

## STYRENE. ENVIRONMENTAL CONSEQUENCES OF A SPILL AT SEA

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### KEY WORDS

### ABSTRACT

#### 1. The substance

Styrene, also known as vinylbenzene or sterol, is an odourless, viscous liquid with a potential to polymerize. It has a molecular mass of 104.15 and the chemical formula  $C_6H_5CH=CH_2$ .

Styrene is highly soluble in benzene and petroleum ether and just marginally soluble in water, ethanol, and water.

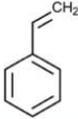
#### 2. Use

Polystyrene polymers and resins are mostly produced using styrene (James and Castor 2005). Polyester resins that have been dissolved in styrene are also utilized to make fiberglass items that are used in boats. Styrene is also utilized as an intermediary in the production of copolymers such as acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) that are used as ion exchange resins (ABS). Styrene-butadiene latex, a similar polymer, is used to create latex paint, paper coatings, and carpet. Materials including pipework, automotive parts, refrigerator liners, plastic drinking glasses, and car battery enclosures are made of SAN and ABS. In products like boat hulls, an additional 7% of styrene is formulated with unsaturated polyester resins (fiberglass reinforcement materials). The remaining amounts of styrene produced are used for several types of applications, including fewer common thermoplastics and even for laboratory and water purification uses (ion-exchange resins) and glues and adhesives (James and Castor 2005). "Styrene copolymers are also frequently used in liquid toner for photocopiers and printers" (HSDB 2009).

The Food and Drug Administration (FDA) permits styrene to be used as a direct additive for synthetic flavouring and an indirect additive in polyester resins, ion-exchange membranes, and in rubber articles (5% by weight maximum) intended for use with foods (HSDB 2009; IARC 1979; NIOSH 1983).



### 3. Physical and chemical properties

General Information	
Chemical name	Styrene
Synonyms	Cinnamene, ethenylbenzene, phenylethylene, styrol, vinylbenzene
Chemical formula	C <sub>8</sub> H <sub>8</sub>
Chemical structure	
Molecular weight	104.15
Color	Colorless to yellow
Odor	Sweet, aromatic (if pure) Sharp, penetrating, unpleasant (commercial grades)
Physical state	Oily liquid
Identification numbers	CAS Registry: 100-42-5 EINICS: 202-851-5 DOT/UN/NA/IMDG shipping: IMDG 3.3; UN 2055

Physical Properties	
Characteristic	Property
Melting point	-30.6 °C
Boiling point	145.2 °C
Critical temperature	373 °C
Solubility	300 mg/L (0.03% wt.vol.)
Water at 20 °C	Soluble in alcohol, ether, acetone, carbon disulfide
Organic solvents	
Partition coefficients	Log
KOW	2.95
Log KOC	2.96
Vapor density (air = 1)	3.6 at 20oC
Vapor pressure at 20 °C	5 mmHG (5 mbar)
Henry's law constant (at 25 °C)	261x10 <sup>-3</sup> atm-m <sup>3</sup> /mol
Rate of evaporation (ether = 1)	12.4 (takes 12.4 times longer to evaporate than ether)

### 4. Spill of styrene and its toxicological effect

#### 4.1 Facts

Spill weight – 2400 tonnes

Volume of the coastal area - 120 \* 109 l

Estimated concentration – 20 mg/L

#### 4.2 Toxicological data

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.
- Dermatitis, chronic dryness.
- Enzyme induction (elevation of gamma-glutamyltransferases).
- Uncertainty regarding possible haematological anomalies Specific effects
- Carcinogenic effects: possible group 2B
- Effect on fertility: not demonstrated
- Teratogenic effects: not demonstrated
- Mutagenic effects: some effects reported

<b>4.3 Ecotoxicological data</b>		
Acute toxicity		
Seaweed	CE (72h)	= 4.9 mg/L
Daphnia magna	CE (48h)	= 4.7 mg/L
Fish	CL (96h)	= 4.02 mg/L
Bacteria	NOEC (16h)	= 72 mg/L
Annelids	CL (14 days)	= 120 mg/kg
Chronic ecotoxicity: no data		

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

Styrene's risk was evaluated in 2003 in accordance with EU procedure 93/793, and the study resulted in intrinsic PNEC values that were accepted by the EU. These numbers represent thresholds below which organisms in the compartments under consideration, like water, sediment, and soil, are no longer affected.

PNEC for water: 0.004 mg/L

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

#### **4.4 Persistence in the environment**

##### **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 hours

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: 1m, current: 1 m/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 biotransformation.

Partition coefficient for octanol/water BCF (fish) = 74 (INERIS, 2000)

BCF (crab) = 12. (Cedre, 2001a) BCF (red fish) = 13.5 (ECB, 2002)

### **Reminder of chemical properties**

- Density and vapour tension 20°C.
- Vapour density: 3.6
- Vapour tension: 0.6 kPa

### **Solubility**

The solubility of styrene in seawater is between 205 and 470 mg/L

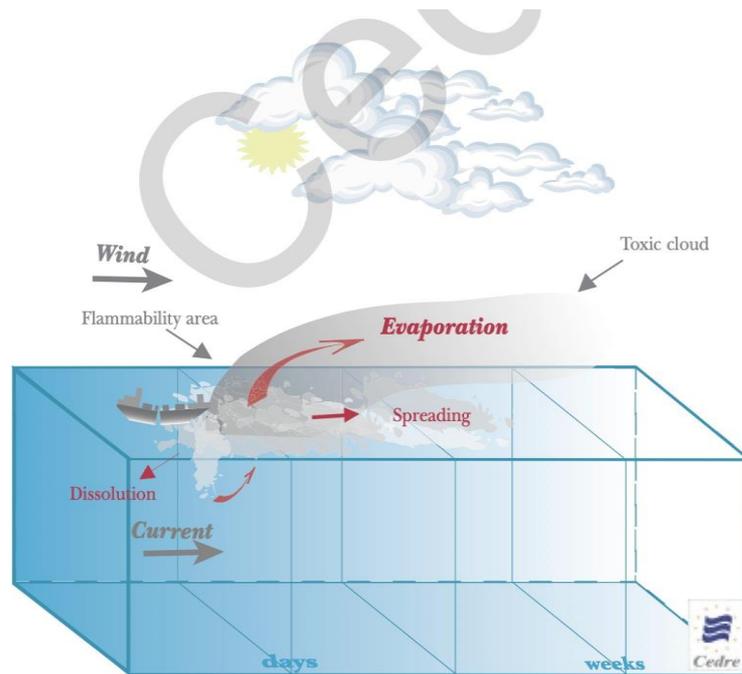
The solubility and vapour tension of styrene are such that it can be classified as a floater/evaporator **(F/E)**

### **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 ( $\rho = 1$ ). The styrene cloud will therefore tend to stay on the water surface.



**Fig. 1. Simulation of the styrene spill**

Source: Cedre, Styrene

If a person eats seafood containing 200  $\mu\text{g}$  of styrene per gramme (body tissue) at a rate of 10 grammes a day, there is no risk to human health. However, consuming 500  $\mu\text{g}$  of styrene per gramme (body tissue) at a rate 150 grammes per week, there will be a risk for human health.

#### 4.5 A record of styrene spill

There were a few styrene leaks, and "levoli Sun" is one among them. The Levoli Sun chemical tanker sunk off the coast of France on October 31st, 2000. It was transporting 4,000 tonnes of styrene monomer, 1,000 tonnes of MEK, and 1,000 tonnes of isopropyl alcohol. This example may serve as a possible outcome in our scenario.

#### Reports

- After the sinking: 3 unidentified slicks were seen
- 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 x 40 m) with occasional "remissions".

#### Styrene in the atmosphere

##### At sea

Samples are taken from around the wreck during the following days (7 air samples) with different techniques

- Tenax (charcoal): 5 samples were positive;
- Draegar 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 the mainland



Styrene was not found in the studies employing Tenax tubes and a mass spectrometer. Styrene concentrations in live organisms 9 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  $\mu\text{g}/\text{kg}$  (meat)

18  $\mu\text{g}/\text{kg}$  (gills)

Jonab crab: 230  $\mu\text{g}/\text{kg}$  (meat)

340  $\mu\text{g}/\text{kg}$  (gills)

## 5. Response

### Recommendations regarding response

Response is possible. The risk of fire increases in this case because a significant amount of spilt styrene evaporates instantly.

Within the first several hours following the spill, surveillance planes must be prohibited. Any effort to approach the spill region at sea in boats or motorboats that might set the vapours on fire is prohibited.

### 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.** Much water should be sprayed on the material that was spilt on the deck before throwing the water overboard. As much water as possible will need to be retrieved and then treated in an inland water context.

To disperse combustible vapours and lower the likelihood of an explosion, spray water. Efficient utilization of fluoroprotein foams can help to reduce evaporation.

Don't come into touch with any styrene liquid, and stay away from styrene vapours.

#### At sea

Whenever possible, keep the slick from reaching the banks or the shore. If necessary, you can utilize water jets or floating boom to keep the liquid styrene contained. Always move upwind of the slick while facing the wind.

Limit access to the risk area and use buoys to identify the slick.

Fishing and other recreational activities are prohibited until the concentration falls to a safe level.

A slick can be skimmed once it has been contained. Using non-flammable sorbents.

## 6. Monitoring the natural system

After the spill, it is necessary to implement systematic methods to observe the effect of the spill. Vapours of styrene pose more dangerous threat to the community living along the bank. Therefore, air monitoring along with water monitoring must be main studies in order to set up appropriate measures.

Bioconcentration of styrene in aquatic organisms is not likely to be significant, based on both a measured BCF for a single goldfish species (BCF = 13.5; Ogata et al. 1984) and an estimated BCF. No data on biomagnification of styrene in the food chain were located. Since significant bioaccumulation is unlikely, this lack of data may not be a major limitation.

Hence, medium scaled analysis for contamination in aquatic species should be taken.



## 7. Conclusion

The spill of 2400 tonnes of styrene can negatively affect the local environment as it quickly evaporates and becomes flammable. The vapours delivered by wind towards the shore and inwards can contaminate the air and form toxic cloud. However, a few people can experience the acute health effects as the concentration of styrene is not that high, but still the people can be exposed to it in a small quantity and as consequence chronic health effects will probably be observed in the long-term. To limit the negative impact, necessary steps and regulation must be done according to the authorized chemical response guide.

Regarding the ecological consequences, the spill may not hugely disrupt the ecosystem, as it tends to float on the surface of the water and its bioaccumulation is not high.

An environmental agency should consider the effect of evaporated styrene as it is almost insoluble in water and less dense than water. The concentration of styrene in the air poses greater danger than in the water.

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