STYRENE

E.U. classification: Xn Noxious

UN N°: 2055

MARPOL classification: B until 31/12/2006
Y from 01/01/2007

SEBC classification: Floater/Evaporator

CHEMICAL RESPONSE GUIDE

STYRENE

PRATICAL GUIDE

INFORMATION

DECISION-MAKING

RESPONSE

This guide was drafted by *CEDRE* with financial support from ATOFINA, TOTAL, French Navy, Technical Committee of ATOFINA, National Chemical Emergency Centre (NCEC, Abingdon, UK) and the Rennes Poison Control Centre.

Published: March 2004

Purpose of this guide

As part of the research funded by the French Navy, TOTAL and ATOFINA, *Cedre* has published a series of response guides intended to mitigate chemical hazards. They can be used to assist in an emergency response, an accident or an incident involving a vessel or a barge carrying hazardous substances likely to pollute the water surface and the water column.

These guides are updates of the 61 "mini response guides" published by *Cedre* at the beginning of the 90s and are intended to afford rapid access to vital information, in addition to providing relevant bibliographical sources to retrieve extra information.

They also contain the results of scenarios relating to accidents having occurred in the Channel, the Mediterranean and in rivers. These scenarios are only intended to provide response authorities with the emergency information they need. Each accident has to be viewed on it's own merits and the response authorities will not be able to forego on *in situ* measures (air, water, sediment and marine fauna) in order to determine exclusion areas.

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

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

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

A hotline is manned 7/24 by Division 7 of the General Department of Health (SD7/DGS).

During opening hours please call :
Tel.: 01 40 56 47 95
Fax: 01 40 56 50 56

Outside normal working hours please call the Prefecture or other relevant authority

Poison control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: 02 41 48 21 21
Bordeaux (Hôpital Pellegrin-Tripode) Tel.: 05 56 96 40 80
Grenoble (Hôpital Albert Michallon) Tel.: 04 76 76 56 46
Lille (Centre Hospitalier Régional Universitaire) Tel.: 08 25 81 28 22
Lyon (Hôpital Edouard Herriot) Tel.: 04 72 11 69 11
Marseille (Hôpital Salvator) Tel.: 04 91 75 25 25
Nancy (Hôpital Central) Tel.: 03 83 32 36 36
Paris (Hôpital Fernand Widal) Tel.: 01 40 05 48 48
Reims (Hôpital Maison Blanche) Tel.: 03 26 78 48 21
Rennes (Hôpital de Pontchaillou) Tel.: 02 99 59 22 22
Rouen (Hôpital Charles Nicolle) Tel.: 02 35 88 44 00
Strasbourg (Hôpitaux Universitaires) Tel.: 03 88 37 37 37
Toulouse (Hôpital de Purpan) Tel.: 05 61 77 74 47

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A

What you need to know about styrene

Definition

Styrene, styrene monomer or vinyl benzene (MARPOL category Y from 01/01/2007) is an oily, floating, flammable and noxious liquid for human beings and the environment. During transport, it is mixed with a polymerisation inhibitor (e.g. para Tertio Butyl Catechol or pTBC).

Risk

- Explosion: if the inhibitor is ineffective (bad quality) or if there is too little of it or if it heats up, the resulting effect may well be an uncontrollable heating of the styrene and a highly exothermal reaction that may turn into an explosion. When polymerisation is slow, solid and inoffensive polystyrene is formed.

- Toxicity: styrene is harmful and causes irritation, regardless of how it is absorbed.

- in the short term: it can cause mild to serious nose and eye irritation, abdominal pain, sleepiness and weakness (concentrations of between 100 and 1,000 ppm). At higher concentrations, styrene can cause coma and even death.
- in the long term: styrene may have an adverse effect on the nervous system, the digestive and the respiratory tracts.

- Fire: vapours are flammable, heavier than air, can cause explosions when in contact with sparks. In the event of a fire, styrene burns and produces toxic and acrid smoke.

Behaviour in the environment

In the event of a spill, styrene forms a slick that spreads on the water surface and evaporates as it spreads. As a general rule, styrene is slightly soluble in water and is volatile. The slick will evaporate to a larger or smaller degree on the water surface depending on wind speed. Small quantities of styrene will dissolve and cause animal mortality in the immediate vicinity of the spill. Dissolved styrene is moderately bio accumulated by fish and crabs and causes tainting.

First line emergency data

- First Aid Information — B1
- ID card — B2
- Physical data — B3
- Flammability data — B4
- Toxicological data — B5
- Ecotoxicological data — B6
- Persistence in the environment — B7
- Classification — B8
- Special risks — B9
- Transportation, handling, storage — B10

First Aid Information (ICSC, 1999)

B1

Remove spotted or soiled clothes immediately.

Poisoning by inhaling

- Take victim outside in the open air;
- Apply oxygen therapy or artificial respiration if necessary;
- Entrust the victim to a healthcare professional (MD);
- When accidentally inhaled, styrene will cause serious lung disorders.

Skin contact, depending on seriousness

- Remove contaminated clothing;
- Rinse exposed skin with a lot of water and soap;
- Treat the skin rashes with products such as Biafine (Baert, A., 2000);
- Refer the victim to healthcare professionals;
- Admit to hospital.

Eye contact

- Rinse with a lot of water for several minutes;
- Remove contact lenses if possible;
- Solutions such as Diphoterine can be used instead of water (Baert, A., 2000);
- Consult a specialist if eyes are irritated when blinking or in the event of a rash (Baert, A., 2000).

Poisoning by ingestion, depending on seriousness

- **Do not cause the person to vomit;**
- Rinse the person's mouth;
- Have the person LEL down;
- Refer the person to a healthcare professional (MD);
- Admit to hospital.

ID card [1]

STYRENE

Empiral formula: C_8H_8

Structural formula: $C_6H_5CH{=}CH_2$

B2

Synonyms

Styrene monomer
Vinyl benzene
Vinylbenzol
Cinnamene
Styrolene
Styrol
Phenylethylene
Phenyletene
Ethenylbenzene
Cinnamol

Classification U.E.

Xn	**Noxious**
R10	Flammable
R20	Noxious if inhaled
R36/38	Irritant for eyes and skin
S23	Do not breathe vapours

CAS n°:	100-42-5
EINECS n°:	202-851-5
Index n°:	601-026-00-0

Classification for transportation

UN n°:	2055
Class:	3

[1] Additional data and sources in annex 1

Physical data

Conversion factor: air (25°C)	1 ppm = 4.26 mg/m³ 1 mg/m³ = 0.23 ppm

B3

Melting point	- 30.6°C
Boiling point	145°C
Critical temperature	373°C
Relative density (water = 1)	0.906 at 20°C
Relative vapour density (air = 1)	3.6 at 20°C
Solubility in freshwater	300 mg/L at 20°C
Solubility in seawater	minimal: 205 - 240 mg/L maximal: 370 - 470 mg/L
Vapour pressure/tension	0.312 kPa at 10°C 0.6 - 0.7 kPa at 20°C
Olfactory threshold	in freshwater: 0.04 - 0.73 ppm * in air: 0.02 - 0.15 ppm
Rate of evaporation (ether = 1)	12.4 (takes 12.4 times longer to evaporate than ether)
Diffusion cœfficient in water	8.10^{-6} cm²/s at 25°C
Airbone diffusion cœfficient	$7.1.10^{-2}$ cm²/s at 25°C
Henry's law constant	275 Pa.m³/mol at 25°C

* odours can be detected when ztyrene concentrations in freshwater are between 0.04 and 0.73 ppm

Definitions in the glossary
Sources in annex 1

Flammability data

• **Explosive limit by volume** (% in air) Lower limit: 1.1 % or 11,000 ppm Upper limit: 6.1 % or 61,000 ppm	INRS, 1997
• **Regression speed:** 5.2 mm/min	CHRIS, 1999
• **Dangerous decomposition products:** Thermal decomposition will produce organic derivatives. In the event of combustion, carbon will be formed in addition to CO and CO_2	FDS ATOFINA, 2003
• **Smoke:** is an irritant or can be toxic in the event of a fire	ICSC, 1999
• **Flash point (in a closed capsule):** 32°C	FDS ATOFINA, 2003
• **Self-ignition point:** 490°C	INRS, 1997

FDS: Safety data card

Definitions in the glossary

Toxicological data

B5

Acute human toxicity

- Ingestion: abdominal pain.
- Skin contact: superficial and regressive lesions, rashes.
- Eye contact: superficial and regressive lesions, rashes and pain.
- Inhalation: dizziness, drowsiness, headaches, nausea, weakness.

Chronic human toxicity

- Depresses the central and peripheral nervous system as of 20 ppm.
- Digestive disorders.
- Irritates the airways.
- Irritates the eyes.
- Dermatosis, chronic dryness.
- Enzyme induction (elevation of gamma-glutamyltransferases).
- Uncertainty regarding possible haematological anomalies.

Threshold toxicological values

IDLH: 700 ppm (2,982 mg/m³) (USA)
TLV-TWA: 20 ppm (85.2 mg/m³) (USA)
TLV-STEL: 40 ppm (170.4 mg/m³) (USA)
AEV: 50 ppm (213 mg/m³) (France)
ELV: 100 ppm (426 mg/m³) (France)
MRL oral: 0.2 mg/kg/day (USA)
MRL inhalation: 0.06 ppm (0.258 mg/m³) (USA)
Value for inhalation: 0.26 µg/m³ full life (E.U.)
TEEL 0: 50 ppm (213 mg/m³) (USA)
ERPG 1: 50 ppm (213 mg/m³) (USA)
ERPG 2: 246 ppm (1,050 mg/m³) (USA)
ERPG 3: 1,000 ppm (4,260 mg/m³) (USA)
DAD: 0.133 mg/kg of body weight per day (USA) *

* additional information to be found on page 29.

Specific effects

Carcinogenic effects: possible group 2B
Effect on fertility: not demonstrated
Teratogenic effects: not demonstrated
Genotoxic effects: overall no
Mutagenic effects: some effects reported

Thresholds for toxic effects

	Time (min)						
Concentration (ppm)	15	30	60	120	240	480	INERIS, 2003
Lethal effect threshold, SEL	5,000	2,500	1,000	500	250	250	
Irreversible effect threshold, SEI	800	500	250	200	100	100	
Reversible effect threshold, SER	200	100	50	50	20	20	

Lethal effects thresholds are in the upper flammability range for styrene and are between 1.1 % and 6.1 % (v/v) namely: 11,000 and 61,000 ppm.

Ecotoxicological data

Acute ecotoxicity

Seaweed (Scenesdesmus capricornutum):	CE_{c50} (72h)	= 4.9 mg/L
Micro-crustacés (Daphnia magna):	CE_{50} (48h)	= 4.7 mg/L
Fish (Pimephales promelas):	CL_{50} (96h)	= 4.02 mg/L
Bacteria (Pseudomonas fluorescens):	NOEC (16h)	= 72 mg/L
Annelids (Eisenia fœtida):	CL_{50} (14 days)	= 120 mg/kg

Chronic ecotoxicity: no data

PNEC (Predicted No-Effect Concentration)

In 2003 styrene was risk assessed according to E.U. procedure 93/793 and the study produced intrinsic PNEC values that were recognized within the E.U. These values represent thresholds below which there is or no longer is any effect on organisms in the considered compartments such as water, sediment and soil.

PNEC for water:	0.004 mg/L
PNEC sediment (calculated):	0.340 mg/kg (dry weight)
PNEC soil:	0.255 mg/kg (dry weight)

Persistence in the environment

B7

Photo-oxidation (ECB, 2002)

Styrene is degraded quickly in the atmosphere by photo-oxidation reactions and is oxidised by OH radical hydroxyls.
It reacts with ozone to form mainly benzaldehyde (41 %) and formaldehyde (37 %).
- Half life in air: 4 h.

N.B.: it will take styrene 50 years to be degraded in the atmosphere by photolysis (CSST, 2002).

Volatilisation from water surfaces (INERIS, 2000)

Styrene evaporates quickly and as a rule it is hardly soluble in water in addition to being highly volatile:
- Half-life: 3 hours (water depth at sea: 1 m, current: 1m/s and wind speed: 3 m/s).
- Half-life: 3 days in a lake at 20°C.
- Half-life: 13 days for an oligotrophic lake at 20°C.

Biodegradation (INERIS, 2000)

Styrene is readily biodegraded in aerobic conditions:
- Half-life in freshwater: 15 days.
- Half-life in underground water: 4 to 30 weeks.
- Half-life in seawater (estimation): 45 days. The fate of styrene in seawater is dominated by evaporation, photo-oxidation and bio-transformation.

Organoleptic alteration of marine organisms (*Cedre*, 2001a)

When crabs are cooked or raw, the olfactory threshold is 5 mg/kg.
For raw muscles the olfactory threshold is 1 mg/kg.

Whenever there is a suspicion about food odours, use the DAD set by the WHO using a consumption scenario.

Partition coefficient for organic carbon and water Koc = 352 litres/kg	ECB, 2002
Partition coefficient for octanol/eau log Kow = 3.02	ECB, 2002
Partition coefficient for octanol/water BCF (fish) = 74 (valour calculated) BCF (crab) = about 12 BCF (red fish) = 13.5	INERIS, 2000 *Cedre*, 2001a ECB, 2002

Classification

IBC classification (IMO, 1998)

- **Risk:** S/P (safety/pollution risk).
- **Vessel type:** 3.
- **Tank type:** 2G (integral gravity tank).
- **Tank clearance:** controlled.
- **Tank atmosphere control:** no.
- **Electrical equipment**
  - class i': T1
  - class i'': IIA
  - class i''': flash point < 60° C
- **Tank level gauge:** R (type à ouverture restreinte).
- **Vapour detection:** F (flammable).
- **Fire extinguishing system:**

  A: foam that resists alcohol (or a multipurpose foam).

  B: ordinary foam, comprising all the foams that do not resist alcohol, in particular fluoroprotein foams and those that form an aqueous film (AFFF).
- Matériaux de construction

  N4: neither copper nor alloys containing copper should be used for manufacturing tanks, piping, valves, accessories and other elements likely to come in contact with styrene or styrene vapours.

  Z: materials normally used with electricity such as copper, aluminium and insulators should wherever possible be protected by protective layers to avoid contact with styrene vapours.

SEBC classification: F/E (Floater/Evaporator)

MARPOL classification: B (definition in annex 3) until 31/12/2006
Y (definition in annex 3b) from 01/01/2007

EU classification

Xn : Noxious

R10	Flammable
R20	Noxious when inhaled
R36/38	Irritates eyes and skin
S23	Do not breathe styrene vapours
202-851-5	EC labelling

Special risks

B9

Polymerisation (Cedre, 2001b)

Styrene is stabilised by a polymerisation inhibitor (such as: para Tertio Butyl Catechol or pTBC) which prevents polymerisation (= solidification), and that can be exothermal. When tanks are immersed in seawater at a temperature of 10°C, a lead-time of 6 months seems reasonable before polymerisation can commence. At the outset, polymerisation is linear up to about 10 % polymer content and is exponential thereafter.

- Little or no spontaneous polymerisation in the following conditions: no light, no oxygen, no or little stirring and a temperature of about 10°C (would be the case of a wreck in the English Channel).

- Polymerisation will occur if the inhibitor is depleted or absent or if the styrene is exposed to polymerisation catalysts (strong acids, peroxides, metallic salts, diazoic compounds), or when stored for a long period at temperatures in excess of 20°C, in the presence of excessive heat (fire, friction heat in a pump...). The increase in temperature catalyses polymerisation.

- **Polymerisation is immediate and uncontrollable when temperatures exceed 65°C** (explosion risk).

pTBC is more soluble in seawater than in styrene, so more the contact surface for seawater and a styrene/pTBC mixture increases, more the pTBC will dissolve in the water column. **It appears necessary to have to add pTBC to styrene for pumping** so as to avoid any risk of further polymerisation. An increase in temperature (from 30°C to 40°C) will also catalyse a polymerisation reaction. At these temperatures, the polymerisation time for styrene is about one week.

Polymerisation of styrene

Danger (CEFIC, 2003)

- If a styrene tank heats up, pressure will build up and the tank may burst and explode. However, risks related to ignition may escalate (fire ball).
- Risk of spontaneous increase in pressure or self-ignition when exposed to heat, light, shock or when coming into contact with other chemicals.
- Toxic and irritating smoke may be formed from heating or combustion.
- Styrene can form explosive mixtures with air at high ambient temperatures.
- Styrene vapour is invisible and heavier than air. It spreads over the ground and can enter sewage systems and underground areas.
- Heat may destroy the inhibitor.

Stability and reactivity (FDS ATOFINA, 2003)

- Comply with following conditions: store far from humidity and heat and maintain a temperature lower than 25°C.
- Reacts explosively with: peroxides (polymerisation), oxidizers (nitric acid, chromic acid), sulphuric acid, chlorosulfonic acid, oleums (increase in temperature and pressure), composite bases of alkaline metals and graphite.
- Dangerous decomposition products: thermal decomposition produces organic derivatives and in the event of combustion can lead to the formation of toxics (carbon, carbon monoxide and carbon dioxide).

Styrene stored in drums

Transportation, handling, storage

Transportation (FDS ATOFINA, 2003)

Road transport:
RID (rail) /ADR (road) (2002)
Danger identification number: 39
Class: 3
Packing group: III
Classification code: F1
Labels: 3

Transportation via inland waterways:
ADN/ADNR (2002)
Danger identification number: 39
Class: 3
Labels: 3
Classification code: F1
Materials identification number (UN number): 2055

Maritime transport:
IMDG (Amendment 31, 2002)
Class: 3
Packing group: III
Marine pollutant (MP): NO
Labels: 3

Air transport:
IATA (2002)
Class: 3
Packing group: III
Labels: 3

Handling (FDS ATOFINA, 2003)

- Provide a ventilation system and appropriate evacuation procedures.
- Provide showers, eye fountain.
- Only use styrene in a closed system.
- Do not use air for transferring and circulating styrene.
- Avoid sprinkle loading styrene as this may cause it to ignite.
- Use small speeds for handling styrene (static electricity).
- When handling, keep well clear of flames.
- Only use explosion proof equipment.

Storage (FDS ATOFINA, 2003)

- Keep recipients tightly closed in a well aired and cool place.
- Keep well clear of all sources of ignition.
- Store far from humidity and heat.
- Maintain temperatures lower than 25°C.
- To avoid uncontrolled polymerisation, maintain inhibitor levels and oxygen concentrations in the liquid phase above minimum levels, (TBC >10 ppm and oxygen >15 ppm).
- Ensure that styrene vapours can be collected.
- Provide a dyked area.
- Ground all electrical equipment if it has to be used in an explosive atmosphere.
- If styrene has to be handled/used at temperatures higher than flash point, store it in an inert gas atmosphere.

Results of accident scenarios

■ Reminder of chemical properties — C1
■ Accident scenarios — C2
■ Consumption scenarios — C3

Reminder of chemical properties

Density and vapour tension (20°C)

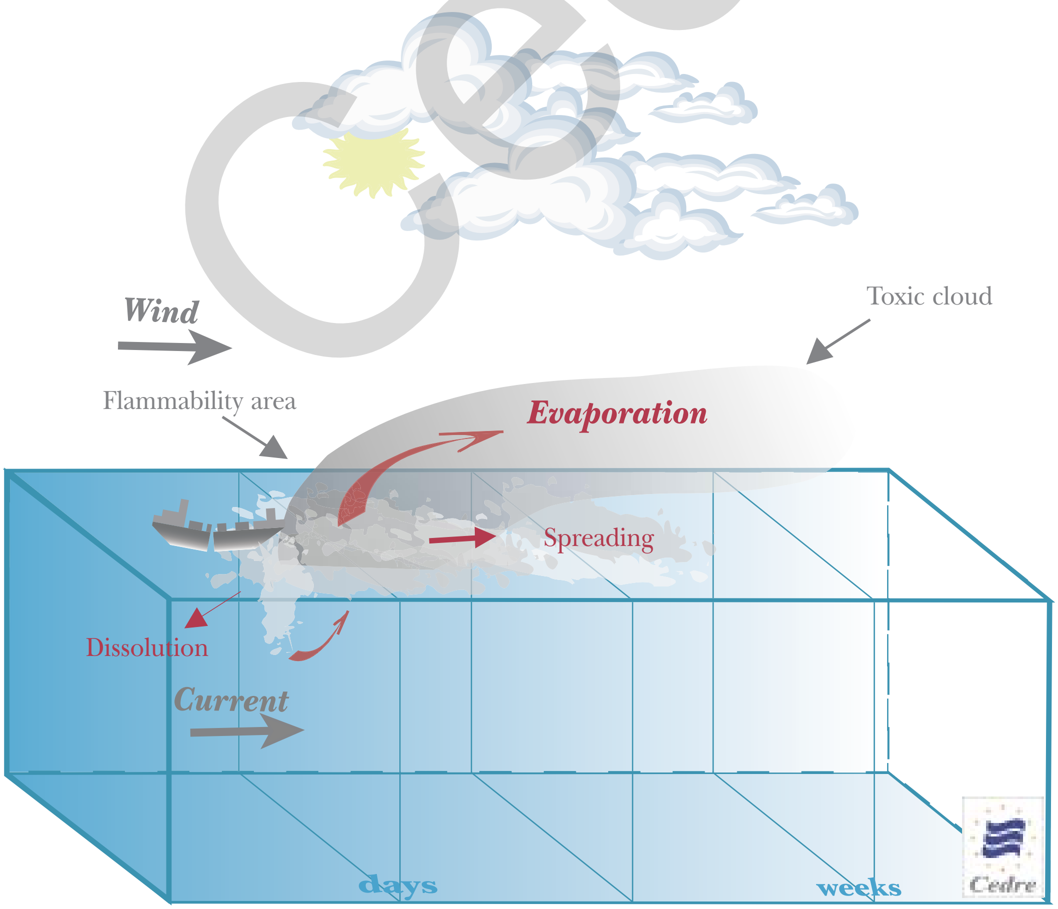
- Density in water: 0.906
- Vapour density: 3.6
- Vapour tension: 0.6 kPa

Solubility

The solubility of styrene in seawater is between 205 and 470 mg/l.
The solubility and vapour tension of styrene are such that it can be classified as **a floater/ evaporator (F/E).**

Behaviour of styrene when spilled in water

- Styrene forms a slick on the water surface.
- It is **volatile.**
  It evaporates quickly depending on how much has been spilled, temperature of air and water and wind speed in the event of atmospheric turbulence.
- Styrene vapours are heavier than air (=1). The styrene cloud will therefore tend **to stay on the water surface.**



C1

Accident scenarios

If a chemical tanker is rammed sideways on, wing cargo tanks containing styrene may be damaged.

Bearing this assumption in mind, three spill scenarios have been defined for four spill rates:

- 10 kg/hour
- 1,000 kg/hour
- 100 t/hour
- 500 t (instantaneous spill)

Ievoli Sun *spill, English channel, 30 october 2000*

C2

The scenarios

"English Channel"
- location 50°N; 1°W (60 km north of Cherbourg)
- air and water temperature: 10°C
- two wind speeds: 3 and 10 m/s
- wave height: 1 m
- current: 0.5 knot

"Mediterranean"
- location 43°10'N; 5°20'E (32 km from Marseille)
- air and water temperature: 20°C
- two wind speeds: 3 and 10 m/s
- wave height: 1 m
- current: 0.5 knot

"River"
- current: 0.5 m/s
- air and water temperature: 10°C
- wind speed: 3 m/s
- release rate: 250 m^3/s

Modelling

ALOHA and CHEMSIS have been used to model hypothetical spillages of styrene in water.

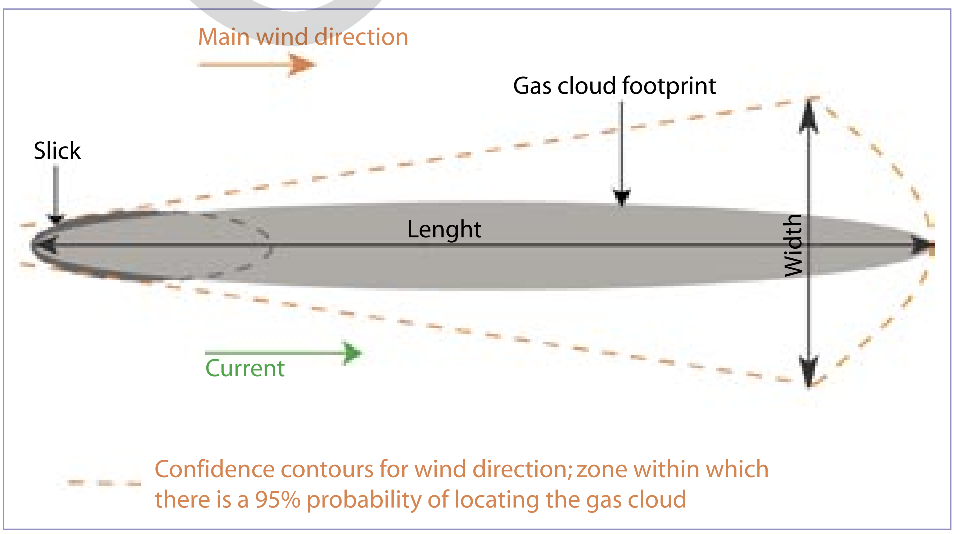
ALOHA is a Gaussian type atmospheric dispersion model developed by NOAA (National Oceanic and Atmospheric Administration) and the EPA, (Environmental Protection Agency) in the USA. ALOHA calculates gas cloud envelopes. **The model will calculate the gas cloud envelope** and it is important to point out that results are only valid for calm sea conditions.

The first three release rates studied (10 kg/h, 1,000 kg/h, 100 t/h) were modelled considering that all the styrene had evaporated.

The instantaneous spill of 500 tonnes of styrene was modelled on a slick 17 mm thick and a surface area of 31,400 sq m.

- Weather conditions chosen were as follows:
- weather stable (wind speed 3 m/s under a cloudy sky, stability class E);
- weather unstable (wind speed 10 m/s under a sunny sky, stability class B);
- average air humidity.
- Surface roughness was 0.01 cm.
- The leakage was located 3 m above sea level.
- The gas cloud is delineated by the following:
- Olfactory threshold: 0.08 ppm;
- TLV-TWA: 20 ppm (weighted average over 8 days and 40 hours a week);
- IDLH: 700 ppm (value below which a worker can, without using a respirator, and without impairing his capacity to escape, reach a safe place, in 30 minutes in the event of sudden exposure);
- LEL (Lower Explosion Limit): 1.1 % = 11,000 ppm;
- UEL (Upper Explosion Limit): 6,1 % = 61,000 ppm.

CHEMSIS is a chemical spill model developed by The National Chemical Emergency Centre (NCEC) (United Kingdom) and **predicts the movement and the fate of a chemical that is spilled water.** It indicates the movement of a chemical on the water surface and how it spreads throughout the environment in addition to how it behaves under the action of wind, waves and current.
The NCEC has done calculations using the CHEMSIS software and has sent Cedre data regarding how styrene moves on the water surface over time (surface volume, dissolved volume and sedimented volume) for the "English Channel" and the "Mediterranean" scenarios.



Results of the "English Channel" scenario

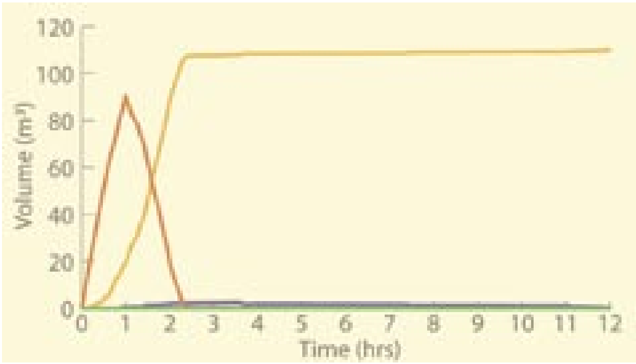
Results of the ALOHA model: atmospheric dispersion

Quantity spilled	Wind	Concentration (ppm)	Maximum distance reached (Length and width)	Protection
10 kg/h	3 m/s	0.08 (olfactory threshold)	1.6 km by 500 m	A
		20 (TLV-TWA)	88 m	B
		700 (IDLH)	16 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	<10 m	D
	10 m/s	0.08 (olfactory threshold)	400 m by 250 m	A
		20 (TLV-TWA)	22 m	B
		700 (IDLH)	11 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	11 m	D
1,000 kg/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 4 km	A
		20 (TLV-TWA)	1 km by 400 m	B
		700 (IDLH)	140 m by 600 m	C
		11,000 (LEL)	31 m	D
		61,000 (UEL)	10 m	D
	10 m/s	0.08 (olfactory threshold)	4.4 km by 3 km	A
		20 (TLV-TWA)	250 m by 150 m	B
		700 (IDLH)	41 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	< 10 m	D
100 t/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 7 km	A
		20 (TLV-TWA)	10 km by 4 km	B
		700 (IDLH)	1.6 km by 1 km	C
		11,000 (LEL)	380 m by 600 m	D
		61,000 (UEL)	120 m by 150 m	D
	10 m/s	0.08 (olfactory threshold)	> 10 km by 8 km	A
		20 (TLV-TWA)	2.8 km by 2 km	B
		700 (IDLH)	500 m by 300 m	C
		11,000 (LEL)	120 m by 80 m	D
		61,000 (UEL)	40 m	D
500 t instantaneous spill	3 m/s	0.08 (olfactory threshold)	> 10 km by 5 km	A
		20 (TLV-TWA)	2.3 km by 1 km	B
		700 (IDLH)	117 m by 150 m	C
		11,000 (LEL)	-	D
		61,000 (UEL)	-	D
	10 m/s	0.08 (olfactory threshold)	5.3 km by 3 km	A
		20 (TLV-TWA)	152 m	B
		700 (IDLH)	100 m	C
		11,000 (LEL)	100 m	D
		61,000 (UEL)	100 m	D

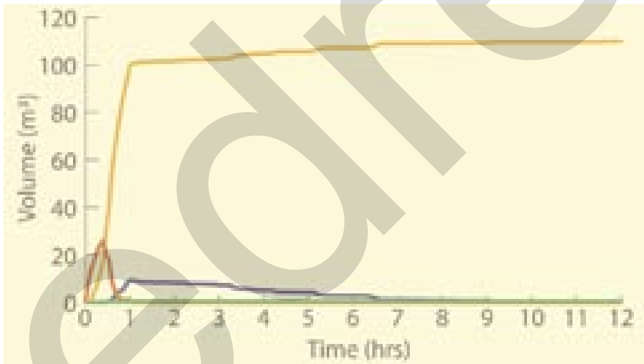
A	Styrene odours are perceptible. No danger.	C	Get PPEs. Use a self-contained breathing apparatus (SCBA).
B	Get PPEs. Use a gas mask.	D	Zone where the styrene concentration has reached explosion limits. Get a self-contained breathing apparatus (SCBA) and use explosion proof equipment.

Results of the CHEMSIS model: Chemical spill in water

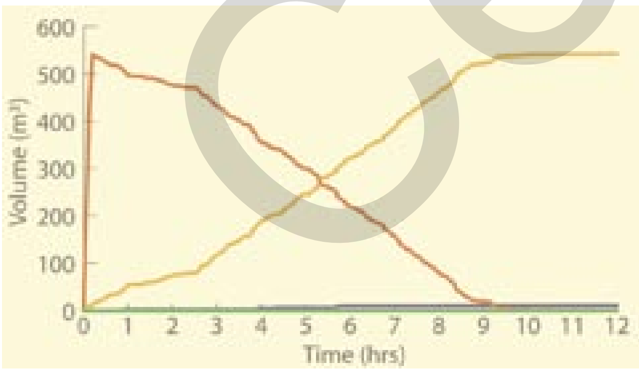
Volume on the surface — Volume evaporated — Volume dispersed in water — Volume dissolved in water — Volume sedimented



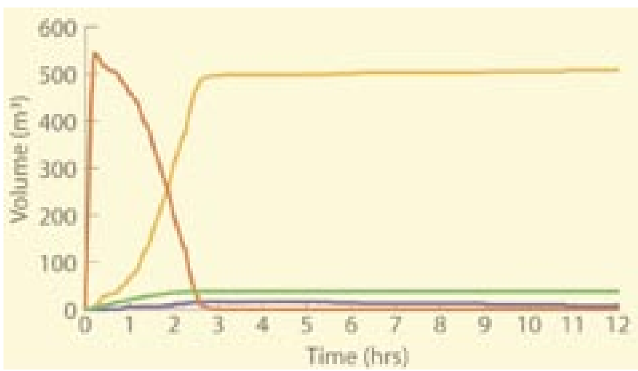
Spill involving 100 tonnes of styrene for an hour
Wind 3m/s



Spill involving 100 tonnes of styrene for a hour
Wind 10 m/s



Spill involving 500 tonnes of styrene at a rate of 3,000 tonnes/hour for 10 minutes
Wind 3 m/s



Spill involving 500 tonnes of styrene at a rate of 3,000 tonnes/ hour for 10 minutes
Wind 10 m/s

Results of the "Mediterranean" scenario

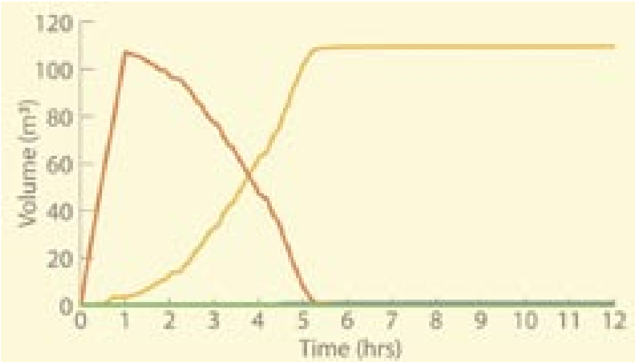
Results of the ALOHA model: atmospheric dispersion

Quantity spilled	Wind	Concentration (ppm)	Maximum distance reached (Length and width)	Protection
10 kg/h	3 m/s	0.08 (olfactory threshold)	1.6 km by 500 m	A
		20 (TLV-TWA)	89 m	B
		700 (IDLH)	17 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	< 10 m	D
	10 m/s	0.08 (olfactory threshold)	410 m by 250 m	A
		20 (TLV-TWA)	23 m	B
		700 (IDLH)	11 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	11 m	D
1,000 kg/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 4 km	A
		20 (TLV-TWA)	1 km by 400 m	B
		700 (IDLH)	150 m by 600 m	C
		11,000 (LEL)	31 m	D
		61,000 (UEL)	10 m	D
	10 m/s	0.08 (olfactory threshold)	4,5 km by 3 km	A
		20 (TLV-TWA)	250 m by 150 m	B
		700 (IDLH)	41 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	< 10 m	D
100 t/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 7 km	A
		20 (TLV-TWA)	10 km by 4 km	B
		700 (IDLH)	1.6 km by 1 km	C
		11,000 (LEL)	380 m by 600 m	D
		61,000 (UEL)	120 m by 150 m	D
	10 m/s	0.08 (olfactory threshold)	> 10 km by 8 km	A
		20 (TLV-TWA)	3 km by 2 km	B
		700 (IDLH)	500 m by 300 m	C
		11,000 (LEL)	120 m by 80 m	D
		61,000 (UEL)	40 m	D
500 t instantaneous spill	3 m/s	0.08 (olfactory threshold)	> 10 km by 5 km	A
		20 (TLV-TWA)	2.3 km by 1 km	B
		700 (IDLH)	117 m by 150 m	C
		11,000 (LEL)	-	D
		61,000 (UEL)	-	D
	10 m/s	0.08 (olfactory threshold)	5.6 km by 3 km	A
		20 (TLV-TWA)	163 m	B
		700 (IDLH)	100 m	C
		11,000 (LEL)	100 m	D
		61,000 (UEL)	100 m	D

A	Styrene odours are perceptible. No danger.	C	Get PPEs. Use a self-contained breathing apparatus (SCBA).
B	Get PPEs. Use a gas mask.	D	Zone where the styrene concentration has reached explosion limits. Get a self-contained breathing apparatus (SCBA) and use explosion proof equipment.

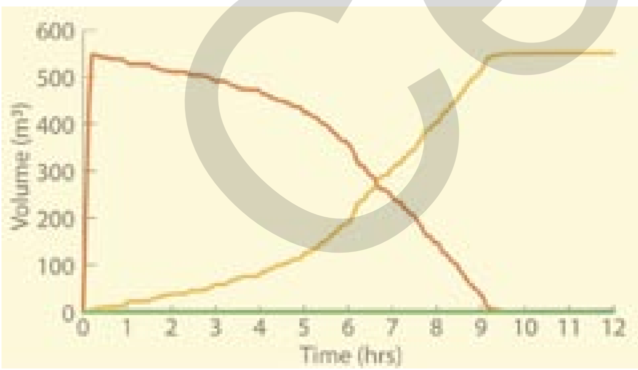
Results of the CHEMSIS model: chemicals spilled in the water

Volume on the surface — Volume evapored — Volume dispersed in water — Volume dissolved in water — Volume sedimented

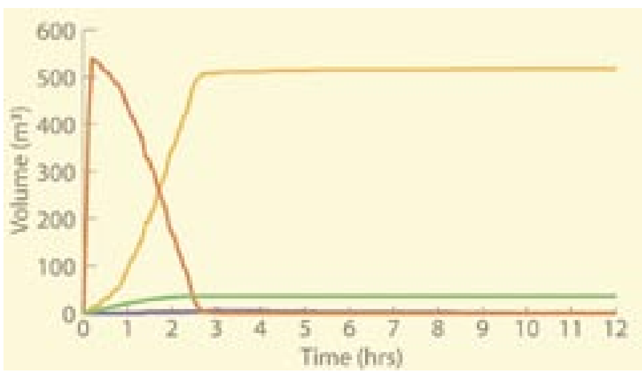


Spill involving 100 tonnes of styrene
in the space of an hour
Wind speed 3 m/s

Spill involving 100 tonnes of styrene
in the space of an hour
Wind speed 10 m/s

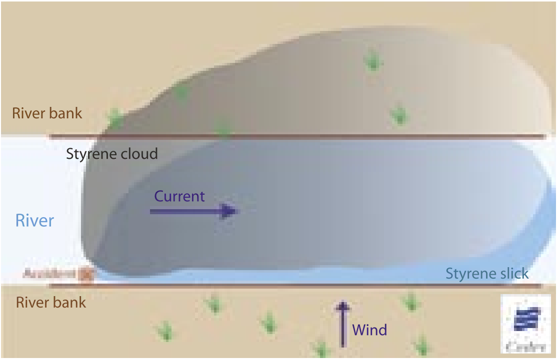


Spill involving 500 tonnes of styrene
at a rate of 3,000 tonnes per hour
for 10 minutes
Wind speed 3 m/s



Spill involving 500 tonnes of styrene
at a rate of 3,000 tonnes per hour
for 10 minutes
Wind speed 10 m/s

Results of "Rivier" scenario



Spill involving styrene in a river. The dispersion of the styrene cloud will depend on current (slick drift) and wind data.

If there was no fire (or explosion) when the spill occurred the liquid styrene slick, contained by the river banks, spreads and evaporates.
Depending on surface current factors, the surface slick will travel a certain distance downstream. The slick will be persistent on the water surface (same as with the English Channel scenario cf page 24) which will determine which length of the river bank is going to be affected.
The banks that are likely to be covered by the toxic cloud will be downwind. When styrene is spilled at a rate of 500 tonnes in 10 minutes in a wind speed of 3 m/s at 10°C, the toxic cloud can only be delineated by three figures: olfactory threshold , TLV-TWA and IDLH.

Results of the ALOHA model: atmospheric dispersion

Quantity spilled	Wind	Concentration (ppm)	Maximum distance reached (Length and width)	Protection
10 kg/h	3 m/s	0.08 (olfactory threshold)	1.6 km by 500 m	A
		20 (TLV-TWA)	88 m	B
		700 (IDLH)	16 m	C
		11,000 (LEL)	11 m	D
		61,000 (UEL)	< 10 m	D
1,000 kg/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 4 km	A
		20 (TLV-TWA)	1 km by 400 m	B
		700 (IDLH)	140 m by 600 m	C
		11,000 (LEL)	31 m	D
		61,000 (UEL)	10 m	D
100 t/h	3 m/s	0.08 (olfactory threshold)	> 10 km by 7 km	A
		20 (TLV-TWA)	10 km by 4 km	B
		700 (IDLH)	1.6 km by 1 km	C
		11,000 (LEL)	380 m by 600 m	D
		61,000 (UEL)	120 m by 150 m	D
500 t instantaneous spill	3 m/s	0.08 (olfactory threshold)	> 10 km by 5 km	A
		20 (TLV-TWA)	2.3 km by 1 km	B
		700 (IDLH)	117 m by 150 m	C

A	Styrene odours are perceptible. No danger.	C	Get PPEs. Use a self-contained breathing apparatus (SCBA).
B	Get PPEs. Use a gas mask.	D	Zone where the styrene concentration has reached explosion limits. Get a self-contained breathing apparatus (SCBA) and use explosion proof equipment.

Consumption scenarios

It is important to point out that when drafting this document in 2003, styrene was still being risk assessed according to Directive 93/793 procedures (first priority list).

At the present time, there is still no Daily Admissible Dose (**DAD**) recognised by the European Union according to the above mentioned procedure. However, there are two figures a DAD/DJA of 7.7 mg/kg body weight/day proposed by the WHO (but only based on drinking water quality Directives dating back to 2000). The other figure is **0.133 mg/kg** body weight/day proposed by a US association that is loosely connected to the EPA. Both figures were included in the AFSSA report after the *Ievoli Sun* wreckage. AS the EU has no official position yet, we are using the most conservative figure available, namely **a full life DAD** of 0.133 mg/kg body weight/day. In the future, prior to any kind of response, responding authorities will need to check what the official EU figure is, (consult the European Chemical Bureau website).

On the next page, a table and corresponding curves are given for Daily Exposure Doses (DED), depending on how much seafood has been eaten (fish, molluscs and crustaceans) in addition to hypothetical concentrations for the same produce.

The calculations in the table and the curves stop when the DED is the same as the DAD.

It is again important to point out that the figures in the table are proportional.
The figures reached may have to be recalculated depending on the DAD used, concentrations found in seafood and actual in situ consumption figures.

The approach consists of comparing reference DAD figures with DED (full life) figures. If the DAD/DED ratio is less than 1 (DAD/DED < 1) it is considered that there is no risk.

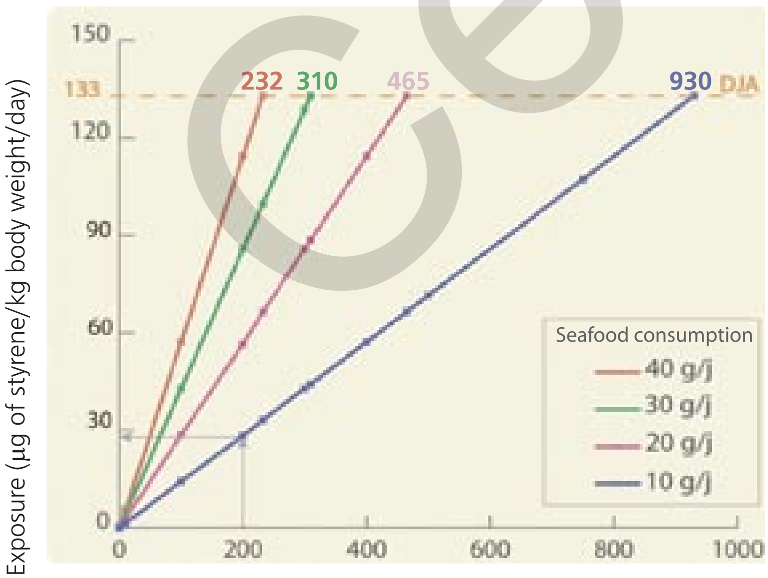
AFSSA in its consumption report for the French population (Enquête INCA; VOLATIER, 2000) gives average consumption figures for seafood for the entire year:
- 6 g/day for crustaceans and molluscs;
- 30 g/day for fish, freshwater and seawater combined (with a variation of between 17.8 g/day for children aged from 3 to 5 and 29.5 for adults).

Daily Exposure Dose (DED) (in µg/g body weight per day) depending on how much seafood you eat (10, 20, 30 and 40 g/day) and the hypothetical concentrations measured in each kind of food.

The colour schemes indicate maximum acceptable concentrations in seafood not to be exceeded (CNE) depending on quantities of seafood eaten (e.g. 232 µg/g in seafood if you eat 40 grammes every day), i.e. when the DAD=DED.

Concentrations in seafood (µg/g)	Seafood consumption (g/day)			
	10	20	30	40
	0	0	0	0
0.01	0.00143	0.00286	0.00429	0.00572
0.1	0.0143	0.0286	0.0429	0.0572
1	0.143	0.286	0.429	0.572
10	1.43	2.86	4.29	5.72
100	14.3	28.6	42.9	57.2
200	28.3	56.6	85.8	114.4
232	33.2	66.4	99.6	133
300	42.9	85.8	128.7	
310	44.3	88.6	133	
400	57.2	114.4		
465	66.5	133		
500	71.5			
750	107.25			
930	133			

Acceptable consumption of seafood depending on concentrations measured in the same produce



Concentrations measured in seafood (µg of styrene per gramme of body tissue)

Example 1: if you eat seafood containing 200 µg of styrene per gramme (body tissue) at a rate of 10 grammes a day, the DED will be 28.3 µg of styrene per kilogramme of body weight per day and the DAD which is 133 µg/kg body weight/day will not be exceeded, **in which case there is no risk to human health.**

Exemple 2: if you eat seafood containing 500 µg of styrene per gramme (body tissue) at a rate of 150 grammes per week which is 20 g/day, the DED will be 143µg of styrene per kg body weight per day and the DAD will be exceeded and there **will be a risk for human health.**

Response

■ Feedback: the *Ievoli Sun* — D1

■ Examples of styrene spills — D2

■ Recommendations regarding response — D3

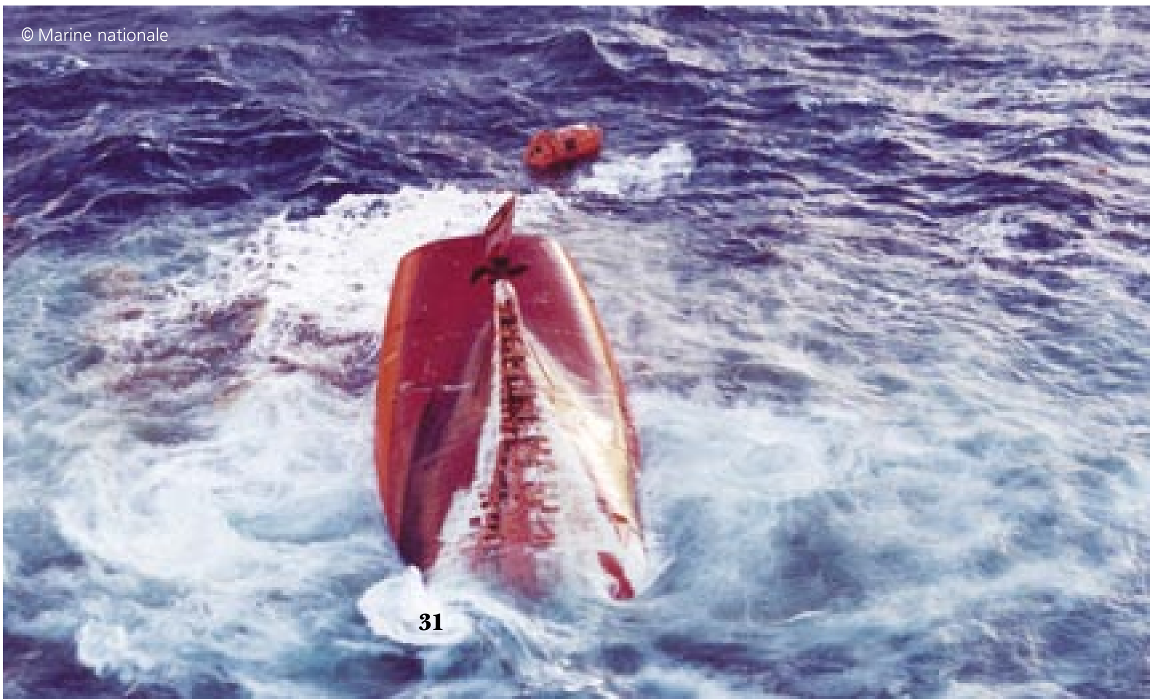
■ Response techniques — D4

■ Choosing PPEs — D5

■ Measuring equipment and waste treatment — D6

D

Ievoli Sun, *wreckage, English Channel,*
30 october 2000



Feedback: the *Ievoli Sun*

The accident

On 31 October 2000 at 0900, the *Ievoli Sun* chemical tanker sank offshore the French coast. She was carrying 4,000 tonnes (10 tanks full) of styrene monomer, 1,000 tonnes (4 tanks) of MEK, and 1,000 tonnes (4 tanks) of isopropylic alcohol.
The wreck sank 90 metres on a sandy bed at an angle of 120°. The area was known as a high tidal current area (6 kn with a tidal coefficient of 110) and a water temperature of 11°C.

Reports

- After the sinking: 3 unidentified slicks were seen (two were 1 nm long* and one was 5 nm long).
- On the following days: a sheen slick 3,000 m long by 10 - 20 m wide evidenced whitish streaks.

The slick persisted on the surface for more than a month after the sinking (1,000 m x 40 m) with occasional "remissions" (200 x 50 m). The IR signature was weak.

* 1 nm = 1,852 m

Mobile lab belonging to the UIISC

Styrene in the atmosphere

At sea

Odours are perceptible at a height of 200 metres in the Customs Department aircraft.
Samples are taken from around the wreck during the following days (7 air samples) with different techniques:
- Tenax (charcoal): 5 samples were positive;
- Draeger tube: 1 tube was positive;
- Atmospheric condition monitor: analyses were negative;
- PID: 6 analyses found to be between 0.1 and 0.5 ppm;

On D+8, the Neuwerk (German response vessel) detected odours between 1.5 and 3 nautical miles from the wreck but the mass spectrometer remained negative.
Another vessel detected a level of 2.5 ppm.
On D+12, 3,000 m from the wreck, the Neuwerk detected concentrations of trichloroethylene lower than **1 mg/m³.**

On the mainland

The analyses conducted by the Marseille Fire Brigade and a UIISC using Tenax tubes and a mass spectrometer did not detect any styrene.
During pumping operations, many Cherbourg inhabitants reported stinging eyes and sore throat.

D1

Styrene in the water column

All the samples taken from the water column were always negative (except for the surface slick).

Styrene concentrations in live organisms
Nine days after the sinking, several samples of seafood were taken less than one nm from the wreck.

The findings were as follows:

spider crab:	5 µg/kg (meat) 18 µg/kg (gills)
Jonas crab:	230 µg/kg (meat) 340 µg/kg (gills)

Prior to the sinking, the skin and the gills of the Jonah crabs fished in the area presented with concentrations lower than 1 µg/kg (except for one 3,8 µg /kg in the gills).

N.B.: by comparison, some food showed concentrations of 25 to 30 µg/kg (yoghurt, butter).

Measures taken by the authorities

- Maritime exclusion area: 5 nm around the wreck and then 2 nm, on 15 November, for vessels in transit.

© Marine nationale

Up welling of styrene from the Ievoli Sun *wreck*

- Aerial exclusion area set up on 31 October 2000 until the beginning of the month of June 2001 over a radius of 2 nm and an initial height of 3,000 feet that was then reduced to 1,500 ft.
- Measuring the stability of the sediment and the vessel.
- ROV surveillance of the wreck.
- Two flights a day.
- Ban on fishing: 500 pots were unusable around this area.

Committees of experts

- MEDD Committee of Experts – Pollution and Risk Prevention Department regarding aerial risks, food risks, fauna and flora.
- Interministerial Steering Committee: Secrétariat Général de la Mer.
- Expert group on "wreck management": Secrétariat Général de la Mer.
- DRIRE/DDE think tank on storing collected waste.
- Building a data bank on analyses and measures taken by the ZDO and *Cedre*.
- Pool of European experts.
- Protection of responders: note drafted by the toxicant monitoring unit of the Rennes Poison Control Centre.

Aircraft in the area

- Planes : Polmar II, air Atlantic (MCA).
- Helicopter.

Vessels in the area

- ***Neuwerk:*** German response vessel was under positive internal pressure and was chartered according to arrangements with the Bonn Agreement. On zone on D+7. Vessel fitted with a mass spectrometer. Assignments:
  - location, identification of the wreck;
  - sampling (air and water) around the wreck;
  - retrieval of pots around the wreck;
  - mapping the polluted area.
- ***Northern Prince:*** chartered by a P&I Club to do wreck reconnaissance work. The ROV turned out to be powerless (in 2.5 m waves and 2.5 kn currents maximum).
- Launch, the ***Iris*** belonging to the Maritime Affairs Department used for surveillance and sampling.
- The ***Gwen Drez*** belonging to IFREMER for taking samples of live organisms and water.
- The ***Audacieux*** patrol boat for air sampling.
- Dispatch boat ***L.V. Lavallée*** to control shipping.
- The ***Alcyon*** pollution response vessel on stand by at Cherbourg.
- The ***Patriote*** trinity vessel for beaconing positioning in the area .

Technical operations (tech-op, cf photo p. 38)

The styrene was pumped as were accessible bunker tanks. The two other chemicals were gradually released into the environment.

Experiments

Evaporation kinetics

Styrene was spilled in a swell tank (10 litres by 10 m^2).
All of the styrene evaporated fully in the space of 8 to 10 hours.
There were pungent odours but the Draeger tube did not detect anything (< 10 ppm).
The explosion test was also negative.

Contamination of live organisms (crabs)

The experiment showed that an exposure of 150 hours in water at a concentration of 2 mg/l of styrene entails a contamination of about 23 mg/kg of drip dried body weight for crab meat (saturation). This level of contamination drops to 0.12 mg/kg of drip dried body weight after putting the animals in clean seawater for 144 hours.
Odours were detectable at concentrations of 5 mg of styrene per kilogramme of fresh crab meat.
Organoleptic tests were organised by IFREMER, MEDD, SHELL, CEA and IPSN.

Polymerisation

- **In lab setting:** styrene does not polymerise at 26°C after a few days.

- **In a tank:** styrene without its polymerisation inhibitor, pTBC, evidenced a polymerisation rate of 1 per cent 35 days after the onset of the test (temperature 8°C). The inhibitor tended to solubilise.

Examples of styrene spills (NOAA, 2003)

Kathie G barge

On 8 September 1988 in the USA, this barge carrying 3 500 tonnes of styrene grounded around midnight in the Mississippi river, 225.3 kms north of Baton Rouge (Louisiana) spilling between 200 and 800 tonnes.

Collisions involving two barges

On 26 January 1992, two barges collided in the Louisiana coastal canal. One of them was carrying a little more than 14,000 tonnes of styrene and spilled its entire load.

N°1 Chung Mu

On 9 March 1995, in the access channel of the port of Zhanjiang (South China), the *N°1 Chon Stone* collided with the *N°1 Chung Mu*, a chemical tanker of 3,500 grt, built in 1994. During the collision, 230 tonnes of styrene monomer were spilled at sea. After this accident, organoleptic tests were done.

Da Yon

On 17 April 2001, the Da Wan rammed the Da Yon that was carrying 3 000 tonnes of styrene in the Yang Tse delta near Shanghai. During the accident, 700 tonnes were spilled at sea over a distance of 80 km.

Smaller styrene spills

On 13 August 1986, a spill of 650 litres of styrene caused by an industrial enterprise in Philadelphia (USA) occurred in the sewage system of the city.

On 3 August 1987, a tank containing styrene, xylene and ethylbenzene spilled its cargo in Chesapeake Bay (Virginia, USA).

On 19 December 1996, a train derailment caused a spill of 56 m^3 of styrene in the Ohio river near Louisville (Kentucky, USA).

On 17 January 1997, a tugboat, the M/V Bronwynne Brent, was pushing 12 barges (two of them containing chloroform and one containing styrene) and grounded on a bank of the Mississippi river 38.6 km north of Memphis (Tennessee, USA).

D2

Fish and shellfish market, China, 1995

Recommendations regarding response

Is response possible ?

- **Yes it is provided** that PPEs are worn and appropriate equipment is used. (cf EPI: p.40). Fire risk was high when the spill occurred and a large quantity of styrene evaporated instantaneously. Responder risks were more tied to possible leaks occurring afterwards rather than to vapour emissions in the hours that followed the spill, which was a massive spill.
- **Surveillance flights** are to be banned during the first few hours after the spill.
- **At sea,** no attempt must be made to approach the spill area with boats of motor boats likely to cause the vapours to ignite.
- **When approaching the scene of the accident,** proceed downwind wear breathing apparatuses and chemical tight suits (cf EPI: p.40), use atmospheric condition monitors, HNU type photo-ionisation vapour detectors fitted with a 9.5 eV lamp and use Draeger tubes (n°67 23301, n°67 33141, n° CH 27 601, 67 28361).

Emergency measures to be taken in the event of a leak or a spill

On board a vessel

- **Eliminate all possible causes of ignition or heat.** Spray a lot of water on the substance spilled on the deck and discard the water overboard. In an inland water setting, as much of the water as possible will have to be recovered and subsequently treated.
- **Spray water to disperse** flammable vapours and to reduce the risk of explosion in addition to protecting response teams.
- **Fluoroprotein foams** can be used efficiently in a bid to limit evaporation.
- **Plug the leak or reduce the leakage rate** if possible (in this case, protect responders by spraying water). If the tank is in a closed area ventilate it before entering.
- **Avoid all contact** with liquid styrene and do not breathe styrene vapours (cf EPI: p. 40).

At sea

- **Whenever possible, prevent the slick from reaching the coast or the banks** and use floating boom or water jets to contain the liquid styrene providing this is not dangerous. Always work into the wind upstream of the slick.
- **Limit access to the danger area** and mark the slick with buoys (Argos PTR buoys).

Emergency measures in the event of a fire

- Using breathing apparatus (cf EPI: p. 40).
- Use extinguishing agents such as: powder, AFFF, foam, CO^2 (ICSC, 1999).

On board boats, try to stop the spill before attempting to extinguish the fire:

On the deck:
- use water spray, foam, (or dry ice, chemical powders if the fire is very small), and do not use full water jets;
- if possible, remove the endangered recipients or cool them down with a lot of water.

Below deck:
- close the hatches;
- use the on-board fire extinguishing system;
- take the same measures as for on deck fires;
- hose exposed recipients down with water whenever flames or heat are present and continue spraying well after the fire has been put out;
- keep well away from the ends of the tanks;
- move immediately out of range if the relief valve starts whistling or if the tank colour changes (owing to the fire).

Near the coast and in rivers (vessel has grounded), keep the general public out of the area because when styrene burns it produces toxic smoke.

If a fire is caused by burning styrene, hose the styrene tanks down with water if they are exposed to heat so as to avoid uncontrolled polymerisation likely to cause an explosion.

Styrene slick at sea during the Ievoli Sun *spill*

Response techniques

Transhipment

If no styrene tank is damages during the grounding, it may be necessary to transfer the cargo and the following precautions will have to be taken:

- If cargo transfer operations have to be conducted at night, spotlighting systems must be explosion proof and equipment must not produce sparks.
- Pressurised styrene tanks must not be emptied; nitrogen atmospheres will be used and slight excess pressure will be maintained during the transfer operation.
- To empty the tank by the top end, reduce vapour tension inside the tank by hosing it down with water or by releasing vapour at short intervals.
- Ensure vapours are evacuated by suction at source.
- Friction heat in a centrifugal pump that is no longer pumping can cause inhibited styrene to polymerise: ensure at all times that the pump is pumping.
- When handling styrene, do not use copper or copper alloys, natural rubber and polychloroprene. We recommend using viton, steel, psilomelane (MnO_2), magnesium and glass alloy.
- Recover styrene in fretted recipients that are grounded or made from galvanised iron (cf storage: p. 18).

Uncontrolled polymerisation in a wreck

To avoid uncontrolled polymerisation (bad quality inhibitor, slight heating, unwanted impurities), a polymerisation inhibitor can be added.

Transferring the styrene cargo to the Smit Pioneer *and the* Angela *chemical tanker during the* Ievoli Sun

Spill response

At sea

- General

As styrene is slightly viscous it will spread quickly and evaporate quickly or not depending on local temperatures. Styrene is colourless but can be evidenced on the water surface by white streaks.
At sea, responding to a styrene spill will be difficult but in some instances (confined areas, harbour areas) it may be possible to envisage recovering and treating the slick before it evaporates.

- Using skimmers and booms

Once a slick has been contained, it can be skimmed (providing the skimmer is made of compatible materials).
Booms covered with hypalon and hoses made from neoprene do not resist styrene very well at all. However, equipment made from stainless steel, aluminium alloy or coated with Teflon (interior) resist well.

- Using sorbents

Sorbents must be non flammable. Polypropylene and cellulose fibres can be used. It is best to use large grain size sorbent (e.g.: polypropylene chippings), at the following ratio, 2:1 namely twice as much sorbent as styrene by volume Styrene will probably be easy to absorb using bulthane (polyurethane powder) because toluene (methyl-benzene), a similar compound can be easily absorbed (with a sorbent to styrene ratio of 0.7 in a lab setting). Trials conducted at *Cedre* have showed however that agglomerate resistance was nil thereby precluding the use of it for high speed trawling at sea during recovery operations.

- Using dispersants

Regarding the dispersion of styrene, lab tests conducted by Cedre have shown that adding 5 % of FINASOL OSR 5 to styrene clearly enhances dispersion. However, when used in situ, dispersant ratios will have to be higher.

In inland waters

- If possible, a slick must be contained by mechanical or chemical booms.
- Styrene must be recovered in a watertight ditch and must not be allowed to burn (if styrene migrates down to the groundwater table it will cause serious pollution).
- Charcoal can be applied to the polluted area (10 per cent of the spilled quantities) if styrene concentrations in water exceed 10 mg/l.
- As styrene is likely to polymerise, water foul will have to be saved and cleaned.
- Non combustible synthetic sorbents can be used to remove all traces of styrene.

On the ground

- Polluted water must not be allowed to enter a sewage system as this may cause a fire or an explosion.
- Non combustible sorbents are recommended (polypropylene, cellulose fibres, cement, fly ash).
- Styrene residues can be absorbed by sand or vermiculite and collected in metal containers.

Choosing PPEs

Ensure maximum protection in the event of high concentrations

Selecting BAs (FINGAS. M., 2000)

Depending on Maximum Use Concentrations (MUC/CME)[2]:

- **Ordinary gas mask:** for concentrations of up to 200 ppm.
- **Respiratory tract protection** to be defined depending on the degree of exposure. Full gas mask with an A2 gas and organic vapour filter for concentrations of up to 500 ppm and 8 hours exposure (Baert. A., 2000).
- **SCBA:** no concentration limit (it is best not to exceed 100,000 ppm).

Selecting protective clothing (Baert.A, 2000/ CSST, 2003 / CEFIC, 2003)

- **Feet:** use long boots (up to the knees).
- Hands: wear gloves that cover forearms sufficiently.
- **Eyes:** Use airtight goggles or full face masks if there is a risk of splashing.
  For better protection, use full suit integrated masks fitted with A2 organic vapour and gas filter cartridges.
- **Clothes:** wear protective clothes: suitable chemical suits to be checked with the suppliers (do not use class 5 disposable overalls).

[2] It is worth noting that the MUC/CME can vary from one manufacturer to another. Contact the manufacturer for special information.

Chemical resistance

Materials	Degradation	Permeability	
Nitrile	Do not expose this fabric to styrene		Not advised
Neoprene	Do not expose this fabric to styrene		Not advised
Polyvinyl alcohol (PVA)	Slight	> 0,9 µg/cm²/min 6 to 50 drops/hour passing through the glove	Very suitable
Polyvinyl chloride (PVC)	Do not expose this fabric to styrene		Not advised
Natural rubber	Do not expose this fabric to styrene		Not advised
Linear Low Density polyethylene (LLDPE)	No degradation test	passage time > 480 min permeability > 0,9 µg/cm²/min 6 to 50 drops/hour passing through the glove	Very suitable

Advice for using SCBAs in a spill situation (FINGAS. M., 2000)

- On demand positive pressure open circuit SCBAs are the best. Their protection factor is about 10 000 (e.g.: ELV = 20 ppm, protection level up to 200 000 ppm of styrene in ambient air).
- Use an SCBA for unknown situations: unknown concentrations or high concentrations of a toxic; places where there may be an oxygen deficit (closed area).
- You can use an on demand air purifying respirator with a high efficiency filter in stable conditions and when the chemical concentrations do not reach an IDLH value and when it is unlikely to increase.
- Warning: some facial features such as a scar, narrow face, or facial hair (e.g.: beard) can prevent a snug fit for the face mask and thus impair protection.
- In warm weather: excessive sweating can impair air tightness of the seal between the mask and the skin.
- In cold weather: ice can form on the pressure valve and mist can cover the face piece.
  If air purifying respirators are used, place the oxygen cylinders in a warm vehicle prior to use. Dampness can freeze the respirator.
- NB: ordinary prescription glasses cannot be worn inside the mask (special frames exist) but contact lenses are allowed because new model respirators allow air exchange (the lenses in this case do not dry and do not stick to the eye ball).
  Adjustment testing is advised for people who are new to using masks and regular trials for experienced users.

Measures to be taken after using PPEs during a spill

- Decontaminate boots after a response job. Foot baths can be used with a mild detergent. Do not forget to treat the contaminated washing water.
- Decontaminate gloves separately using a bucket and a mild detergent.

Measuring equipment and waste treatment

Portable measuring equipment
(Environnement Canada, 2001)

Instruments	Manufacturer
Lovibond 2000 MkII	Lovibond The Tintometer
Comparator(a)	Compagny
Snapshot	Photovac

Field measuring equipment
(Baert, A., 2000)

Air monitoring can be done by pumps with charcoal filters (secondary thermal desorption) for calculating average exposure via Draeger tubes which afford instantaneous readings.

Recommendations for treating polluted water

- Polluted water can be air treated so as to ensure they are evacuated safely. The air will have to be burned if the liquid is highly polluted.
- Once all insoluble compounds have been removed polluted waters can be shipped to a facility where they will be treated biologically.
- Whatever cannot be retreated will have to incinerated.

Addresses where special industrial waste can be treated in France

Companies likely to treat such waste can also be found at the following web address: http://www.observatoire-dechets-bretagne.org

GEREP
route Jacquart
77299 Mitry Mory
Tel.: 01 64 27 16 97 / fax: 01 64 27 43 35

SEDIBEX
route industrielle
76430 Sandouville
Tel.: 02 32 79 54 10 / fax: 02 35 20 56 92

Soredi Groupe SARP industries ONYX
route Plessis Bouchet
44800 St Herblain
Tel.: 02 51 80 64 80 / fax: 02 40 43 45 48

SARP Industries
route de Hazay
78520 Limay
Tel.: 01 34 97 25 25 / fax: 01 34 77 22 25

Manufacturers
(CHIMEDIT, 2004)

ATOFINA, Shell Chemicals, Union Carbide, BP Chemicals

Supplementary information

- Bibliography — E1
- Glossary — E2
- Acronyms — E3
- Useful Internet adresses — E4

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OMI. *MARPOL 73/78 Edition récapitulative de 2002 : Articles, protocoles, annexes et interprétations uniformes de la Convention internationale de 1973 pour la prévention de la pollution par les navires, telle que modifiée par le Protocole de 1978 y relatif.* Londres : OMI, 2002. 547 p.

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Available at: http://www.reptox.csst.qc.ca (page consulted in March, 2003).

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Available at: http://www.cdc.gov/niosh/ipcs/french.htm (page consulted in March, 2003).

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Available at: http://www.incidentnews.gov/incidents/history.htm (page consulted in May, 2003).

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Available at: http://tis.eh.doe.gov/web/chem_safety/teel.html (page consulted in March, 2003).

Glossary

Admissible daily dose (ADD)
For humans this dose is the quantity of a substance that can be ingested by an organism in the space of a day for the rest of its life without presenting a health hazard for the organism in question.

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.

AEGLs (Acute Exposure Guideline Levels)
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 : is the airborne concentration (expressed as ppm (parts per million) or mg/m^3 (milligrams per cubic meter) 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 not disabling and are transient and reversible upon cessation of exposure.
AEGL 2 : is the airborne concentration (expressed as ppm or mg/m^3) 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 : is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

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

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

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

Bioconcentration factor, BCF
According to EPA guidelines, "the BCF is defined as the ratio of chemical concentration in the organism to that in surrounding water. Bio concentration occurs through uptake and retention of a substance from water only, through gill membranes or other external body surfaces. In the context of setting exposure criteria it is generally understood that the terms "BCF" and "steady-state BCF" are synonymous. A steady-state condition occurs when the organism is exposed for a sufficient length of time that the ratio does not change substantially."

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

BLEVE (Boiling Liquid Expanding Vapour Explosion)
A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has failed.

Boiling point (cf diagramme on page 44)
(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 thus measured depends on atmospheric pressure.

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

Critical temperature (cf figure on following page)
Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

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

Decompositon products
Products stemming from chemical or thermal disaggregation of a substance.

Diffusion coefficient in air (and in water) (cm^2/s at ambient temperature)
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).

Efficient concentration 50 (EC_{50})
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 intended to protect the population at large.
ERPG1: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odour.
ERPG2: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.
ERPG3: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

Exposure limit value (ELV)
Ceiling exposure value measured for a maximum duration of 15 minutes.

Flash point
The lowest temperature at which a substance generates vapours that ignite or burn immediately when approached by a flame.

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

Henry's law constant
Property of a substance to divide itself into two distinct phases of a binary air/water system.

Immediately Dangerous to Life or Health (IDLH)
Level below which a worker can, without availing himself of a respirator and without impairing his ability to escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere.

Irreversible effect threshold (IET)
Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

Lethal effect threshold (LET)
Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

Lower Explosive Limit (LEL)
Minimum airborne concentration above which vapours ignite.

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

MARVS (Max Admissible Relief Valve System)
Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

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

Median lethal concentration (LC_{50})
Concentration of a substance deduced statistically that should, during exposure and for a given period of time or subsequently, cause the death of 50% of the animals exposed during a given period of time.

Melting point (cf page 44)
Temperature at which solid and liquid state co-exist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

Minimum Risk Level (MRL)
This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic harmful effect on health for a specific exposure duration.

Miscible
Matter that mixes readily with water.

No Observed Effect Concentration (NOEC)
Concentration measured after chronic toxicity testing and for which no effect has been observed. The substance does not cause 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.

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.

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

Organic carbon/water partition coefficient (Koc) (for organic substances)
Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

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

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

Protective equipment
This means the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).
Level A: an SCBA (Self contained breathing apparatus/respirator) and fully air and chemical-tight suit (that resists permeation).
Level B: an SCBA and a suit that protects against liquid spray (splash proof).
Level C: a full face mask or goggles and a suit that protects responders against chemicals (splash-proof).
Level D: overalls without a respirator.

Rate of evaporation or volatility (ether = 1)
The rate of evaporation expresses the number of times that a product takes to evaporate as compared with a benchmark substance (ether for instance) This rate varies with the nature of the product and temperature.

Regression speed
Speed at which a burning liquid slick reduces in thinness.
For a given liquid, this speed is constant regardless of the slick surface (slick diameter bigger than 2 metres). Regression speed allows to estimate the total duration of a fire if no-one tries to extinguish it. For instance for a 1,000 mm thick slick, the regression speed may be 10 mm/minute, the fire lasts for 1000/10 = 100 minutes.

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

Relative vapour density
Weight of a volume of vapour or pure gas (without air) compared to that of an equal volume of dry air at the same temperature and pressure. A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When the vapour density is higher than 1 vapour is heavier than air and will tend to stay near ground level and spread.

Self-ignition temperature
Minimal temperature at which vapours ignite spontaneously.

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

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

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

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

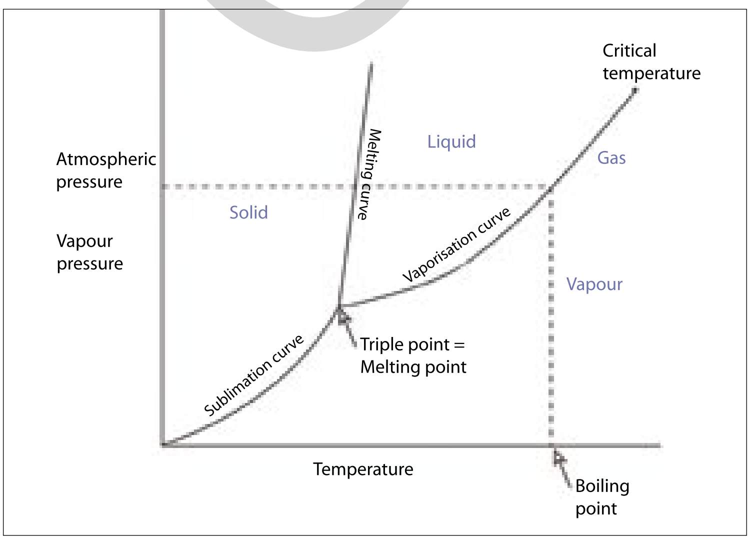
Temporary Emergency Exposure Limits (TEEL)
Exposure times when there is no ERPG.
TEEL 0 is the threshold concentration below which a large part of the population will experience no effect on health.
TEEL 1 is equivalent to ERPG1, TEEL 2 is equivalent to ERPG2 and TEEL 3 is equivalent to ERPG3.

Threshold Limit Value (TLV)
Average limit value (weighted as a function of time) that people can be exposed to regularly at work 8 hours a day, 5 days a week without experiencing harmful effects. This value was defined and determined by ACGIH.
TLV-STEL
Mean weighted 15 minutes concentration that must never be exceeded at any time during the day.
TLV-TWA
Man weighted values for an eight hour period per day and forty hours a week.
TLV-ceiling
Ceiling values never to be exceeded not even for an instant.

Unconfined Vapour Cloud Explosion (UVCE)
Explosion of a gas cloud or slick of combustible vapours in an unconfined environment.

Upper Explosive Limit (UEL)
Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

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



Phase diagramme of a pure substance

Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ADN	Accords De Navigation
ADR	Accords européens relatifs au transport international des marchandises dangereuses par route
AIHA	American International Health Alliance
AFSSA	Agence Française de Sécurité Sanitaire des Aliments
ALOHA	Areal LOcations of Hazardous Atmospheres
AFFF	Agent Formant un Film Flottant
APRA	Appareil de Protection Respiratoire Autonome
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bio Concentration Factor
CAS	Chemical Abstracts Service
CE	Concentration Efficace
CEA	Commissariat à l'Energie Atomique
CEDRE	Centre de Documentation de Recherche et d'Expérimentations sur les Pollutions Accidentelles des Eaux
CEFIC	Conseil Européen des Fédérations de l'Industrie Chimique
CHRIS	Chemical Hazards Response Information System
CL	Concentration médiane Létale
CME	Concentration Maximale d'Emploi
CSST	Commission de la Santé et de la Sécurité du Travail
CSTEE	Comité Scientifique sur la Toxicité, l'Ecotoxicité et l'Environnement
DDASS	Direction Départementale des Affaires Sanitaires et Sociales
DDE	Direction Départementale de l'Equipement
DJA	Dose Journalière Admissible
DJE	Dose Journalière d'Exposition
DRASS	Direction Régionale des Affaires Sanitaires et Sociales
DRIRE	Direction Régionale de l'Industrie, de la Recherche et de l'Environnement
ECB	European Chemicals Bureau
EINECS	European INventory of Existing Chemical Substances
EPI	Equipement de Protection Individuelle
ERPG	Emergency Response Planning Guidelines
HSDB	Hazardous Substances Data Bank
IATA	International Air Transport Association
IBC	International Bulk chemical Code
ICSC	International Chemical Safety Cards
IDLH	Immediately Dangerous to Life or Health concentrations
IFREMER	Institut Français de Recherche pour l'Exploitation de la MER
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
INCA	Enquête Individuelle et Nationale sur les Consommations Alimentaires
INCHEM	INternational CHEMical industries

INERIS	Institut National de l'Environnement Industriel et des RISques
INRS	Institut National de Recherche et de Sécurité
IPCS	International Programme on Chemical Safety
IPSN	Institut de Protection et de Sécurité Nucléaire
IUCLID	International Uniform Chemical Information Database
LIE	Limite Inférieure d'Explosivité
LSE	Limite Supérieure d'Explosivité
MARPOL	MARine POLlution
MCA	Maritime and Coastgard Agency
MEDD	Ministère de l'Ecologie et du Développement Durable
MRL	Minimum Risk Level
NOAA	National Oceanic and Atmospheric Administration
NIOSH	National Institute for Occupational Safety and Health
NOEC	No Observed Effect Concentration
OMI	Organisation Maritime Internationale
OMS	Organisation Mondiale pour la Santé
PEC	Predicted Effect Concentration
PID	Photo-Ionisation Detector
PNEC	Predicted No-Effect Concentration
ppm	Partie par million
pTBC	para Tertio Butyl Catéchole
ROV	Remot Operated Vehicle
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
TEEL	TEmporary Exposure Limits
TGD	Technical Guidance Document
TNO	Toegepast - Natuurwetenschappelijk Onderzoek. Nom anglais : the Netherlands Organisation for Applied Scientific Research
TLV-ceiling	Threshold Limit Values - ceiling
TLV-STEL	Threshold Limit Values - Short Term Exposure Limit
TLV-TWA	Threshold Limit Values - Time Weighted Average
US EPA	United States-Environmental Protection Agency
UIISC	Unité d'Instruction et d'Intervention de la Sécurité Civile
VHF	Very High Frequency
VLE	Valeur Limite d'Exposition
VME	Valeur Moyenne d'Exposition
ZDO	Zone de Défense Ouest

Useful Internet adresses

Accord de Bonn, Système européen de classification, [on line],
Available at: http://www.bonnagreement.org/fr/html/counter pollution_manual/chapitre25.htm

AFSSA (Agence Française de Sécurité Sanitaire des Aliments), [on line],
Available at: http://www.afssa.fr

ATOFINA, [on line],
Available at: http://www.atofina.com/groupe/gb/f_elf_2.cfm

ATSDR (Agency for Toxic Substances and Disease Registry), [on line],
Available at: www.atsdr.cdc.gov/tfacts53.pdf

Cedre (Centre de documentation de recherche et d'expérimentations sur les pollutions accidentelles des eaux), [on line],
Available at: http://www.cedre.fr

CEFIC (Conseil Européen des Fédérations de l'Industrie Chimique), [on line],
Available at: http://www.ericards.net

Chemfinder : [on line],
Available at: http://chemfinder.cambridgesoft.com

CHRIS (Chemical Hazards Response Information System), [on line],
Available at: http://www.chrismanual.com

CRIOS (Carcinogenic Risk In Occupational Settings), [on line],
Available at: http://cdfc.rug.ac.be/HealthRisk/default.htm

CSST (Commission de la Santé et de la Sécurité du Travail), [on line],
Available at: http://www.reptox.csst.qc.ca

CSTEE (Comité Scientifique sur la Toxicité, l'Ecotoxicité et l'Environnement), [on line],
Available at: http://europa.eu.int/comm/food/fs/sc/sct/out117_en.pdf

CTE (Centre de Technologie Environnementale du Canada) [on line],
Available at: http://www.etc-cte.ec.gc.ca/etchome_f.html

Environnement Canada : Mesure de la pollution, [on line],
Available at: http://www.etcentre.org/databases/fuelcalc_f.html

European Chemicals Bureau, Risk Assessment, [on line]
Available at: http://ecb.jrc.it/existing-chemicals

Hygiène et sécurité du travail, Listes des Valeurs Limites d'Exposition et des Valeurs Moyennes d'Exposition, [on line],
Available at: http://www.inrs.fr/produits/pdf/nd2098.pdf

ICSC (International Chemical Safety Cards) Programme International sur la Sécurité des Substances Chimiques (Fiches), [on line],
Available at: http://www.cdc.gov/niosh/ipcs/french.html

IDLH Documentation for Immediately Dangerous to Life or Health concentrations, Liste de 387 produits (originale et révisée) [on line],
Available at: http://www.cdc.gov/niosh/idlh/intridl4.html

INCHEM (INternational CHEMical Industries . Inc.), [on line],
Available at: http://www.inchem.org et http://inchem.org/pages/ilodb.html (liste des ERPG)

INERIS (Institut National de l'Environnement industriel et des RISques), [on line],
Available at: http://www.ineris.fr

INRS (Institut National de Recherche et de la Sécurité pour la prévention des accidents du travail et des maladies professionnelles, [on line],
Available at: http://www.inrs.fr/index_fla.html

IPCS (International Programme on Chemical Safety) [on line],
Available at: http://www.ilo.org/public/english/protection/safework/cis/products/icsc

Lyondell, entreprise chimique : [on line],
Available at: http://www.lyondell.com/html/products/products/sm.shtml

NIOSH (National Institute for Occupational Safety and Health), [on line],
Available at: http://www.cdc.gov/niosh/homepage.html

NOAA (National Oceanic and Atmospheric Administration), historical incident search page, [on line],
Available at: http://www.incidentnews.gov/incidents/history.htm

Sécaline (Système d'informations et de conseils sur les produits et déchets toxiques), [on line],
Available at: http://www.secaline.alison-envir.com

SHELL, Fiches de sécurité (MSDS), [on line],
Available at: http://www.euapps.shell.com/MSDS/GotoMsds

UIC (Union des Industries Chimiques), [on line],
Available at: http://www.uic.fr

Université de Nancy-Metz, Fiche de sécurité, [on line],
Available at: http://www.ac-nancy-metz.fr/enseign/physique/chim/sc_fds.htm

US Departement of Energy's, Chemical Safety Program, liste des ERPG, [on line],
Available at: http://tis.eh.doe.gov/web/chem_safety/teel.html

U.S.-EPA (Environmental Protection Agency), [on line],
Available at: http://www.epa.gov

US EPA, liste des AEGLs, [on line],
Available at: http://www.epa.gov/oppt/aegl/chemlist.htm

ANNEXES

Annex 1: Additional physical and toxicological data

Annex 2: Fax format data card

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ANNEX 1: ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification (CHRIS, 1999 and INRS, 1997)

CAS N°: 100-42-5
EINECS N°: 202-851-5
UN N°: 2055
EC index N°: 601-026-00-0
Class: 3

Physical data

Conversion factor

in air (25°C): 1 ppm = 4.26 mg/m³ ; 1 mg/m³ = 0.23 ppm

INERIS, 2000

Molar mass: 104.15 g/mol

HSDB (2000), IUCLID (1996), Merck (1996), Weiss (1986) in INERIS, 2000

Liquid volume mass: 905.9 kg/m³ at 20°C

FDS ATOFINA, 2003

Volume mass of vapour: 3.04 kg/m³ at 145°C

FDS ATOFINA, 2003

Physical state:
Appearance: liquid is oily, viscous and floats.
Colour: colourless to pale yellow.
Odour: pleasant, rather floral at low concentrations, unpleasant and heady at high concentrations.

CHRIS, 1999 and CSST, 2002 and FDS ATOFINA, 2003

Density:

Relative density (freshwater = 1):	0.9237 at 0°C	CSST, 2002
	0.9060 at 20°C	INRS, 1997
	0.8346 at 100°C	CSST, 2002
Relative vapour density (air = 1):	3.6 at 20°C	INRS, 1997
Relative density of air/vapour mixture (air = 1):	1.2	ICSC, 1999

Solubility:
Solubility in freshwater at 20°C: 300 mg/L

HSDB (2000), IUCLID (1996), Verschueren (1996) in INERIS, 2000

Solubility in seawater: (mg/L)

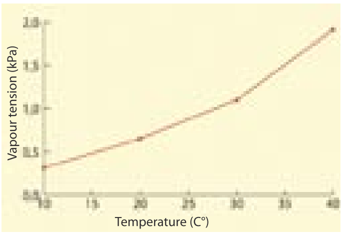
Cedre, 2003

Average energy	Without filtration (dissolved fraction and emulsioned fraction)	370 - 470
	With filtration	210 - 230
No energy	205 - 240	

increases when temperatures increase and drop when salinity increases.

Solubility in distilled water at 25°C: 320 mg/litre	Kirk-Othmer (1983) in INERIS, 2000
Solubility in other compounds: Soluble in methanol and carbon sulphide and miscible in acetone, carbon tetrachloride, benzene, ether, ethanol, n-Heptane hydrocarbons and ethylic ether.	Enviroguide, 1985 and FDS ATOFINA, 2003
Solubility of water in styrene: Soluble up to 0.07 g/100 ml at 25°C.	Environment Canada, 1985 and FDS ATOFINA, 2003
Emulsification: dissolved and emulsioned fraction, with a lot of energy (ultra turax): 840 mg/l (extreme value)	*Cedre*, 2003

Vapour tension: INRS, 1997



Important temperature:

Boiling point at 1 atm: 145° C	FDS ATOFINA, 2003
Melting point: -30.6°C	FDS ATOFINA, 2003
Flash point: 32°C	FDS ATOFINA, 2003
Self-ignition temperature: 490°C	INRS, 1997
Critical temperature: 373°C	CHRIS, 1999
Latent vaporisation heat: 44.6 kJ/mol (25°C)	Environment Canada, 1985
Polymerisation heat: 74.48 kJ/mol	Environment Canada, 1985

Other properties:

Henry's law constant : 275 Pa.m3/mol (at 25°C)	HSDB (2000), US EPA (1996) in INERIS, 2000
Diffusion coefficient in air : 7.1.10-2 cm2/s (at 25°C)	US EPA (1996) in INERIS, 2000
Diffusion coefficient in freshwater: 8.10-6 cm2/s (at 25°C)	US EPA (1996) in INERIS, 2000 Guide de la chimie (1999), Kirk-Othmer (1983) in INERIS, 2000
Dynamic viscosity: 0.763.10-3 Pa.s at 20°C	CHRIS, 1999
Surface tension : 0.03086 N/m at 20°C	Kirk-Othmer (1983) in INERIS, 2000
Interface tension/freshwater: 35.48 mN/m	CHRIS, 1999
Rate of evaporation (ether =1): 12.4	CSST, 2002

Olfactory threshold:

In air: 0.02 - 015 ppm	Kirk-Othmer (1983), NIOSH (1978), TNO (1997) in INERIS, 2000
In freshwater: 0.04 – 0.73 ppm	Prager (1995), TNO (1977) in INERIS, 2000

Toxicological data

Threshold toxicological values

IDLH: 700 ppm (2 982 mg/m^3)	CHRIS, 1999
TLV-TWA: 20 ppm (85.2 mg/m^3)	US/ACGIH (2003) in FDS ATOFINA, 2003
TLV-STEL: 40 ppm (170.4 mg/m^3)	US/ACGIH (2003) in FDS ATOFINA, 2003
AEV: 50 ppm (213 mg/m^3)	INRS, 1997
ELV: 100 ppm (426 mg/m^3)	FDS Shell, 2003
DJA/DAD: 0.133 mg/kg body weight per day	AFSSA, 2000
MRL oral: 0.2 mg/kg/day	ATSDR, (1992) in INERIS, 2000
MRL inhaled: 0.06 ppm (0.258 mg/m^3)	ATSDR (1992) in INERIS, 2000
Guide value by inhalation: 0.26 µg/m3 full life	OMS, 2000
TEEL 0: 50 ppm (213 mg/m^3)	US Department of Energy's Chemical Safety Program, 2002
ERPG 1: 50 ppm (213 mg/m^3): slight transitory effects	AFSSA, 2000
ERPG 2: 246 ppm (1 050 mg/m^3): reversible non dangerous effects	AFSSA, 2000
ERPG 3: 1000 ppm (4 260 mg/m^3): life threatening effects	US Department of Energy's Chemical Safety Program, 2002

General toxicity

Acute human toxicity: INRS, 1997 and ICSC, 1999

- By inhalation: dizziness, sleepiness, headaches, nausea, dyspnoea.
  At 500 ppm, irritation of eye and respiratory mucosa.
  At 1,000 ppm, impairment of the central nervous system.
- Skin and eyes: superficial and regressive lesions, rashes, pain.
- Ingestion: abdominal pain

Chronic human toxicity: INRS, 1997

- Can depress the CNS and PNS as of 20 ppm.
- Digestive disorders.
- Irritates the airways and respiratory tract.
- Irritates eye mucosa.
- Dermatoses, chronic dryness of the skin.
- Enzyme induction (elevation of gamma-glutamyltransferases).
- Uncertain as to haematological complications.

Specific effects:

Carcinogenic effects: styrene is a possible carcinogenic substance group 2B (CIRC-IARC).	INERIS, 2000
Effects on fertility: not demonstrated.	FDS ATOFINA, 2003
Teratogenic effects: not demonstrated.	FDS ATOFINA, 2003
Genotoxic effects: overall, no.	FDS ATOFINA, 2003
Mutagenic effects : some effects have been reported.	INRS, 1997

Ecotoxicological data

Acute ecotoxicity:

Seaweed (Scenesdesmus capricornutum)	CE_{50c}* (72h) = 4.9 mg/L	Cushman et al. (1997) in INERIS, 2000
Micro-crustaceans (Daphnia magna)	CE_{50} (48h) = 4.7 mg/L	Cushman et al. (1997) in INERIS, 2000
Fish (Pimephales promelas)	CL_{50} (96h) = 4.02 mg/L	Geiger et al. (1990) in INERIS, 2000
Bacteria (Pseudomonas fluorescens)	NOEC (16h) = 72 mg/L	Bringmann (1973) in INERIS, 2000
Annelids (Eisenia fœtida)	CL_{50} (14 days) = 120 mg/kg	Cushman et al. (1997) in INERIS, 2000

Chronic ecotoxicity:

ECB, 2002

PNEC water 0.004 mg/l
PNEC sediment (calculated) 0.340 mg/kg dry weight
PNEC soil 0.255 mg/kg dry weight

In 2003 styrene was risk assessed according to the EU 93/793 procedure, and the study produced intrinsic PNEC values (PNEC = Predicted No Effect Concentration) that are recognised inside the E.U. These values are thresholds below which there is or no longer is any effect on the organisms of the considered compartment such as water, sediment and soil.

* : growth

ANNEX 2: FAX FORMAT DATA CARD

STYRENE
Vinyl benzene, Cinnamene, Styrolene, Styrol, Phenylethylene, Phenylethene, Ethenylbenzene, Styropor, Cinnamol, Phenethylene.

$C_6H_5CH{=}CH_2$

CAS N°: 100-42-5
EINECS N°: 202-851-5
EC N°: 601-026-00-0
UN N°: 2055
Class: 3

First aid data

Inhalation: take the victim outside into the open air. Oxygen or artificial respiration if necessary. Place under medical surveillance. Accidental pulmonary aspiration may cause serious lung disorders.
Skin contact: remove contaminated clothing. Rinse and wash the skin with a lot of water and use soap also. Rashes can be treated with products such as Biafine. Refer the patient to a healthcare professional (MD). Admit to hospital.
Poisoning by ingestion: rinse the mouth. DO NOT CAUSE PATIENT TO VOMIT.Rest. Refer to a healthcare professional. Admit to hospital.
Eye contact: first rinse the mouth a lot with water for several minutes, remove contact lenses if possible.

Physical data

Conversion factor : in air at 25°C 1 ppm = 4.26 mg/m^3; 1 mg/m^3 = 0.23 ppm

Relative density (water=1): 0.906 at 20°C
Relative vapour density (air = 1): 3.6 at 20°C
Solubility in freshwater: 300 mg/l at 20°C
Solubility in seawater: minimum: 205 - 240 mg/l
maximum: 370 - 470 mg/l
Vapour pressure/tension: 0.312 kPa at 10°C
0.6-0.7 kPa at 20°C
Olfactory threshold: in freshwater: 0.170 – 3.11 mg/m^3
in air : 0.08 – 0.63 mg/m^3
Rate of evaporation (ether=1): 12.4
Diffusion coefficient in water: 8.10^{-6} cm^2/s at 25°C
Diffusion coefficient in air: 7.1.10^{-2} cm^2/s at 25°C
Henry's law constant: 275 Pa.m3/mol at 25°C
Flash point: 32°C
Melting point: -30.6°C
Boiling point: 145°C

Xn-Noxious

R10 - Flammable
R20 – Harmful when inhaled
R36/38 - Irritates eyes and skin
S23 – Do not breathe vapours
202-851-5 EU classification and labelling

Toxicological data

Threshold toxicological values

IDLH: 700 ppm (2,982 mg/m³)
TLV-TWA (8h): 20 ppm (85.2 mg/m³)
TLV-STEL (15 min): 40 ppm (170.4 mg/m³)
DAD: 0.133 mg/kg body weight per day
MRL oral: 0.2 mg/kg/day
MRL inhalation: 0.06 ppm (0.258 mg/m³)
SEL: 5,000 ppm (15 min) 1,000 ppm (60 min)
SEI: 800 ppm (15 min) 250 ppm (60 min)
SER: 200 ppm (15 min) 50 ppm (60 min)
AEV: 50 ppm (213 mg/m³)
LEV: 100 ppm (426 mg/m³)
TEEL 0: 50 ppm (213 mg/m³)
ERPG 1: 50 ppm (213 mg/m³)
ERPG 2: 246 ppm (1,050 mg/m³)
ERPG 3: 1,000 ppm (4,260 mg/m³)
Guide value by inhalation: 0.26 µg/m^3 full life

Specific effects

Carcinogenic effects: possible/ group 2B.
Effects on fertility: not demonstrated.
Teratogenic effects: not demonstrated.
Genotoxic effects: overall, no.
Mutagenic effects: some effects reported.

Acute human toxicity

Ingestion: abdominal pain.
Skin contact: superficial and regressive lesions, rashes.
Eye contact: superficial and regressive lesions, rashes, pain.
Inhalation: dizziness, drowsiness, headaches, nausea, dyspnoea.

Chronic human toxicity

- Depresses the CNS and PNS from 20 ppm upwards.
- Digestive disorders.
- Irritates the respiratory tract.
- Irritates the eye mucosa.
- Dermatosis, chronic dryness.
- Enzyme induction (elevation of gamma-glutamyltransferases).
- Uncertainty regarding possible blood disorders or anomalies.

Ecotoxicological data

- **Acute ecotoxicity:**

Seaweed (*Scenesdesmus capricornutum*) CEc50 (72h) = 4.9 mg/l
Micro-crustaceans (*Daphnia magna*) CE50 (48h) = 4.7 mg/l
Fish (*Pimephales promelas*) CL50 (96h) = 4.02 mg/l
Bacteria (*Pseudomonas fluorescens*) NOEC (16h) = 72 mg/l
Annelids (*Eisenia foetida*) CL50 (14 days) = 120 mg/kg

- **Chronic ecotoxicity:** no data

PNEC water: 0.004 mg/l
PNEC sediment: (calculated) 0.340 mg/kg dry weight
PNEC soil: 0.255 mg/kg dry weight

Persistence in the environment

- **Photo-oxidation:** styrene degrades in the air by oxidation with hydroxyl radicals (OH) and by reacting with ozone. Formaldehyde and benzaldehyde are the most important degradation products. In air: t1/2 life = 4 h.

- **Volatilisation:** evaporation is rapid: t1/2 life = 3h (at a depth of 1 m, current 1m/s and a wind speed of 3 m/s), for a lake t1/2 life = 3 days and for an oligotrophic lake t1/2 life=13 days.

- **Biodegradation:**

- Freshwater: t1/2 life = 15 days

- Underground water: t1/2 life = 4 to 30 weeks

- Seawater (estimation): t1/2 life = 45 days

- **MARPOL classification:**
  B until 31/12/2006
  Y from 01/01/2007

- **Classification SEBC: F/E**
  (Floater/Evaporator)

- **Partition coefficient for octanol/water:**
  log Kow = 3.02

- **Partition coefficient for organic carbon/water:**
  Koc = 352 L/kg

BCF (fish) = 74
BCF (crab) = 12
BCF (red fish) = 13.5

Special risks

Polymerisation:
Styrene monomer is stabilised by para Tertio Butyl Catechol (pTBC) which inhibits polymerisation (=solidification). Polymerisation can be exothermal and even explosive.

Danger:
- If a styrene tank heats up, pressure will build up and the tank may burst and explode. However, risks related to ignition may escalate (fire ball).
- Risk of spontaneous increase in pressure or self-ignition when exposed to heat, light, shock or when coming into contact with other chemicals.
- Toxic and irritating smoke may be formed from heating or combustion.
- Styrene can form explosive mixtures with air at high ambient temperatures.
- Styrene vapour is invisible and heavier than air. It spreads over the ground and can enter sewage systems and underground areas.
- Heat may destroy the inhibitor.

Fire:
- Explosion limits in air (%): LEL : 1.1; UEL : 6.1
- Smoke: smoke will be an irritant or toxic in the event of a fire.
- Self-ignition point: 490°C.
- Regression speed: 5.2 mm/min

Stability and reactivity
- Conditions to be complied with:
Store far from damp and heat.
Store at temperatures lower than 25°C.
- Reacts explosively with: peroxides, oxidisers, sulphuric acid, chlorosulfonic acid, oleums, bases, composites of alkaline metals and graphite.
- Dangerous decomposition products:
Thermal decomposition produces organic derivatives.
By combustion, formation of toxic products : carbon, carbon monoxide carbon dioxide.

Transportation

General data: Class: 3
Labels: 3

Road transport
RID/ADR Danger identification number: 39
Packing group: III
Classification code: F1

ADN/ADNR Materials number: 2055
Danger identification number: 39
Identification code: F1

Sea and air transportation
IMDG IATA packing group: III

Handling

- Provide a ventilation system and appropriate evacuation procedures.
- Provide showers, eye fountain.
- Only use styrene in a closed system.
- Do not use air for transferring and circulating styrene.
- Avoid sprinkle loading styrene as this may cause it to ignite.
- Use small speeds for handling styrene (static electricity).
- When handling, keep well clear of flames.
- Only use explosion proof equipment.

Storage

- Keep recipients tightly closed in a well aired and cool place.
- Keep well clear of all sources of ignition.
- Store far from humidity and heat.
- Maintain temperatures lower than 25°C.
- To avoid uncontrolled polymerisation, maintain inhibitor levels and oxygen concentrations in the liquid phase above minimum levels,
(TBC >10 ppm and oxygen >15 ppm).
- Ensure that styrene vapours can be collected.
- Provide a dyked area.
- ground all electrical equipment if it has to be used in an explosive atmosphere.
- If styrene has to be handled/used at temperatures higher than flash point, maintain an inert gas atmosphere.

ANNEX 3: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Dangerous goods (IMO, 2002)

Regulations governing the carriage in bulk of hazardous liquid substances (MARPOL Annex II) provide valuable indications on the hazards that such substances can produce during transportation.
Noxious liquid substances are classified into 4 categories (A, B, C, D) starting with the most dangerous substances (MARPOL A) and ending with the least dangerous ones (MARPOL D).
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).

Category A - Noxious liquid substances which, if discharged into the sea from tank washing or defalcating operations, are deemed to present a major hazard to marine resources or human health or can cause serious harm to amenities or other legitimate uses of the sea and therefore justify the implementation of strict pollution response measures.

Category B - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to present a hazard to marine resources or human health and can harm amenities or other legitimate uses of the sea and therefore justify the implementation of special pollution response measures.

Category C - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a minor risk for marine resources or human health or cause, to some extent, harm to amenities or other legitimate uses of the sea and therefore require special operating conditions.

Category D - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a noticeable risk for marine resources or human health or have a very slight effect on amenities or other legitimate uses of the sea and therefore require certain precautions concerning operating conditions.

ANNEX 3b: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Revised MARPOL Annex II (IMO, 2005)

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

The new categories are:

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

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

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

Other Substances: substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning of deballasting operations. The discharge of bilge or ballast water or other residues or mixtures containing these substances are not subject to any requirements of MARPOL Annex II.