com

**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, *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) and the French Navy 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 and in ports and 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)  
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 methyl methacrylate

A

## Definition

Methyl methacrylate is a colourless liquid with a slightly irritating, acrid odour which can be detected from 0.05 ppm. It is a highly flammable irritant which is volatile and soluble in water. Its vapours are heavier than air and can explode in confined spaces, or cause flash-back.

## Uses (IPCS INCHEM, 1998)

Methyl methacrylate is mainly used in manufacturing cast acrylic sheets, acrylic emulsions and moulding and extrusion resins. Polymers and copolymers of methyl methacrylate are present in many products: surface coatings, adhesives, sealants, leather and paper coatings, inks, floor polishes, textile finishes, dental prostheses, surgical bone cements, leaded acrylic radiation shields, synthetic fingernails, shoe inserts...

## Risks

- Polymerisation in the absence of air or an inhibitor and in the case of high temperatures. This reaction is exothermic and is liable to degenerate into an uncontrolled reaction.
- Fire: methyl methacrylate is highly flammable (closed cup flash point: 2°C). Vapours can form explosive mixtures with air.
- Toxicity: this compound is irritating to the respiratory tract and skin. It may cause sensitisation by skin contact.

## Behaviour in the environment

When spilt in water, methyl methacrylate will float (density 0.94), some will dissolve in the water (solubility 16 g/L), but the main part will evaporate forming noxious vapours which are heavier than air.

According to its Kow value of 1.38, bioaccumulation of methyl methacrylate is unlikely. Methyl methacrylate is harmful to aquatic organisms.

# 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**



## First aid information

(ARKEMA SDS, 2007; ICSC, 2003)

**Immediately remove all soiled or spotted clothes. In the event of contact or inhalation, seek medical advice.**

### Intoxication by inhalation

- Take the victim into the fresh air.
- Supply oxygen or apply artificial respiration if necessary.
- In case of persistent problems: consult a doctor.

**B1**

### Skin contact

- Remove contaminated clothing.
- Immediately wash thoroughly with soap and water.
- In case of persistent irritation of the skin, consult a doctor.

### Eye contact

- Wash well-open eyes immediately, abundantly and thoroughly with water (remove contact lenses where possible).
- In case of persistent problems, consult a doctor.

### Intoxication by ingestion

- Rinse out the mouth.
- Do not induce vomiting.
- Consult a doctor.

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

## ID card<sup>1</sup>

# Methyl methacrylate

Gross formula:  $C_5H_8O_2$

Semi-developed formula:  $CH_2 = C(CH_3)COOCH_3$

### Synonyms

MMA; Methacrylic acid methyl ester; Methyl alpha-methacrylate; Methyl ester; 2-methyl-2-propenoic acid; Methyl 2-methyl-2-propenoate; Methyl 2-methylpropenoate.

B2

### EU classification

**F: Highly flammable.**

**Xi: Irritant.**

R11: Highly flammable.

R43: May cause sensitisation by skin contact.

R37/38: Irritating to respiratory system and skin.

S24: Avoid contact with the skin.

S37: Wear suitable gloves.

S46: If swallowed seek medical advice immediately and show the container or label.

CAS n°: 80-62-6

EC n° (EINECS): 201-297-1

Index n°: 607-035-00-6

### Classification for transportation<sup>2</sup>

UN n°: 1247

Class: 3

<sup>1</sup> Additional data in Annex 1

<sup>2</sup> IMO data page 15

## Physical data

### Conversion factors:

1 ppm = 4.10 mg/m<sup>3</sup>

1 mg/m<sup>3</sup> = 0.244 ppm

1 atm = 1.013×10<sup>5</sup> Pa

B3

Melting point	- 48.2°C <small>DIPPR, 2006</small>
Boiling point	100.3°C <small>DIPPR, 2006</small>
Critical temperature	292.8°C <small>DIPPR, 2006</small>
Relative density (water = 1) (g/cm <sup>3</sup> )	0.944 <small>INERIS, 2004; ICSC, 2003; ECB, 2002; ARKEMA SDS, 2007</small>
Relative vapour density (air = 1)	3.45 <small>INRS, 1997; CSST, 2006</small>
Solubility in seawater	8 g/L at 10°C 9.8 g/L at 20°C <small>CEDRE, 2008</small>
Solubility in fresh water	16 g/L at 20°C <small>ARKEMA SDS, 2007; ECB, 2002</small> 11.5 g/L at 10°C 12.8 g/L at 20°C <small>CEDRE, 2008</small>
Vapour pressure/tension	3.9 kPa at 20°C <small>ARKEMA SDS, 2007; INRS, 1997; CSST, 2006</small> 16.6 kPa at 50°C
Viscosity at 20°C	0.56 mPa.s <small>ARKEMA SDS, 2007</small>
Olfactory threshold	0.05 ppm <small>CSST, 2006</small>
Evaporation rate (n-butyl acetate = 1)	3.1 (takes 3.1 times longer to evaporate than n-butyl acetate) <small>INRS, 1997</small>
Diffusion coefficient in water	No data available
Diffusion coefficient in air	No data available
Henry's law constant	26.3 Pa.m <sup>3</sup> .mol <sup>-1</sup> <small>ECB, 2002</small> 3.2×10 <sup>-4</sup> atm.m <sup>3</sup> .mol <sup>-1</sup> <small>HSDB, 2005</small>
Molecular mass	100.11 g.mol <sup>-1</sup> <small>DIPPR, 2006</small>
Volumic mass (20°C)	943 kg/m <sup>3</sup> <small>ARKEMA SDS, 2007</small>
Surface tension	28 mN/m at 20°C <small>HSDB, 2005</small> 61 mN/m <small>ECB, 2002</small>

# Flammability data

## Explosive limits by volume (% in air)

Lower limit (LEL): 2.1% or 21,000 ppm ARKEMA SDS, 2007

Upper limit (UEL): 12.5% or 125,000 ppm ARKEMA SDS, 2007

## Flash point

Closed cup: 2°C ARKEMA SDS, 2007; CSST, 2006

Open cup: 10°C CSST, 2006

## Self-ignition point

421°C CSST, 2006; INRS, 1997; ICSC, 2003

430°C ECB, 2002; ARKEMA SDS, 2007

Methyl methacrylate can form flammable vapours with air and can ignite in the presence of heat or a source of ignition.

INRS, 1997; CSST, 2006

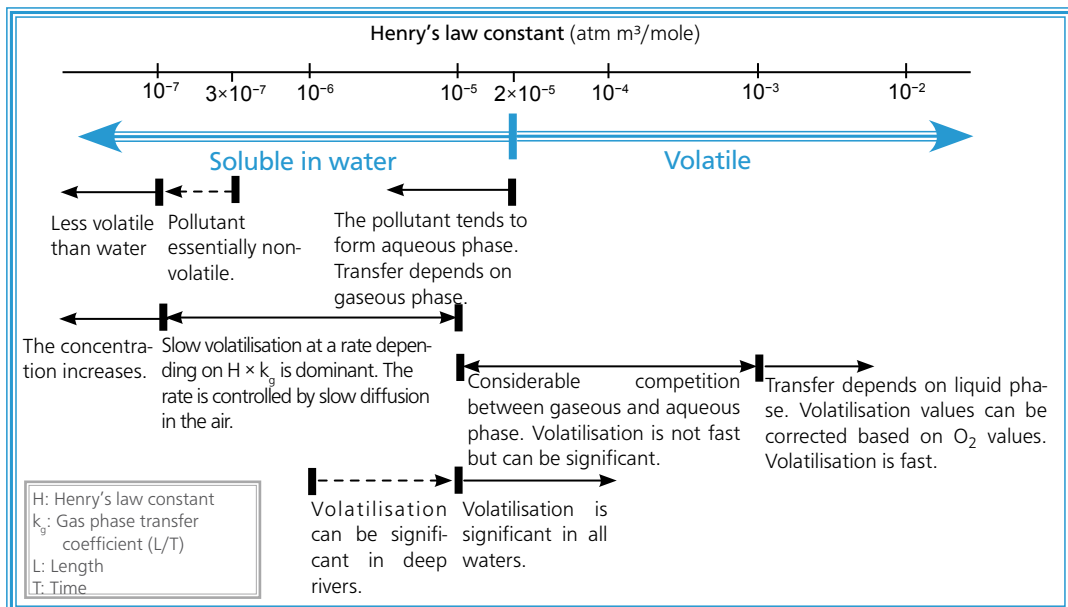
## Dangerous products of decomposition CSST, 2006

Carbon monoxide, carbon dioxide

## Regression speed

No data available

B4



Characteristics of volatilisation associated with different Henry's law constant values (Lyman et al., 1990).

## Toxicological data

### Acute human toxicity

(ICSC, 2003; CANUTEC, 2008; ARKEMA SDS, 2007)

- By inhalation: cough, shortness of breath, sore throat, irritation of the nose and throat and, at high concentrations, nausea and dizziness. The inhalation of concentrated vapours can lead to anaesthesia-like conditions.
- By skin contact: redness, irritation, possibility of dermatitis.
- By ingestion: irritation of the mouth, throat, oesophagus and stomach, nausea, vomiting, abdominal pains.
- By eye contact: pain, redness, watering.

### Threshold toxicological values

#### Occupational exposure values

(ARKEMA SDS, 2007)

MEV: 100 ppm; 410 mg/m<sup>3</sup> (France)

ELV: 200 ppm; 820 mg/m<sup>3</sup> (France)

TLV-TWA: 50 ppm; 205 mg/m<sup>3</sup> (US ACGIH)

TLV-STEL: 100 ppm; 410 mg/m<sup>3</sup> (US ACGIH)

TLV-ceiling: no data available

#### Risk management values for the population

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

IDLH: 1,000 ppm; 4,100 mg/m<sup>3</sup> (NIOSH, 2005)

TEEL 0: 400 ppm; 1,640 mg/m<sup>3</sup>

TEEL 1: 400 ppm; 1,640 mg/m<sup>3</sup>

TEEL 2: 400 ppm; 1,640 mg/m<sup>3</sup>

TEEL 3: 4,000 ppm; 16,400 mg/m<sup>3</sup>

ERPG 1: no data available

ERPG 2: no data available

ERPG 3: no data available

### Chronic human toxicity

(ICSC, 2003; CANUTEC, 2008)

Repeated or prolonged contact can cause skin sensitisation, allergic reactions and dermatitis. Methyl methacrylate may have effects on the peripheral nervous system and, if exposure continues, loss of consciousness may occur with possible damage to the liver and kidneys.

### Specific effects

(CSST, 2006; INRS, 1997; HSDB, 2004; ARKEMA SDS, 2007; ECB, 2002)

Carcinogenic effects: no carcinogenic effects according to the IARC. No causal relationship between occurrences of cancer and exposure to the substance in epidemiological investigations.

Effects on fertility: no effect on reproductive organs.

Teratogenic effects and/or effects on foetal development: not demonstrated in humans; in animals, effects on development (significant decrease in foetal weight, delayed ossification) have been observed at doses which are toxic for mothers.

Mutagenic effects: not demonstrated in humans or animals.

#### Proposed AEGLs (EPA, 2006)

Concentrations (ppm)	10 min	30 min	60 min	240 min	480 min
AEGL 1	17	17	17	17	17
AEGL 2	150	150	120	76	50
AEGL 3	720	720	570	360	180

## Ecotoxicological data

### Acute ecotoxicity (HSDB, 2004; ECB, 2002; ARKEMA SDS, 2007)

Bacteria ( <i>Pseudomonas putida</i> )	EC <sub>5</sub> (16 h)	= 100 mg/L (fresh water)
Bacteria ( <i>Uronema parduczi</i> )	EC <sub>5</sub> (20 h)	= 556 mg/L (fresh water)
Bacteria ( <i>Chilomonas paramecium</i> )	EC <sub>5</sub> (72 h)	= 178 mg/L (fresh water)
Algae ( <i>Raphidocelis subcapitata</i> )	EC <sub>50</sub> (96 h)	= 170 mg/L (fresh water)
Crustacean ( <i>Daphnia magna</i> )	EC <sub>50</sub> (48 h)	= 69 mg/L (fresh water)
	EC <sub>50</sub> (24 h)	= 720 mg/L (fresh water)
Fish ( <i>Lepomis macrochirus</i> )	LC <sub>50</sub> (72 h)	= 264 mg/L (fresh water)
	LC <sub>50</sub> (96 h)	= 191 mg/L (fresh water)
Fish ( <i>Oncorhynchus mykiss</i> )	LC <sub>50</sub> (96 h)	> 79 mg/L (fresh water)
	NOEC (96 h)	= 40 mg/L (fresh water)

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### Chronic ecotoxicity (ARKEMA SDS, 2007)

Algae ( <i>Scenedesmus quadricauda</i> )	EC <sub>3</sub> (8 d)	= 37 mg/L (fresh water)
Algae ( <i>Microcystis aeruginosa</i> )	EC <sub>3</sub> (8 d)	= 120 mg/L (fresh water)
Algae ( <i>Raphidocelis subcapitata</i> )	NOEC (96 h)	= 100 mg/L (fresh water)
Crustacean ( <i>Daphnia magna</i> )	NOEC (21 d)	= 37 mg/L (fresh water)

### PNEC (ECB, 2002) (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<sub>water</sub> is 740 µg/L. A safety factor of 50 is applied to the lowest value (data for the crustacean *Daphnia magna*).

## Persistence in the environment

**Volatilisation** (HSDB, 2005; ARKEMA SDS, 2007; HEALTH CANADA, 2004; ECB, 2002)

According to Henry's law constant, the evaporation half-life of methyl methacrylate in a 1 m deep river with a current speed of 1 m/s and a wind speed of 3 m/s is 6 hours.

According to the calculated Koc value, its adsorption in soil and sediments is low. This low level of adsorption together with the product's high vapour tension mean that it evaporates quickly from the ground.

**Biodegradation** (ECB, 2002; HSDB, 2005)

Methyl methacrylate is considered readily biodegradable in water. Biodegradation measurements reached 94% after 14 days in an aerobic environment (OECD 301 C test guideline, modified MITI test) (ECB, 2002).

Methyl methacrylate is completely degraded by activated sludge in approximately 20 hours (HSDB, 2005).

**Photolysis (HEALTH CANADA, 2004; ECB, 2002)**

The ultraviolet/visible absorption maximum is 231 nm. Methyl methacrylate should therefore not absorb radiation greater than 290 nm (the radiation reaching the earth's surface) and photolyze.

Free radicals formed in natural waters by the action of light might react with methyl methacrylate, however data is limited. Once in the atmosphere, the substance is degraded by a photochemical reaction with hydroxyl radicals ( $t_{1/2 \text{ life}} = 1.1 \text{ to } 9.7 \text{ h}$ ).

**Hydrolysis** (HEALTH CANADA, 2004; ECB, 2002)

Hydrolysis is not significant at neutral and acidic pH. The hydrolysis half-life of methyl methacrylate is estimated to be 3.9 years at pH 7 and 14.4 days at pH 9.

**Bioaccumulation** (FDS ARKEMA, 2007; ECB, 2002)

The bioaccumulation of methyl methacrylate calculated from its Kow value is not significant.

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### Organic carbon/water partition coefficient:

Log Koc = 1.17 to 2.13 (HEALTH CANADA, 2004)

Log Koc = 1.53 (ARKEMA SDS, 2007)

### Octanol/water partition coefficient:

Log Kow = 0.7 to 1.38 (INERIS, 2004; HEALTH CANADA, 2004; ECB, 2002)

### Bioconcentration factor (BCF):

Calculated BCF = 3 (TGD 1996 method) (INERIS, 2004; HEALTH CANADA, 2004; ECB, 2002)

Calculated BCF according to ECETOC = 2 to 6.59

# Classification

## IBC classification (IMO, 2007)

- Hazards: S/P (safety/pollution risk)
- Ship type: 2
- Tank type: 2G (integral gravity tank)
- Tank vents: controlled
- Controlled venting: no
- Electrical equipment:
  - i': Temperature class: T2
  - ii': Apparatus group: IIA
  - iii': Flash point: no (< 60°C)

- Gauging: R (restricted gauging)
- Vapour detection: F-T (flammable and toxic vapours)
- Fire protection: A (alcohol-resistant foam or multipurpose foam)

**SEBC classification:** ED (evaporates/dissolves)

**MARPOL classification:** Y

B8

## EU classification



F: Highly flammable



Xi: Irritant

R11	Highly flammable.
R43	May cause sensitisation by skin contact.
R37/38	Irritating to respiratory system and skin.
S24	Avoid contact with the skin.
S37	Wear suitable gloves.
S46	If swallowed seek medical advice immediately and show this container or label.
EC n° (EINECS)	201-297-1.

## GESAMP classification of methyl methacrylate (GESAMP, 2006)

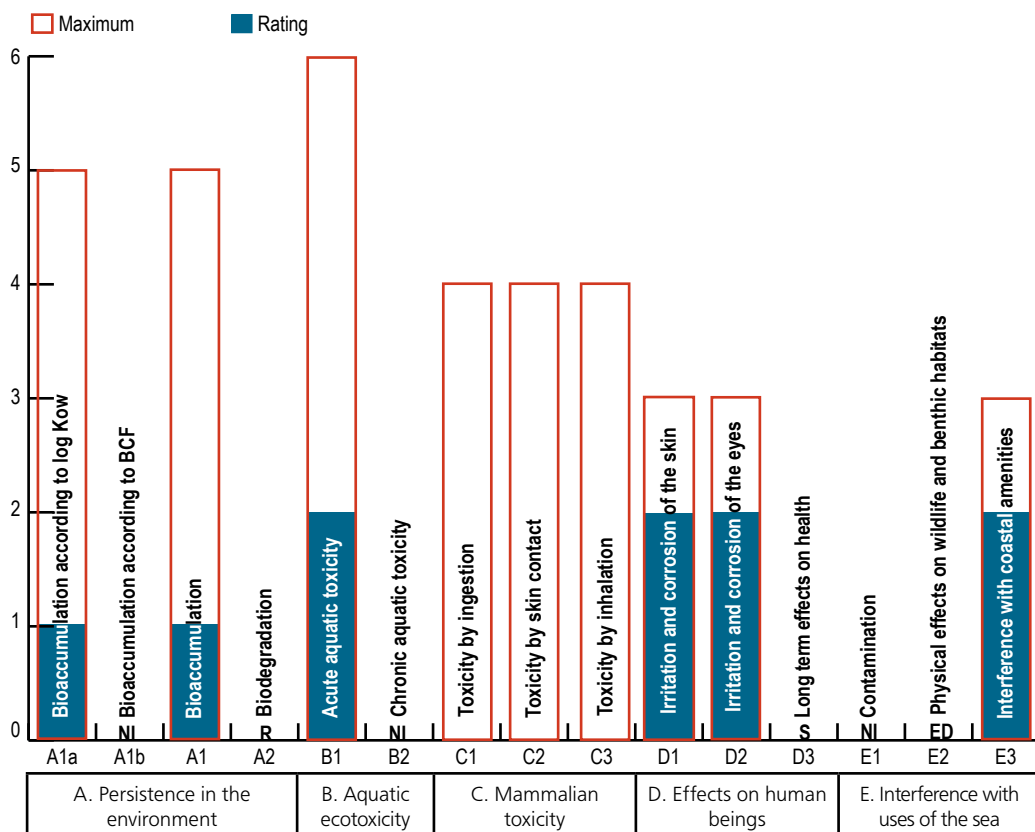


Figure 1: GESAMP classification of methyl methacrylate

- A1a: very slight potential to bioaccumulate in aquatic organisms.
- A1b: **NI**: No Information.
- A1: very slight potential to bioaccumulate in aquatic organisms.
- A2: **R**: Readily biodegradable.
  
- B1: moderate acute aquatic toxicity.
- B2: **NI**: No Information.
  
- C1: negligible toxicity when ingested by mammals.
- C2: negligible toxicity by skin contact with mammals.
- C3: negligible toxicity through inhalation by mammals.
  
- D1: irritating to the skin.
- D2: irritating to the eyes.
- D3: **S**: Sensitising.
  
- E1: **NI**: No Information.
- E2: product which Evaporates and Dissolves.
- E3: moderately objectionable, possible closure of amenities.

## Particular risks

### **Polymerisation** (ARKEMA SDS, 2007; INRS, 1997; CSST, 2006)

Polymerisation is stabilised by phenolic derivatives, most often 10 to 20 mg/kg of hydroquinone monomethyl ether or hydroquinone, or 2 to 20 mg/kg of 6-tert-butyl-2,4-xylenol. Free oxygen is essential to stabilize the product and the efficiency of stabilisation decreases if the temperature exceeds 30°C.

Methyl methacrylate is a highly reactive compound which polymerises readily at room temperature if it is not sufficiently stabilised. Polymerisation is caused or accelerated by heat, light and contact with oxidising products such as peroxides, nitrates, iron oxides, strong bases and strong acids, even as trace elements.

### **Danger** (CEFIC ERICARD, 2005)

- Heating the receptacle causes an increase in pressure leading to a risk of the container bursting and a possibility of explosion.
- A spontaneous increase in pressure or auto-ignition may be caused by exposure to heat, light, impact or contact with other chemicals.

- Release of toxic, irritating fumes by heating or combustion.
- Invisible vapours heavier than air when the product is spilt on land. These vapours spread out and can enter sewers and basements.
- The stabilising additive may be destroyed by heat.
- Can be narcotic and result in loss of consciousness when inhaled.

### **Stability and reactivity** (ARKEMA SDS, 2007; INRS, 1997)

- Safety precautions: keep away from light, heat and sources of ignition and keep at temperatures not exceeding 30°C. The inhibitor concentration and oxygen must be maintained for the product to remain stable.
- Substances to be avoided: free radical generators, activated carbon (explosive reaction), peroxides, strong oxidizing agents, strong acids, strong bases, rust.
- Stabilised methyl methacrylate can be transported and stored at room temperature.

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## Transportation, handling, storage

### Transportation (ARKEMA SDS, 2007)

Identification n° (UN): 1247

#### Land transportation:

RID (rail) /ADR (road)

Danger n°: 339

Class: 3

Packaging group: II

Classification code: F1

Danger labels: 3

#### Transportation via inland waterways:

ADN/ADNR

Class: 3

Danger labels: 3

Classification code: F1

#### Maritime transport: IMDG

Class: 3

Packaging group: II

Marine pollutant (MP): No

Danger labels: 3

#### Air transport: IATA

Class: 3

Packaging group: II

Danger labels: 3

### Handling (ARKEMA SDS, 2007)

- Provide appropriate exhaust ventilation at machinery.
- Do not use activated carbons to capture odours of methacrylates.
- Provide showers and eye baths.
- Transfer by pump or atmospheric pressure containing between 5 and 21% oxygen.
- Never bring into contact with an atmosphere made up only of inert gases.
- Take precautionary measures against static discharges.
- Keep away from flames.
- Only use fireproof equipment.

### Storage (ARKEMA SDS, 2007)

- Keep container in a well ventilated place.
- Maintain in contact with an atmosphere containing between 5 and 21% oxygen.
- Keep away from sources of ignition. Do not smoke.
- Protect against light.
- Avoid long storage periods.
- Keep below 30°C.
- Continuously monitor product temperature.
- Monitor the product's clarity.
- Maintain inhibitor levels.
- Ground the material and electric equipment used in explosive atmospheres.
- Provide a retention tank.

### Incompatible products (ARKEMA SDS, 2007)

Oxidizing agents, rust, peroxides, polymerization initiators, activated carbon.

### Recommended packaging materials

High density polyethylene, polypropylene, polytetrafluoroethylene, stainless steel 316 L (preferably), mild steel, aluminium.

### Packaging materials to be avoided

Natural or synthetic rubber.

# Results of accident scenarios

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



## Reminder of properties

### Transportation

Methyl methacrylate is transported in tanks in liquid form.

### Vapour density and tension

- Relative density: 0.944 at 20°C
- Vapour density: 3.45
- Vapour tension: 3.9 kPa at 20°C

### Solubility

Methyl methacrylate is soluble in water (solubility in fresh water = 16 g/L at 20°C). Its solubility and vapour tension mean that this product is classed ED, i.e. it evaporates and dissolves (according to the SEBC classification).

### Behaviour of methyl methacrylate when spilt in water

When methyl methacrylate is spilt at sea, it briefly forms a colourless slick at the spill location which evaporates and dissolves.

Methyl methacrylate vapours are heavier than air. In a stable atmosphere, the cloud will tend to remain at the water surface. However, vapours can travel to a source of ignition and flash back.

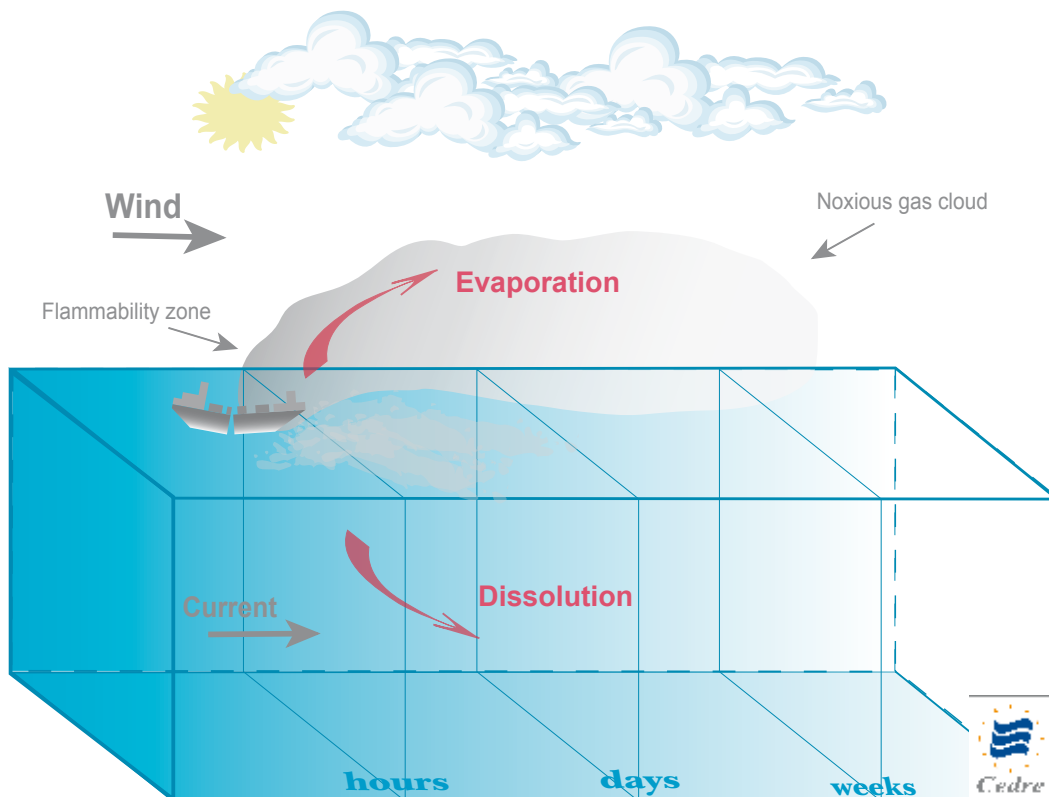


Figure 2: Behaviour of methyl methacrylate when spilt in water

## Accident scenarios

The scenarios defined here are simply designed to give an indication of the possible behaviour of methyl methacrylate. In the event of a real spill, the results of simulations will naturally be different from those given here. We used CHEMMAP and ALOHA behaviour models, the emergency response models available to *Cedre*. Other more sophisticated models exist, but require response times which are incompatible with an emergency situation.

Situation: a chemical tanker enters into a collision, causing a breach in one of its tanks containing methyl methacrylate. Four methyl methacrylate spill scenarios are given here with different quantities of chemical spilt:

- an **open sea** scenario (Channel) with three different spill rates:

1 t/h  
100 t/h    |    ➔    5 hours

500 t        ➔    instantaneous

- a **river** scenario with two different spill rates:

1 t/h  
100 t/h    |    ➔    5 hours

- a **wreck** scenario (Channel) with one spill rate: 1,000 t over 48 hours

- a **port** scenario (Cherbourg) with two instantaneous spills: 1 t  
100 t    |    ➔    instantaneous

### The scenarios

#### Channel scenario

- Location: 50°N; 3°W
- Air and water temperature: 10°C
- Two wind speeds: 3 and 10 m/s (NW)
- Tidal currents
- Spill depth: 1 m
- Model time step: 15 minutes
- Duration of spills: 5 hours and instantaneous

#### Wreck scenario

- Location: 49°27N; 3°15W
- Air and water temperature: 10°C
- Wind speed: 3 m/s (NW)
- Tidal currents
- Spill depth: between 80 and 90 m
- Model time step: 15 minutes
- Duration of spill: 48 hours

#### River scenario

- Depth: 4 to 5 m; width: 150 m
- Air and water temperature: 15°C
- Wind speed: 3 m/s (NW)
- Current speed: 0.74 m/s
- Model time step: 15 minutes
- Duration of spill: 5 hours

#### Port scenario

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

## Modelling

CHEMMAP software was used to model hypothetical spillages of methyl methacrylate in the aquatic environment.

CHEMMAP is a chemical spill model designed by ASA (Applied Science Associates, Inc - USA) which predicts the movement and fate of the spilt 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 fifteen minutes. Atmospheric modelling (for spills in a port environment with no current) was realised

using the ALOHA software programme (US Environmental Protection Agency). Responders are familiar with the ALOHA programme. It is a simple Gaussian atmospheric modelling programme.

The spill scenarios used in this guide take place on the same day at the same time: 15/05/2007 at 16h00. In the case of a continuous spill, the surface drift generated by currents must be taken into account, in this case with a mean high water spring tide and currents reaching a maximum of 2.3 knots in the area studied.

**The scenarios presented in this guide involve a release 1 m below the water surface (except wreck scenario).**



Figure 3: location of a hypothetical spill in the Channel



Figure 4: view of the dissolved part after 2 hours

- ☒ Spill location
- Section line

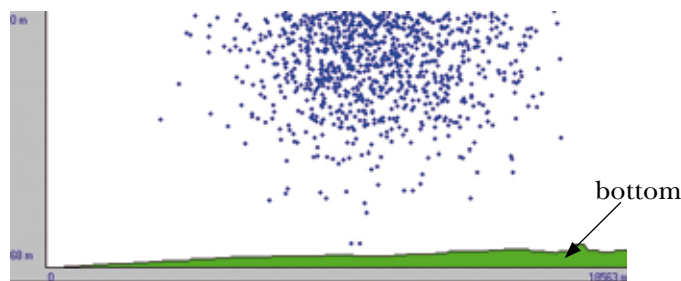
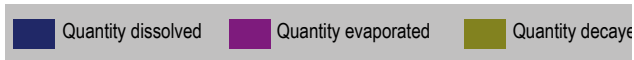


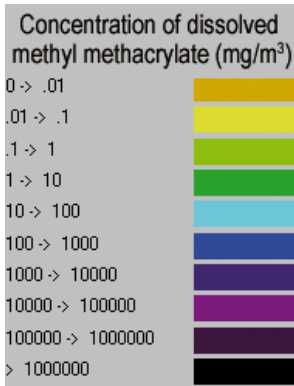
Figure 5: cross-section of the dissolved part along the section line

### Key used in this guide

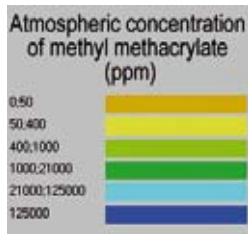
- for the graphs



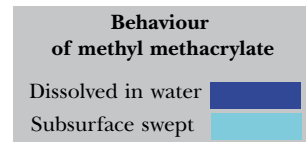
- for the concentrations in the water column



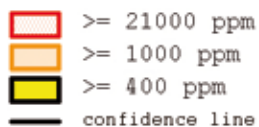
- for the atmospheric concentrations of methyl methacrylate



- for the behaviour of methyl methacrylate in water

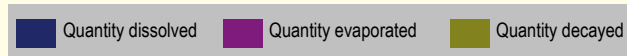
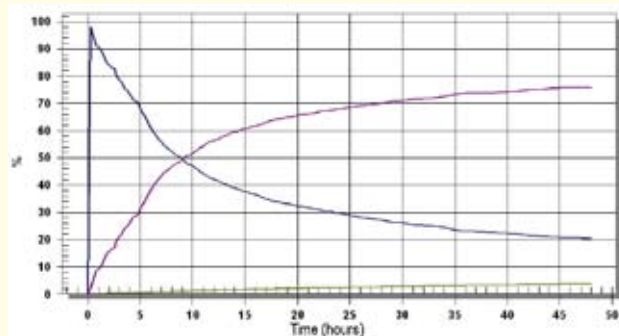


- for atmospheric concentrations (ALOHA software)



## Results of the Channel scenario

### 1- Spill of 1 t/h of methyl methacrylate for 5 hours, with a wind speed of 3 m/s



Graph 1: overall distribution for a spill of 1 t/h and 100 t/h for 5 hours

Five hours after the beginning of the spill, 70% of the chemical has dissolved in the water column, while the rest has evaporated into the atmosphere. Forty-eight hours after the spill, around 76% of the methyl methacrylate has evaporated into the atmosphere after having been dissolved in the water column, while 20% remains in the water column and 4% has been broken down. The overall distribution is much the same with a wind speed of 10 m/s.

#### 1.1- Behaviour of methyl methacrylate according to the wind speed (3 and 10 m/s)

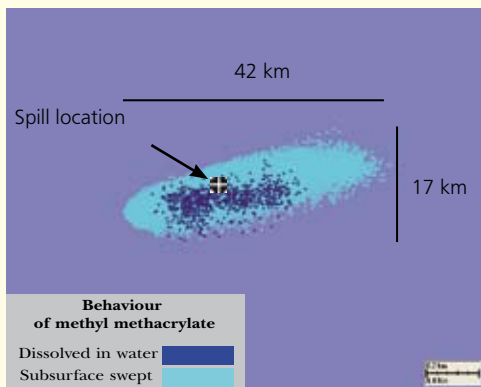


Figure 6: behaviour of the chemical with a wind speed of 3 m/s

For a NW wind at a speed of 3 m/s, the surface area liable to be affected reaches 42 km from east to west and 17 km from north to south, for a 48 hour study.

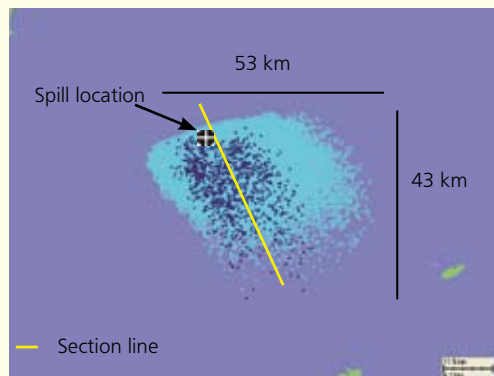


Figure 7: behaviour of the chemical with a wind speed of 10 m/s

For a NW wind at a speed of 10 m/s, the surface area liable to be affected reaches 53 km from east to west and 43 km from north to south, for a 48 hour study.

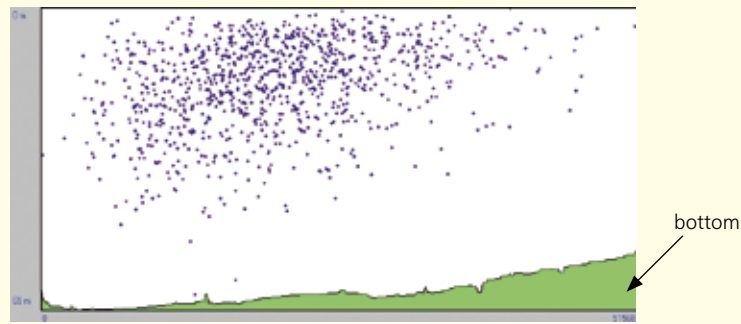


Figure 8: behaviour of methyl methacrylate with a 10 m/s wind, cross-section

Figure 8 above indicates the depth of the water mass affected by the methyl methacrylate with a wind speed of 10 m/s, 48 hours after the beginning of the spill. The chemical spreads through the entire depth of the water column. The distribution of the product in the water mass is influenced by the wind.

**1.2- View of the dissolved part after a spill of 1 t/h of methyl methacrylate for 5 hours.  
Wind speed of 3 m/s.  
Results obtained 2 hours after the beginning of the spill.**

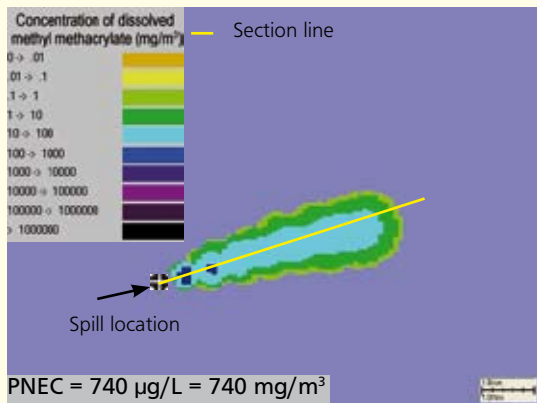


Figure 9: aerial view of dissolved part at flood tide

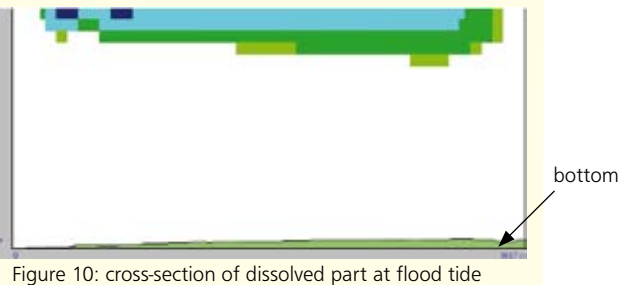


Figure 10: cross-section of dissolved part at flood tide

Concentrations greater than or equal to the PNEC ( $740 \text{ mg/m}^3$ ) will travel a distance of up to 2.2 km east of the spill location. This distance will be reached 2 hours after the beginning of the spill. The depth reached at this point by the dissolved part is around 15 m.

**1.3- Atmospheric concentrations of methyl methacrylate,  
with a NW wind at a speed of 3 m/s and 10 m/s**

According to CHEMMAP: the atmospheric concentrations are less than 50 ppm (TLV-TWA) after the first 5 minutes following the beginning of the spill with a NW wind at a speed of 3 and 10 m/s.

## 2- Spill of 100 t/h of methyl methacrylate for 5 hours, with a wind speed of 3 m/s

The overall distribution is identical for a spill of 1 t/h and 100 t/h for 5 hours (see Graph 1).

### 2.1- Behaviour of methyl methacrylate according to the wind speed (3 and 10 m/s)

The behaviour of methyl methacrylate is identical for a spill of 1 t/h for 5 hours and for a spill of 100 t/h for 5 hours (see Figures 6, 7 and 8).

### 2.2- View of the dissolved part after a spill of 100 t/h of methyl methacrylate for 5 hours. Wind speed of 3 m/s.

Results obtained 5 h 30 and 10 h 45 after the beginning of the spill.

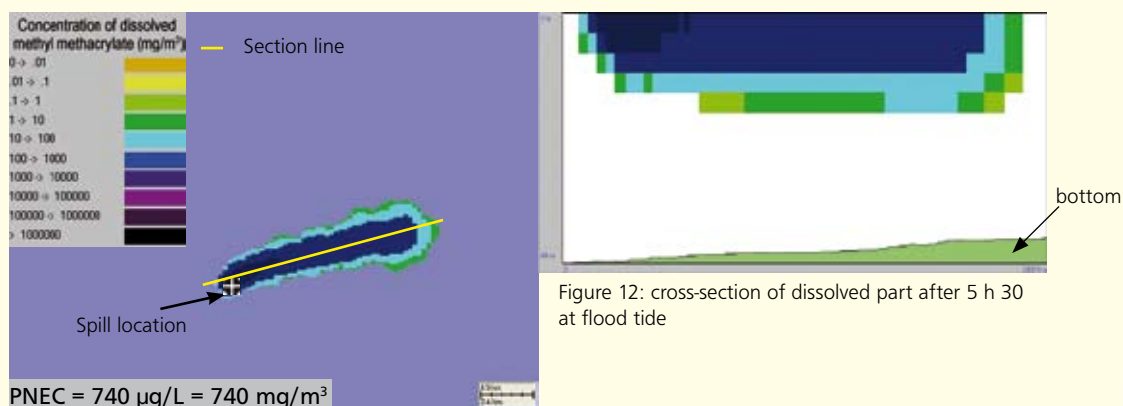


Figure 11: aerial view of dissolved part after 5 h 30 at flood tide

Concentrations greater than or equal to the PNEC ( $740 \text{ mg/m}^3$ ) will travel a distance of up to 17 km east-north-east of the spill location. This distance will be reached 5 h 30 after the beginning of the spill. The depth reached at this point is around 30 m. Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is  $40,000 \text{ mg/m}^3$ .

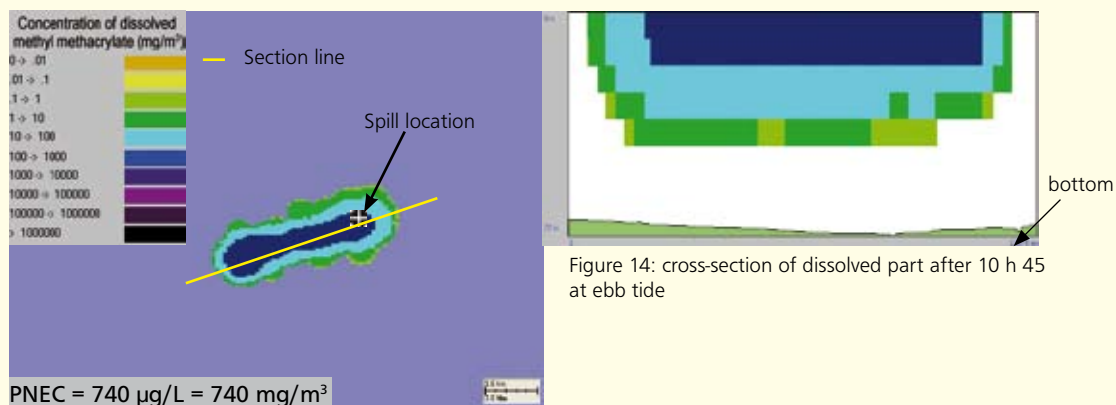


Figure 13: aerial view of dissolved part after 10 h 45 at ebb tide

Ten hours and forty-five minutes after the beginning of the spill, the tide is falling. This is the time needed for the concentrations greater than or equal to the PNEC ( $740 \text{ mg/m}^3$ ) to travel the maximum distance of 16 km west-south-west of the spill location. The depth reached at this point is around 45 m.

### 2.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s.

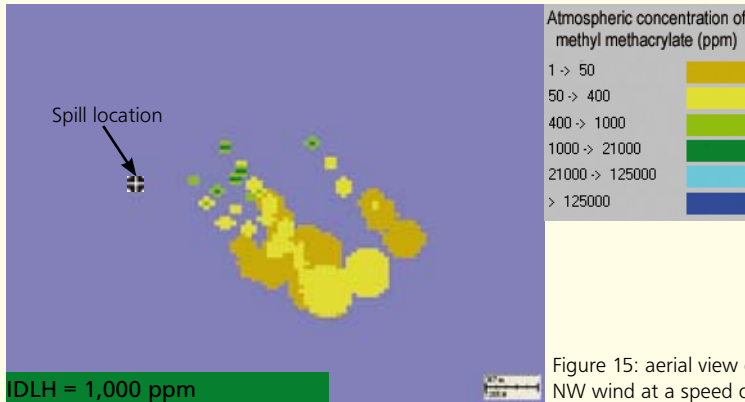


Figure 15: aerial view of evaporated part,  
NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is 1.3 km east of the spill location. This distance is reached 5 minutes after the beginning of the spill.

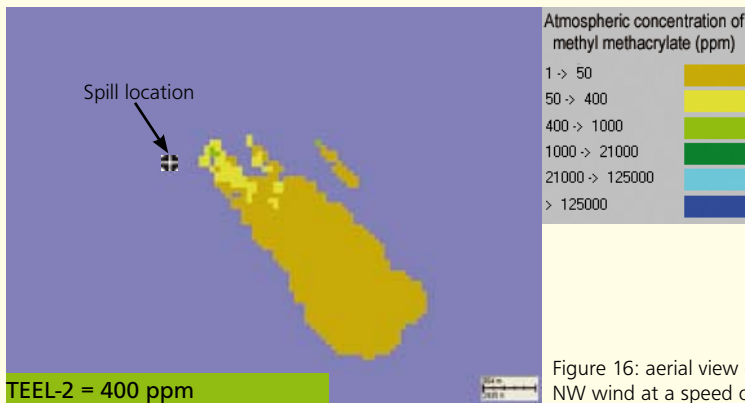


Figure 16: aerial view of evaporated part,  
NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 2.5 km east of the spill location. This distance is reached 20 minutes after the beginning of the spill.

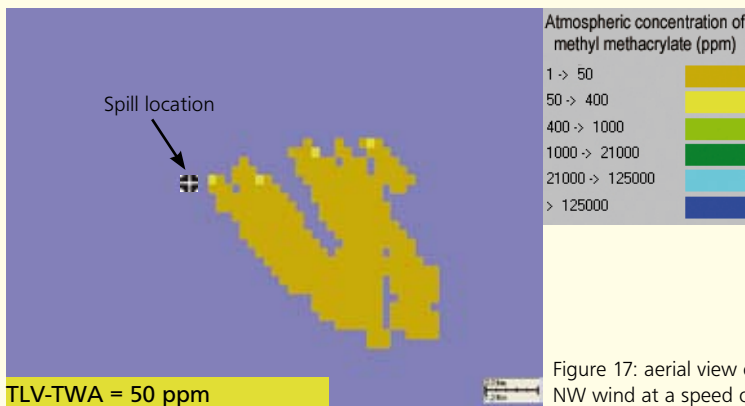


Figure 17: aerial view of evaporated part,  
NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TLV-TWA is 8.3 km east of the spill location. This distance is reached 2 hours after the beginning of the spill.

## 2.4 Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 10 m/s.

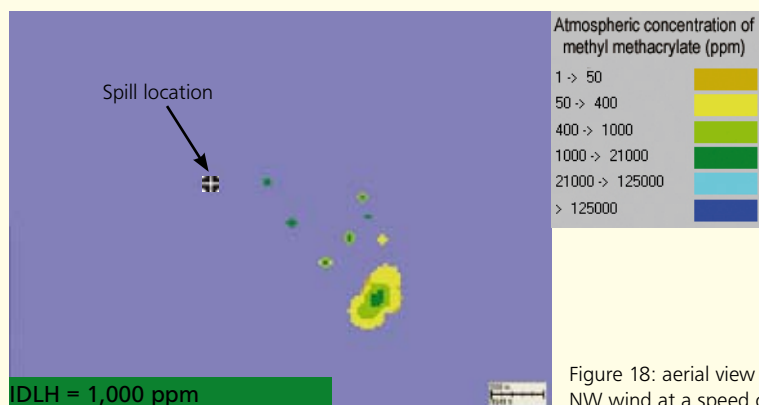


Figure 18: aerial view of evaporated part, NW wind at a speed of 10 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is 2 km south-east of the spill location. This distance is reached a few minutes after the beginning of the spill.



Figure 19: aerial view of evaporated part, NW wind at a speed of 10 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 3 km east of the spill location. This distance is reached 1 hour after the beginning of the spill.

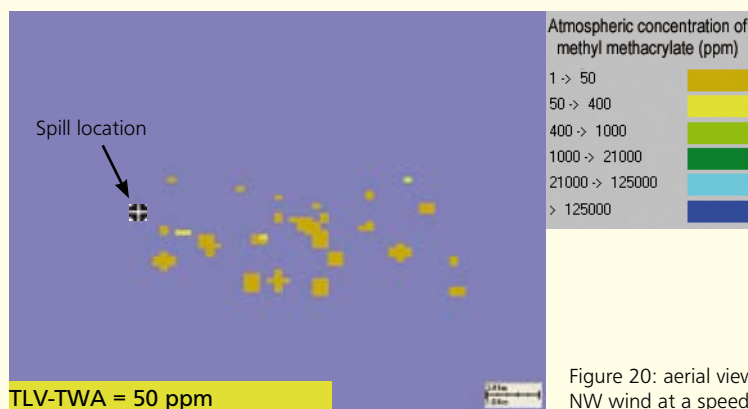
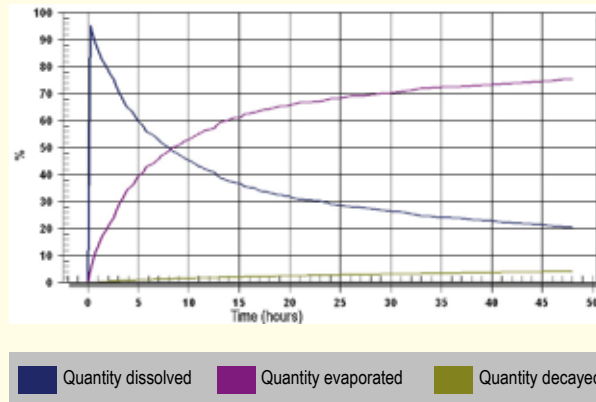


Figure 20: aerial view of evaporated part, NW wind at a speed of 10 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TLV-TWA is 19 km east of the spill location. This distance is reached 5 hours after the beginning of the spill.

### 3- Instantaneous spill of 500 tonnes of methyl methacrylate, with a wind speed of 3 m/s



Graph 2: overall distribution for an instantaneous spill of 500 tonnes

One hour after the spill, 90% of the methyl methacrylate is found dissolved in the water column and 10% has evaporated into the atmosphere. Forty-eight hours after the spill, 76% of the product has evaporated, 20% is found in the water column and 4% has been broken down.

#### 3.1- Behaviour of methyl methacrylate according to the wind speed (3 and 10 m/s)

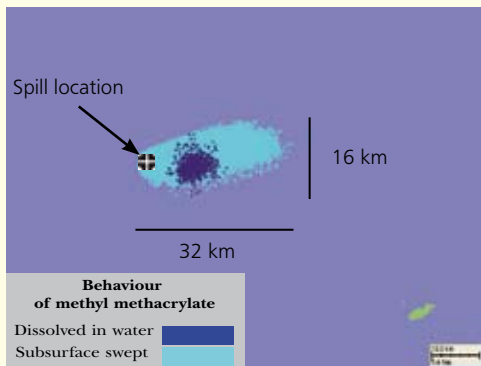


Figure 21: behaviour of the chemical with a wind speed of 3 m/s

For a NW wind at a speed of 3 m/s, the surface area liable to be affected reaches 32 km from east to west and 16 km from north to south, for a 48 hour study.

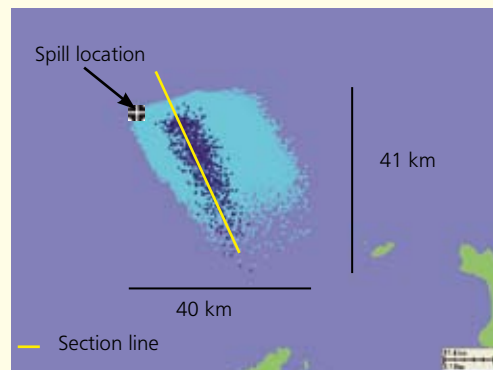


Figure 22: behaviour of the chemical with a wind speed of 10 m/s

For a NW wind at a speed of 10 m/s, the surface area liable to be affected reaches 40 km from east to west and 41 km from north to south, for a 48 hour study.

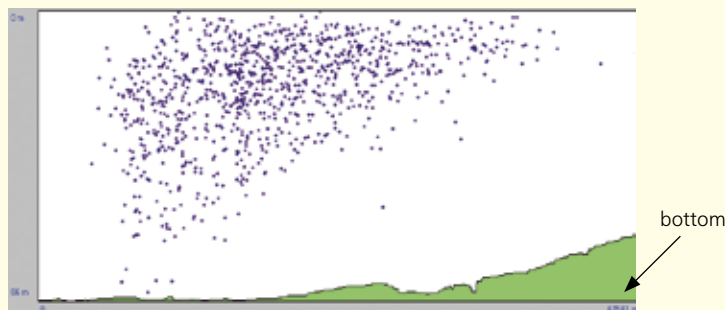


Figure 23: behaviour of methyl methacrylate with a 10 m/s wind, cross-section

Figure 23 above indicates the depth of the water mass affected by the methyl methacrylate with a wind speed of 10 m/s, 48 hours after the spill. The chemical spreads through the entire depth of the water column. The distribution of the product in the water mass is influenced by the wind.

**3.2- View of the dissolved part after an instantaneous spill of 500 tonnes of methyl methacrylate. Wind speed of 3 m/s. Results obtained 30 hours after the beginning of the spill.**

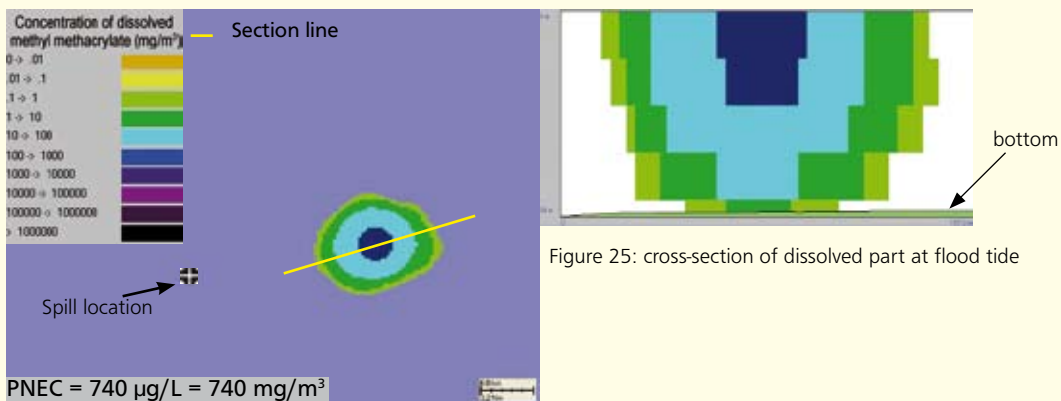


Figure 24: aerial view of dissolved part at flood tide

Concentrations greater than or equal to the PNEC ( $740 \text{ mg/m}^3$ ) will travel a distance of up to 24 km east-north-east of the spill location. This distance will be reached 30 hours after the spill. Thirty hours after the spill, the product is spread throughout the entire depth of the water column (between 60 and 70 m).

Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is  $680,000 \text{ mg/m}^3$ . At ebb tide, the area affected will not go beyond the spill location in a west-south-westerly direction.

### 3.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s.

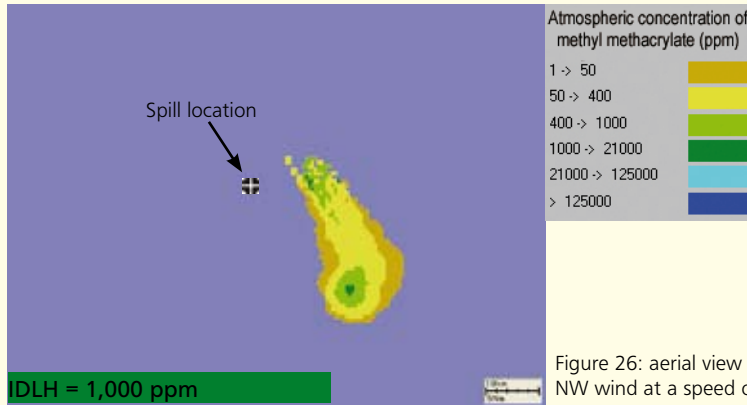


Figure 26: aerial view of evaporated part, NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is 3 km south-east of the spill location. This distance is reached 15 minutes after the spill.

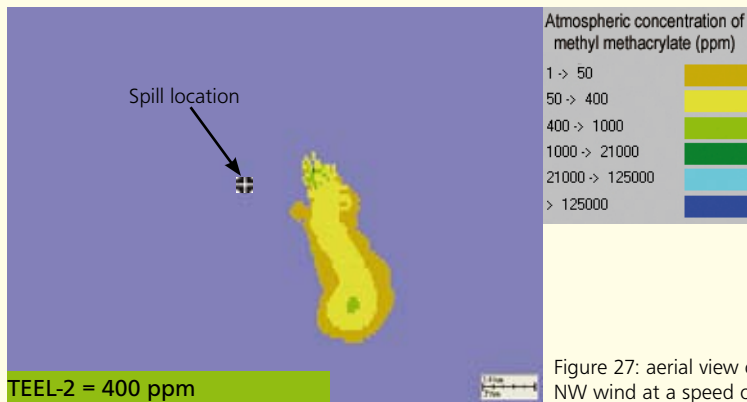


Figure 27: aerial view of evaporated part, NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 4.6 km south-east of the spill location. This distance is reached 20 minutes after the spill.



Figure 28: aerial view of evaporated part, NW wind at a speed of 3 m/s

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TLV-TWA is 17 km east of the spill location. This distance is reached 4 h 30 after the spill.

### 3.4 Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 10 m/s.

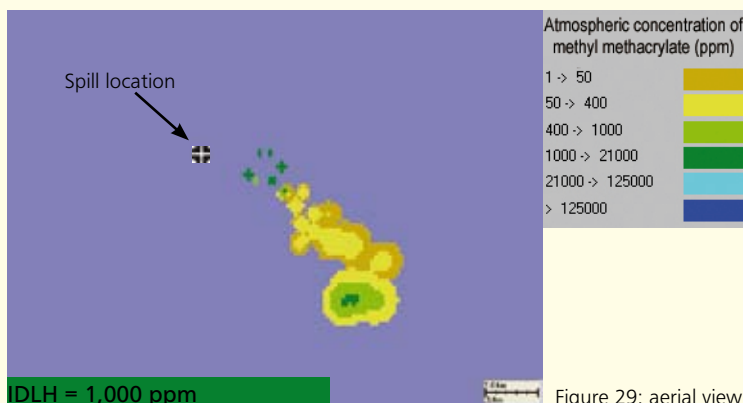


Figure 29: aerial view of evaporated part, 10 m/s wind

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is 4.5 km south-east of the spill location. This distance is reached 5 minutes after the spill.



Figure 30: aerial view of evaporated part, 10 m/s wind

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 6.5 km south-east of the spill location. This distance is reached less than 10 minutes after the spill.

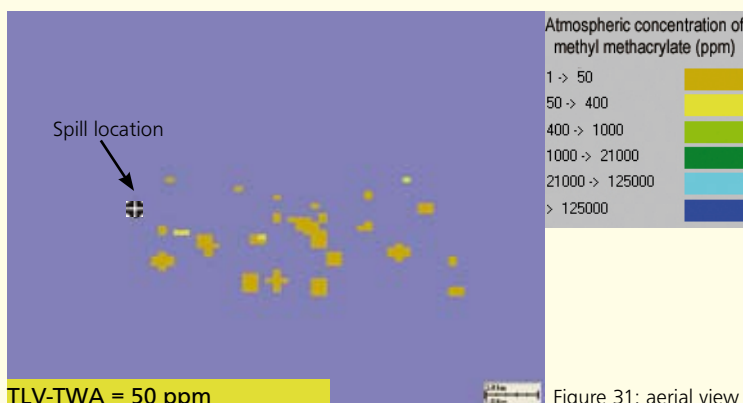
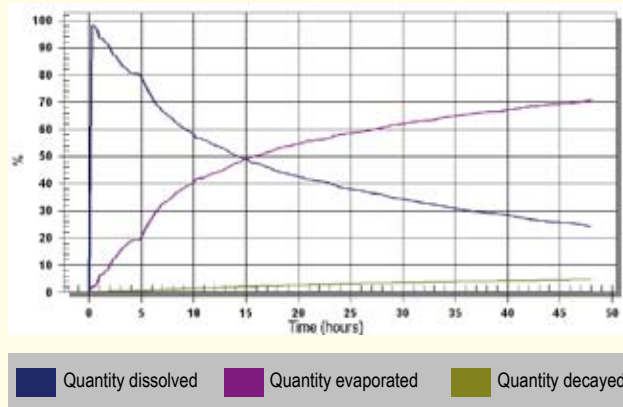


Figure 31: aerial view of evaporated part, 10 m/s wind

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TLV-TWA is 25 km east of the spill location. This distance is reached 18 hours after the spill.

## Results of the river scenario

### 4- Spill of 1 t/h of methyl methacrylate for 5 hours, with a NW wind at a speed of 3 m/s and a current speed of 0.74 m/s



Graph 3: overall distribution for a spill of 1 t/h and 100 t/h for 5 hours

Five hours after the spill, 80% of the methyl methacrylate is found dissolved in the water column and 20 % has evaporated. Forty-eight hours after the spill, 70% of the product has evaporated, 25% is found in the water column and 5% has been broken down.

#### 4.1- Behaviour of methyl methacrylate 48 hours after the spill

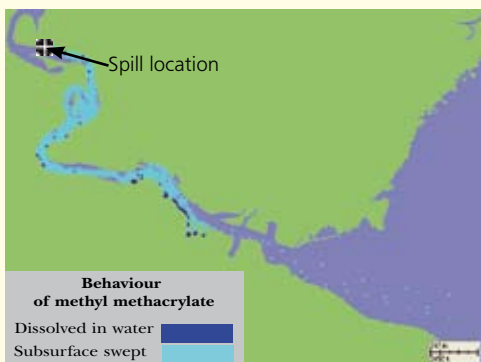


Figure 32: behaviour of methyl methacrylate, aerial view

The methyl methacrylate is dissolved in the water column over a distance of 10 km downstream of the spill location. The product is distributed throughout the entire depth of the water column (5 m).

#### 4.2- Concentrations of dissolved methyl methacrylate 48 hours after the spill

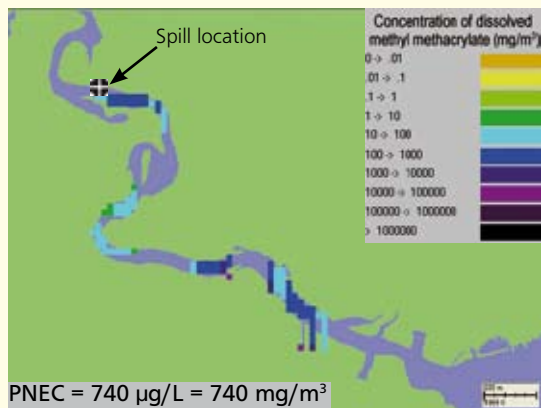


Figure 33: aerial view of dissolved part

Concentrations greater than or equal to the PNEC (740 mg/m<sup>3</sup>) will travel a distance of up to 6 km downstream of the spill location. This area remains affected by these concentrations until the end of the scenario (48 h).

The entire depth of the water column is affected by the methyl methacrylate (5 m).

Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is  $1.5 \times 10^5$  mg/m<sup>3</sup>.

#### 4.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s

According to CHEMMAP: the atmospheric concentrations are less than or equal to 50 ppm (TLV-TWA), after the first 5 minutes following the beginning of the spill.

### 5- Spill of 100 t/h of methyl methacrylate for 5 hours, with a NW wind at a speed of 3 m/s and a current speed of 0.74 m/s

The overall distribution is identical for a spill of 1 t/h and 100 t/h for 5 hours (see Graph 3).

#### 5.1- Behaviour of methyl methacrylate 48 hours after the spill

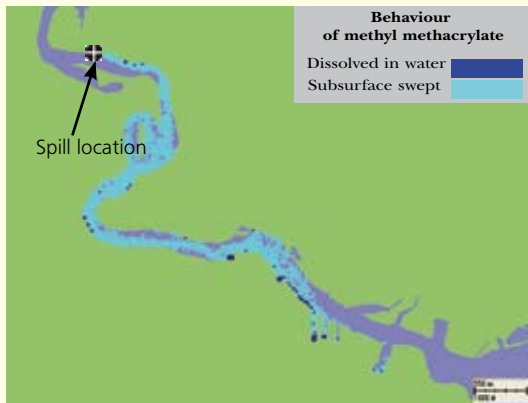


Figure 34: behaviour of methyl methacrylate, aerial view

The methyl methacrylate is dissolved in the water column over a distance of 6.5 km downstream of the spill location. The product is distributed throughout the entire depth of the water column (5 m).

#### 5.2- Concentrations of dissolved methyl methacrylate 48 hours after the spill

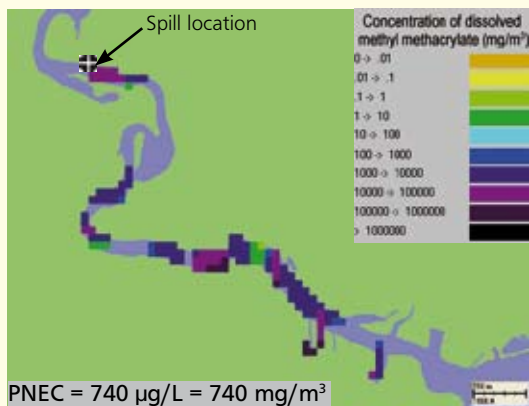


Figure 35: aerial view of dissolved part

Concentrations greater than or equal to the PNEC ( $740 \text{ mg/m}^3$ ) will travel a distance of up to 6.5 km downstream of the spill location. This area remains affected by these concentrations until the end of the scenario (48 h). The entire depth of the water column is affected by the methyl methacrylate (5 m). Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is  $3.4 \times 10^7 \text{ mg/m}^3$ .

### 5.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s

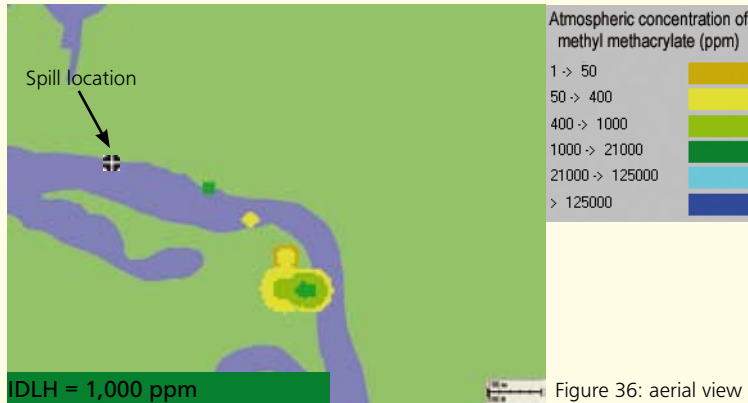


Figure 36: aerial view of evaporated part

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is 900 m south-east of the spill location. This distance is reached around 5 minutes after the beginning of the spill.



Figure 37: aerial view of evaporated part

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 1.1 km south-east of the spill location. This distance is reached a few minutes after the beginning of the spill.

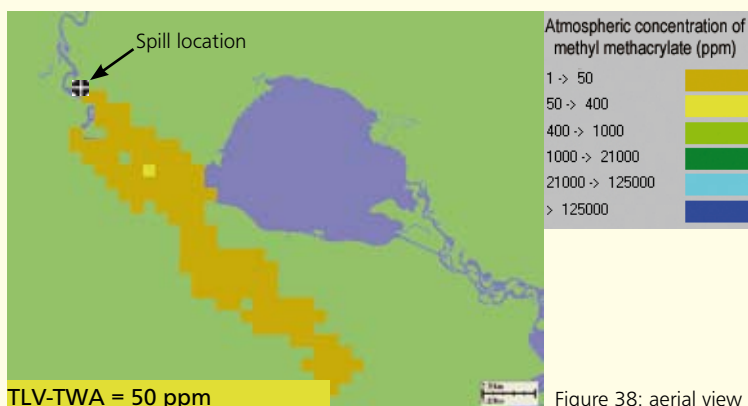


Figure 38: aerial view of evaporated part

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TLV-TWA is 4.5 km south-east of the spill location. This distance is reached 16 hours after the beginning of the spill.

## Results of the wreck scenario

A wreck is lying on the seabed between 80 and 90 m below the surface not far from an inhabited coastline and begins to leak.

The leak leads to the continuous release of 1,000 tonnes of methyl methacrylate over 48 hours from the tanks of the wreck.

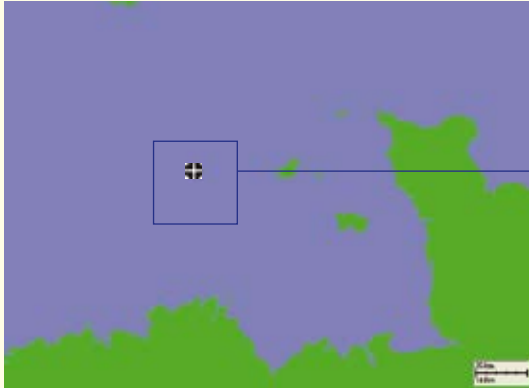


Figure 39: location of the wreck

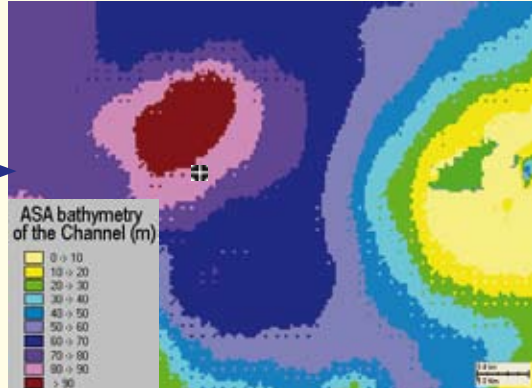
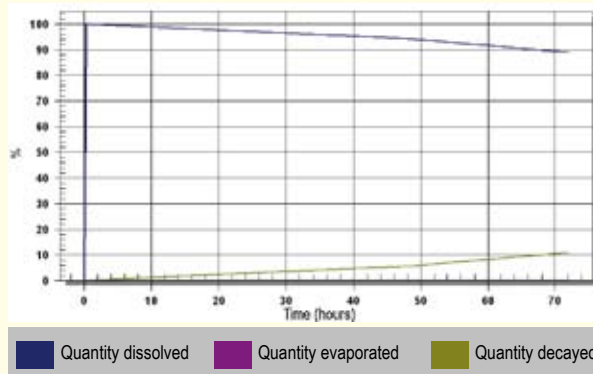


Figure 40: bathymetry of the Channel

### 6- Spill of 1,000 tonnes of methyl methacrylate over 48 hours (rate of approximately 20.8 t/h) from the seabed in the Channel



Graph 4: overall distribution for a spill of 1,000 tonnes over 48 hours

Forty-eight hours after the beginning of the spill, 94% of the product has dissolved in the water column, while 6% has been broken down. There is no evaporation of the product from the surface.

### 6.1- Behaviour after 48 hours of 1,000 tonnes of methyl methacrylate released from the seabed

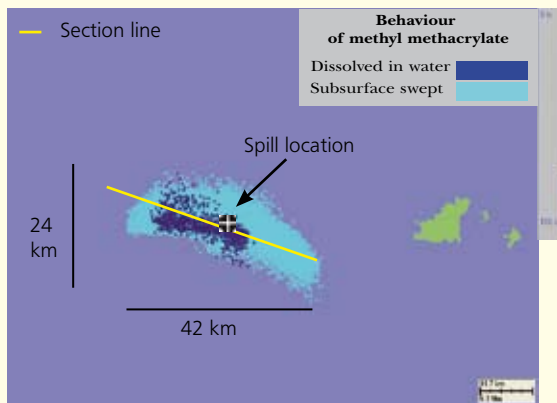


Figure 41: behaviour of methyl methacrylate, aerial view

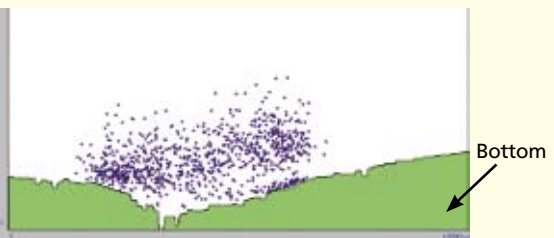


Figure 42: behaviour of methyl methacrylate, cross-section

The methyl methacrylate released dissolves in the water column over a depth of around 60 m from the seabed upwards. The chemical spreads over an area of 42 km from east to west and 24 km from north to south.

### 6.2- Concentrations of dissolved methyl methacrylate, obtained 9 h 30 after the beginning of the spill

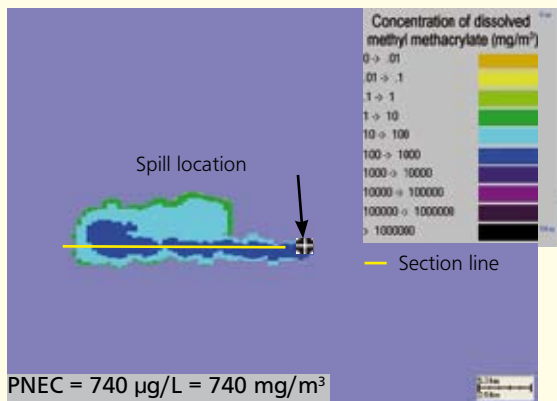


Figure 43: aerial view of dissolved part after 9 h 30 at ebb tide

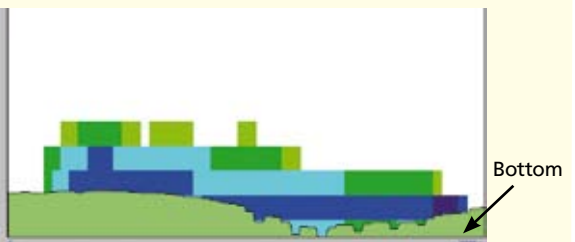


Figure 44: cross-section of dissolved part after 9 h 30 at ebb tide

Concentrations greater than or equal to the PNEC (740 mg/m<sup>3</sup>) will travel a distance of up to 22.9 km west of the spill location. This distance will be reached 9 h 30 hours after the beginning of the spill.

The methyl methacrylate will affect the water column over a depth of around 50 m from the seabed upwards. Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is 11,200 mg/m<sup>3</sup>.

### Concentrations of dissolved methyl methacrylate, obtained 28 hours after the beginning of the spill

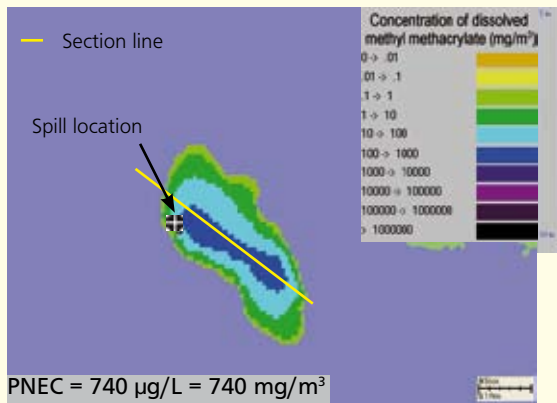


Figure 45: aerial view of dissolved part after 28 h at flood tide



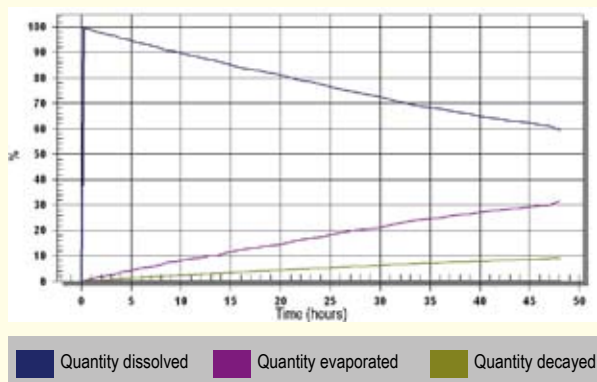
Figure 46: cross-section of dissolved part after 28 h at flood tide

Concentrations greater than or equal to the PNEC (740 mg/m<sup>3</sup>) will travel a distance of up to 23 km east-south-east of the spill location. This distance will be reached 28 hours after the beginning of the spill.

The methyl methacrylate will affect the entire depth of the water column.

## Results of the port scenario

### 7- Instantaneous spill of 1 tonne of methyl methacrylate in a port, with a NW wind at a speed of 3 m/s. The spill occurs 1 m below the surface.



Graph 5: overall distribution for an instantaneous spill of 1 tonne and 100 tonnes.

The methyl methacrylate is initially found in the water column, but gradually evaporates. Five hours after the spill, 95 % of the product is found dissolved in the water column, while 5% has evaporated into the atmosphere. Forty-eight hours after the spill, around 60% of the product has dissolved, 30% has evaporated after having been dissolved in the water column and 10% has been broken down.

The overall distribution is the same as for an instantaneous spill of 100 tonnes.

#### 7.1- Behaviour of methyl methacrylate 48 hours after the spill

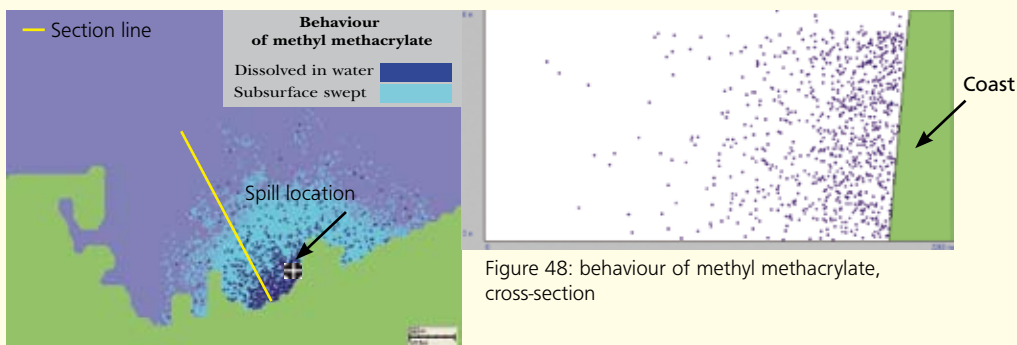


Figure 47: behaviour of methyl methacrylate, aerial view

Figure 48: behaviour of methyl methacrylate, cross-section

Forty-eight hours after the spill, the methyl methacrylate spill spreads over an area of 6.3 km<sup>2</sup> (3 km by 2.1 km) around the spill location. The entire depth of the water column (3 m) is affected.

## 7.2- Concentrations of dissolved methyl methacrylate, obtained 42 hours after the spill

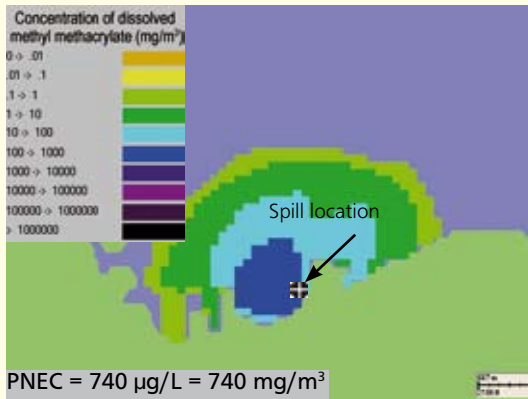


Figure 49: aerial view of dissolved part

Concentrations greater than or equal to the PNEC (740 mg/m<sup>3</sup>) will travel a distance of up to 900 m around the spill location. This distance will be reached around 42 hours after the spill. The methyl methacrylate will affect the entire depth of the water column (3 m). Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is 31,700 mg/m<sup>3</sup>.

## 7.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s

According to CHEMMAP: the atmospheric concentrations are greater than or equal to 50 ppm (TLV-TWA), up to 4 minutes after the beginning of the spill. Thereafter, the concentrations remain below 50 ppm.

The ALOHA modelling programme however gave us the following information:

**7.4- Atmospheric concentrations of methyl methacrylate. Instantaneous spill of 10 kg of methyl methacrylate (1% of 1 t) with a wind speed of 3 m/s.**

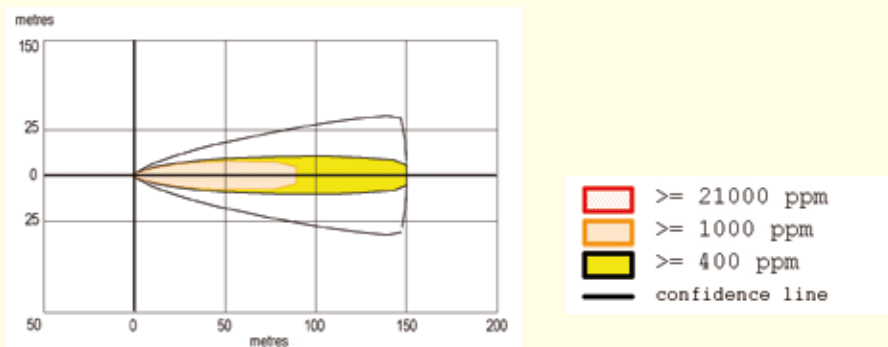


Figure 50: evaporated part, wind speed of 3 m/s

The results were obtained 1 hour after the spill. No concentrations greater than the LEL (21,000 ppm) are detected. Concentrations greater than the IDLH (1,000 ppm) are detected up to 100 m east of the spill location and concentrations greater than the TEEL-2 (400 ppm) are detected up to around 150 m.

## 8- Instantaneous spill of 100 tonnes of methyl methacrylate in a port, with a NW wind at a speed of 3 m/s. The spill occurs 1 m below the surface.

The overall distribution is identical for an instantaneous spill of 1 tonne and 100 tonnes (see Graph 5).

### 8.1- Behaviour of methyl methacrylate 48 hours after the spill

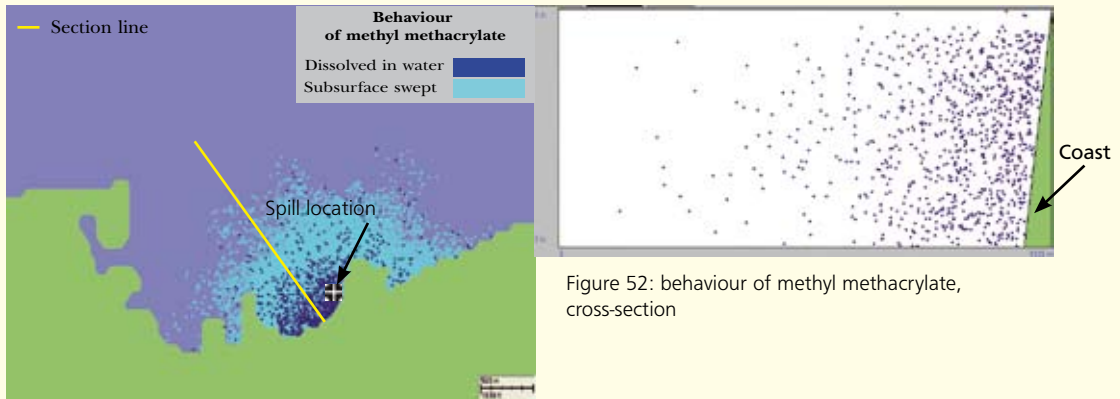


Figure 51: behaviour of methyl methacrylate, aerial view

Forty-eight hours after the spill, the methyl methacrylate spill spreads over an area of 6.7 km<sup>2</sup> (3.2 km by 2.1 km) around the spill location. The entire depth of the water column (3 m) is affected.

### 8.2- Concentrations of dissolved methyl methacrylate, obtained 48 hours after the spill

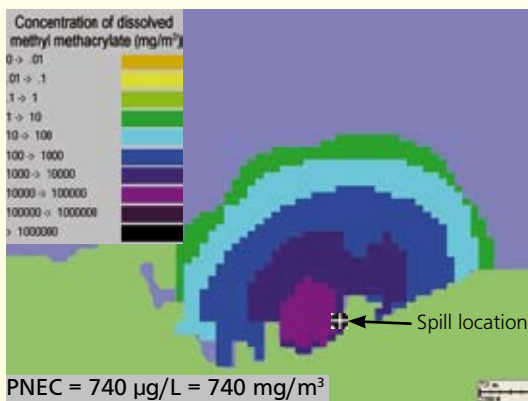


Figure 53: aerial view of dissolved part

Concentrations greater than or equal to the PNEC (740 mg/m<sup>3</sup>) will travel a distance of up to 2.1 km around the spill location. This distance will be reached 48 hours after the spill. The methyl methacrylate will affect the entire depth of the water column (3 m).

Throughout the entire duration of the scenario (48 h), the maximum concentration observed in the water column is  $3.17 \times 10^6$  mg/m<sup>3</sup>.

### 8.3- Atmospheric concentrations of methyl methacrylate, with a NW wind at a speed of 3 m/s, according to CHEMMAP.

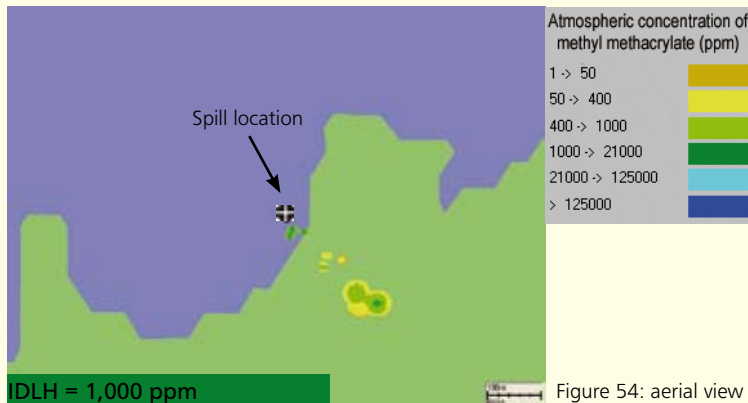


Figure 54: aerial view of evaporated part

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the IDLH is nearly 500 m (485 m according to the model) south-east of the spill location. This distance is reached a few minutes after the spill.

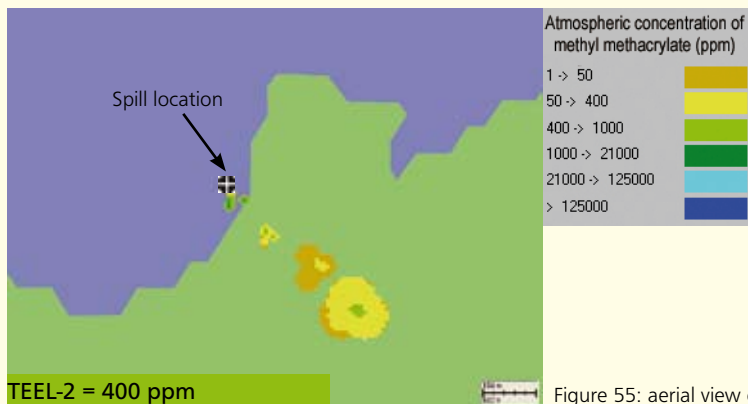


Figure 55: aerial view of evaporated part

The **maximum** distance travelled by the chemical at concentrations greater than or equal to the TEEL-2 is 660 m south-east of the spill location. This distance is reached less than 5 minutes after the beginning of the spill.

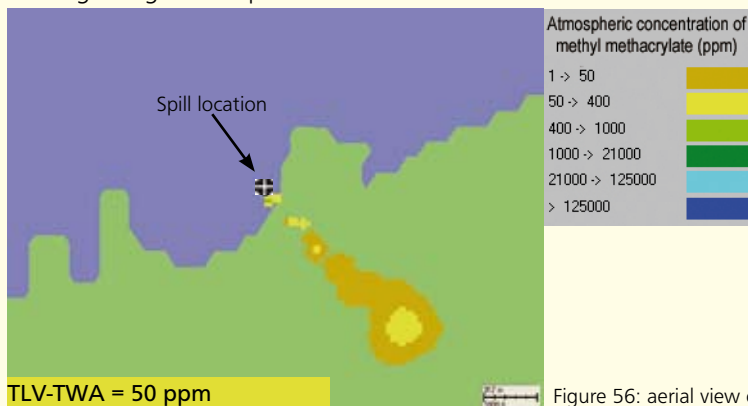


Figure 56: aerial view of evaporated part

Concentrations greater than or equal to the TLV-TWA travel a **maximum** distance of around 1.5 km (1.3 km according to the model) south-east of the spill location. This distance is reached around 5 minutes after the spill.

The ALOHA modelling programme however gave us the following information:

**8.4- Atmospheric concentrations of methyl methacrylate. Instantaneous spill of 1 tonne of methyl methacrylate (1% of 100 t) with a wind speed of 3 m/s.**

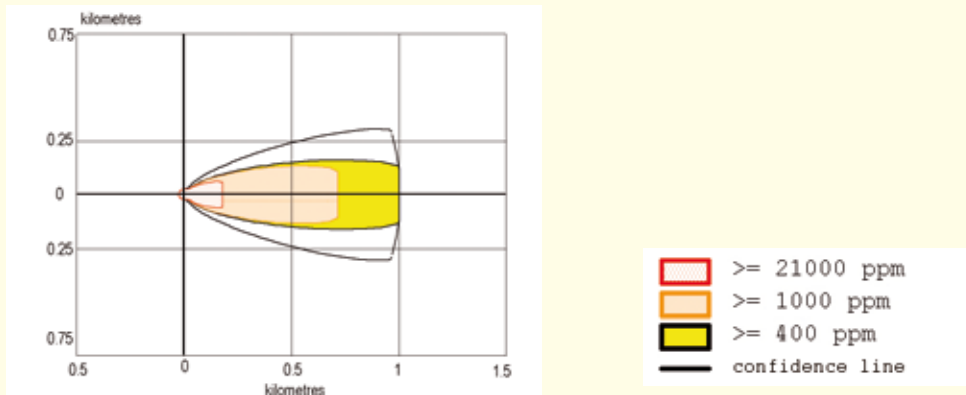


Figure 57: evaporated part, wind speed of 3 m/s

The results were obtained 1 hour after the spill. Concentrations greater than the LEL (21,000 ppm) are detected over a distance of around 180 m to the east of the spill location. Concentrations greater than the IDLH (1,000 ppm) are also detected up to 750 m and concentrations greater than the TEEL-2 (400 ppm) up to around 1 km.

## Consumption scenarios

Due to the very low tendency of methyl methacrylate 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.

# Response

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

## Examples of spills

### Maritime transport (United Kingdom, 1991) (BARPI)

On 6 May 1991 in Bradford, UK, a Swedish cargo ship lost part of its cargo, in total 4 semi-trailers containing 24 tonnes of methyl methacrylate. Two tanks washed up on a beach. A gas cloud escaped from one of the tanks. Sixty people were intoxicated by the irritating vapours and were taken to hospital. A thousand people located inland were evacuated. The emergency services poured concrete onto the pebble beach and attempted to siphon the contents out of the trailer.

### Interurban transport of goods by road (Soisson, France, 1993) (BARPI)

On 4 March 1993 in Soisson, a road tanker transporting 22,400 litres of methyl methacrylate overturned on the carriageway. The emergency services worked at the scene for 20 hours. An exclusion zone was established, which affected 31 households (72 inhabitants were evacuated). A sand berm was built and the drains plugged to prevent all risk of infiltration.

### Interurban transport of goods by road (Hoerdt, France, 2001) (BARPI)

On 27 August 2001 in Soisson, a road tanker containing 2,700 litres of methyl methacrylate overturned on the motorway. The driver of the vehicle was killed. A small chemical leak was caused. The motorway was closed in both directions and an exclusion zone of 400 m was established while the tanker was lifted and its contents transferred into another tank; 130 employees of companies located within the exclusion zone were evacuated. The transfer of the chemical was delayed to avoid the hottest hours of the day, as the chemical involved was volatile.

### Manufacture of industrial chemicals (Lauterbourg, France, 2004) (BARPI)

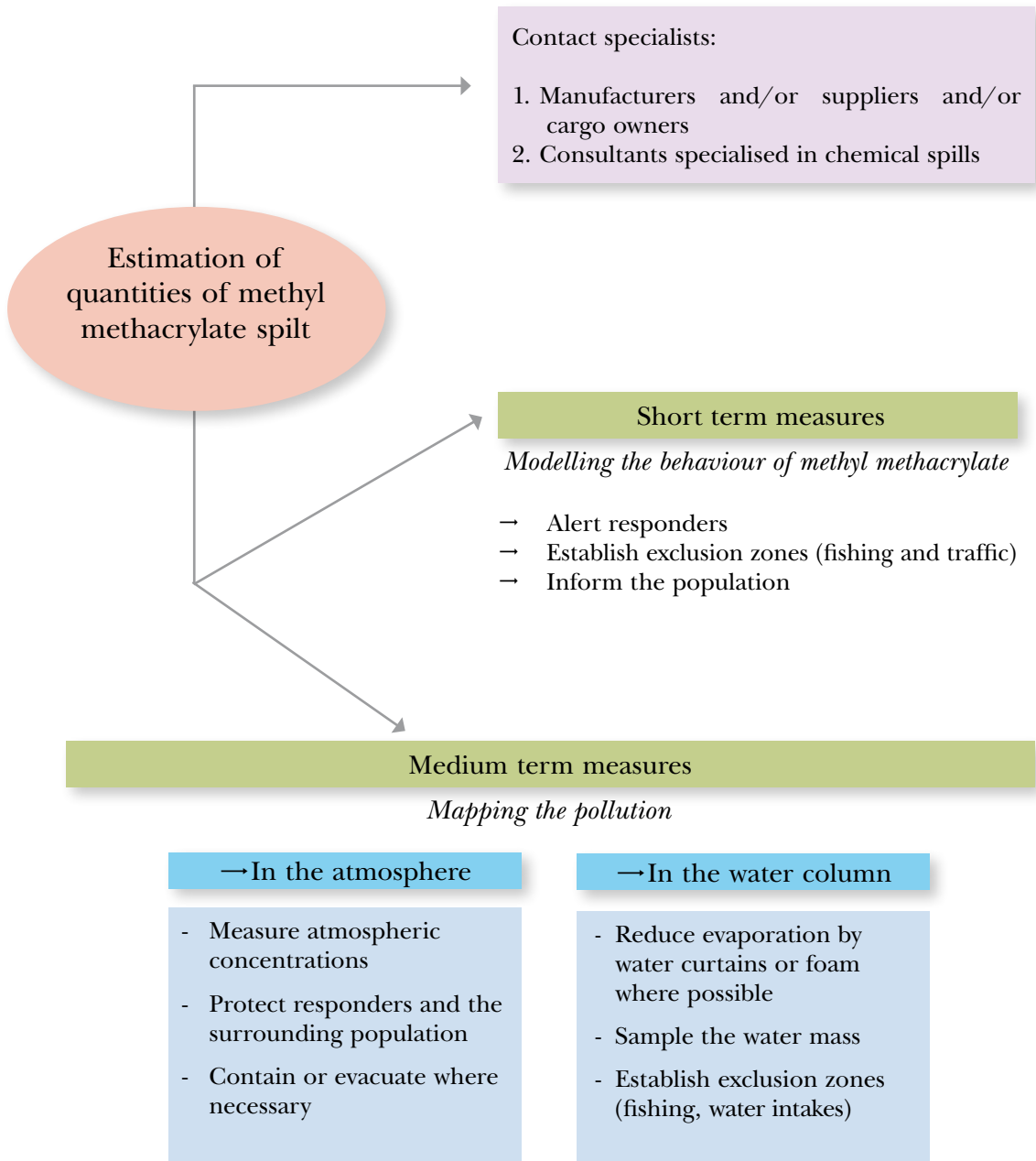
On 17 May 2007 in Lauterbourg, a road tanker transporting methyl methacrylate arrived at the car park entrance for heavy goods vehicles for a delivery to a chemical plant. A leak of the product in the car park was reported and the plant activated its contingency plan. A site safety team, assisted by the emergency services, treated the pollution: sorbents were applied to the 100 litre spill of methyl methacrylate which had spread over the road surface, and the traffic was interrupted for two hours. The truck's top manhole, thought not to have been properly closed, is likely to have been the source of the leak.

### Methyl methacrylate spill in the port of Kwai Chung (Hong Kong, China, 2007) (BARPI)

On 5 July 2007, in the port of Kwai Chung in Hong Kong, six people were taken to hospital following a spill of methyl methacrylate while unloading. An estimated quantity of 20 tonnes leaked from a container during transfer from the ship *OOCL Keelung* to the terminal. The 23 crew members were evacuated. Two fireboats and twelve fire engines were mobilised following the distress call from the ship. Among the six people hospitalised, two men were members of the crew and the four others were dock workers. Some inhabitants living one kilometre from the spill location had to leave their homes due to an irritating odour. The spokesman for the ship announced that the *OOCL Keelung* was able to leave Hong Kong only a few hours later than planned.

# Response recommendations

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



D2

### Is response possible? (CEFIC, 2005; CANUTEC, 2008)

If an incident occurs, as an immediate prevention measure, set up an exclusion zone with a minimum radius of 50 metres around the location of the spill or leak. If the leak continues and becomes increasingly heavy, evacuation within a distance of 300 metres downwind must initially be considered. Intervention may be considered if the following precautions are taken:

- Approach the accident area from upwind, equipped with Personal Protective Equipment (PPE), explosimeters and vapour sensing apparatus such as Dräger tubes.
- 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 measures in the event of a leak or spill (CANUTEC, 2008)

- Evacuate the area downwind of the leak or the slick of spilt product.
- Find and remove all sources of ignition.
- All equipment used for handling must be earthed.
- Avoid all contact with the liquid and do not inhale the vapours.
- Stop the leak, if doing so is not dangerous.
- On land, prevent infiltration into waterways, sewers, basements and closed spaces.
- Protect response personnel from the cloud of methyl methacrylate by using a vapour suppressing foam to reduce vapours.
- On board, absorb or cover with sand or some other non-combustible material and transfer to containers.
- Use non-sparking tools to collect absorbed material.

- In the case of a leak in the open sea, the only possible method is exclusion (fishing, navigation) and analytical monitoring.

### Emergency measures in the case of a tank fire (CANUTEC, 2008; CEFIC, 2005)

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

- Recommended fire extinguishers: dry chemical powder, carbon dioxide, water spray and alcohol-resistant foam.

#### In the event of a major fire

- Cool the containers exposed to flames with water spray, continuing the operation until well after the fire is out.
- Knock down vapours with water spray.
- Move away if the hissing of the safety mechanisms becomes louder or if the tank discolors.
- Recommended fire extinguishers: alcohol-resistant foam and water spray or mist.
- Use remote-controlled hoses or water cannons in order to fight the fire from as far away as possible.

## Response techniques

### Response

(FICHES RÉFLEXES D'INTERVENTION ANTIPOLLUTION " PRODUITS EN SURFACE : LIQUIDES ÉVAPORANTS ET FLOTTANTS " ; " PRODUITS DANS LA COLONNE D'EAU ET SUR LE FOND : LIQUIDES SOLUBLES ET COULANTS " ; FICHE GUIDE N°3 : " LUTTE EN MILIEU AQUATIQUE " ; FICHES STRATÉGIES ET MOYENS N°S 1, 2, 3, 4, 5, 12, CEDRE 2004)

#### On land

Before taking any response actions, the explosive limits and flammability limits in the atmosphere must be checked.

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

It is important to respond as rapidly as possible to prevent the substance from infiltrating the sewer system, or any other confined space, by building dams out of earth or sand to contain and absorb the substance.

#### At sea and in ports and harbours

In most cases, it will not be possible to respond directly to the spill. Response actions will be limited to stopping the leak, controlling the vapour cloud and spreading, and even the dissolution, of the substance. In ports and harbours, evaporation can be controlled by a layer of foam or by water curtains. The extent of the gas plume can be modelled using forecast models checked against in situ measurements using gas detectors.

#### Transshipment (ARKEMA, 2007)

- If the vessel must be lightered, transfer the chemical by pump or atmospheric pressure containing between 5 and 21% oxygen.
- Never bring into contact with an atmosphere made up only of inert gases.
- Take precautionary measures against static discharges.
- Use fireproof equipment.

# Choosing Personal Protective Equipment (PPE)

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

## Choosing breathing apparatus (FINGAS, M., 2000)

According to Maximum Use Concentrations (MUC)<sup>3</sup>:

- Gas mask up to 1,000 ppm for a short period of time.
- SCBA (Self-Contained Breathing Apparatus): for response in areas of high concentrations (over 1,000 ppm) or in the case of prolonged exposure.

## Choosing protective clothing

(ARKEMA SDS, 2007; CCHST, 2006; CEFIC, 2005; ERICARDS, 2005)

- Wear chemical protective clothing, consider wearing classic fire clothing underneath the suit and wearing boots.
- Protective breathing apparatus: in the case of insufficient ventilation, wear a suitable respirator.
- Eye protection: wear chemical safety glasses and/or a face shield in areas where there is a risk of splashes. Prepare an emergency eye-bath and quick-drench facilities in the work area.
- Hand protection: gloves made of PVA (polyvinyl alcohol) are recommended.

## Recommendations for use in the event of a spill (FINGAS M., 2000)

- Open-circuit, pressure demand SCBAs give the best safety protection. Their protection factor is around 10,000 (e.g. ELV = 50 ppm, protection up to 500,000 ppm of product in ambient air temperatures).
- Use SCBA to face unknown situations or to enter an area with unknown or high concentrations of a toxic substance or areas where there may be a lack of oxygen (an enclosed space).

- Certain facial features such as a scar, facial hair (even two day stubble), a thin face-shape or glasses may prevent the mask from being water tight. Special lens holders exist that fit into the face piece. Contact lenses can now be used, as new contact lenses allow for gas exchange and thus do not dry out and stick to the eyeball.
- Problems due to temperature:
  - . In hot weather, excessive perspiration can cause face-seal problems with the mask.
  - . In cold weather, ice may form on the regulator and the mask may steam up.

Mask adjustment tests are recommended for new users and regular fit 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.
- Wear chemical protective clothing and self-contained breathing apparatus when helping other responders to remove their protective clothing and when handling contaminated equipment.
- Recover decontamination effluents in reservoirs which comply with the storage conditions outlined in the chapter on "Transportation, handling, storage".

D4

<sup>3</sup> Maximum Use Concentrations (MUC) can vary according to the make and model. Contact the manufacturer for more information.

## Measuring devices and waste treatment

### Methods of detection and measurement in air (INRS, 1997)

- Instantaneous response: Dräger pump equipped with 50/a detector tube; Gastec pump equipped with detector tube 141.
- Infrared spectrometry (portable spectrometers equipped with a long-path cell).
- Sampling on porous material, desorption by carbon sulphide and quantification by gas phase chromatography.

### Waste treatment

Methyl methacrylate can be pumped into an inert safety reservoir. The rest must be absorbed with an inert sorbent (sand, earth). Methyl methacrylate should be disposed of by incineration. Do not release this chemical into the environment and prevent it from entering the sewer system.

### European manufacturers of methyl methacrylate

ARKEMA, BASF, Hœchst, Rohm and Haas France SA, Union Carbide Benelux.



# Further information

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

# 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 (AEGLs)

Defined by the National Research Council's Committee on Toxicology (USA), AEGLs are three levels above which the general population may experience certain effects. These three AEGLs 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 solid or liquid particles 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)

The relationship between the concentration of the chemical compound in the living organism and the concentration in the environment (water/air/ground). This factor is used to determine the bioaccumulation.

## 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.

### **Dermatitis**

Inflammation of the skin

### **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 (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.

### **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 (see p. 11)**

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.

### **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 (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.

### 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

### MITI test

Test used to determine how easily a product breaks down in the aqueous phase (aerobic conditions).

### Narcotic

A product which induces sleep or stupor and has a numbing effect.

### 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.

### pKa

The term pKa is the cologarithm of Ka, the acid dissociation constant to distinguish acids and bases.

$$K_a = \frac{[\text{base}] \times [\text{H}_3\text{O}^+]}{[\text{acid}]}$$

$$\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]}$$

### 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.

#### **Source of ignition**

Examples of sources of ignition: heat, sparks, flame, static electricity and friction. Sources of ignition should always be eliminated when handling flammable products or responding to an emergency in risky areas (use explosion proof pumps and VHF walky-talkies).

#### **Surface roughness**

Length of a transfer area between the atmospheric layer and a contact surface. This will depend on the average size of the roughness of the contact and atmospheric parameters near the water surface. When the sea is calm it is of the order of 0.02 to 0.06 cm.

#### **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.

#### **Temporary Emergency Exposure Limits (TEEL)**

Exposure times when there is no ERPG.

TEEL 0 is the threshold concentration below which a large part of the population will experience no effect on health. TEEL 1 is equivalent to ERPG1, TEEL 2 is equivalent to ERPG2 and TEEL 3 is equivalent to ERPG3.

#### **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.

#### **Unconfined Vapour Cloud Explosion (UVCE)**

Explosion of a gas cloud or slick of combustible vapours in an unconfined environment.

#### **Upper Explosive Limit (UEL)**

Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

#### **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
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
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
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
DIPPR	Design Institute for Physical Properties
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
ESTC	Environmental Science and Technology Centre
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
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
MARPOL	Marine Pollution
MARVS	Maximum Allowable Relief Valve Setting
MCA	Maritime and Coastguard Agency
MEEDDAT	Ministère de l'Écologie, de l'Énergie, du Développement durable et de l'Aménagement du Territoire
MEV	Mean Exposure Value
MMA	Methyl methacrylate
MP	Marine Pollutant
MRL	Minimum Risk Level
MSDS	Safety Data Sheet
MUC	Maximum Use Concentrations
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
OELV	Occupational Exposure Limit Value
PEC	Predicted Effect Concentration
PID	Photo Ionisation Detector
PNEC	Predicted No-Effect Concentration
PPE	Personal Protective Equipment
ppm	Parts per million
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
ROV	Remote Operated Vehicle
SCBA	Self-Contained Breathing Apparatus
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
SIDS	Screening Information Data Set
SINOE	Système d'Information et d'Observation de l'Environnement
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
VHF	Very High Frequency

## Useful websites

**AFSSA (Agence Française de Sécurité Sanitaire des Aliments)**

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

**ARKEMA**

Available at <http://www.arkemagroup.com>

**ATSDR (Agency for Toxic Substances and Disease Registry)**

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

**Bonn Agreement, European Classification System**

Available at <http://www.bonnagreement.org>

**Cedre (Centre of Documentation, Research and Experimentation on Accidental Water Pollution)**

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

**CEFIC (European Chemical Industry Council)**

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

**Chemfinder**

Available at <http://chemfinder.cambridgesoft.com>

**CHRIS (Chemical Hazards Response Information System)**

Available at <http://www.chrismanual.com>

**CSST (Commission de la Santé et de la Sécurité du Travail)**

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

**ECB (European Chemicals Bureau), Risk Assessment**

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

**ESTC (Environmental Science and Technology Centre)**

Available at [http://www.etc-cte.ec.gc.ca/home/about\\_e.html](http://www.etc-cte.ec.gc.ca/home/about_e.html)

**ICSC (International Chemical Safety Cards)**

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

**INERIS (Institut National de l'Environnement industriel et des Risques)**

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

**INRS (Institut National de Recherche et de Sécurité)**

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

**IPCS (International Programme on Chemical Safety)**

Available at <http://www.ilo.org/public/english/protection/safework/cis/products/icsc>

**NIOSH (National Institute for Occupational Safety and Health)**

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

**NOAA (National Oceanic and Atmospheric Administration), Historical incident search page**

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

**TRANSPORT CANADA, CANUTEC - Emergency Response Guide Book 2004**

Available at <http://www.tc.gc.ca/canutec/en/guide/guide.htm>

**TROCS, REMPEC (Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea) chemical transport database**

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

**UIC (Union des Industries Chimiques)**

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

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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°: 80-62-6  
EC n° (EINECS): 201-297-1  
UN n°: 1247  
Class: 3

### Physical data

#### Conversion factors

1 ppm = 4.10 mg/m<sup>3</sup>

1 mg/m<sup>3</sup> = 0.244 ppm

1 atm = 1.013×10<sup>5</sup> Pa

CSST, 2006

#### Physical state at 20°C

Appearance: liquid

Colour: colourless

Odour: irritating, fruity

ARKEMA SDS, 2007

#### Molecular mass

100.11 g.mol<sup>-1</sup>

DIPPR, 2006

#### Volumic mass

943 kg/m<sup>3</sup> at 20°C

ARKEMA SDS, 2007

#### Density

Relative density (water = 1): 0.944

INERIS, 2004; ICSC, 2003; ECB, 2002

Relative vapour density (air = 1): 3.45

INRS, 1997; CSST, 2006

#### Solubility

In fresh water: 16 g/L at 20°C

ARKEMA SDS, 2007; ECB, 2002

11.5 g/L at 10°C

CEDRE, 2008

12.8 g/L at 20°C

CEDRE, 2008

In seawater: 8 g/L at 10°C

CEDRE, 2008

9.8 g/L at 20°C

CEDRE, 2008

#### Vapour pressure/tension

3.9 kPa at 20°C

ARKEMA SDS, 2007; INRS, 1997

16.6 kPa at 50°C

CSST, 2006

#### Key temperatures

Boiling point: 100.3°C

DIPPR, 2006

Melting point: - 48.2°C

DIPPR, 2006

Flash point (closed cup): 2°C

ARKEMA SDS, 2007; CSST, 2006

(open cup): 10°C

CSST, 2006

Self-ignition point: 421°C

CSST, 2006; INRS, 1997; ICSC, 2003

: 430°C

ECB, 2002; ARKEMA SDS, 2007

#### Explosivity

LEL = 2.1 % or 21,000 ppm

ARKEMA SDS, 2007

UEL = 12.5 % or 125,000 ppm

#### Other properties

Viscosity at 20°C: 0.56 mPa.s

ARKEMA SDS, 2007

Henry's law constant: 26.3 Pa.m<sup>3</sup>.mol<sup>-1</sup>

ECB, 2002

3.2×10<sup>-4</sup> atm.m<sup>3</sup>.mol<sup>-1</sup>

HSDB, 2005

Surface tension: 28 mN/m at 20°C

HSDB, 2005

61 mN/m

ECB, 2002

Evaporation rate (n-butyl acetate = 1): 3.1

INRS, 1997

Olfactory threshold: 0.05 ppm

CSST, 2006

## Toxicological data

### Threshold toxicological values

Occupational exposure values

MEV: 100 ppm (410 mg/m<sup>3</sup>)

ARKEMA SDS, 2007

ELV: 200 ppm (820 mg/m<sup>3</sup>)

ARKEMA SDS, 2007

TLV-TWA: 50 ppm (205 mg/m<sup>3</sup>)

ARKEMA SDS, 2007

TLV-STEL: 100 ppm (410 mg/m<sup>3</sup>)

ARKEMA SDS, 2007

TLV-ceiling: no data available

Risk management values for the population

IDLH: 1,000 ppm (4,100 mg/m<sup>3</sup>)

NIOSH, 2005

TEEL 0: 400 ppm (1,640 mg/m<sup>3</sup>)

TEEL 1: 400 ppm (1,640 mg/m<sup>3</sup>)

US DEPARTMENT OF ENERGY'S CHEMICAL  
SAFETY PROGRAM, 2005

TEEL 2: 400 ppm (1,640 mg/m<sup>3</sup>)

TEEL 3: 4,000 ppm (16,400 mg/m<sup>3</sup>)

Proposed AEGLs (EPA, 2006)

Concentrations (ppm)	10 min	30 min	60 min	240 min	480 min
AEGL 1	17	17	17	17	17
AEGL 2	150	150	120	76	50
AEGL 3	720	720	570	360	180

## General toxicity

**Acute human toxicity** (ICSC, 2003; CANUTEC, 2008; ARKEMA SDS, 2007)

- By inhalation: cough, shortness of breath, sore throat, irritation of the nose and throat and, at high concentrations, nausea and dizziness. The inhalation of concentrated vapours can lead to anaesthesia-like conditions.
- By skin contact: redness, irritation, possibility of dermatitis.
- By ingestion: irritation of the mouth, throat, oesophagus and stomach, nausea, vomiting, abdominal pains.
- By eye contact: pain, redness, watering.

**Chronic human toxicity** (ICSC, 2003; CANUTEC, 2008)

Repeated or prolonged contact can cause skin sensitisation, allergic reactions and dermatitis. Methyl methacrylate may have effects on the peripheral nervous system and, if exposure continues, loss of consciousness may occur with possible damage to the liver and kidneys.

**Specific effects** (CSST, 2006; INRS, 1997; HSDB, 2004; ARKEMA SDS, 2007; ECB, 2002)

- Carcinogenic effects: no carcinogenic effects according to the IARC. No causal relationship between occurrences of cancer and exposure to the substance in epidemiological investigations.
- Effects on fertility: no effect on reproductive organs.
- Teratogenic effects and/or effects on foetal development: not demonstrated in humans; in animals, effects on development (significant decrease in foetal weight, delayed ossification) have been observed at doses which are toxic for mothers.
- Mutagenic effects: not demonstrated in humans or animals.

## Ecotoxicological data

### Acute ecotoxicity (HSDB, 2004; ECB, 2002; ARKEMA SDS, 2007)

Bacteria ( <i>Pseudomonas putida</i> )	EC <sub>5</sub> (16 h)	=	100 mg/L (fresh water)
Bacteria ( <i>Uronema parduczi</i> )	EC <sub>5</sub> (20 h)	=	556 mg/L (fresh water)
Bacteria ( <i>Chilomonas paramecium</i> )	EC <sub>5</sub> (72 h)	=	178 mg/L (fresh water)
Algae ( <i>Raphidocelis subcapitata</i> )	EC <sub>50</sub> (96 h)	=	170 mg/L (fresh water)
Crustacean ( <i>Daphnia magna</i> )	EC <sub>50</sub> (48 h)	=	69 mg/L (fresh water)
	EC <sub>50</sub> (24 h)	=	720 mg/L (fresh water)
Fish ( <i>Lepomis macrochirus</i> )	LC <sub>50</sub> (72 h)	=	264 mg/L (fresh water)
	LC <sub>50</sub> (96 h)	=	191 mg/L (fresh water)
Fish ( <i>Oncorhynchus mykiss</i> )	LC <sub>50</sub> (96 h)	>	79 mg/L (fresh water)
	NOEC (96 h)	=	40 mg/L (fresh water)

### Chronic ecotoxicity (ARKEMA SDS, 2007)

Algae ( <i>Scenedesmus quadricauda</i> )	EC <sub>3</sub> (8 d)	=	37 mg/L (fresh water)
Algae ( <i>Microcystis aeruginosa</i> )	EC <sub>3</sub> (8 d)	=	120 mg/L (fresh water)
Algae ( <i>Raphidocelis subcapitata</i> )	NOEC (96 h)	=	100 mg/L (fresh water)
Crustacean ( <i>Daphnia magna</i> )	NOEC (21 d)	=	37 mg/L (fresh water)



**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<sub>water</sub> is 740 µg/L. A safety factor of 50 is applied to the lowest value (data for the crustacean *Daphnia magna*). (ECB, 2002)

## ANNEX 2: FAX FORMAT DATA CARD

<p><b>Methyl Methacrylate</b> MMA; Methacrylic acid methyl ester; Methyl alpha-methacrylate; Methyl ester; 2-methyl-2-propenoic acid; Methyl 2-methyl-2-propenoate; Methyl 2-methylpropenoate.</p>	<p><math>C_5H_8O_2</math></p>	<p>CAS n°: 80-62-6 EC n° (EINECS): 201-297-1 Index n°: 607-035-00-6 UN n°: 1247 Class: 3</p>
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<b>First aid information</b>	
Immediately remove all soiled or spotted clothes. In the event of contact or inhalation, seek medical advice.	
<p><b>Intoxication by inhalation</b> Take the victim into the fresh air. Supply oxygen or apply artificial respiration if necessary. In case of persistent problems: consult a doctor.</p>	<p><b>Eye contact</b> Wash well-open eyes immediately, abundantly and thoroughly with water (remove contact lenses where possible). In case of persistent problems, consult a doctor.</p>
<p><b>Skin contact</b> Remove contaminated clothing. Immediately wash thoroughly with soap and water. In case of persistent irritation of the skin, consult a doctor.</p>	<p><b>Intoxication by ingestion</b> Rinse out the mouth. Do not induce vomiting. Consult a doctor.</p>

<b>Physical data</b>			
<b>Conversion factors</b>			
1 ppm = 4.10 mg/m <sup>3</sup>			
1 mg/m <sup>3</sup> = 0.244 ppm			
1 atm = 1.013×10 <sup>5</sup> Pa			
Melting point:	-48.2°C	Vapour pressure/tension:	3.9 kPa at 20°C
Boiling point:	100.3°C		16.6 kPa at 50°C
Critical temperature:	292.8°C	Viscosity at 20°C:	0.56 mPa.s
Relative density (water = 1):	0.944	Olfactory threshold:	0.05 ppm
Relative vapour density (air = 1):	3.45	Henry's law constant:	26.3 Pa.m <sup>3</sup> .mol <sup>-1</sup>
Solubility in fresh water:	16 g/L at 20°C		3.2×10 <sup>-4</sup> atm.m <sup>3</sup> .mol <sup>-1</sup>
	11.5 g/L at 10°C (CEDRE)	Evaporation rate	
	12.8 g/L at 20°C (CEDRE)	(n-butyl acetate = 1):	3.1
Solubility in seawater:	8 g/L at 20°C	Surface tension:	28 mN/m at 20°C
	9.8 g/L at 10°C		61 mN/m

<b>EU classification:</b>		
		
F: Highly flammable	Xi: Irritant	
		<p>R11 Highly flammable R43 May cause sensitisation by skin contact. R37/38 Irritating to respiratory system and skin. S24 Avoid contact with the skin. S37 Wear suitable gloves. S46 If swallowed seek medical advice immediately and show this container or label.</p>

## Toxicological data

### Threshold toxicological values

MEV: 100 ppm (410 mg/m<sup>3</sup>)  
 ELV: 200 ppm (820 mg/m<sup>3</sup>)  
 TLV-TWA: 50 ppm (205 mg/m<sup>3</sup>)  
 TLV-STEL: 100 ppm (410 mg/m<sup>3</sup>)  
 TLV-ceiling: no data available  
 IDLH: 1,000 ppm (4,100 mg/m<sup>3</sup>)  
 TEEL 0: 400 ppm (1,640 mg/m<sup>3</sup>)  
 TEEL 1: 400 ppm (1,640 mg/m<sup>3</sup>)  
 TEEL 2: 400 ppm (1,640 mg/m<sup>3</sup>)  
 TEEL 3: 4,000 ppm (16,400 mg/m<sup>3</sup>)

### Acute human toxicity

- By ingestion: cough, shortness of breath, sore throat, irritation of the nose and throat and, at high concentrations, nausea and dizziness. The inhalation of concentrated vapours can lead to anaesthesia-like conditions.
- By skin contact: redness, irritation, possibility of dermatitis.
- By ingestion: irritation of the mouth, throat, oesophagus and stomach, nausea, vomiting, abdominal pains.
- By eye contact: pain, redness, watering.

### Chronic human toxicity

Repeated or prolonged contact can cause skin sensitisation, allergic reactions and dermatitis. Methyl methacrylate may have effects on the peripheral nervous system and, if exposure continues, loss of consciousness may occur with possible damage to the liver and kidneys.

### Specific effects

Carcinogenic effects: no carcinogenic effects according to the IARC. No causal relationship between occurrences of cancer and exposure to the substance in epidemiological investigations.

Effects on fertility: no effect on reproductive organs.

Teratogenic effects and/or effects on foetal development: not demonstrated in humans; in animals, effects on development (significant decrease in foetal weight, delayed ossification) have been observed at doses which are toxic for mothers.

Mutagenic effects: not demonstrated in humans or animals.

## Ecotoxicological data

### Acute ecotoxicity

Bacteria (*Pseudomonas putida*) EC<sub>5</sub> (16 h) = 100 mg/L\*  
 Bacteria (*Uronema parduczi*) EC<sub>5</sub> (20 h) = 556 mg/L\*  
 Bacteria (*Chilomonas paramecium*) EC<sub>5</sub> (72 h) = 178 mg/L\*  
 Algae (*Raphidocelis subcapitata*) EC<sub>50</sub> (96 h) = 170 mg/L\*  
 Crustacean (*Daphnia magna*) EC<sub>50</sub> (48 h) = 69 mg/L\*  
 EC<sub>50</sub> (24 h) = 720 mg/L\*  
 LC<sub>50</sub> (72 h) = 264 mg/L\*  
 LC<sub>50</sub> (96 h) = 191 mg/L\*  
 Fish (*Lepomis macrochirus*) LC<sub>50</sub> (96 h) = 79 mg/L\*  
 Fish (*Oncorhynchus mykiss*) LC<sub>50</sub> (96 h) = 79 mg/L\*  
 NOEC (96 h) = 40 mg/L\*

(\* fresh water)

### Chronic ecotoxicity

Algae (*Scenedesmus quadricauda*) EC<sub>3</sub> (8 d) = 37 mg/L\*  
 Algae (*Microcystis aeruginosa*) EC<sub>3</sub> (8 d) = 120 mg/L\*  
 Algae (*Raphidocelis subcapitata*) NOEC (96 h) = 100 mg/L\*  
 Crustacean (*Daphnia magna*) NOEC (21 d) = 37 mg/L\*  
 (\* fresh water)

**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<sub>water</sub> is 740 µg/L. A safety factor of 50 is applied to the lowest value (data for the crustacean *Daphnia magna*).

## Persistence in the environment

### Volatilisation

According to Henry's law constant, the evaporation half-life of methyl methacrylate in a 1 m deep river with a current speed of 1 m/s and a wind speed of 3 m/s is 6 hours.

According to the calculated Koc value, its adsorption in soil and sediments is low. This low level of adsorption together with the product's high vapour tension mean that it evaporates quickly from the ground.

### Biodegradation

Methyl methacrylate is considered readily biodegradable in water. Biodegradation measurements reached 94% after 14 days in an aerobic environment (OECD 301 C test guideline, modified MITI test).

Methyl methacrylate is completely degraded by activated sludge in approximately 20 hours.

### Photolysis

The ultraviolet/visible absorption maximum is 231 nm. Methyl methacrylate should therefore not absorb radiation greater than 290 nm (the radiation reaching the earth's surface) and photolyze. Free radicals formed in natural waters by the

action of light might react with methyl methacrylate, however data is limited. Once in the atmosphere, the substance is degraded by a photochemical reaction with hydroxyl radicals ( $t_{1/2, \text{OH}} = 1.1$  to 9.7 h).

### Hydrolysis

Hydrolysis is not significant at neutral and acidic pH. The hydrolysis half-life of methyl methacrylate is estimated to be 3.9 years at pH 7 and 14.4 days at pH 9.

### Bioaccumulation

The bioaccumulation of methyl methacrylate calculated from its Kow value is not significant.

### Organic carbon/water partition coefficient:

log Koc = 1,53  
 1.17 to 2.13

**Octanol/water partition coefficient:** log Kow = 0.7 to 1.38

**Bioconcentration factor:** BCF = 3

**SEBC classification:** ED (evaporates/dissolves)

**MARPOL classification:** Classification on 1<sup>st</sup> January 2007: Y (definition in Annex 3)

### Particular risks

#### Polymerisation

Polymerisation is stabilised by phenolic derivatives, most often 10 to 20 mg/kg of hydroquinone mono-methyl ether or hydroquinone, or 2 to 20 mg/kg of 6-tert-butyl-2,4-xylenol. Free oxygen is essential to stabilize the product and the efficiency of stabilisation decreases if the temperature exceeds 30°C.

Methyl methacrylate is a highly reactive compound which polymerises readily at room temperature if it is not sufficiently stabilised. Polymerisation is caused or accelerated by heat, light and contact with oxidising products such as peroxides, nitrates, iron oxides, strong bases and strong acids, even as trace elements.

#### Danger

- Heating the receptacle causes an increase in pressure leading to a risk of the container bursting and a possibility of explosion.
- A spontaneous increase in pressure or auto-ignition may be caused by exposure to heat, light, impact or contact with other chemicals.

- Release of toxic, irritating fumes by heating or combustion.
- Invisible vapours heavier than air when the product is spilt on land. These vapours spread out and can enter sewers and basements.
- The stabilising additive may be destroyed by heat.
- Can be narcotic and result in loss of consciousness when inhaled.

#### Stability and reactivity

Safety precautions: keep away from light, heat and sources of ignition and keep at temperatures not exceeding 30°C. The inhibitor concentration and oxygen must be maintained for the product to remain stable. Substances to be avoided: free radical generators, activated carbon (explosive reaction), peroxides, strong oxidizing agents, strong acids, strong bases, rust. Stabilised methyl methacrylate can be transported and stored at room temperature.

Transportation	Handling	Storage
<p>Identification n° (UN): 1247                      - Land transportation: RID (rail) /ADR (road)                      Danger n°: 339                      Class: 3                      Packaging group: II                      Classification code: F1                      Danger labels: 3                      - Transportation via inland waterways:                      ADN/ADNR                      Class: 3                      Danger labels: 3                      Classification code: F1                      - Maritime transport: IMDG                      Class: 3                      Packaging group: II                      Marine pollutant (MP): no                      Danger labels: 3                      - Air transport: IATA                      Class: 3                      Packaging group: II                      Labels: 3</p>	<ul style="list-style-type: none"> <li>- Provide appropriate exhaust ventilation at machinery.</li> <li>- Do not use activated carbons to capture odours of methyl methacrylate.</li> <li>- Provide showers and eye baths.</li> <li>- Transfer by pump or atmospheric pressure containing between 5 and 21% oxygen.</li> <li>- Never bring into contact with an atmosphere made up only of inert gases.</li> <li>- Take precautionary measures against static discharges.</li> <li>- Keep away from flames.</li> <li>- Only use fireproof equipment.</li> </ul>	<ul style="list-style-type: none"> <li>- Keep container in a well ventilated place.</li> <li>- Maintain in contact with an atmosphere containing between 5 and 21% oxygen.</li> <li>- Keep away from sources of ignition. Do not smoke.</li> <li>- Protect against light.</li> <li>- Avoid long storage periods.</li> <li>- Keep below 30°C.</li> <li>- Continuously monitor product temperature.</li> <li>- Monitor the product's clarity.</li> <li>- Maintain inhibitor levels.</li> <li>- Ground the material and electric equipment used in explosive atmospheres.</li> <li>- Provide a retention tank.</li> </ul>

#### Incompatible products

Oxidizing agents, rust, peroxides, polymerization initiators, activated carbon.

#### Packaging materials to be avoided

Natural or synthetic rubber.

#### Recommended packaging materials

High density polyethylene, polypropylene, polytetrafluoroethylene (PTFE), stainless steel 316 L (preferably), mild steel, aluminium.

## ANNEX 3: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

### 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 (Group of Experts on the Scientific Aspects of Marine Pollution).

### Revised MARPOL Annex II (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.

**Category OS (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.