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Environmental Parameter Effects on the Fate of a Chemical Slick

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1. Introduction

Recent data highlights the growing trend in the transport of dangerous substances and the consequent evolution in legislation concerning such substances, whether on a European level (evolution of the Standard European Behaviour Classification, or SEBC code) or on a worldwide scale (new MARPOL-Annex II classification which entered into force on 1st January 2007, the OPRC-HNS Protocol, as well as the HNS Convention). This evolution is however based exclusively on data from the literature which all too often cannot be applied to spills, as it does not take into account the influence of factors in the marine environment on the physico-chemical characteristics of the product spilt.

Yet, following a spill at sea of a bulk liquid chemical, the response authorities must immediately take measures in order to reduce the risks of exposure of the surrounding population as well as to prevent contamination of the marine ecosystem as a whole and, more widely, to protect all life forms. To succeed in this effort that forms a part of emergency response, it is vital to know which compartment of the ecosystem will be affected (atmosphere, water surface, water column, sediments...) and to monitor the evolution of concentrations in order to define the environmental risks.

The accident of the chemical tanker *Ievoli Sun* which sank in the English Channel in 2000 releasing approximately 1,000 tonnes of styrene into the sea (Law et al., 2003) has raised concerns about the fate of this compound at sea. In the aquatic environment, styrene is often reported to be of low risk for chronic effects due to its volatility and low bioaccumulation potential. Hence, the potential for styrene to produce long term adverse environmental impacts appears to be negligible. However, most of these statements are based on tests performed in fresh water environments whilst very few data exist concerning the marine environment. Also, the value of some of these tests can on some occasions be questionable as they are reliant on a static mode of exposure and measurements of the actual exposure concentrations are not performed during the tests. Hence, although styrene's volatility and biodegradability would in most cases significantly reduce the levels in water, the behaviour and bioavailability of styrene in saline water is not very well known. Thereby, a better

evaluation of the actual toxic effects of this compound in marine aquatic organisms is needed. In the recent example of the *levoli Sun* vessel, a relatively large amount of styrene was discharged in a relatively short time. Yet, studies showed that only low levels of styrene contamination were measured in edible tissues of crabs caught in the immediate vicinity of the wreck site (Law et al., 2003). Bioaccumulation does not necessarily represent the real uptake of a contaminant as many aquatic organisms including fish and crustaceans are able to efficiently biotransform the mother compounds into more polar metabolites, thereby considerably reducing the bioaccumulation factor of the mother compound. Even at low concentrations, it is known that some substances can disturb important biochemical pathways which can impair biochemical functioning of cells and lead to deleterious effects in tissue, like cancer development, in the longer term (Alexander, 1997; Vaghef & Hellman, 1998; Moller et al., 2000). Furthermore, the styrene released from the wreck lying on the floor of the Channel, whose density is lower than that of seawater, rose through the water column to form slicks at the sea surface. These slicks drifted under the combined influence of the wind and marine currents, without ever reaching the coast. Under the effect of the wind and sunshine, the styrene evaporated to form an invisible cloud whose fate was then dependent, both in terms of drift and dilution on aerial currents alone. Following this succession of physico-chemical events, the response authorities had to deal with contamination of the atmosphere, in addition to water pollution, by a product recognised as being particularly neurotoxic (Laffon et al., 2002). The French Customs operators conducting aerial surveillance above the spill area were not prepared for this new risk and were exposed to styrene vapours, resulting in disabling headaches. Just as concerning, on the inhabited island of Aurigny, naval firefighters sporadically yet repeatedly detected the presence of styrene in the air. The inability to predict, i.e. to anticipate, arrivals of styrene gas on the coast rendered contingency plans ineffective for the protection of the population. While no consequences on the health of neighbouring populations were reported in this incident, as the concentrations always remained below the ADI for styrene, things could have been quite different with other more toxic substances.

While classifications can be used to predict the theoretical fate of a product in the event of a spill in the environment, they do not take into account the specificities of this environment and should therefore be used cautiously. For instance, wind and sunshine can significantly affect chemicals' evaporation. A similar observation can be made for the salinity and temperature of seawater and the chemicals' hydrosolubility. Furthermore, while the prediction of a substance's fate in the event of a spill has been facilitated by the emergence of forecast software (CLARA, CHEMMAP...), these predictions must nevertheless be validated by field measurements. Forecasting predicts behaviour, i.e. the fate of products in the environment, from the physico-chemical characteristics of products as determined in laboratory conditions, to which mathematical equations are applied which often underestimate certain environmental parameters such as the influence of surface agitation on the spreading of the slick or sunshine on evaporation. This software also has difficulty in predicting the interaction of chemicals with the sea water matrix in the case of a leaking wreck, due to a lack of information on the effects of pressure, temperature and salinity on dissolution processes (Le Floch et al., 2007; 2009).

This work aimed to obtain experimental data on the behaviour of 3 liquid chemicals when released at sea and to characterise them through *in situ* experiments. For this purpose,

experimental open cells were set up in Brest Bay, each of them made of a 9 square metre surface surrounded with a 3 metre high nylon skirt set on a metal structure. As the cell sides were flexible, the contained water was subject to the influence of swell and waves. As the cells were not covered, the sea surface was subject to atmospheric influences (wind, sunshine and rain). After releasing the products at the surface, weathering processes were studied by measuring the viscosity of the slick, solubility in the water column and gas cloud formation.

2. Fate of chemicals in the environment after accidental release

Several international, regional and national authorities, aware of the risk connected with the transport of chemicals by sea, have published operational guides to describe the possible response options. For instance, IMO has published several manuals (IMO, 1987, 1992, 2006) and REMPEC has done the same for the Mediterranean area (REMPEC, 1996, 1999, 2004). We can also mention the Helsinki Baltic Sea Convention manuals (HELCOM, 1991, 2002, 2007) and the North Sea Bonn Agreement manuals (Bonn Agreement, 1985, 1994). At a national level in France, *Cedre* has produced response guides, each of which is specifically dedicated to a given chemical.

Alongside this information, which ranges from general (i.e. in the case of a guide on response at sea to hazardous substances) to specific (i.e. guides that characterize the behaviour and identify the risks related to a given product), the Standard European Behaviour Classification system or SEBC code determines the short term behaviour of any chemical as long as its physico-chemical characteristics are known. This tool is of the utmost importance for operational staff in charge of response, as it can be used in an emergency to indicate the main components of the ecosystem that will be affected. However, experience has made it clear that this code can be tricky to use as it can be difficult to understand how environmental factors (wind, sunshine, water and air temperature, etc.) will affect the chemicals' categorization. Indeed these parameters have a very significant influence on the short-term fate of chemicals in the marine environment, in particular on their evaporation kinetics (transfer from the water surface to the atmosphere), their dissolution kinetics (transfer from the water surface to the water column) and their transport and transformation processes in the aqueous phase.

2.1 Fate of substances with low reactivity

In the case of a spill, response usually follows three generally accepted scenarios: i) response is not possible because the spill occurred in a geographical environment that is incompatible with reasonable response times; ii) response is not possible due to the reactivity of the substances (major, imminent danger); iii) response is possible.

If, in the latter scenario, the substance spilled is not particularly reactive, it is important to bear in mind that the slick formed will evolve. Immediately after its accidental release into the marine environment, the substance will tend to move into different components of the ecosystem, i.e. the atmosphere, the sea surface, the water column and the seafloor. These different forms of distribution are gathered under the umbrella term of "fate", for which we generally distinguish short term behaviour (a few hours) and longer term behaviour (up to several years).

2.2 Short term fate

Short term behaviour covers a duration ranging from a few minutes to a few hours, and it must be known in order to implement response measures and techniques. It was in light of this observation that the Standard European Behaviour Classification, or SEBC code, was developed (Cedre, 1988; Bonn Agreement, 1994; GESAMP, 2002).

This code classifies the behaviour of chemical substances according to their state and some of their physical properties, i.e. density, vapour pressure and solubility. The state of the substance refers to whether it is in the form of a gas, a liquid or a solid at 20°C. The density, defined as the mass per unit volume compared to that of seawater (1.03 g.cm⁻³, at 20°C), determines whether or not a substance will float. The vapour pressure is defined as the partial vapour pressure of a compound in equilibrium with its pure condensed phase (liquid or solid). It is generally accepted that a floating substance will not evaporate if its vapour pressure is lower than 0.3 kPa and it will evaporate rapidly if its vapour pressure is higher than 3 kPa. For dissolved substances, evaporation occurs when the vapour pressure is greater than 10 kPa. Solubility is defined as the maximum abundance of a compound per unit volume in the aqueous phase when the solution is in equilibrium with the pure compound in its initial state. It is usually measured at 20°C, at a pressure of 1 atmosphere, in distilled water (zero salinity). The criteria used are different according to the physical state of the substance. A substance is considered insoluble if its solubility is less than 0.1% for liquids and less than 10% for solids. At the other end of the scale, the phenomenon of dilution will take place if the solubility is greater than 5% for liquids and greater than 100% for solids.

These limits are presented in Figure 1 and can be used to identify 12 types of behaviour, which are summarized in Table 1.

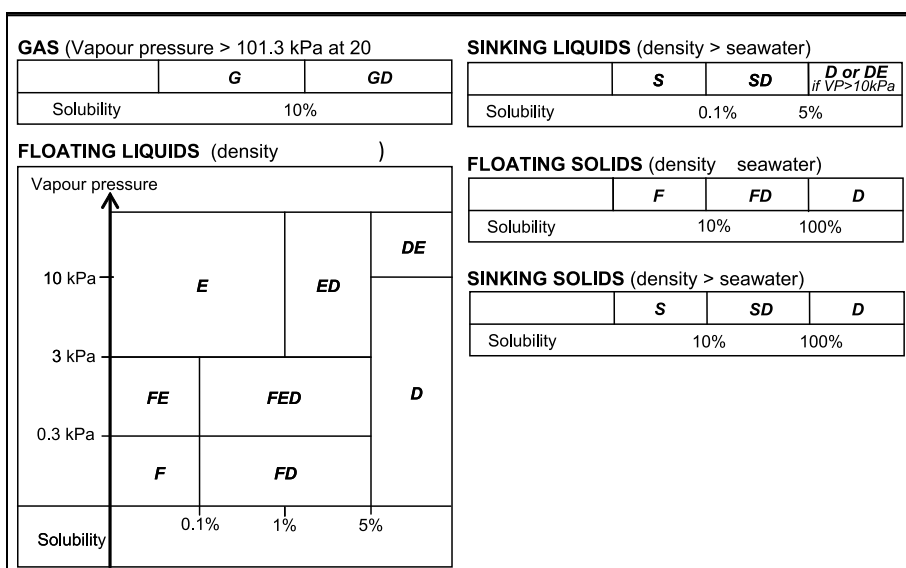


Fig. 1. SEBC Classification of Chemical Products according to their Physical State and Physical Properties

| Main group | | Subgroup | |
|------------|------------|----------|---------------------------------------|
| G | Gas | GD | Gas that dissolves |
| E | Evaporator | ED | Evaporator that dissolves |
| F | Floater | FE | Floater that evaporates |
| | | FD | Floater that dissolves |
| | | FED | Floater that evaporates and dissolves |
| D | Dissolver | DE | Dissolver that evaporates |
| S | Sinker | SD | Sinker that dissolves |

Table 1. The 12 Behaviour Groups according to the Standard European Behaviour Classification System

2.3 Long term fate

In terms of response, it is also useful to be aware of longer term behaviour as it provides information on the fate of a pollutant that cannot be removed from the environment through response operations. The residual chemical will spread through the atmosphere and/or the water column where it may become associated with sediment particles in suspension before settling. In water and air, the ultimate fate of chemicals will depend on the processes of dispersion, breakdown and other physical, chemical or biological transformations. These processes can extend over periods ranging from a few months to several years when the substance remains in the environment.

In terms of fate, all these phenomena will contribute, in the best case scenario, to the disappearance of the product and, in the worst case scenario, to its accumulation or even its transfer into another part of the ecosystem.

2.4 Influence of environmental factors on fate

Spill response fundamentally requires rapid identification of the compartment(s) of the ecosystem in which the pollutant will accumulate so as to implement the appropriate means to reduce, or even eliminate, its impact. While the SEBC code provides initial elements of response, the operational personnel in charge of response must interpret this classification critically so as to assess whether or not the specificities of the environment in which the incident has occurred will alter the results. This critical interpretation may go as far as altering the categorization of a substance as in the case of the industrial incident at the Jilin plant in China.

On 13 November 2005, an explosion occurred in a petrochemical plant resulting in a spill of around one hundred tonnes of various substances into the Songhua River. Analyses conducted by the Chinese Research Academy of Environmental Science showed that the water contained benzene and nitrobenzene concentrations 30 to 100 times higher than the accepted standards, of 0.01 mg.L⁻¹ and 0.017 mg.L⁻¹ respectively (Ambrose, 2006; UNEP, 2006). The pollution was carried by the current, and concentrations 34 times higher than standard levels were found in Harbin, 380 km downstream of Jilin, and 10 times higher than standard levels in Jiamusi, 550 km downstream. This decrease can be explained both by the

processes of dilution and adsorption of the chemicals by organic matter present in the water, either in suspension, or on the banks (Levshina et al., 2009). These unexpectedly high concentrations can be explained by the particularly harsh weather conditions on site at this time of year (negative temperatures [$< -10\text{ }^{\circ}\text{C}$] and river partially frozen) which restricted evaporation, promoting dilution.

With this as a background, *Cedre* developed an experimental system designed to study the fate of chemicals when released into the marine environment in field conditions, i.e. as close as possible to those encountered in the event of a spill.

3. Materials and methods

The aim of this experimental investigation was to characterise the fate of liquid chemicals released at the sea surface.

3.1 Floating cell enclosures

Six floating cells were constructed by *Cedre* and moored in Brest Bay, France ($48^{\circ}22'32\text{N}$ and $4^{\circ}29'32\text{W}$) to study the influence of natural conditions (i.e., prevailing air and sea temperatures, wind, radiant energy) on the weathering of products spilled onto the sea surface (Figure 2). Each cell consisted of a $3 \times 3\text{ m}$ rigid aluminium framework surrounded by a nylon skirt which extended approximately 2 m below and 0.6 m above the sea surface. As cells were not covered and were open to the sea at the base, evaporation and dissolution processes were unimpaired but lateral dispersion at the sea surface was restricted. Observations have shown that while wind-induced capillary waves were reduced by the presence of the skirt, the majority of the mixing action of the sea passed into the cell almost unimpeded. The volume of seawater inside the skirt of each floating cell was approximately 18 m^3 . As the floating cell enclosures were independent of each other, replica experiments could be conducted simultaneously. During this research programme only 3 of the 6 cells were used.



Fig. 2. Floating cell enclosure

3.2 Chemical products tested

Following an investigation into the chemicals transported most frequently and in the greatest quantities, three products were selected: xylene, methyl methacrylate and methyl ethyl ketone.

Xylene is a volatile aromatic hydrocarbon produced through petrochemistry. It is in liquid form at room temperature and is often a mixture of isomers (ortho, para and meta - often the most dominant) containing variable proportions of ethylbenzene, although always below <15%. In France, xylene is the most commonly used hydrocarbonated solvent, with 34,000 tonnes in 2004, in particular in the paint, varnish, glue and printing ink industries. The main physico-chemical characteristics of this substance indicate that it will, in theory, behave as a floater/evaporator with very low solubility ($V_p = 8.9 \text{ hPa}$ at 20°C , density of 0.88 g.cm^{-3} , and solubility between 175 and 200 mg per litre of seawater; Cedre, 2007 and Lyman et al., 1996).

Methyl methacrylate (MMA) is described as a transparent volatile liquid with a characteristic smell that can be detected at very low concentrations (< 1 ppm in air). It is mainly used in the polymer and copolymer industry (plastic sheets such as Plexiglas®, Perspex® and Lucite...). Its vapour pressure is 3.9 kPa at 20°C , its solubility 15 g.L^{-1} and its density 0.944 g.cm^{-3} (Cedre, 2008).

Methyl ethyl ketone (MEK) is a sweet-smelling colourless liquid. It is a volatile organic compound, that is readily flammable and is of little harm to the environment. MEK is an eye and respiratory irritant as well as a central nervous system depressant in humans. It is mainly used as a solvent in various coatings including vinyl, nitrocellulose and acrylic coatings. It is also used as an extraction agent in certain oils as well as in the processing of products and food ingredients. Its vapour pressure is 10.5 kPa at 20°C , its solubility 158 g.L^{-1} and its density 0.805 g.cm^{-3} . It is therefore a highly evaporative and soluble product, with particularly low persistence at the water surface (Cedre, 2009).

3.3 Experimental protocol

The test, replicated for each product, required 25 litres to be released at the sea surface of each floating cell. To monitor physical oceanographic conditions that may influence the behavioural processes of products, weather conditions, prevailing light, wind speed and temperature conditions were recorded, for both air and sea.

3.3.1 Slick sampling

Slicks were sampled daily, with a funnel equipped with a tap, in order to characterise the emulsification processes. Samples were transferred into 0.5 L amber bottles and brought back to the laboratory for viscosity measurement and water content determination.

Before the release of xylene, the internal standard pentacosane, a non-evaporating and insoluble substance, was introduced. By measuring the pentacosane/xylene ratio throughout the trial, it was possible to monitor the disappearance kinetics of xylene at the water surface.

3.3.2 Water column sampling

The natural dispersion of the products in the water column was monitored by performing *in situ* fluorescence measurements at 2 positions in each floating cell at 3 depths (0.5, 1 and 1.50 m). In addition, for each *in situ* fluorescence measurement (at a given position and a given depth), a sample of seawater (1 L) was taken. All samples were placed in an amber

bottle and were stored in a refrigerator before analysis, performed the following day. These samples, which were analysed by GC-MS after liquid-liquid extraction, were used to correct data obtained by fluorimetry measurements (Katz, 1987).

3.3.3 Air monitoring

During the tests, evaporation was monitored by measuring the Volatile Organic Carbon using two Photo Ionization Detectors (PID MiniRAE 2000, RAE systems). A stationary PID was placed in a corner of the floating cell, while the second was placed on a wind vane so as to monitor evaporation independently of the wind direction.

During these trials, an infrared hyperspectral SPIM camera was deployed to assess its capacity to monitor the formation and movement of a gas cloud formed from slicks of MMA.

4. Results and discussion

4.1 Xylene

To study the fate of xylene, two 25 litre releases were performed.

4.1.1 Field observations

Photo 1, taken at T_0 , illustrates the chemical release. One hour after the release, the slick began to emulsify and, two hours later, the emulsion covered the entire surface of the floating cell. After 5 hours, the slick began to fragment and several small slicks scattered across the entire cell appeared (Photo 2).

4.1.2 Prevailing sea and weather conditions

The week of the trials was marked by relatively harsh weather conditions, with a slight sea according to the Douglas sea scale (sea 3), a north-easterly wind at force 3 on the Beaufort scale (12 to 19 $\text{km}\cdot\text{h}^{-1}$) and low temperatures (between 3 and 5°C). Several snow showers occurred during this week.



Photo 1. Xylene release (T_0)



Photo 2. Xylene slick at T_{+5h}

4.1.3 Slick persistence

Figure 3 shows the persistence of the xylene slicks at the water surface. The results are expressed as a percentage of the quantity spilt at T_0 . After 2 hours, over 50% of the slick had disappeared, and after 5 hours, less than 30% of the initial quantity remained. The quantities lost were either transferred from the surface to the air (evaporation) or from the surface to the water column (natural dispersion). After day 2, no traces of the slick remained visible at the surface. The time during which the slick was present was estimated at 34 hours.

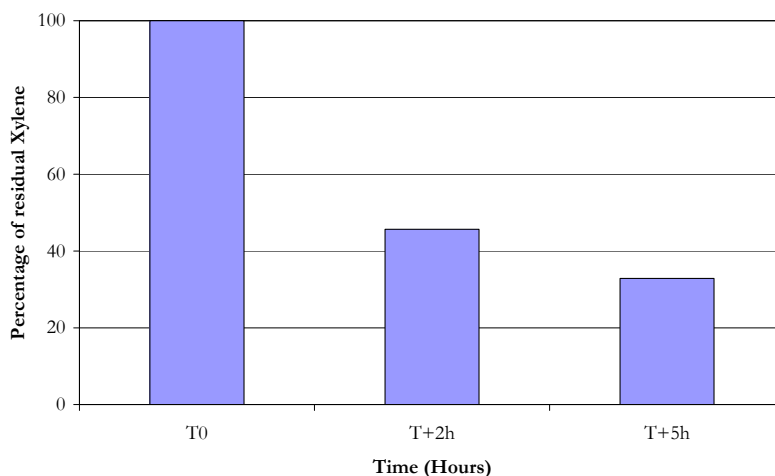


Fig. 3. Evolution over time of the slicks remaining at the surface (average of results obtained using samples taken from cells 1 and 2).

4.1.4 Monitoring of emulsification

The emulsification kinetics could only be monitored during the first day of the experiment (Figure 4).

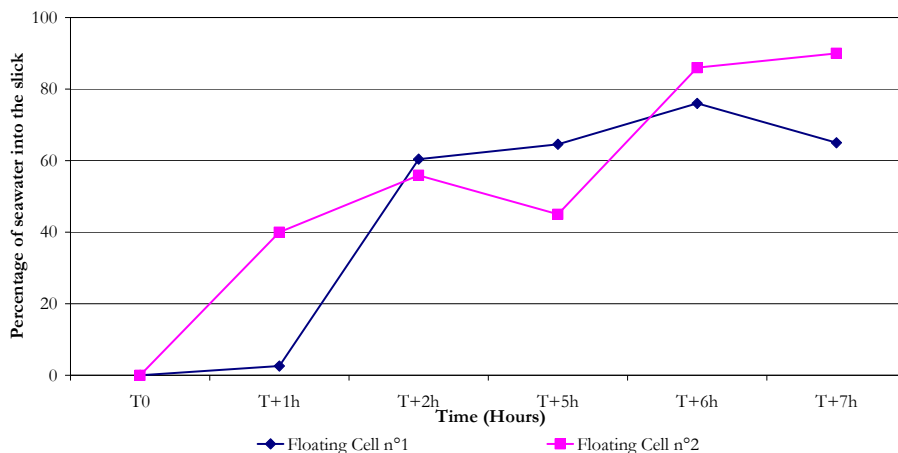


Fig. 4. Emulsification kinetics of xylene slicks within cells 1 and 2.

Xylenes have a high water sorption capacity and rapidly form emulsions. At T+7h the water content of slicks in cells 1 and 2 were respectively 65% and 90%. However, these emulsions are unstable as they are non-persistent: from day 2, it was no longer possible to sample the surface slick due to insufficient quantities, and on day 3, no pollution remained visible.

4.1.5 Monitoring of dispersion in the water column

Figures 5 and 6 show the xylene concentrations in the water column, respectively in cells 1 and 2, at the three sampled depths (0.5, 1 and 1.5 m) over time. After 29 hours, concentrations of the substance were no longer detected.

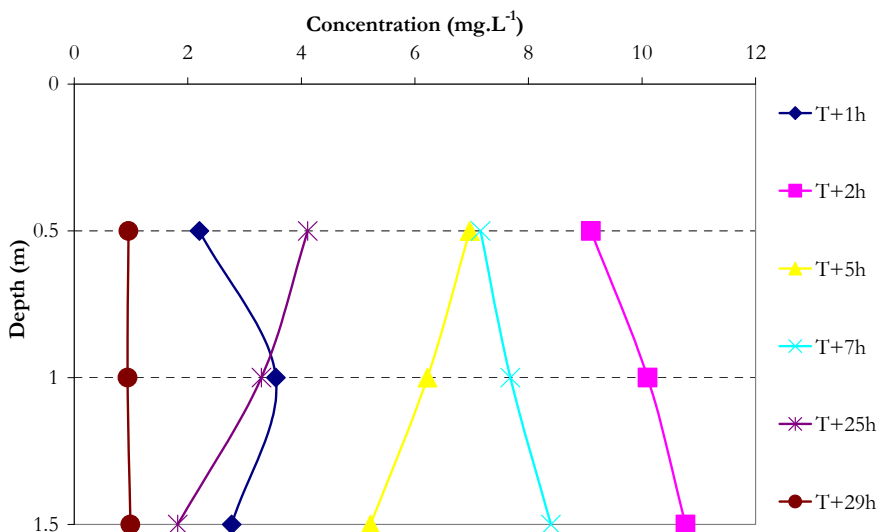


Fig. 5. Evolution over time of xylene concentrations in the water column in cell 1.

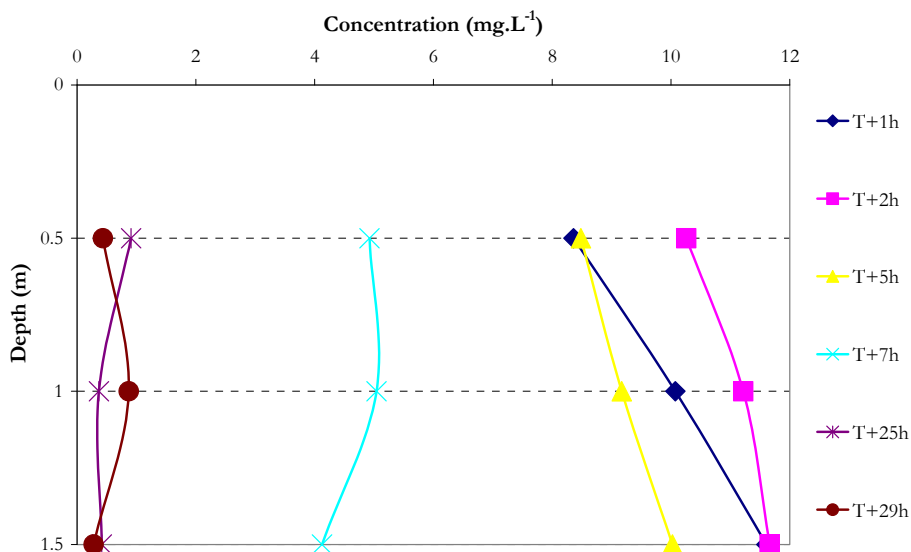


Fig. 6. Evolution over time of xylene concentrations in the water column in cell 2.

In the two cells, the maximum concentrations were obtained at T_{+2h} (10.8 and 11.7 mg.L^{-1} , respectively in cells 1 and 2), and represented a quantity of around 200 g of dispersed xylenes. These concentrations then gradually decreased over time, and dropped below 1 mg.L^{-1} at T_{+29h} . Beyond this sample time, traces of xylene were no longer detected in the water column.

During these *in situ* trials, the natural dispersion of xylenes in the water column (dissolution + emulsification) showed rapid kinetics, and the concentrations measured were higher than expected: 100 times higher than the theoretical solubility found in the literature.

4.1.6 Fate of xylenes

These trials demonstrated that the persistence of a slick of xylenes at the water surface is relatively short-lived (around 2 days in these trial conditions, not very conducive to evaporation) and that this disappearance could be explained by dissolution processes which were higher than expected (in the literature this chemical is identified as having low solubility). In terms of the transfer of the chemical into the atmosphere, evaporation kinetics could not be measured due to the particularly harsh weather conditions (the snow interfered with the photoionisator). However, by comparing it to styrene (this chemical was previously tested and these two products have an equivalent vapour pressure and are classified as FE according to the SEBC code), it can be presumed that xylenes evaporate less quickly than theory predicts: after 5 hours, the entire styrene slick had disappeared, while this took 34 hours with xylenes. These results can be explained by emulsification processes: the xylene slicks rapidly emulsified to a great extent during the first day (90% at T_{+7h}), a process which does not take place with styrene. This raises the question of surface tension which is not taken into account in the SEBC classification; yet it is this factor that defines a product's capacity to emulsify, and emulsification promotes natural dispersion in the water column.

The results obtained *in situ* therefore directly contradict the literature which mainly describes the behaviour of a xylene slick in terms of transfer into the atmosphere. It is clear that the slick will initially emulsify, causing evaporation kinetics to slow down and promoting transfer into the water column by natural dispersion processes (dissolution and emulsification). It is important, however, to remember that the sea and weather conditions on site should be taken into account when considering these results, as, in these trials, the low temperatures curbed evaporation processes and surface agitation promoted emulsification. This fate is in accordance with what was observed during the benzene spill in Jilin (higher dissolution than predicted and low evaporation processes).

In terms of response, this means that all the issues related to pollution by soluble products (contamination of the water column and problem of water intakes, impact on benthic flora and fauna...) must be taken into account even if the product is classified as a floater and evaporator. Nevertheless, the gas cloud must not be overlooked, as it presents a risk for responders both in terms of intoxication and as an explosion hazard. In the case of xylene, vapours are heavier than air and will move around just above the water surface, pushed by the wind. This danger is even greater if the spill occurs in a coastal area, or even in a port or harbour, where the population density is liable to be high.

4.2 Methyl methacrylate

Methyl methacrylate (or MMA) is classed ED according to the SEBC classification, and its main behaviour is evaporation according to its Henry's law constant.

4.2.1 Observations

The MMA spread out across the water surface forming a heterogeneous slick: various sized clusters of floating droplets were observed (Photo 3). This phenomenon was only temporary, as in less than two hours all of the substance had disappeared.



Photo 3. Appearance of the MMA slick immediately after the spill

4.2.2 Prevailing sea and weather conditions

The prevailing weather conditions onsite at the time of the trial are presented in Table 2. The key point is the presence of wind.

| Date | 25/06 | 25/06 | 25/06 |
|---------------------------------------|-------------|-------------|-------------|
| Time | 11:00-12:00 | 12:00-13:00 | 13:00-14:00 |
| Air T (°C) | 16.4 | 16.7 | 17.1 |
| Wind speed (m/s) | 5.5 | 5.6 | 5.6 |
| Solar intensity (mW/cm ²) | 61.5 | 71.2 | 83.4 |

Table 2. Evolution of weather conditions during the release of MMA

4.2.3 Evaporation

The MMA evaporated very rapidly: it was released at 11:18 and the PIDs began to detect significant values from 11:25 (1 ppm at 11:24, then 53 ppm at 11:25). A peak in concentration was reached at 11:27 with 130 ppm, the time at which a local maximum was recorded for light intensity (130 mW/cm²), while the wind varied little throughout the duration of measurements (5 to 6 m/s on average with peaks at 7 m/s and minima at 4 m/s). These results, illustrated in Figure 6, show the importance in evaporation processes of sunshine, which had a greater influence than the wind: positive correlation between solar peaks and evaporation peaks (T₊₉, T₊₁₄, T₊₃₅, T₊₄₉, T₊₅₆, T₊₇₄ min).

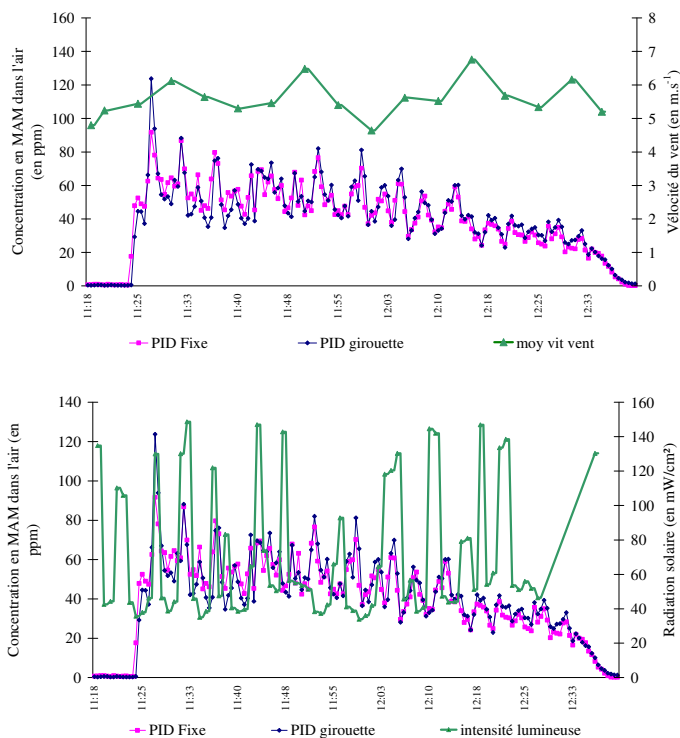


Fig. 7. MMA concentrations in the air measured using PIDs (stationary and on the wind vane) and variations in wind and sun intensity throughout the experiment.

The advantage of using the wind vane to monitor the concentration of the product in the atmosphere can be observed in Figure 7: while the shapes of the two curves (stationary PID and PID on wind vane) match, the concentration peaks are more intense for the PID on the wind vane and, in general, its curve shows slightly higher values, indicating better quantification of the vapours emitted by the slick. This result was obtained despite a relatively constant wind direction throughout the experiment (250 - 270°), therefore suggesting that the gain would be even greater in the case of quantification with a swirling wind.

4.2.4 Dissolution

Despite its solubility (10 g.L⁻¹), the MMA did not dissolve at all in these experimental conditions: the chemical was not detected at any of the three depths sampled (0.5, 1 and 1.5 m).

4.2.5 Fate of methyl methacrylate

MMA is listed as ED according to the SEBC code, i.e. it is first and foremost an evaporator, but also dissolves. In the prevailing weather conditions during the trial, this product only evaporated, and it did so with rapid kinetics: in less than 90 minutes, no traces of MMA were visible at the water surface or detected by the PIDs. Given its negligible dissolution, an atmospheric transfer coefficient can be estimated at around 4.1 litres per square metre per hour (4.1 L.m⁻².h⁻¹), in these experimental conditions.

In the event of a spill, response should therefore focus on the gas cloud as it will be explosive (MMA can form flammable vapours with air) and toxic (TEEL¹ of 400 ppm). It is therefore essential to have operational tools to visualise the formation and movement of a gas cloud as well as a computer forecast model.

Due to its marked evaporation, MMA was selected to test the SPIM camera. Using this camera, three periods were identified:

- Beginning of detection at T_{+30min} and until T_{+40min} the cloud has spread little and appears denser around the outside (Photo)
- Between T_{+40min} and T_{+60min}, the cloud spreads and the edges become more diffuse, while remaining detectable by the SPIM
- Between T_{+60min} and T_{+75min}, the cloud no longer spreads but the wind promotes its dilution so that it completely disappears.

These results, although partial, are very promising in order to monitor the formation and movement of an invisible gas cloud. This technology, already employed for the detection of gas leaks at industrial facilities, could be put to good use in the field of pollution response.

4.3 Methyl ethyl ketone

Methyl ethyl ketone (MEK), like MMA, is classed ED.

¹ TEEL = TEmporary Exposure Limit



Photo 5. Infrared image of the MMA gas cloud near the floating cells

4.3.1 Observations

Immediately after the spill, the MEK spread across the entire water surface within the floating cell to form a homogeneous, colourless slick that was difficult to detect. This observation is consistent with the results obtained in the laboratory on MEK-water interfacial tension which predict complete spreading, or even infinite spreading in the absence of containment. This high degree of spreading promoted the transfer of the product into the atmosphere and the water column, resulting in complete disappearance of the slick in less than 1 hour and the end of sampling and PID measurements at 12:00 (no signal from PID).

4.3.2 Prevailing sea and weather conditions

The prevailing weather conditions on site at the time of the experiment are presented in Table 3, and can be summarised as alternating sunny spells and threatening clouds due to the constant wind.

| Date | 25/06 | 25/06 | 25/06 |
|---------------------------------------|-------------|-------------|--------------|
| Time | 10:25-11:00 | 11:00-11:30 | 11:30 -12:00 |
| Air T (°C) | 15.6 | 15.7 | 15.7 |
| Wind speed (m/s) | 5.1 | 5.1 | 5.2 |
| Solar intensity (mW/cm ²) | 93.1 | 106.1 | 104.6 |

Table 3. Evolution of weather conditions during the MEK release

Note that the mean solar intensity on this day was higher than that measured during the MMA trial.

4.3.3 Evaporation

The MEK evaporated very swiftly and to a great extent: less than 5 minutes after the spill, a peak in concentration was measured both by the stationary PID and the PID on the wind vane (350 ppm). Concentrations then gradually decreased and levelled out at around 20 ppm at $T_{+30 \text{ min}}$ before disappearing completely at $T_{+90 \text{ min}}$ (Figure 8). The evaporation of MEK was so intense that it was unaffected by the wind or sun; no peaks could be correlated with a gust of wind or spell of sunshine.

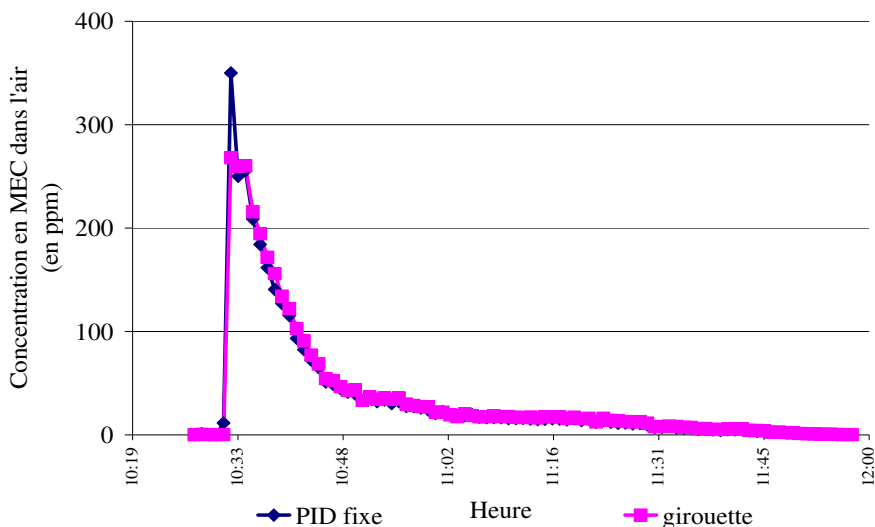


Fig. 8. MEK concentrations in the air measured by the PIDs (stationary and wind vane) during the trial.

4.3.4 Dissolution

Despite its high solubility ($\approx 300 \text{ g.L}^{-1}$ i.e. 30 times higher than MMA), MEK did not dissolve at all in the conditions of this experiment: the chemical was not detected at any of the three depths sampled (0.5, 1 and 1.5 m).

4.3.5 Fate of methyl ethyl ketone

MEK is listed as ED according to the SEBC code, i.e. it is first and foremost an evaporator, but also dissolves. In the weather conditions during this trial, the product only evaporated, and did so with intense, rapid kinetics: in less than 5 minutes, an evaporation peak was observed and thereafter concentrations in the air continually decreased. This behaviour was similar to MMA with, however, even faster evaporation kinetics, unaffected by the wind or sun. This trend can be explained by MEK's capacity to spread widely at the water surface

and to form a homogeneous slick. The coefficient is the same as for MMA, i.e. $4.1 \text{ L.m}^{-2}.\text{h}^{-1}$, bearing in mind that for MEK it is not constant throughout evaporation. It is estimated that 80% of the slick evaporated in 15 minutes, giving a coefficient of $8.9 \text{ L.m}^{-2}.\text{h}^{-1}$, while the remaining 20% took around 75 minutes, giving a considerably lower transfer coefficient of around $0.45 \text{ L.m}^{-2}.\text{h}^{-1}$.

In the event of a spill, response should therefore focus on the gas cloud which will form rapidly and will be flammable and toxic.

5. Conclusion

In the event of a chemical spill at sea, it is crucial to be aware of the behaviour of the substances involved to determine the most appropriate response strategy. While classifications exist and are valuable tools, they are based on laboratory data for which the influence of environmental parameters is not taken into consideration, i.e. the effects of wind and sunshine on evaporation and of surface agitation on dissolution are not taken into account. Moreover, they consider the physico-chemical properties of substances independently of each other, while in the event of a spill, dissolution and evaporation processes will occur simultaneously. Therefore, if evaporation kinetics are rapid, dissolution processes will not have time to occur and a product, even if soluble, could evaporate completely into the atmosphere. With this in mind, *Cedre* developed an experimental tool, floating cells, which can be used to characterise the main processes governing a substance's fate after its release at sea.

This paper presents the results obtained during a series of trials in these floating cells, which aimed to characterise the behaviour of three chemicals: xylene, methyl methacrylate and methyl ethyl ketone.

These trials provided two vital pieces of information on these chemicals, to add to the information provided by the SEBC classification. The first relates to xylene which is listed as FE. It became apparent that, in certain weather conditions, xylene will indeed behave as a Floater/Evaporator, however if the temperature drops and especially if the surface agitation and wind are sufficient (wind speed greater than 3 m.s^{-1}), it will form an emulsion and will mainly dissolve, thus exhibiting FDE behaviour. The two other products (MMA and MEK) are classed ED while, in these experimental conditions, they behaved only as Evaporators.

These results highlight the need to study *in situ* the behaviour of chemicals to add to the theoretical classification based only on laboratory data, especially as it is clear that factors such as surface agitation, wind, sunshine and outside temperature significantly affect the transfer of products from the surface to another environmental compartment. The floating cells, developed by *Cedre*, adequately fulfil this purpose, and, what's more, are an innovative tool which, in addition to helping to define a response strategy in the event of a spill, can be used routinely as realistic input for forecast software.

Concretely, such experiments on the behaviour of HNS releases in sea water provide:

- i. further information in addition to the chemical emergency response guides. For example, on the one hand, xylene, which is considered as a Floater/Evaporator, can

behave as a FDE; in the case of emergency response in the same weather conditions as the trials, the attention of the intervention team must also be focused on the water column. On the other hand for both other substances (MMA and MEK), the atmospheric compartment has to be especially considered by the intervention team which has, firstly, to protect itself against the gas cloud.

- ii. experimental data for the implementation of existing software. Forecast software is a useful tool but few programs are validated by field experiments. Here, results are used to validate the Clara software which is fully dedicated to predicting the behaviour of HNS at sea.
- iii. the Authorities in charge of the response with operational information. They require accurate data in order to organize the most appropriate response.

6. Acknowledgments

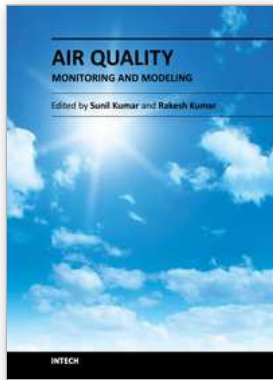
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