METHYL ETHYL KETONE



UN n°: 1193

MARPOL classification: Z SEBC classification: ED (evaporates/dissolves)





CHEMICAL RESPONSE GUIDE



METHYL ETHYL **KETONE**

PRACTICAL GUIDE

INFORMATION **DECISION-MAKING**

RESPONSE

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

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

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In the same collection

Warning

mend that you check them.

Certain data, regulations, values and

norms may be liable to change sub-

sequent to publication. We recom-

Ammonia, Benzene, Dichloroethane, Dimethyl disulphide, Ethyl acrylate, Phosphoric acid, Sodium hydroxide, Stabilised methyl methacrylate, Styrene, Sulphuric acid, Unleaded gasoline, Vinyl Chloride, Xylene.

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Purpose of this guide

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

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

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

They also contain the results of scenarios relating to fictitious 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)241482121 Bordeaux (Hôpital Pellegrin-Tripode) Tel.: + 33 (0)556964080 Grenoble (Hôpital Albert Michallon) Tel.: + 33 (0)476765646 Lille (Centre Hospitalier Universitaire) Tel.: + 33 (0)476765646 Lille (Centre Hospitalier Universitaire) Tel.: + 33 (0)472116911 Marseille (Hôpital Edouard Herriot) Tel.: + 33 (0)472116911 Marseille (Hôpital Salvator) Tel.: + 33 (0)491752525 Nancy (Hôpital Central) Tel.: + 33 (0)383323636 Paris (Hôpital Fernand Widal) Tel.: + 33 (0)140054848 Reims (Hôpital Maison Blanche) Tel.: + 33 (0)29592222 Rouen (Hôpital Charles Nicolle) Tel.: + 33 (0)235884400 Strasbourg (Hôpitaux Universitaires) Tel.: + 33 (0)388373737 Toulouse (Hôpital de Purpan) Tel.: + 33 (0)561777447

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What you need to know about methyl ethyl ketone

Definition

Methyl ethyl ketone (MEK) is a colourless liquid with a sharp sweet odour. It is a volatile organic compound, is readily flammable, an irritant and causes little environmental harm. Methyl ethyl ketone is an eye irritant. It can cause drowsiness and dizziness.

Uses and sources of emission (CCOHS, 2008; CSST, 2004)

Methyl ethyl ketone is mainly used as a solvent for various coatings such as vinyl, adhesives, nitrocellulose, or acrylic coatings, but also in paint removers, lacquers, varnishes, glues, printing inks, resins... It is present in dewaxing lubricating oils. It is also used as a chemical intermediate and catalyst. It serves as an extraction solvent in the processing of foodstuffs and food ingredients. It is found in some fruits and vegetables and occurs naturally in blood, urine and exhaled air.

Human activity can be a source of emission of methyl ethyl ketone into the atmosphere. In particular, it is present in vehicle exhaust gases and cigarette smoke.

Risks (CSST, 2004; ARKEMA SDS, 2008)

- Toxicity

Methyl ethyl ketone is irritating to the eyes. Repeated exposure can cause dryness or cracking of the skin. Inhalation of methyl ethyl ketone vapours can cause drowsiness and dizziness.

- Explosion

Methyl ethyl ketone vapours can form flammable mixtures with air.

Methyl ethyl ketone can react violently with strong oxidants and strong inorganic acids. Its vapours are denser than air and can travel as far as a heat source and ignite.

- Fire

Methyl ethyl ketone is a highly flammable liquid at room temperature. This substance breaks down at over 500°C to form toxic and irritating products. Concentrated aqueous solutions of the product may be flammable.

Behaviour in the environment

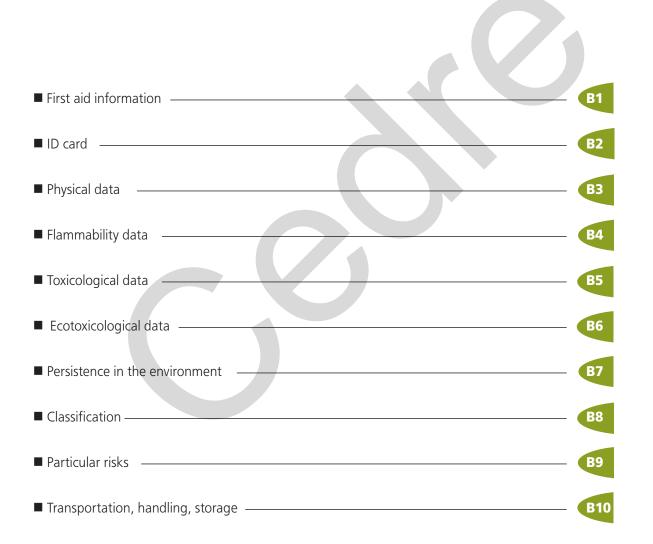
(ARKEMA SDS, 2008; ICSC, 1998)

Methyl ethyl ketone is highly soluble (271 g/l at 20°C) in water with rapid kinetics. It is a highly volatile compound. When spilt on the ground, it evaporates. The vapours are denser than air and can spread at ground level and enter the sewer system and basements. Methyl ethyl ketone is slightly bioaccumulable in aquatic organisms. It is readily biodegradable and not very harmful for the aquatic environment. It can however temporarily and locally affect the environment.

Response strategy

As methyl ethyl ketone is a colourless liquid which is very soluble in water, it is difficult to locate slicks in water and to respond to a spill. Response actions will be limited to stopping the leak, controlling the vapour cloud, preventing spreading and, if possible, reducing the dissolution of the substance.

First line emergency data



First aid information

(ARKEMA SDS, 2008; ICSC, 1998; CCOHS, 1997; CANUTEC, 2008)

Immediately remove all soiled or spotted clothes with suitable gloves.

Intoxication by inhalation

- Move the victim into the open air and lie them down.
- Supply oxygen or apply artificial respiration if necessary.
- Consult a doctor if effects persist.

Skin contact

- Remove contaminated clothing.
- Immediately flush under water.
- Flush again if irritation persists.

Eye contact

- Flush with water for 20 minutes holding the eyelids wide open
- (remove contact lenses if possible).
- Consult an ophthalmologist wherever possible.

Intoxication by ingestion

- Rinse out the mouth.
- Drink large quantities of water.
- Do not induce vomiting.
- Consult a doctor.

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

ID card

Methyl Ethyl Ketone

Gross formula: C₄H₈O **Semi-developed formula:** CH₃-CO-CH₂CH₃

Synonyms (other names)

2-Butanone; Butanone; MEK; Methyl acetone; Butan-2-one; Methylpropane-2; Butanone-2; 2-oxobutane; 3-Butanone; Ethyl methyl ketone; Methylethylketone; Ethylmethylketone.

EU Classification

F: Highly flammable.

Xi: Irritant.

R11: Highly flammable.

R36: Irritating to eyes.

R66: Repeated exposure may cause skin dryness or cracking.

R67: Vapours may cause drowsiness and dizziness.

S2: Keep out of reach of children.

S9: Keep container in a well ventilated place.

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

CAS n°:	78-93-3
EC n° (EINECS):	201-159-0
Index n°:	606-002-00-3

Classification for transportation

UN n°: 1193 Class 3

¹ Additional data in Annex 1

Physical data

1 ppm = 2.95 mg/m ³ - 1	Conversion factor: $mg/m^3 = 0.339 \text{ ppm} - 1 \text{ atm} = 1.013x10^5 \text{ Pa}$	
Melting point	- 86°C (ARKEMA SDS, 2008; ICSC, 1998; HSDB, 1997) - 86.6°C (CSST, 2004; DIPPR, 2006)	
Boiling point	79.6°C (INRS, 2003; ARKEMA SDS, 2008; CHRIS, 1999; ECB, 2000; DIPPR, 2006; CSST, 2004)	
Critical temperature	261.4°C (DIPPR, 2006)	
Relative density (water = 1) at 20°C	0.805 g/cm ³ (INRS, 2003; ARKEMA SDS, 2008; CSST, 2004; HSDB, 1997)	
Relative vapour density (air = 1) at 20°C	2.5 (INRS, 2003; CHRIS, 1999)	
Relative density of air/vapour mixture at 20°C	1.1 (ICSC, 1998)	
Solubility in seawater at 25°C	158 g/l (cedre, 2001)	
Solubility in fresh water	10°С: 353 g/l (есв, 2000) 20°С: 271 g/l (аккема sds, 2008) 25°С: 223 g/l (сеdre, 2001)	
Solubility in solvent	Soluble in most organic solvents (ARKEMA SDS, 2006)	
Vapour pressure/tension	at 20°C: 10.1 kPa (ARKEMA SDS, 2008; ECB, 2000) at 25°C: 13.3 kPa (INRS, 2003) at 41.6°C: 26.7 kPa (INRS, 2003)	
Critical pressure	41 atm (HSDB, 1997, DIPPR, 2006)	
Viscosity at 20°C	0.41 mPa.s (HSDB, 1997)	
Olfactory threshold	5.4 ppm (arkema sds, 2008)	
Evaporation rate (ether=1)	2.6 (CSST, 2004) 2.7 (HSDB, 1997; INRS, 2003)	
Diffusion coefficient in water:	No data available	
Diffusion coefficient in air	No data available	
Henry's law constant *	5.66 Pa.m ³ /mol - 5.59×10 ⁻⁵ atm.m ³ /mol (ARKEMA SDS, 2008; ECB, 2000)	
Molecular mass	72.10 g/mol (Arkema SDS, 2008; INRS, 2003; DIPPR, 2006)	
Density at 20°C	805 kg/m³ (arkema sds, 2008)	
Vapour density at 20°C	3.11 kg/m ³ (Arkema sds, 2008)	
Surface tension at 20°C	0.246 mN/cm (HSDB, 1997)	

* See Henry's law constant diagram p 66

Flammability data

Explosive limits by volume (% in air):

Lower limit (LEL): 1.8 % or 18,000 ppm (arkema sds, 2008; ICSC, 1998; ECB, 2000; CSST, 2004; HSDB, 1997) Upper limit (UEL): 11.5 % or 115 000 ppm (arkema sds, 2008; ICSC, 1998; ECB, 2000; CSST, 2004)

Combustion rate: 4.1 mm/min (CHRIS, 1999)

Flash point:

Closed cup: Open cup: - 6°C (ARKEMA SDS, 2008; ECB, 2000; DIPPR, 2006) - 4°C (INRS, 2003; CSST, 2004)

Auto-ignition temperature:

516°C (ARKEMA SDS, 2008; ECB, 2000; DIPPR, 2006)

Dangerous products of decomposition (ARKEMA SDS, 2008; CSST, 2004)

Thermal decomposition products: carbon monoxide, carbon dioxide, organic derivatives. Prolonged exposure of methyl ethyl ketone to ultraviolet rays can generate dangerous products of decomposition: ethane, methane, ethylene, diacetyl and carbon monoxide.

Behaviour when in contact with other products (INRS, 2003; CSST, 2004)

- Methyl ethyl ketone can react vigorously with strong oxidising agents such as chromic acid, nitric acid, ozone and peroxides, in particular hydrogen peroxide.
- If methyl ethyl ketone oxidises, it can cause the formation of unstable peroxides.
- It can react violently with inorganic acids such as fuming sulphuric acid and chlorosulphuric acid. The product may ignite in the presence of potassium t-butoxide.
- It can react violently with certain chlorinated hydrocarbons such as trichloromethane, in the presence of a strong base (sodium or potassium hydroxide).
- Methyl ethyl ketone is not corrosive for metals, but attacks certain plastics and materials including natural rubber, nitrile rubber, polyvinyl chloride, Viton®, certain acrylics and celluloses.

Vapour (INRS, 2003; CSST, 2004)

The vapours are heavier than air and can travel as far as a heat source and ignite. Methyl ethyl ketone vapours can form flammable mixtures with air.

Heat (INRS, 2003)

Aqueous solutions of methyl ethyl ketone can ignite if heated.

Toxicological data

Acute human toxicity (ARKEMA SDS, 2008; ICSC, 1998)

Exposure to this product can cause various effects.

- By inhalation: cough, dizziness, drowsiness, headache, nausea, vomiting.
- By skin contact: light irritation.
- By eye contact: irritation, redness, pain. The vapours are irritating to the eyes.
- By ingestion: loss of consciousness, cough, dizziness, drowsiness, headache, nausea, vomiting.

Chronic human toxicity (Arkema SDS, 2008; ICSC, 1998; INRS, 2003; CHRIS, 1999; CSST, 2004)

- Repeated or prolonged exposure of the skin can cause dryness or cracking, dermatitis and whitening of the skin.

Threshold toxicological values

Occupational exposure values (INRS, 2003; CHRIS, 1999; HSDB, 1997)

MEV: 200 ppm = 590 mg/m³

ELV: 300 ppm = 885 mg/m³

TLV-TWA (ACGIH): 200 ppm = 590 mg/m³

TLV-STEL (ACGIH): 300 ppm = 885 mg/m³

TLV-ceiling (ACGIH): no data available.

Risk management values for the population

(NIOSH, 2003; US DEPARTEMENT OF ENERGY'S CHEMICAL SAFETY PROGRAM)

IDLH: 3,000 ppm = 8,850 mg/m ³
TEEL-0: 200 ppm = 590 mg/m ³

TEEL-1: 200 ppm = 590 mg/m³

TEEL-2: 2,700 ppm = 7,965 mg/m³

TEEL-3: 4,000 ppm = 11,800 mg/m³

ERPGs: no data available.

- Repeated or prolonged exposure can cause irritation of the skin and dermatosis due to the product's degreasing properties.
- Methyl ethyl ketone could be a central nervous system depressant at very high concentrations. A study reported that a worker exposed to methyl ethyl ketone by inhalation and skin contact for at least 2 years showed reversible symptoms such as shaking, malcoordination (dizziness) and involuntary muscle movements.

AEGLs for methyl ethyl ketone

Cor	ncentrations (ppm)	10 min	30 min	1 h	4 h	8 h
	AEGL 1	200	200	200	200	200
	AEGL 2	4,900	3,400	2,700	1,700	1,700
	AEGL 3	* *	* *	4,000	2,500	2,500

Specific effects

(ICSC, 1998; INRS, 2003; CSST, 2004; CCOHS, 2008)

Effects on reproduction: presence of congenital malformations in animals. Methyl ethyl ketone passes through the placenta in humans. Data does not allow an adequate evaluation of postnatal effects.

Genotoxic effects: no data available.

Carcinogenic effects: absence of cancer in workers. The IARC has not assessed this product's carcinogenicity.

Ecotoxicological data

Acute ecotoxicity (ECB, 2000; HSDB, 1997; ARKEMA SDS, 2008)

LC ₅₀ (24 h)	= 5,640 mg/l
LC ₅₀ (96 h)	= 4,467 mg/l = 5,600 mg/l = 3,200 mg/l
LC ₅₀ (24 h) LC ₅₀ (48 h)	= 2,400 mg/l = 4,600 mg/l
EC ₅₀ (48 h)	= 8,890 mg/l = 1,382 mg/l = 5,091 mg/l > 520 mg/l < 70 mg/l = 1,950 mg/l
2	 = 1,150 mg/l ≥ 2,982 mg/l ≥ 190 mg/l = 5,100 mg/l
EC ₃ (7 d) EC ₃ (7 d)	≥ 4,300 mg/l ≥ 1,200 mg/l
	NOEC (96 h) LC_{50} (24 h) LC_{50} (24 h) LC_{50} (24 h) LC_{50} (24 h) LC_{50} (24 h) LC_{50} (24 h) LC_{50} (48 h) EC_{50} (48 h) EC_{50} (24 h) EC_{50} (24 h) EC_{50} (24 h) EC_{50} (27 h) EC_{50} (5 min) EC_{50} (5 min)

PNEC (Predicted No-Effect Concentration):

According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated $PNEC_{water}$ is 1.4 mg/L (1,400 mg/m³). A safety factor of 1,000 is applied to the lowest value of the three trophic levels.

Persistence in the environment

Evaporation (HSDB, 1997)

According to Henry's law constant*, the evaporation half-life of methyl ethyl ketone in a 1 m deep river with a current speed of 1 m/s and a wind speed of 3 m/s is 16 hours.

For a 1 m deep lake model, with a current speed of 0.05 m/s and a wind speed of 0.5 m/s, the product's evaporation half-life is 7.3 days.

Methyl ethyl ketone is expected to evaporate from dry ground.

Abiotic degradation (ECB, 2000; HSDB, 1997)

Methyl ethyl ketone breaks down rapidly in air (half-life of 8 days). It undergoes photodecomposition in sunlight, producing ethane, methane, ethylene, diacetyl and carbon monoxide.

In an anaerobic environment, 100 % of the product is broken down after 8 days of adaptation by methane-enriched cultures.

In the atmosphere, rapid degradation occurs by hydroxyl radicals, with a half-life of around 7 days.

Biodegradation (Arkema SDS, 2008; HSDB, 1997; ECB, 2000)

Methyl ethyl ketone is readily biodegradable. In the presence of activated sludge, 80% of methyl ethyl ketone is biodegraded in 20 hours. In optimal biodegradation conditions, the degradation rate is 76% in 5 days and 89% in 20 days.

Bioaccumulation (ARKEMA SDS, 2008)

According to its log Kow value, methyl ethyl ketone is practically non bioaccumulable.

Mobility (ARKEMA SDS, 2008)

Methyl ethyl ketone is a high mobility liquid. In water, the product is highly soluble (271 g/l at 20° C).

According to its log Koc value, methyl ethyl ketone has low adsorption to solids in the ground and in sediments. It remains dissolved in interstitial water.

Octanol/water partition coefficient: Log Kow = 0.29 (ARKEMA SDS, 2008)

Organic carbon/water partition coefficient: Log Koc = 0.71 (ARKEMA SDS, 2008)

Bioconcentration factor BCF: not measured

^{*} See Henry's law constant diagram p 66

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Classification

IBC classification (IMO, 2007)

- Hazards: P (Pollution risk)
- Ship type: 3
- Tank type: 2G (integral gravity tank)
- Tank vents: controlled venting
- Tank environmental control: no
- Electrical equipment: class i''': no (flash point < 60°C)
- Gauging: R (restricted gauging)

- Vapour detection: F (flammable vapours)
- Fire protection: A (alcohol-resistant foam or multipurpose foam)
- Eye protection: no special requirements

SEBC classification: ED (evaporates and dissolves) MARPOL classification: Z (definition in Annex 3)

E.U. Classification:

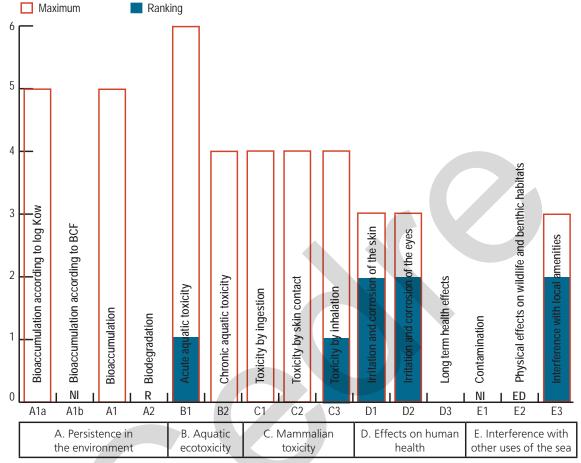






Xi: Irritant

R11	Highly flammable.
R36	Irritating to eyes.
R66	Repeated exposure may cause skin dryness or cracking.
R67	Vapours may cause drowsiness and dizziness.
S2	Keep out of reach of children.
S9	Keep container in a well ventilated place.
S16	Keep away from sources of ignition - No smoking.
EC n° (EINECS)	201-159-0



GESAMP classification of methyl ethyl ketone: (GESAMP, 2007)

GESAMP classification of methyl ethyl ketone

- A1a: Non bioaccumulable substance.
- A1b: NI: No Information
- A1: Non bioaccumulable substance.
- A2: Readily biodegradable.
- B1: Practically non-toxic
- B2: Negligible chronic aquatic toxicity
- C1: Negligible toxicity when ingested by mammals
- C2: Negligible toxicity by skin contact with mammals
- C3: Low toxicity through inhalation by mammals
- D1: Irritating to skin
- D2: Irritating to eyes
- D3: No long term effects
- E1: NI: No Information
- E2: ED: Evaporates and Dissolves
- E3: Moderately objectionable, possible closure of amenities.

Particular risks

Polymerisation

N/A

Danger (INRS, 2003; ARKEMA SDS, 2008; CANUTEC, 2008)

- Methyl ethyl ketone vapours can form flammable mixtures with air.
- A source of heat or ignition can cause it to ignite.
- The vapours are invisible and denser than air. They spread out across the ground and can infiltrate sewer systems and basements.
- The vapours can travel towards a source of ignition and ignite.

Stability and reactivity (INRS, 2003; ARKEMA SDS, 2008)

- Safety precautions: keep away from heat, sources of ignition and light.
- This is a stable product in normal storage and handling conditions.
- Methyl ethyl ketone can react vigorously with strong oxidising agents such as chromic acid, nitric acid, ozone and peroxides, in particular hydrogen peroxide. Oxidation of methyl ethyl ketone can, in some cases, lead to the formation of peroxide.
- The reaction of potassium t-butoxide with a small quantity of product can cause ignition. It can react violently with certain chlorinated hydrocarbons (e.g. trichloromethane) in the presence of a strong base (e.g. sodium or potassium hydroxide).

- Methyl ethyl ketone is not corrosive to metals but attacks certain plastics.

Safety precautions (INRS, 2003; ARKEMA SDS, 2008)

- Store away from all sources of heat and ignition, in an airtight container in a cool, dry and well ventilated place, away from oxidising agents and direct sunlight. Containers should be electrically grounded.

- Use non-sparking tools.

Transportation, handling, storage

Transportation (ARKEMA SDS, 2008)

Identification n° (UN): 1193

Land transportation: RID (rail) /ADR (road)

Hazard identification n°: 33 Classification code: F1 Class: 3 Packaging group: II Danger labels: 3

Transportation via inland waterways: ADN/ADNR

Hazard identification n°: 33 Classification code: F1 Class: 3 Packaging group: II Danger labels: 3

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, 2008; INRS, 2003)

- Provide appropriate exhaust ventilation at machinery.
- Provide showers and eye baths.
- Ensure that there is a water supply nearby.
- Provide self-contained breathing apparatus nearby.
- Eliminate all sources of sparks and ignition. Do not smoke.

- Do not use air for transfers.
- Do not use air to dry the equipment.
- Take precautionary measures against static discharges.
- Use only fireproof equipment.

Storage (ARKEMA SDS, 2008; INRS, 2003)

- Store in tightly closed containers in a cool, well ventilated area.
- Store away from heat and ignition sources.
- Store at ambient temperature.
- Provide a retention tank.
- Ground the electric equipment suitable for use in explosive atmospheres.

Incompatible products (INRS, 2003)

Avoid strong oxidising agents (chromic acid, nitric acid, hydrogen peroxide and ozone), potassium t-butoxide, chlorinated hydrocarbons (trichloromethane) and strong bases (sodium or potassium hydroxide).

Recommended packaging materials (ARKEMA SDS, 2008; INRS, 2003)

Methyl ethyl ketone can be stored in iron, steel or aluminium containers. Glass can also be used for small quantities; in this case cylinders can be protected by a more resistant, suitably adjusted metal envelope.

Packaging materials to be avoided (ARKEMA SDS, 2008)

Rubber, polyethylene, plastics.

Results of accident scenarios



Reminder of properties

Transportation

Methyl ethyl ketone is transported in liquid form in stainless steel or ordinary steel tanks.

Vapour density and tension

- Relative density: 0.805 g/cm³ at 20°C
- Relative vapour density: 2.5 at 20°C
- Vapour tension: 10.1 kPa at 20°C

Solubility

C1

Methyl ethyl ketone is highly soluble in water with rapid kinetics (solubility of 271 g/l at 20°C in freshwater).

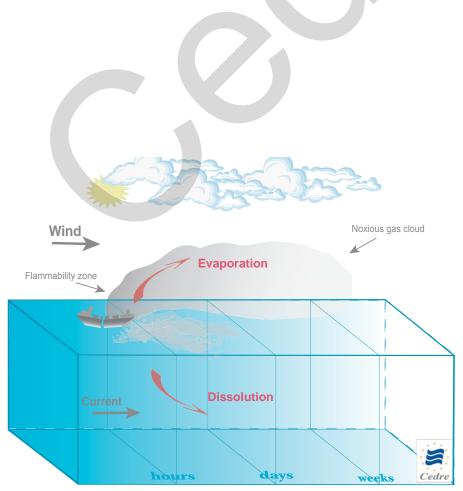
Behaviour in the environment

Its solubility in water and vapour tension mean that this product is classed ED, i.e. it evaporates and dissolves (according to the SEBC classification).

Methyl ethyl ketone is highly volatile. It therefore dissipates rapidly in the atmosphere.

When spilt on the ground, methyl ethyl ketone evaporates. Its vapours are denser than air and can spread at ground level and enter the sewer system.

According to its log Kow value, methyl ethyl ketone is practically non bioaccumulable in aquatic organisms.

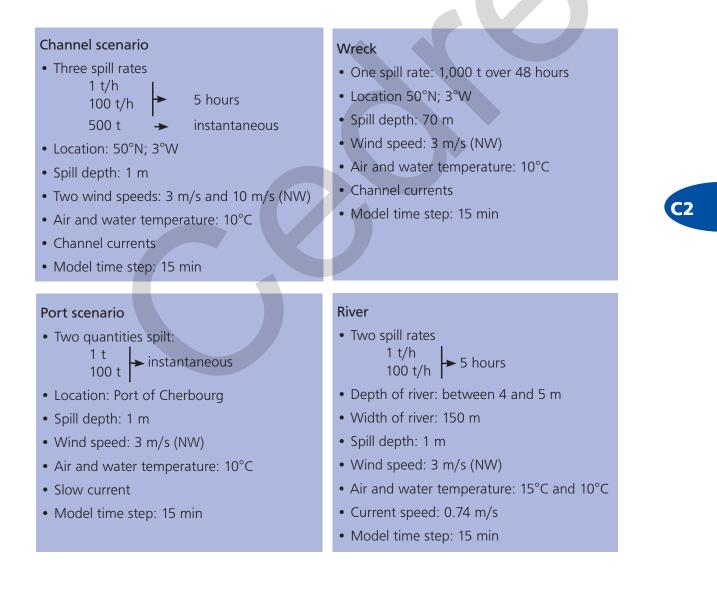


Behaviour of methyl ethyl ketone spilt in water

Accident scenarios

The scenarios defined here are simply designed to give an indication of the chemical's possible behaviour. In the event of a real spill, the results of simulations will naturally be different from those given here. These simulations were performed using the CHEMMAP behaviour model, the emergency response model employed by *Cedre*. Other more sophisticated models exist, but require response times which are incompatible with an emergency situation.

Four spill scenarios are given here with different quantities of chemical spilt:



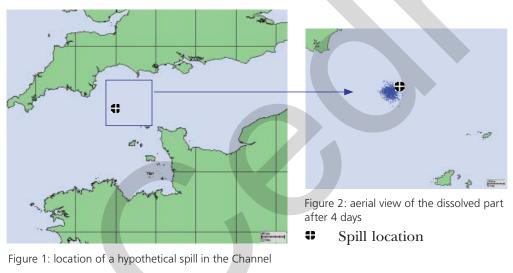
Modelling

CHEMMAP software was used to model hypothetical spillages of methyl ethyl ketone in the aquatic environment. This chemical spill model, designed by ASA (Applied Science Associates, Inc. - USA), predicts the movement and fate of the spilt product in fresh and sea water. CHEMMAP indicates both the movement of the product when spilt and its distribution in the environment (air, surface, water column, sediment...).

In the case of a continuous spill at sea, the surface drift generated by the current must be taken into account. Here the **tidal coefficient was 73** (moderate tide) and the **current speed** reached a maximum of **1.73 m/s** in the area studied.

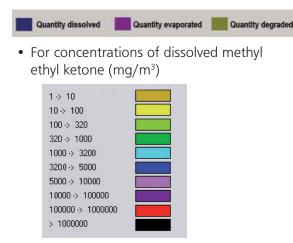
The spill scenarios used in this guide take place on the same day at the same time: on 11/12/2007 at 12:00 noon.

Example presentation of results obtained after 4 days, following a spill of 1 t/h of methyl ethyl ketone for 5 hours

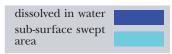


Key used in this guide

• For the distribution by mass



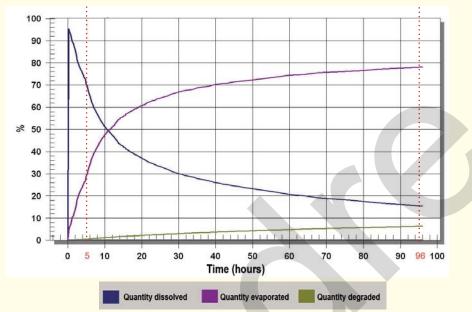
• For the behaviour of methyl ethyl ketone



• For atmospheric concentrations of methyl ethyl ketone (ppm)

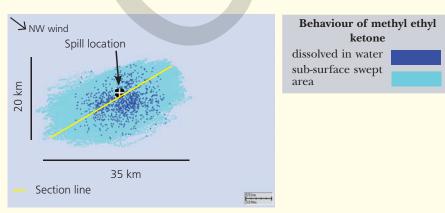
1 -> 50	
50 -> 200	
200 -> 300	
300 -> 1000	
1000 -> 3000	
3000 -> 5000	
5000 -> 18000	
> 18000	

Results of the Channel scenario



1. Spill in the Channel of 1 t/h of methyl ethyl ketone for 5 hours, with a 3 m/s NW wind.

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. After 4 days, 15% of the initial quantity is in the water column while 78% has evaporated and 7% has been broken down.



1.1 Behaviour of methyl ethyl ketone after 4 days

Figure 3: aerial view of the chemical's behaviour

With a NW wind at a speed of 3 m/s, the surface area liable to be affected is 35 km from east to west and 20 km from north to south, for a 4 hour study.

This area is approximately the same for a spill of 100 t/h with a wind speed of 3 m/s.

Graph 1: distribution by mass of a spill of 1 t/h and 100 t/h for 5 hours with a wind speed of 3 m/s $\,$

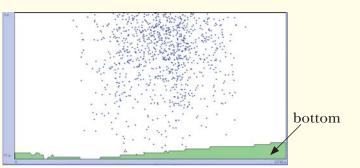
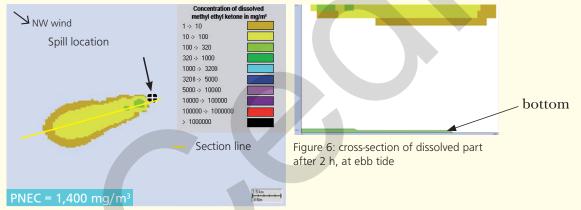


Figure 4: cross-section of the chemical's behaviour

Figure 4 below shows the depth of the water column affected by the methyl ethyl ketone with a wind speed of 3 m/s. The chemical affects the entire water column (around 70 m), 4 days after the beginning of the spill.



1.2 Concentrations of methyl ethyl ketone dissolved in the water column

Throughout the entire duration of the scenario (4 days), the maximum concentration observed in the water column is 320 mg/m^3 . This concentration is obtained 2 hours after the beginning of the spill, up to 1.75 km from the spill location. The PNEC (1,400 mg/m³) is therefore not reached. At that time, an approximate depth of 15 m of the water column is affected.

1.3 Atmospheric concentrations of methyl ethyl ketone

According to the CHEMMAP model, the maximum atmospheric concentrations remain below 50 ppm throughout the spill (5 hours). These concentrations are detected up to a maximum distance of 6.5 km south-west of the spill location, the distance covered by the dissolved part over 5 hours.

Figure 5: aerial view of dissolved part after 2 h, at ebb tide



2. Spill in the Channel of 1 t/h of methyl ethyl ketone for 5 hours, with a 10 m/s NW wind.

Graph 2: distribution by mass of a spill of 1 t/h and 100 t/h for 5 hours with a wind speed of 10 m/s $\,$

Five hours after the beginning of the spill, 80% of the chemical has dissolved in the water column, while the rest has evaporated into the atmosphere. After 4 days, 38% of the initial quantity is in the water column, 50% has evaporated and 12% has been broken down.

2.1 Behaviour of methyl ethyl ketone after 4 days

The behaviour of methyl ethyl ketone is identical for a spill of 1 t/h and 100 t/h for 5 hours, with wind speeds of 3 and 10 m/s (cf. Figures 3 and 4).

2.2 Concentrations of methyl ethyl ketone dissolved in the water column

Throughout the entire duration of the scenario (4 days), the maximum concentration observed in the water column is 300 mg/m^3 . This concentration is obtained 30 minutes after the beginning of the spill, up to 1 km from the spill location. The PNEC (1,400 mg/m³) is therefore not reached. At that time, an approximate depth of 20 m of the water column is affected.

2.3 Atmospheric concentrations of methyl ethyl ketone

According to the CHEMMAP software, during the first minute following the spill, the methyl ethyl ketone concentrations were higher than or equal to the IDLH (3,000 ppm). Thereafter, the atmospheric concentrations remain below 50 ppm throughout the scenario (4 days).

3. Spill in the Channel of 100 t/h of methyl ethyl ketone for 5 hours, with a 3 m/s NW wind.

The distribution by mass is identical to that of a spill of 1 t/h for 5 hours (cf. Graph 1).

3.1 Behaviour of methyl ethyl ketone after 4 days

The behaviour of methyl ethyl ketone is identical for a spill of 1 t/h and 100 t/h for 5 hours, with wind speeds of 3 and 10 m/s (cf. Figures 3 and 4).

3.2 Concentrations of methyl ethyl ketone dissolved in the water column

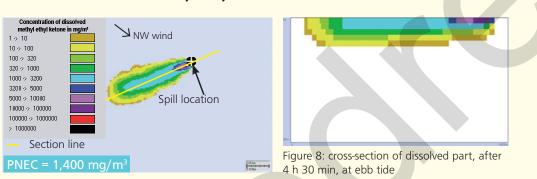


Figure 7: aerial view of dissolved part, after 4 h 30 min, at ebb tide

Concentrations greater than or equal to the PNEC $(1,400 \text{ mg/m}^3)$ will travel a maximum distance of up to 10 km west-south-west of the spill location. This distance will be reached 4 h 30 min after the beginning of the spill. The depth affected at this time is around 20 m.

Throughout the duration of the scenario (4 days), the maximum concentration observed in the water column is $40,000 \text{ mg/m}^3$, a value obtained 1 hour after the beginning of the spill near the spill location.

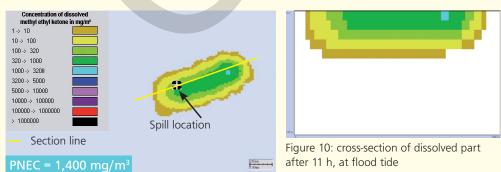


Figure 9: aerial view of dissolved part after 11 h, at flood tide

Concentrations greater than or equal to the PNEC $(1,400 \text{ mg/m}^3)$ will travel a maximum distance of up to 8.6 km east of the spill location. This distance will be reached 11 hours after the beginning of the spill. The depth affected at this time is around 35 m.

3.3 Atmospheric concentrations of methyl ethyl ketone

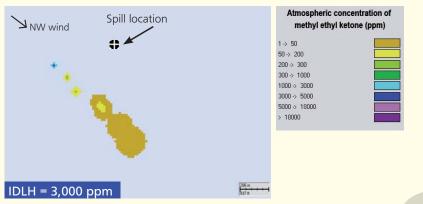


Figure 11: aerial view of the evaporated part, after 12 min

With a 3 m/s NW wind, the maximum distance covered by concentrations higher than or equal to the IDLH (3,000 ppm) is 700 m from the spill location. This distance is reached 12 minutes after the beginning of the spill, west-south-west of the spill location.

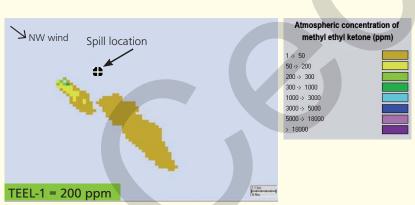


Figure 12: aerial view of the evaporated part, after 39 min

The maximum distance travelled by concentrations greater than or equal to the TEEL-1 (200 ppm) is 2 km west-south-west of the spill location. This distance is reached 39 minutes after the beginning of the spill.

4. Spill in the Channel of 100 t/h of methyl ethyl ketone for 5 hours, with a 10 m/s NW wind.

The distribution by mass is identical to that of a spill of 1 t/h for 5 hours, with a wind speed of 10 m/s (cf. Graph 2).

4.1 Behaviour of methyl ethyl ketone after 4 days

The chemical's behaviour is identical for a spill of 1 t/h and 100 t/h for 5 hours, with wind speeds of 3 and 10 m/s (cf. Figures 3 and 4).

4.2 Concentrations of methyl ethyl ketone dissolved in the water column

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a maximum distance of 8.4 km west-south-west of the spill location. This distance will be reached 4 h 45 min after the beginning of the spill. The depth affected at this time is around 35 m.

Throughout the entire duration of the scenario (4 days), the maximum concentration observed in the water column is 29,000 mg/m³. This concentration is obtained 30 minutes after the beginning of the spill, near the spill location.

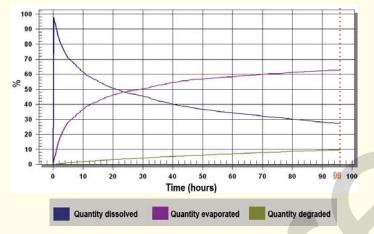
4.3 Atmospheric concentrations of methyl ethyl ketone

The maximum distance travelled by the chemical at concentrations greater than or equal to the LEL (18,000 ppm) is 65 m west of the spill location. This distance is reached 1 minute after the beginning of the spill.

The maximum distance travelled by the chemical at concentrations greater than or equal to the IDLH is 210 m west of the spill location. This distance is reached 4 minutes after the beginning of the spill.

The maximum distance travelled by the chemical at concentrations greater than or equal to the TEEL-1 is 4.7 km south-east of the spill location. This distance is reached 4 h 05 min after the beginning of the spill.

5. Instantaneous spill of 500 tonnes of methyl ethyl ketone in the Channel, with a 3 m/s NW wind



Graph 3: distribution by mass of an instantaneous spill of 500 t, with a wind speed of 3 $\ensuremath{\text{m/s}}$

Immediately after the spill, the entire volume spilt is found in the water column. After 4 days, 30% of the initial quantity is in the water column while 60% has evaporated and 10% has been broken down.

5.1 Behaviour of methyl ethyl ketone after 4 days

The surface area liable to be affected by an instantaneous spill of 500 t of methyl ethyl ketone stretches 30 km from east to west and 20 km from north to south. The methyl ethyl ketone affects the entire water column, after 4 days.



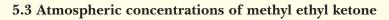
5.2. Concentrations of methyl ethyl ketone dissolved in the water column

Figure 13: aerial view of dissolved part after 5 h, at ebb tide

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a maximum distance of up to 12 km west-south-west of the spill location. This distance will be reached 5 hours after the spill. The depth affected at this time is around 35 m.

Concentrations higher than or equal to the PNEC are not found east of the spill location (at flood tide).

Throughout the scenario (4 days), the maximum concentration observed is approximately 250,000 mg/m³. This concentration is reached 30 minutes after the spill.



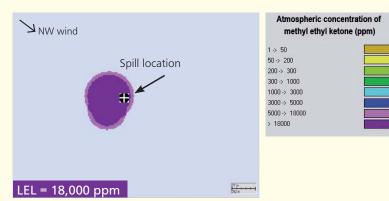


Figure 15: aerial view of the evaporated part, after 1 min

The maximum distance travelled by the chemical at concentrations greater than or equal to the LEL (18,000 ppm) is 125 m west of the spill location. This distance is reached 1 minute after the spill.

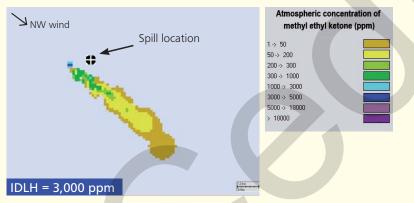


Figure 16: aerial view of the evaporated part, after 32 min

The maximum distance travelled by the chemical at concentrations greater than or equal to the IDLH (3,000 ppm) is 1.4 km west-south-west of the spill location. This distance is reached 32 minutes after the spill.

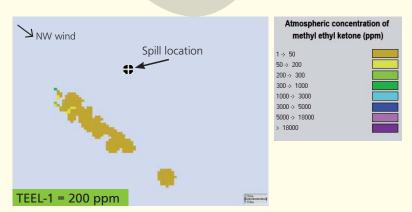


Figure 17: aerial view of the evaporated part, after 4 h 20 min

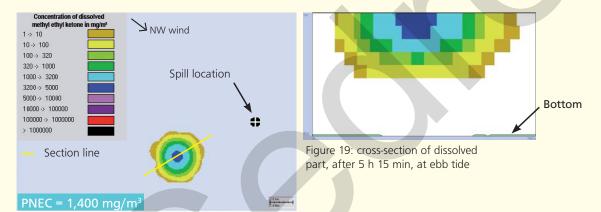
The maximum distance travelled by concentrations greater than or equal to the TEEL-1 (200 ppm) is 11.4 km west-south-west of the spill location. This distance is reached 4 h 20 min after the spill.

6. Instantaneous spill of 500 tonnes of methyl ethyl ketone in the Channel, with a 10 m/s NW wind

The distribution by mass is identical to that of an instantaneous spill of 500 tonnes, with a 3 m/s NW wind (cf. Graph 3).

6.1 Behaviour of methyl ethyl ketone after 4 days

The chemical's behaviour is identical to that of an instantaneous spill of 500 tonnes, with a wind speed of 3 m/s.



6.2 Concentrations of methyl ethyl ketone dissolved in the water column

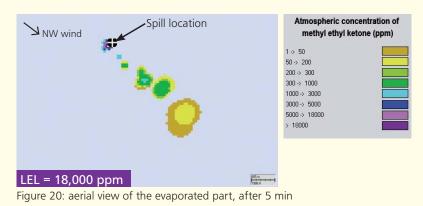
Figure 18: aerial view of dissolved part, after 5 h 15 min, at ebb tide

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a distance of up to 11.3 km south-west of the spill location. This distance will be reached 5 h 15 min after the spill. The depth affected at this time is around 35 m.

Concentrations higher than or equal to the PNEC are not found east of the spill location (at flood tide).

Throughout the duration of the scenario (4 days), the maximum concentration observed is approximately 190,000 mg/m³, 30 minutes after the spill, 200 m west-south-west of the spill location.

Methyl Ethyl Ketone Chemical Response Guide



6.3 Atmospheric concentrations of methyl ethyl ketone

The maximum distance travelled by the chemical at concentrations greater than or equal to the LEL (18,000 ppm) is 230 m south-west of the spill location. This distance is reached 5 minutes after the spill.

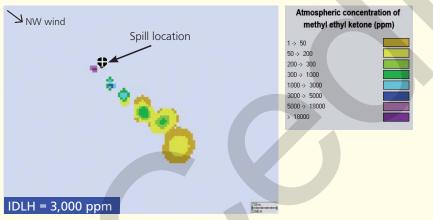


Figure 21: aerial view of the evaporated part, after 6 min

The maximum distance travelled by the chemical at concentrations greater than or equal to the IDLH (3,000 ppm) is 720 m south-south-east of the spill location. This distance is reached 6 minutes after the spill.

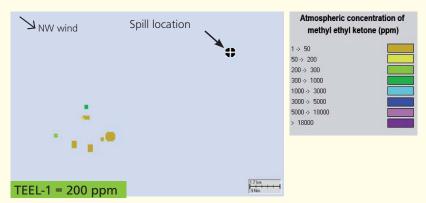


Figure 22: aerial view of the evaporated part, after 3 h 30 min

The maximum distance travelled by the concentrations greater than or equal to the TEEL-1 (200 ppm) is 9 km south-west of the spill location. This distance is reached 3 h 30 min after the spill.

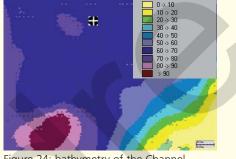
Results of the wreck scenario

A wreck is lying on the seabed 70 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 ethyl ketone over 48 hours from the tanks of the wreck.



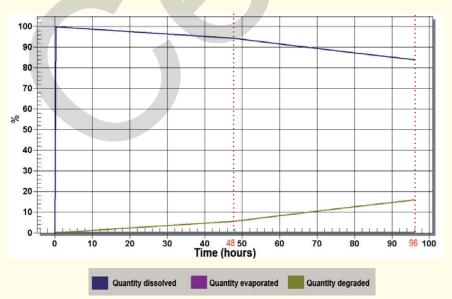
Figure 23: location of the wreck in the Channel



ASA bathymetry

Figure 24: bathymetry of the Channel

7. Spill of 1,000 tonnes of methyl ethyl ketone in the Channel, over 48 hours (approximately 20.8 t/h), from the wreck

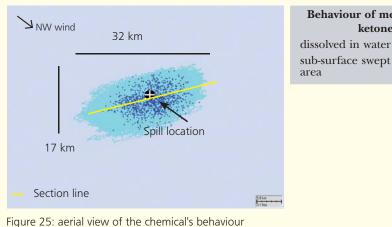


Graph 4: distribution by mass of a spill of 1,000 t over 48 h

Four days after the beginning of the spill, 85% of the chemical is found in the water column and 15% has been broken down. There is no evaporation.

Methyl Ethyl Ketone Chemical Response Guide

7.1. Behaviour of methyl ethyl ketone after 4 days



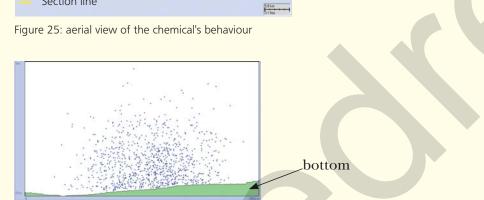


Figure 26: cross-section of the chemical's behaviour

The methyl ethyl ketone affects an area of 32 km from east to west and 17 km from north to south.

Behaviour of methyl ethyl

ketone

The chemical affects the entire depth of the water column.

7.2. Concentrations of methyl ethyl ketone dissolved in the water column

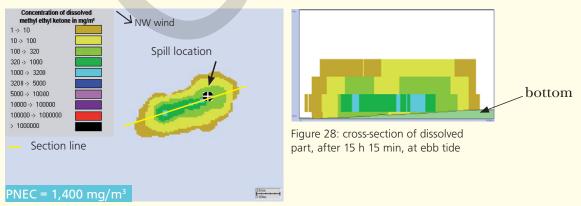
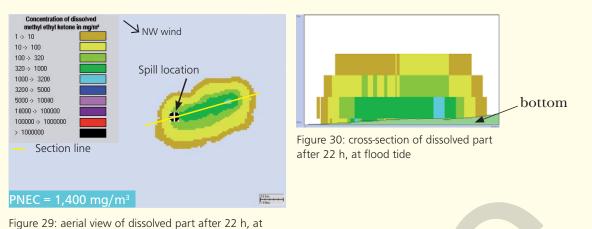


Figure 27: aerial view of dissolved part after 15 h 15 min at ebb tide

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a maximum distance of 7.7 km west-south-west of the spill location. This distance will be reached 15 h 15 minutes after the beginning of the spill. The methyl ethyl ketone affects a depth of 35 m from the bottom of the water column.



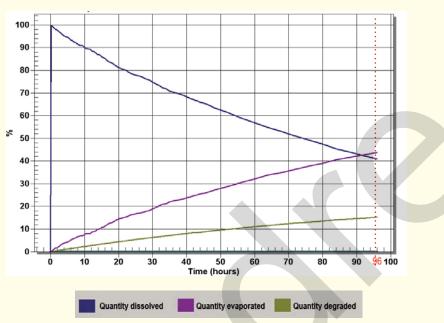
flood tide

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a distance of up to 9.3 km east-north-east of the spill location. This distance will be reached 22 hours after the beginning of the spill. The methyl ethyl ketone affects a depth of 45 m from the bottom of the water column.

Throughout the entire duration of the scenario (4 days), the maximum concentration observed in the water column is 9,200 mg/m³.

Results of the port scenario

8. Instantaneous spill of 1 tonne of methyl ethyl ketone in a port, with a 3 m/s NW wind



Graph 5: distribution by mass of an instantaneous spill of 1 t and 100 t, with a wind speed of 3 m/s $\,$

After 4 days, 40% of the initial quantity is in the water column while 45% has evaporated and 15% has been broken down.

8.1. Behaviour of methyl ethyl ketone after 4 days

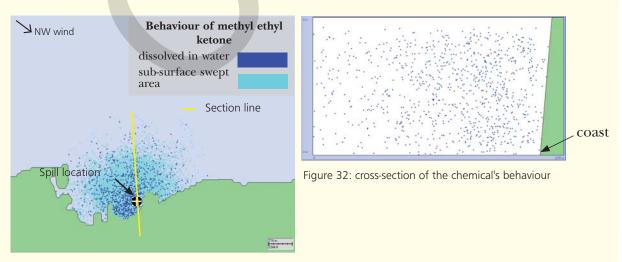
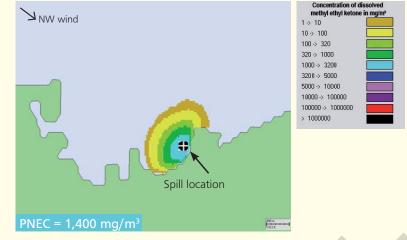


Figure 31: aerial view of the chemical's behaviour

After four days, the methyl ethyl ketone stretches over a radius of 3 km around the spill location. The chemical affects the entire depth of the water column. The same results are obtained for a spill of 100 t with a wind speed of 3 m/s.



8.2 Concentrations of methyl ethyl ketone dissolved in the water column

Figure 33: aerial view of dissolved part, after 3 h 45 min

Concentrations greater than or equal to the PNEC (1,400 mg/m³) will travel a distance of up to 300 m around the spill location. This distance will be reached 3 h 45 min after the spill. Throughout the entire duration of the scenario (4 days), the maximum concentration observed is 22,000 mg/m³, after 30 minutes.

8.3 Atmospheric concentrations of methyl ethyl ketone

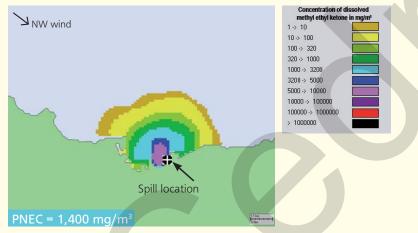
According to the CHEMMAP software, the atmospheric concentrations are lower than 50 ppm during the first minutes, and thereafter are too low to be detected.

9. Instantaneous spill of 100 tonnes of methyl ethyl ketone in a port, with a 3 m/s NW wind

The distribution by mass is identical to that of an instantaneous spill of 1 t (cf. Graph 5).

9.1 Behaviour of methyl ethyl ketone after 4 days

The behaviour is identical for an instantaneous spill of 1 t and 100 t (cf. Figures 31 and 32).

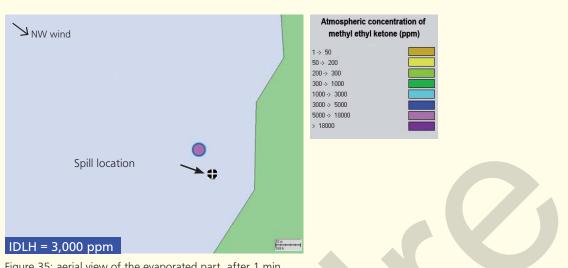


9.2 Concentrations of methyl ethyl ketone dissolved in the water column

Concentrations greater than or equal to the PNEC will travel a maximum of 1.9 km from the spill location. This distance is reached 3 days after the spill.

Throughout the entire duration of the scenario (4 days), the maximum concentration observed is $2,000,000 \text{ mg/m}^3$, reached after 30 minutes.

Figure 34: aerial view of dissolved part, after 3 days



9.3 Atmospheric concentrations of methyl ethyl ketone

Figure 35: aerial view of the evaporated part, after 1 min

The maximum distance travelled by the chemical at concentrations greater than or equal to the IDLH (3,000 ppm) is 80 m from the spill location. This distance is reached 1 minute after the beginning of the spill.

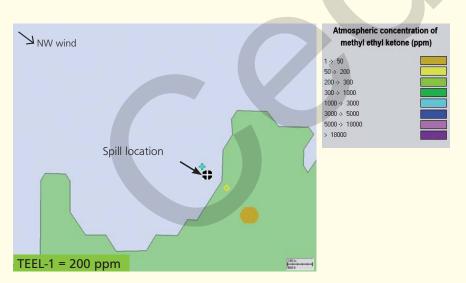
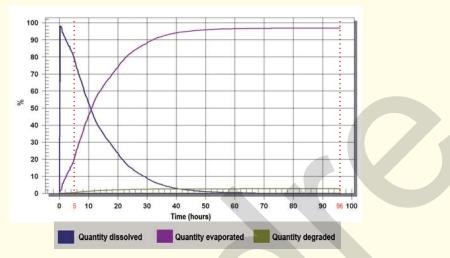


Figure 36: aerial view of the evaporated part, after 3 min

The maximum distance travelled by concentrations greater than or equal to the TEEL-1 (200 ppm) is 130 m south-east of the spill location. This distance is reached 3 minutes after the beginning of the spill.

Results of the river scenario

10. Spill of 1 t/h of methyl ethyl ketone for 5 hours, in a river, with a 3 m/s NW wind and a current speed of 0.74 m/s $\,$



Graph 6: distribution by mass of a spill of 1 t/h and 100 t/h for 5 hours with a wind speed of 3 m/s

Five hours after the beginning of the spill, 80% of the chemical has dissolved in the water column, while the rest has evaporated into the atmosphere. After 4 days, 1% of the initial quantity is in the water column while 96% has evaporated and 3% has been broken down.

10.1 Behaviour of methyl ethyl ketone after 4 days

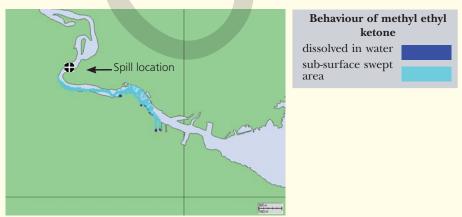


Figure 37: aerial view of the chemical's behaviour

The area liable to be affected by the methyl ethyl ketone is 7 km (\pm 1 km) downstream of the spill location.

The methyl ethyl ketone, pushed by the current, will affect the entire depth of the water column. The results obtained are the same for a spill of 100 t/h for 5 hours.

10.2 Concentrations of methyl ethyl ketone dissolved in the water column

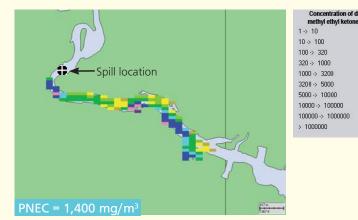


Figure 38: aerial view of dissolved part, after 9 hours

Concentrations greater than or equal to the PNEC $(1,400 \text{ mg/m}^3)$ will travel a distance of up to 3.5 km downstream of the spill location. This distance will be reached 9 hours after the beginning of the spill.

10.3 Atmospheric concentrations of methyl ethyl ketone

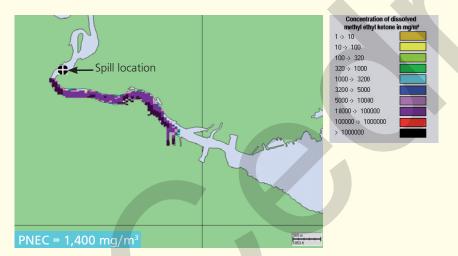
According to the CHEMMAP software, the atmospheric concentrations are lower than 50 ppm for 10 minutes, then less than 50 ppm sporadically along the river in terms of the dissolved concentrations greater than or equal to the PNEC.

11. Spill of 100 t/h of methyl ethyl ketone for 5 hours, in a river, with a 3 m/s NW wind and a current speed of 0.74 m/s

The distribution by mass is identical to that of a spill of 1 t/h for 5 hours (cf. Graph 6).

11.1 Behaviour of methyl ethyl ketone after 4 days

The behaviour is identical for a spill of 1 t/h and 100 t/h for 5 hours (cf. Figure 37).

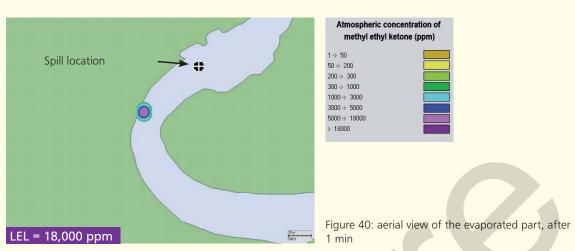


11.2 Concentrations of methyl ethyl ketone dissolved in the water column

Figure 39: aerial view of dissolved part, after 5 h 45 min

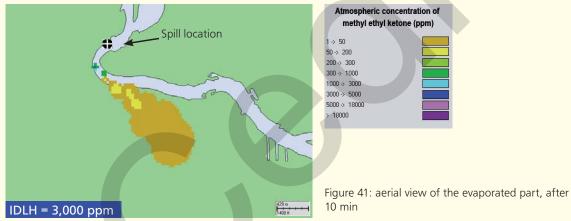
Concentrations greater than or equal to the PNEC $(1,400 \text{ mg/m}^3)$ will travel a distance of up to 3.5 km downstream of the spill location. This distance will be reached 5 h 45 min after the beginning of the spill.

Note: Concentrations greater than or equal to the PNEC are present throughout the scenario (4 days).



11.3 Atmospheric concentrations of methyl ethyl ketone

The maximum distance travelled by the chemical at concentrations greater than or equal to the LEL (18,000 ppm) is 250 m south-west of the spill location. This distance is reached 1 minute after the beginning of the spill.



The maximum distance travelled by the chemical at concentrations greater than or equal to the IDLH (3,000 ppm) is 360 m south-west of the spill location. This distance is reached 10 minutes after the beginning of the spill.

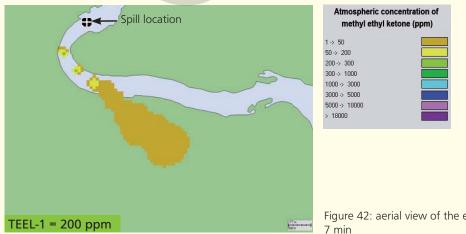


Figure 42: aerial view of the evaporated part, after 7 min

The maximum distance travelled by concentrations greater than or equal to the TEEL-1 (200 ppm) is 450 m south-south-west of the spill location. This distance is reached 7 minutes after the beginning of the spill.

Consumption scenarios

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



C3

D

Spill response

Experience feedback	D1
Examples of spills	D2
Response recommendations	D3
Response techniques	D4
Choosing Personal Protective Equipment (PPE)	D5
Measuring devices and waste treatment	D6

Experience feedback

(CEDRE, 2006; MARINE NATIONALE, 2006)

Sinking of the *IEVOLI SUN* (France, October 2000)

The incident

On Monday 30 October 2000 at 4:30 am, the MRCC Corsen received a distress call from an Italian-registered chemical tanker, the *levoli Sun*. The ship was 45 nautical miles north of Batz Island in Brittany. It was travelling from Fawley (UK) to Barcelona with 6,000 t of chemicals onboard, including 1,000 t of methyl ethyl ketone. The captain reported a leak in the ship's double hull, at the bow.

The French maritime authorities sent the tug *Abeille Flandre*, the crew of the *Super Frelon* helicopter and an assessment team on site. At 8:05 am, they observed the severe state of the ship and proceeded to airlift the crew to safety. At 12:00 noon, the authorities activated the Polmar sea contingency plan. Upon arrival, the *Abeille Flandre* discovered a spill at the front of the ship (styrene slick).

Given the sea and weather conditions, the risk of grounding causing a major spill on the Breton shoreline rapidly became apparent. This survey confirmed that the chemical tanker was whole and that it was lying on its left side, 70 m deep.

On 8 November, the *Northern Prince* was mobilised with a ROV to conduct a complete survey of the wreck. It was supported by the specialised German vessel *Neuwerk*, mobilised by the French authorities through the Bonn Agreement, which surveyed the zone to detect any contamination during the operation. No leaks of methyl ethyl ketone were detected.

Neutralisation operations considered

The neutralisation of the wreck was studied by a steering committee and a college of experts from 9 November 2000. In-depth discussions, led by the French Secretary-General of the Sea, were held between national experts and the shipowner's experts, on the technical solutions to respond to the risk generated by this wreck.

Upon agreement by the French and English authorities, the shipowner and his P&I Club signed a contract with *Smit Tak Co*, on 10 April 2001, to deal with the *levoli Sun*'s cargo.

After assessing the possible options, the *levoli*

Sun was taken in tow by the Abeille Flandre. On 31 October, at 9:00 am, the *levoli Sun* sank two-thirds of the way to shelter at Cotentin, 9 nautical miles north of Les Casquets (12 NM from Aurigny and 20 NM from the tip of La Hague), in waters 70 m deep.

State of the wreck

The wreck was located on 1st November by sonar, and subsequently by the *Poisson Auto Propulsé* (PAP) of the French Navy minehunter *Céphée*.



Several treatment options were considered:

- controlled release of the chemical into the sea
- pumping of the chemical from the wreck into another vessel
- leaving the chemical in the tanks of the wreck
- refloating the wreck to empty it.

The French authorities accepted for the methyl ethyl ketone to undergo controlled release. This method promoted neutralisation given the compatibility between the volume of pollutant (or release rate) and its dilution possibilities in the environment.

Behaviour of methyl ethyl ketone

The dissolution kinetics of methyl ethyl ketone were studied in a 3.5 m high by 16 cm in diameter plexiglass column filled with seawater at *Cedre*. The chemical was injected using a pump at various depths and rates. Organol red dye was added so as to visualise the behaviour of the methyl ethyl ketone.

At slow rates, dissolution was relatively rapid and complete. A decrease in the surface area and number of bubbles confirmed this dissolution as the chemical rose. A high release rate of methyl ethyl ketone could cause a surface slick to form, which could potentially affect the environment and responders.

The chemical was therefore released slowly, at a rate of less than 100 m^3/h .

Controlled release

Operations began on 12 April 2001 with the arrival of the *Smit Pioneer*.

The controlled release of the methyl ethyl ketone was carried out in 5 stages:

- 1. identification of tanks
- 2. installation of base plates and drilling of outer hull
- 3. inspection of the area between the hulls
- 4. drilling of the inner hull
- 5. direct release of the chemical at a controlled rate.

The operation was completed on 7 May, without measurable consequences for the environment. The exclusion zone for this chemical was 1 km.

Expert committees

- Expert committee under the French Ministry in charge of Ecology on the risks in terms of aerial dispersion, food, flora and fauna
- Inter-ministerial steering committee: Secrétariat Général de la Mer
- "Wreck management" expert group:
 Secrétariat Général de la Mer
- DRIRE/DDE think tank on the storage of recovered substances
- Constitution of a databank on the analyses and measures taken: ZDO/Cedre
- Operator protection: note by the Toxicovigilance Unit at Rennes Poison Control Centre
- European expert group.

Examples of spills

Plastic parts factory (France, 2006)

(BARPI, 2006)

On 11 January 2006, in Saint-Marcellin, France, a 200 litre metal drum containing spray booth cleaning solvents exploded in a factory in which plastic parts for the automotive industry were painted and varnished. The consequences were grim: 8 people injured, including 2 badly, and 1 person killed. The drum, containing 50% methyl ethyl ketone and 50% butyl acetate, was projected upwards and hit the ceiling. The factory personnel managed to control the fire which followed the explosion. Around 100 firemen, medical teams and policemen arrived on site. The water used to extinguish the fire was collected. The operator was required to provide an accident report describing how the factory functioned, as well as the causes of the accident and the human and environmental consequences. The affected line was not authorised to recommence. work until an inspection report had been established including a specific study on the electrostatic risks of the future set-up of the line.

Road freight transport (France, 2005) (BARPI, 2005)

On 14 April 2005, in Espeluche, France, a lorry transporting 16,000 litres of methyl ethyl ketone overturned due to the driver taking ill. A fire broke out but was rapidly extinguished with a powder extinguisher. The driver was slightly injured. A leak of diesel was contained with a dyke. The lorry was transporting a container of 20 pallets of 4 drums of methyl ethyl ketone, a highly flammable product. Explosivity measurements were between 10 and 20% with a significant odour indicating a leak. As the drums could not be transported in their current condition, the fire brigade covered them with foam to lift the lorry. A sorbent boom was set up around the vehicle. Once upright, the lorry was moved and a 150 m safety zone was set up.

Leak in a heat exchanger (Canada,

2004) (ENVIRONMENT CANADA, 2005)

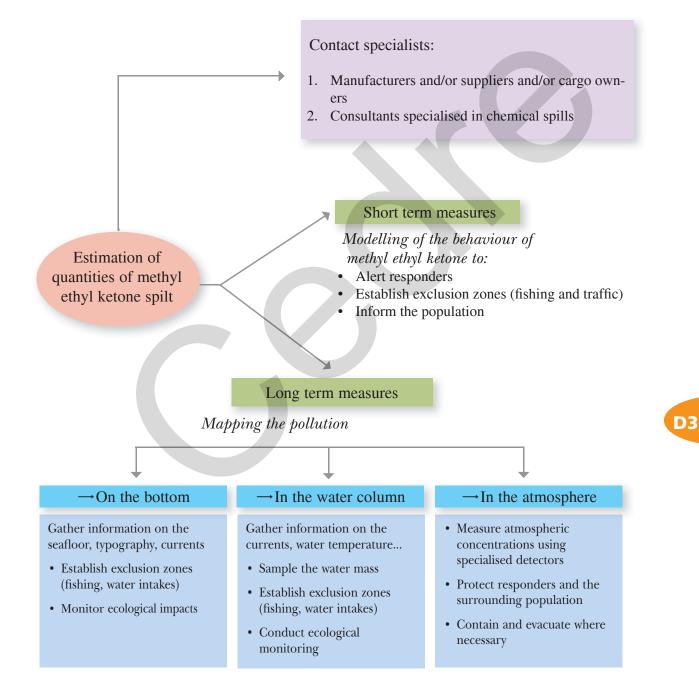
In February 2004, a leak of ketone in a heat exchanger belonging to Pétrolier Impérial contaminated 170,000 litres of cooling water discharged into the St Clair River in Ontario. Two chemicals were involved: methyl ethyl ketone and methyl isobutyl ketone. A study by the Investigations and Enforcement Branch of the Ministry of the Environment estimated that 85,700 kg of ketone had been spilt. Analyses confirmed that the contaminated water discharged had made the outflow deleterious for a short period. The company was fined \$300,000 after having pleaded guilty to charges of breaching the Fisheries Act.

Wholesale trade of chemicals (France, 1999) (BARPI 1999)

On 23 March 1999 in Saint-Herblain, France, during the loading of a lorry at a chemical wholesalers, a 48 kg drum of methyl ethyl ketone fell from a pallet and was crushed by a power lift truck. A spark caused an explosion and a fire which spread to other drums of solvents. The internal contingency plan was activated. Vast emergency means, including a mobile chemical response unit, were mobilised to support the internal health and safety team. The incident was controlled within 20 minutes. The water used to extinguish the fire was collected in the existing retention tanks. No environmental impact was detected. The damaged drums were evacuated for disposal at an authorised treatment centre.

Response recommendations

Diagram showing response actions in the event of a spill



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

As an immediate prevention measure, evacuate the area within a minimum radius of 50 m around the site of the spill or leak. Response may be envisaged if the following precautions are taken:

- Approach the accident area from upwind equipped with personal protective equipment (PPE), self-contained breathing apparatus (SCBA) as mentioned in the chapter "Choosing Personal Protective Equipment", explosimeters and apparatus to measure methyl ethyl ketone in air.
- Avoid all sources of ignition, sparks and heating, and only use fireproof equipment.
- Ventilate closed environments before entering and avoid depressions in the ground.

Emergency measures in the event of

a leak or spill (Arkema SDS, 2008; CEFIC, 2005; CANUTEC, 2008)

- For a major spill, consider initially evacuating within a distance of 300 m downwind of the spill.
- 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.
- Control the explosive limits.
- On land, prevent infiltration into waterways, sewers, basements and closed spaces.
- A vapour suppressing foam can be used to stop evaporation.
- Absorb or cover with dry earth, sand or some other non-combustive material and transfer into containers.
- Use non-sparking tools to collect absorbed material.

Emergency measures in the case of a

tank fire (Arkema SDS, 2008; CANUTEC, 2008)

- If a tank or trailer is involved in a fire, consider initially evacuating within 800 m in every direction. People in the nearby area should remain indoors with all doors and windows closed and stop all ventilation.

In the event of a minor fire

- Eliminate all sources of sparks and ignition, do not smoke.
- Cool the containers/tanks by spraying with water.
- Recommended fire extinguishers: dry chemical powder, CO_2 , water spray and alcoholresistant foam.

In the event of a major fire

- Recommended fire extinguishers: water spray or mist or alcohol-resistant foam.
- Remove containers from fire area if this can be done safely.
- Eliminate all sources of sparks and ignition, do not smoke.
- Cool the containers/tanks by spraying with water, do not use a solid water jet.
- Spray water to beat vapours down towards the ground and dilute the cloud of dangerous gases in the atmosphere.
- Wear protective clothing and self-contained breathing apparatus.
- Prevent the product from entering sewers and basements.
- Do not attempt to extinguish a fire that is too far on.

Tank, trailer or wagon fire.

- Fight the fire at a maximum distance or use remote controlled hoses or water canons.
- Cool the containers with plenty of water for a long time after the fire has been extinguished.
- Move away if the hissing of the safety mechanisms becomes louder or if the tank discolours.
- Always stay well away from a tank swallowed up in flames.
- For a major fire, use remote controlled hoses or water canons. Where possible, move away and leave to burn.

Response techniques

Response

(ARKEMA SDS, 2008; FICHES RÉFLEXES D'INTERVENTION ANTI-POLLUTION "PRODUIT DANS LA COLONNE D'EAU ET SUR LES FONDS" & "ATMOSPHÈRE ET SURFACE", CEDRE, 2004; FICHES GUIDES DE DÉCISION N°2 & 3, CEDRE, 2004; FICHES STRATÉGIES ET MOYENS N°1, 2, 3, 4, 5, 6, 8, 10, 12, 13, 14, CEDRE, 2004)

BEWARE OF METHYL ETHYL KETONE VAPOURS.

On land

Before any response actions, the atmospheric concentrations must be tested and checked against the explosive limits. It is essential to intervene as rapidly as possible in order to prevent any polluted water from reaching the sewer system or a waterway, by containing the spill with bunds made of earth, sand or other materials or using specialised sorbents. These bunds can be completed with a layer of foam to reduce evaporation of the chemical. This product must not be released into the environment. The product recovered, as well as all waste, must be eliminated by incineration in compliance with local and national regulations.

In inland waters

As methyl ethyl ketone is highly soluble, it is difficult to respond to a spill in water.

Where possible, deflect polluted waters immediately after the spill for subsequent storage and treatment.

If polluted waters cannot be deflected, a possible response option involves diluting the methyl ethyl ketone.

Dilution may come about naturally (for instance in the case of a small stream flowing into a larger river with a faster flow).

Whatever the volume spilt, mark the progress of the pollution front using fluorescein or

rhodamine and regularly measure the concentration of the product in the water mass. Water intakes must be closed.

Accumulation of the methyl ethyl ketone can also be prevented by promoting dilution (agitation of the water mass by propellers).

Aquatic toxicity should be monitored and assessed or measured.

At sea

Methyl ethyl ketone is a colourless liquid; it is therefore difficult to locate a slick on water. Response actions will be limited to stopping the leak, controlling the vapour cloud, preventing spreading and, if possible, reducing the dissolution, of the substance. The extent of the gas plume can be simulated using provisional models with in situ measurements using gas detectors.

Transshipment

- Do not use air for transfers.
- Take precautionary measures against static discharges.
- Eliminate all sources of sparks or ignition. Do not smoke.
- Use only fireproof equipment.
- Avoid transfer the product with fireproof pumps into plastic storage tanks (polyethylene, polypropylene, butyl).
- Never enter tanks.

Choosing Personal Protective

Equipment (PPE)

Ensure maximum protection in the case of high or unknown concentrations of methyl ethyl ketone.

Choosing breathing apparatus (CCOHS, 1998)

- Up to 3,000 ppm (IDLH) choose between:
 - an organic vapour cartridge respirator
 - a powered air-purifying respirator with organic vapour cartridge
 - a gas mask with organic vapour canister
 - full-facepiece SCBA.
- Emergency or planned entry into an area in which concentrations are unknown or IDLH:
 - positive pressure SCBA or SAR with full facepiece
 - auxiliary positive pressure SCBA.
- Escape:
 - gas mask with organic vapour canister
 - escape-type SCBA.

Choosing protective clothing (Arkema SDS, 2008; CCOHS, 1998; CSST, 2004)

- Eyes: watertight cup goggles or a watertight mask are recommended if there is a risk of splashes. In certain cases (e.g. corrective glasses), a face shield may be recommended.
- Hands: wear gloves made from either:
 - PVC with a permeation index according to EN 374 with a breakthrough time of over 10 minutes
 - Multilayer polyethylene/vinyl alcohol and ethylene/polyethylene
 - Polyvinyl alcohol (PVA)
 - Linear Low Density Polyethylene (LLDPE). A breakdown test was not carried out for this chemical. However, the breakthrough time being > 8 hours, the breakdown ranking should be good or excellent. The permeation time is greater than 480. Its permeability resistance is excellent: 0 to 1/2 drop per hour

passes through the glove.

• Clothing: wear protective cotton overalls. Salopettes, boots and/or other cotton protective clothing resistant to the chemical may be necessary.

Recommendations for use in the

event of a spill (INRS, 2003; FINGAS M., 2001)

Self-contained breathing apparatus (SCBA) provides the best protection as it supplies air from an uncontaminated source. The user is independent of the surrounding atmosphere.

Certain facial features such as a scar, facial hair (even two day stubble), a thin face-shape or glasses may prevent the mask from being watertight. 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.

Measures to take after using PPE in a spill situation (ARKEMA SDS, 2008; CCOHS, 1997)

Used PPE should be placed in closed containers, then washed with soap and water, or even placed with the waste for incineration according to local and national regulations.

Measuring devices and waste treatment

Methods of detection and measurement in air (INRS, 2003)

- Detector tubes: Dräeger acetone 100/b; Gastec methyl ethyl ketone 152; MSA acetone.
- Sampling by passive diffusion (badge) or pumping of the atmosphere onto a tube with a carbonate molecular sieve. Desorption with carbon disulphide. Assay by gas phase chromatography, detection by flame ionisation.

Recommendations for elimination (ARKEMA SDS, 2008)

- Eliminate the product and packaging by incineration in compliance with local and national regulations.
- Do not release methyl ethyl ketone into the environment.
- Clean the recipient with water and recover waste water for subsequent treatment.

Manufacturers

ARKEMA, Exxon Chemical, Shell France...

Further information

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Glossary

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.

Auto-ignition temperature

Minimal temperature at which vapours ignite spontaneously.

Bioaccumulation

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

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.

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.

Catalyst

Substance that increases the speed of a chemical reaction. Catalysts participate in reactions but are neither products nor reactants and therefore do not appear in the chemical equation.

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.

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 (EC₅₀)

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

Emergency Response Planning Guidelines (ERPG)

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

<u>ERPG1</u>: 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.

<u>ERPG2</u>: 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.

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

Exposure limit value (ELV)

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

Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately when in contact with a flame.

Foam

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

Henry's law constant

Value indicating a substance's volatility.

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 concentration (LC_{50})

Statistically deduced concentration of a substance which will cause the death of 50% of animals exposed during or following a given period of exposure.

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.

Mean exposure value (MEV)

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

Median lethal concentration (LC₅₀)

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

Melting point

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

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.

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).

<u>Level A</u>: 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).

<u>Level C</u>: 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

The rate of evaporation expresses the relationship between the time that a product takes to evaporate and the time taken by a control substance of an equal volume. This rate varies with the nature of the product and the temperature. Diethyl ether, for instance, is the reference product for which most data is available.

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

 \rightarrow 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.

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 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.

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

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

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

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
ADN	European Agreement concerning the International Carriage of Dangerous Goods by
	Inland Waterways
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
AEGL	Acute Exposure Guideline Level
AIHA	American International Health Alliance
ALOHA	Areal Locations of Hazardous Atmospheres
BCF	Bio Concentration Factor
BLEVE	Boiling Liquid Expanding Vapour Explosion
CANUTEC	Canadian Transport Emergency Centre
CAS	Chemical Abstracts Service
CCOHS	Canadian Centre for Occupational Health and Safety
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
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
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
GESAMP	Group of Experts on Scientific Aspects of Marine Environmental Protection
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IATA	International Air Transport Association
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
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
MCA	Maritime and Coastguard Agency
MEEDDM	Ministère de l'écologie, de l'énergie, du Développement durable et de la Mer
MEK	Methyl Ethyl Ketone
MEV	Mean Exposure Value
MP	Marine Pollutant
MUC	Maximum Use Concentration
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
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
RID	International carriage of dangerous goods by rail
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
SCBA	Self-Contained Breathing Apparatus
SDS	Safety Data Sheet
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
TEEL	Temporary Exposure Limit
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
TRANSAID	Agreement between UIC (French Chemical Industry Association) & the French Government
TROCS	Transport of Chemical Substances - database created by REMPEC
UEL	Upper Explosive Limit
VHF	Very High Frequency

Useful websites

ARKEMA Available at http://www.arkemagroup.com 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 CHRIS (Chemical Hazards Response Information System) Available at http://www.chrismanual.com/findform.htm CSST (Commission de la Santé et de la Sécurité du Travail) Available at http://www.reptox.csst.qc.ca ECB (European Chemicals Bureau) Available at http://ecb.jrc.it EFMA (European Fertilizer Manufacturer Association) Available at http://www.efma.org HSDB (Hazardous Substances DataBank) Available at http://toxnet.nlm.nih.gov ICSC (International Chemical Safety Cards) Available at http://www.cdc.gov/niosh/ipcs/nicstart.html INRS (Institut National de Recherche et de Sécurité) Available at http://www.inrs.fr NIOSH (National Institute for Occupational Safety and Health) Available at http://www.cdc.gov/niosh NPI (National Pollutant Inventory) Available at http://www.npi.gov.au TRANSPORT CANADA, CANUTEC - Emergency Response Guidebook 2008 Available at http://www.tc.gc.ca/eng/canutec/guide-menu-227.htm

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ANNEXES

Annex 1: Summary and additional physical and toxicological data

Annex 2: Fax format data card

Annex 3: Classification of noxious liquid substances

ANNEX 1: SUMMARY AND ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification

CAS n°: 78-93-3 EC n° (EINECS): 201-159-0 UN n°: 1193 INDEX n°: 606-002-00-3 Class: 3

Physical data

Melting point: - 86°C - 86.6°C Boiling point: 79.6°C

Critical temperature: 261.4° C Relative density (water = 1) at 20° C: 0.805 g/cm^{3} Relative vapour density (air = 1) at 20° C: 2.5Relative density of air/vapour mixture (air=1) at 20° C: 1.1 Solubility in seawater at 25° C: 158 g/l Solubility in freshwater at 10° C: 353 g/l at 20° C: 271 g/l at 25° C: 223 g/l Solubility in solvents:

Soluble in most organic solvents Vapour pressure/tension: at 20°C: 10.1 kPa at 25°C: 13.3 kPa at 41.6°C: 26.7 kPa Critical pressure: 41 atm

Viscosity at 20°C: 0.41 mPa.s Olfactory threshold: 5.4 ppm Evaporation rate (ether=1): 2.6 2.7

Diffusion coefficient in water: no data available. Diffusion coefficient in air: no data available. Henry's law constant: 5.66 Pa.m³/mole 5.59×10⁻⁵ atm.m³/mole Molar mass: 72.10 g/mol Density at 20°C: 805 kg/m³

Vapour density at 20°C: 3.11 kg/m³ Surface tension at 20°C: 0.246 mN/cm (ARKEMA SDS, 2008; ICSC, 1998; HSDB, 1997) (CSST, 2004; DIPPR, 2006) (INRS, 2003; ARKEMA SDS, 2008; CHRIS, 1999; ECB, 2000; DIPPR, 2006; CSST, 2004) (DIPPR, 2006) (INRS, 2003; ARKEMA SDS, 2008; CSST, 2004; HSDB, 1997) (INRS, 2003; CHRIS, 1999)

(ICSC, 1998) (CEDRE, 2001) (ECB, 2000) (ARKEMA SDS, 2008) (CEDRE, 2001)

(ARKEMA SDS, 2008) (ARKEMA SDS, 2008; ECB, 2000) (INRS, 2003) (INRS, 2003) (HSDB, 1997; DIPPR, 2006) (HSDB, 1997) (ARKEMA SDS, 2008) (CSST, 2004) (HSDB, 1997; INRS, 2003)

(ARKEMA SDS, 2008; ECB, 2000)

(ARKEMA SDS, 2008; INRS, 2003; DIPPR, 2006) (ARKEMA SDS, 2008) (ARKEMA SDS, 2008) (HSDB, 1997)

Toxicological data

Threshold toxicological values

Occupational exposure values (INRS, 2003; CHRIS, 1999; HSDB, 1997)

MEV: 200 ppm = 590 mg/m³ ELV: 300 ppm = 885 mg/m³ TLV-TWA: 200 ppm = 590 mg/m³ TLV-STEL: 300 ppm = 885 mg/m³ TLV-ceiling: no data available.

Risk management values for the population (NIOSH, 2003; US department of energy's chemical safety program)

IDLH: 3,000 ppm = 8,850 mg/m³ TEEL-0: 200 ppm = 590 mg/m³ TEEL-1: 200 ppm = 590 mg/m³ TEEL-2: 2,700 ppm = 7,965 mg/m³ TEEL-3: 4,000 ppm = 11,800 mg/m³ ERPGs: no data available.

Proposed AEGLs (US EPA, 2007)

Duration	10 min	30 min	1 hour	4 hours	8 hours
AEGL-1 (ppm)	200	200	200	200	200
AEGL-2 (ppm)	4,900	3,400	2,700	1,700	1,700
AEGL-3 (ppm)	**	**	4,000	2,500	2,500

**AEGL-3 - 10 min/30 min = 10,000 ppm

General toxicity

Acute human toxicity (ARKEMA SDS, 2008; ICSC, 1998)

Exposure to this product can cause various effects.

- By inhalation: cough, dizziness, drowsiness, headache, nausea, vomiting.
- By skin contact: light irritation.
- By eye contact: irritation, redness, pain. The vapours are irritating to the eyes.

- By ingestion: loss of consciousness, cough, dizziness, drowsiness, headache, nausea, vomiting. **Chronic human toxicity** (ARKEMA SDS, 2008; ICSC, 1998; INRS, 2003; CHRIS, 1999; CSST, 2004)

- Repeated or prolonged exposure of the skin can cause dryness or cracking, dermatitis and whitening of the skin.
- Repeated or prolonged exposure can cause irritation of the skin and dermatosis due to the product's degreasing properties.
- Methyl ethyl ketone can be a central nervous system depressant at very high concentrations. A study reported that a worker exposed to methyl ethyl ketone by inhalation and skin contact for at least 2 years showed reversible symptoms such as shaking, malcoordination (dizziness) and involuntary muscle movements.

Specific effects (ICSC, 1998, INRS, 2003; CSST, 2004; CCOHS, 2008)

Effects on reproduction: presence of congenital malformations in animals. Methyl ethyl ketone passes through the placenta in humans. Data does not allow adequate evaluation of postnatal effects. Genotoxic effects: no data available.

Carcinogenic effects: absence of cancer in workers. The IARC has not assessed this product's carcinogenicity.

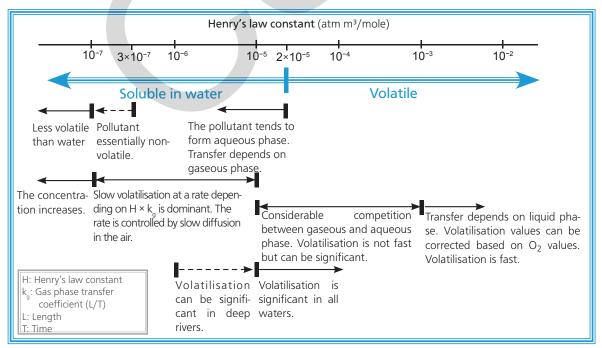
Ecotoxicological data

Acute ecotoxicity (ECB, 2000; HSDB 1997; ARKEMA SDS, 2008)

5 (
Fish (Pimephales promelas) Fish (Lepomis macrochirus)	LC ₅₀ (96 h) LC ₅₀ (24 h) LC ₅₀ (96 h)	3,200 mg/l 5,640 mg/l 4,467 mg/l
Fish <i>(Gambusia affinis)</i>	LC ₅₀ (96 h) NOEC (96 h)	5,600 mg/l 3,200 mg/l
Fish (Carassius auratus) Fish (Leuciscus idus) Fish (Lebistes reticulatus)	LC ₅₀ (24 h) LC ₅₀ (48 h) LC ₅₀ (24 h)	2,400 mg/l 4,600 mg/l 5,700 mg/l
Fish (Cyprinodon variegatus)	LC ₅₀ (24 h)	> 400 mg/l
Crustacean (Daphnia magna)	LC ₅₀ (24 h) LC ₅₀ (48 h) EC ₅₀ (48 h)	8,890 mg/l 1,382 mg/l 5,091 mg/l > 520 m g/l
	NOEC (48 h)	< 70 mg/l
Crustacean (Artemia salina)	LC ₅₀ (24 h)	1,950 mg/l
Bacterium (Pseudomonas putida) Bacterium (Chilomonas paramaecium) Bacterium (Entosiphon sulcatum) Bacterium (Photobacterium phosphoreum)	EC_{3} (16 h) EC_{5} (48 h) EC_{5} (72 h) EC_{50} (5 min)	1,150 mg/l ≥ 2 982 mg/l ≥ 190 mg/l 5,100 mg/l
Chronic ecotoxicity		

Alga (Scenedesmus quadricauda)	EC ₃ (7 d)	≥ 4,300 mg/l
Alga (Microcystis aeruginosa)	EC ₃ (7 d)	≥ 1,200 mg/l

PNEC (Predicted No-Effect Concentration): According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated PNEC_{water} is 1.4 mg/l (1,400 mg/m³). A safety factor of 1,000 is applied to the lowest value of the three trophic levels.



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

ANNEX 2: FAX FORMAT DATA CARD

C₄H₈O

Methyl Ethyl Ketone

2-Butanone; Butanone; MEK; Methyl acetone; Butan-2-one; Methylpropane-2; Butanone-2; 2-oxobutane; 3-Butanone; Ethyl methyl ketone; Methylethylketone; Ethylmethylketone. CAS n°: 78-93-3 EC n° (EINECS): 201-159-0 INDEX N°: 606-002-00-3 UN n°: 1193 Class: 3

First aid information

Immediately remove all soiled or spotted clothes with suitable gloves.

Intoxication by inhalation

- Move the victim into the open air and lie them down.
- Supply oxygen or apply artificial respiration if necessary.
- Consult a doctor if effects persist.
 Skin contact
- Remove contaminated clothing.
- Immediately flush under water.
- Flush again if irritation persists.

- Eye contact
- Flush with water for 20 minutes holding the eyelids wide open.
- (remove contact lenses if possible)
- Immediately consult an ophthalmologist.
- Intoxication by ingestion
- Rinse out the mouth.
- Drink large quantities of water.
- Do not induce vomiting.
- Consult a doctor.

Physical data

Olfactory threshold: 5.4 ppm Molar mass: 72.10 g/mol Melting point: - 86°C / - 86.6°C Boiling point: 79.6°C Critical temperature: 261.4°C Critical pressure: 41 atm Relative density (water = 1) at 20°C: 0.805 g/cm³ Relative vapour density (air = 1) at 20°C: 2.5 Relative density of air/vapour mixture (air=1) at 20°C: 1.1 Solubility in seawater at 25°C: 158 g/l Solubility in fresh water at 10°C: 353 g/l at 20°C: 271 g/l at 25°C: 223 g/l Solubility in solvents: soluble in most organic solvents Viscosity at 20°C: 0.41 mPa.s Henry's law constant: 5.66 Pa.m³/mol -5.59×10⁻⁵ atm./mol Evaporation rate (ether=1): 2.6 / 2.7 Surface tension: 0.246 mN/cm at 20°C Vapour pressure/tension: at 20°C: 10.1 kPa at 25°C: 13.3 kPa at 41.6°C: 26.7 kPa Vapour density at 20°C: 3.11 kg/m³ Density at 20°C: 805 kg/m³

EU classification:



F: Highly flammable



- R11: Highly flammable.
- R36: Irritating to eyes.
- R66: Repeated exposure may cause skin dryness or cracking.
- R67: Vapours may cause drowsiness and dizziness.
- S2: Keep out of reach of children
- **S9:** Keep container in a well ventilated place.
- **S16:** Keep away from sources of ignition No smoking.

Toxicological data

Acute human toxicity

Exposure to this product can cause various effects.

- By inhalation: cough, dizziness, drowsiness, headache, nausea, vomiting.
- By skin contact: light irritation.
- By eye contact: irritation, redness, pain. The vapours are irritating to the eyes.
- By ingestion: loss of consciousness, cough, dizziness, drowsiness, headache, nausea, vomiting.

Chronic human toxicity

- Repeated or prolonged exposure of the skin can cause dryness or cracking, dermatitis and whitening of the skin.
- Repeated or prolonged exposure can cause irritation of the skin and dermatosis due to the product's degreasing properties.
- Methyl ethyl ketone can be a central nervous system depressant at very high concentrations. A study reported that a worker exposed to methyl ethyl ketone by inhalation and skin contact for at least 2 years showed reversible symptoms such as shaking, malcoordination (dizziness) and involuntary muscle movements.

Specific effects

Effects on reproduction: presence of congenital malformations in animals. Methyl ethyl ketone passes through the placenta in humans. Data does not allow adequate evaluation of postnatal effects. Genotoxic effects: no data available.

Carcinogenic effects: absence of cancer in workers. The IARC has not assessed this product's carcinogenicity.

Threshold toxicological values

Occupational exposure values: MEV: 200 ppm = 590 mg/m³ ELV: 300 ppm = 885 mg/m³ TLV-TWA (ACGIH): 200 ppm = 590 mg/m³ TLV-STEL (ACGIH): 300 ppm = 885 mg/m³ TLV-ceiling (ACGIH): no data available. Risk management values for the population: IDLH: 3,000 ppm = 8,850 mg/m³ TEEL-0: 200 ppm = 590 mg/m³ TEEL-1: 200 ppm = 590 mg/m³ TEEL-2: 2,700 ppm = 7,965 mg/m³ TEEL-3: 4,000 ppm = 11,800 mg/m³ ERPGs: no data available.

AEGLs of methyl ethyl ketone with **AEGL-3: 10 min/30 min = 10,000 ppm

Duration	10 min	30 min	1 hour	4 hours	8 hours
AEGL-1 (ppm)	200	200	200	200	200
AEGL-2 (ppm)	4,900	3,400	2,700	1,700	1,700
AEGL-3 (ppm)	**	**	4,000	2,500	2,500

Ecotoxicological data Acute ecotoxicity LC₅₀ (96 h) Pimephales promelas 3,200 mg/l Fish LC₅₀ (24 h) LC₅₀ (96 h) LC₅₀ (96 h) Lepomis macrochirus 5,640 mg/l 4,467 mg/l Gambusia affinis 5,600 mg/l NOEC (96 h) 3,200 mg/l Carassius auratus 2,400 mg/l LC₅₀ (24 h) LC₅₀ (48 h) Leuciscus idus 4,600 mg/l LC₅₀ (24 h) 5,700 mg/l Lebistes reticulatus Cyprinodon variegatus LC₅₀ (24 h) > 400 mg/l LC₅₀ (24 h) 8,890 mg/l Crustacean Daphnia magna LC₅₀ (48 h) EC₅₀ (48 h) 1,382 mg/l 5,091 mg/l > 520 g/l NOEC (48 h) < 70 mg/l Artemia salina LC₅₀ (24 h) 1,950 mg/l Pseudomonas putida EC₃ (16 h) 1,150 mg/l Bacterium EC_{5} (48 h) Chilomonas paramaecium ≥ 2,982 mg/l Entosiphon sulcatum EC₅ (72 h) ≥ 190 mg/l Photobacterium phos-EC₅₀ (5 min) 5,100 mg/l phoreum Chronic ecotoxicity Alga Scenedesmus quadricauda EC₃ (7 d) ≥ 4,300 mg/l ≥ 1,200 mg/l Microcystis aeruginosa EC₃ (7 d)

PNEC (Predicted No-Effect Concentration): According to the Technical Guidance Document corresponding to commission regulation (EC) 1488/94 on risk assessment of chemical substances, the calculated $PNEC_{water}$ is 1.4 mg/l (1,400 mg/m³). A safety factor of 1000 is applied to the lowest value of the three trophic levels.

Persistence in the environment

Volatilisation

According to Henry's law constant, at 25°C, the evaporation half-life of methyl ethyl ketone in a 1 m deep river with a current speed of 1 m/s and a wind speed of 3 m/s is 16 hours.

Methyl ethyl ketone is expected to evaporate from dry ground.

Abiotic degradation

Methyl ethyl ketone breaks down rapidly in air (half-life of 8 days). It undergoes photodecomposition in sunlight, producing ethane, methane, ethylene, diacetyl and carbon monoxide.

In an anaerobic environment, 100 % of the product is broken down after 8 days of adaptation by methane-enriched cultures

In the atmosphere, rapid degradation occurs by hydroxyl radicals, with a half-life of around 7 days.

Biodegradation

Methyl ethyl ketone is readily biodegradable. In the presence of activated sludge, 80% of methyl ethyl ketone is biodegraded in 20 hours. In optimal biodegradation conditions, the degradation rate is 76% in 5 days and 89% in 20 days.

Bioaccumulation

According to its log Kow value, methyl ethyl ketone is practically non bioaccumulable

Mobility

Methyl ethyl ketone is a high mobility liquid. In water, the product is highly soluble (271 g/l at 20°C).

According to its log Koc value, methyl ethyl ketone has low adsorption to solids in the ground and in sediments. It remains dissolved in interstitial water.

MARPOL classification: Z

SEBC classification: ED

Octanol/water partition coefficient: Log Kow = 0.29

Organic carbon/water partition coefficient: Log Koc = 0.71

in particular hydrogen peroxide, ozone... Oxidation of methyl ethyl ketone can, in some cases, lead to the formation of peroxide.

The reaction of potassium t-butoxide with a small quantity of prod-

uct can cause ignition. It can react violently with certain chlorinated

hydrocarbons (trichloromethane) in the presence of a strong base

Methyl ethyl ketone is not corrosive to metals but attacks certain

Store away from all sources of heat and ignition, in an airtight container in a cool, dry and well ventilated place, away from oxidis-

ing agents and direct sunlight. Containers should be electrically

(sodium or potassium hydroxide).

Particular risks

plastics.

grounded.

Safety precautions

Use non-sparking tools.

Polymerisation

N/A

Danger

- Methyl ethyl ketone vapours can form flammable mixtures with air.
- A source of heat or sources of ignition can cause it to ignite.
- The vapours are invisible and denser than air. They spread out across the ground and can infiltrate sewer systems and basements.
- The vapours can travel towards a source of ignition and ignite. Stability and reactivity
- Safety precautions: keep away from heat, sources of ignition and liaht.
- This is a stable product in normal storage and handling conditions
- Methyl ethyl ketone can react vigorously with strong oxidising
- agents such as chromic acid, nitric acid, ozone and peroxides,

Transportation

Land transportation: RID (rail) /ADR (road) Hazard identification n°: 33 Classification code: F1

Class: 3 Packaging group: II Danger labels: 3

Transportation via inland waterways: ADN/ADNR

Hazard identification n°: 33 Classification code: F1 Class: 3 Packaging group: II Danger labels: 3

Maritime transport: IMDG

Class: 3 Packaging group: II Marine pollutant (MP): NO Danger labels: 3

Air freight: IATA Class: 3 Packaging group: II Danger labels: 3

Provide showers and eye baths. Ensure that there is a water supply nearby - Provide self-contained breathing apparatus

Handling

- nearby.
- Eliminate all sources of sparks and ignition. Do not smoke
- Do not use air for transfers.
- Do not use air to dry the equipment. - Take precautionary measures against static
- discharges.

machinery.

- Use only fireproof equipment.

- Provide appropriate exhaust ventilation at -Store in tightly closed containers in a cool, well ventilated area.
 - Store away from heat and ignition sources.
 - Store at ambient temperature.
 - Provide a retention tank
 - Ground the material and electric equipment used in explosive atmospheres.

Incompatible products: avoid strong oxidising agents (chromic acid, nitric acid, hydrogen peroxide and ozone), potassium t-butoxide, chlorinated hydrocarbons (trichloromethane) and strong bases (sodium or potassium hvdroxide).

Recommended packaging materials: methyl ethyl ketone can be stored in iron, steel or aluminium containers. Glass can also be used for small quantities; in this case cylinders can be protected by a more resistant, suitably adjusted metal envelope

Packaging materials to be avoided: rubber, polyethylene, plastics.

Storage

ANNEX 3: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Dangerous goods

Regulations governing the carriage in bulk of hazardous liquid substances (Annex II of MARPOL Convention) 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 Annex II of MARPOL classification (IMO, 2005)

This revision, adopted in October 2004, includes a new classification of the dangers of noxious liquid substances transported by sea in bulk and entered into force on 1st January 2007.

The new categories are:

Category X: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a major hazard to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment.

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

Category Z: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment.

Other Substances – Substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning of 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.