

## Hazardous and Noxious Substances (HNS) Spills: Evaporation and Dissolution of Styrene and Vinyl Acetate Spilled in Sea Water

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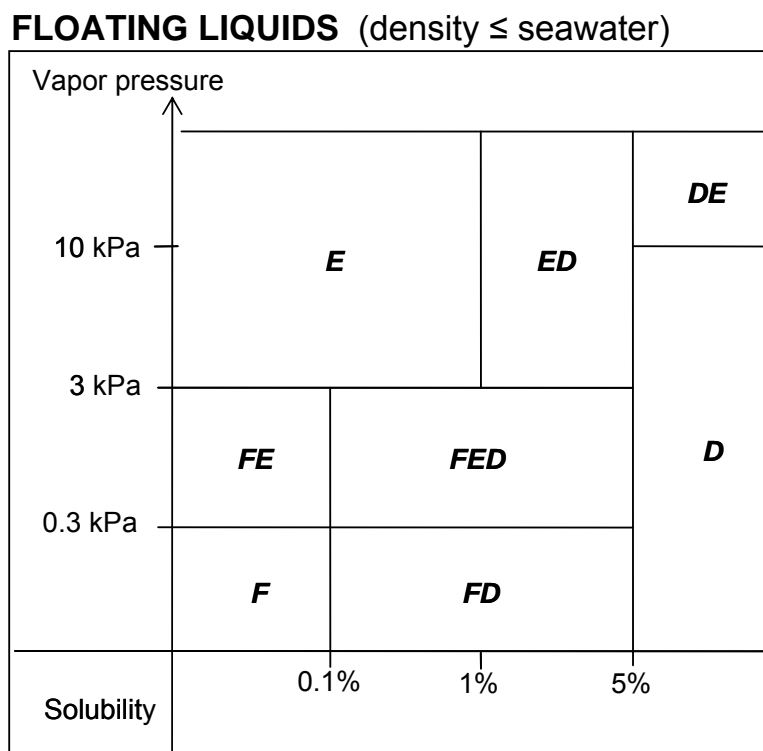
### Abstract

This paper reports an accurate method to define the behavior of chemical products spilled in sea water according to weather conditions. The main purpose of this study is to determine the evaporation and the dissolution behavior of styrene and vinyl acetate spilled in sea water in order to provide a prompt response to accidental sea water pollution involving marine Hazardous and Noxious Substances (HNS). Some home-made waterborne frameworks, called floating cells, were used in order to host the release of a chemical substance. The on site characterization of the gaseous cloud, *i.e.* the evaporation of the chemicals, was performed with a Photo-Ionization Detectors (PID MiniRAE 2000) coupled to a meteorological station (Serpe-Iesm). The *in situ* characterization of the water column, *i.e.* the dissolution of the chemicals, was carried out thanks to a spectrofluorometer (10AU Field Fluorometer from Turner Designs) coupled to a classical sampling. The taken water samples were analyzed some later time in the laboratory. The *in situ* measurements and the common sampling techniques were used concomitantly to improve data processing on natural samples. Considering the meteorological conditions, some results obtained during *in situ* experiments on the evaporation and the dissolution of chemicals as styrene and vinyl acetate will be presented.

### 1 Introduction

The increase of the maritime traffic, and particularly the transport of chemical products, leads to a need of the enhancement of the prevention and the intervention towards the spills of chemicals in the environment. Since 2004, the European Maritime Safety Agency (EMSA) has a legal obligation in the field of response to ship sourced pollution within European Union waters (EMSA, 2004). The Agency was tasked to provide a framework for developing pollution response actions at European level. This task was grown through the Action Plan for HNS Pollution Preparedness and Response (EMSA, 2007).

The Standard European Behavior Classification (SEBC code, Bonn Agreement 1991) gives a theoretical behavior of chemical substances according to their chemico-physical properties. For example, the SEBC classification of floating liquids, as styrene and vinyl acetate, is presented Figure 1. It is generally accepted that a floating substance will not evaporate if its vapor pressure is lower than 0.3 kPa and it will evaporate rapidly if its vapor pressure is higher than 3 kPa. For dissolved substances, evaporation occurs when the vapor 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). A substance is considered insoluble if its solubility is less than 0.1% and the phenomenon of dilution will take place if the solubility is greater than 5%.



**Figure 1: SEBC Classification of Floating liquids according to their Physical Properties.**  
*E: Evaporator; F: Floater; D: Dissolver*

However such a code does not take in consideration the weather conditions. The wind speed, the solar radiation, the air temperature or the sea water temperature can affect the behavior of the chemical products spilled in sea water. In order to define a strategy of intervention in case of urgency state, Cedre (Centre de documentation, de recherche et d'expérimentations sur les pollutions accidentelles des eaux) leads, in collaboration with the Ceppol (Centre d'expertises pratiques de lutttes antipollution) from the Marine Nationale, a research project on Hazardous and Noxious Substances (HNS) behavior. This project aimed to determine the behavior of chemical substances spilled in sea water considering the weather conditions by the monitoring of a slick drifting (Le Floch *et al.*, 2011). The experimental behavior of the tested substances was added to the chemical emergency response guides and to the database of simulation software.

## 2 Operational and Instrumentation

The deployment of the home-made waterborne frameworks needs an important logistical support. The Figure 2 presents the successive steps to launch the floating cells. The Figure 2 a) shows the mean of carrying of the home-made waterborne frameworks. The Figure 2 b) presents how the floating cells were hanged thanks to a crane-truck before the launch (Figure 2 c). The floating cells were then towed until the experimental zone with a ship and a rubber dinghy (Figure 2 d).

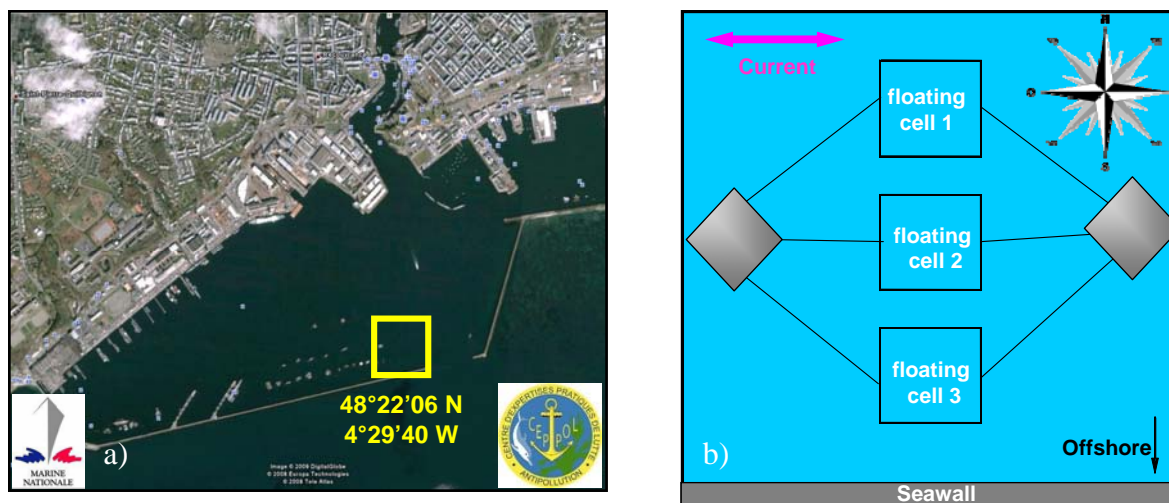
These floating cells were moored in Brest harbor, France (48°22'32"N and 4°29'32"W). The experimental zone was defined with the help of the Marine Nationale (Figure 3 a). The experimental zone was exposed to the meteorological conditions. The scheme of the arrangement of the floating cells (Figure 3 b) shows that the floating cells were positioned perpendicularly to the marine current. The seawall protected them against the oceanic swell.



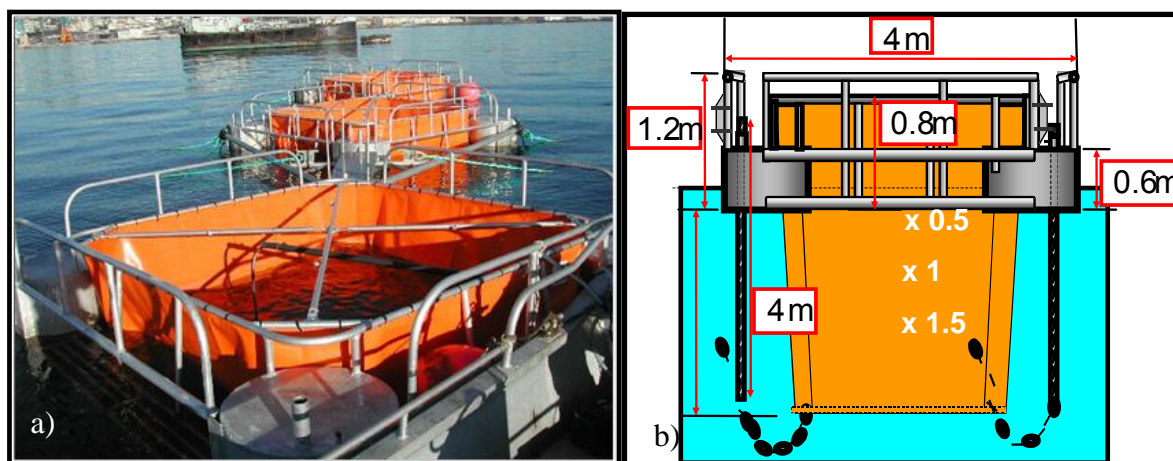
**Figure 2: a) The lift of the home-made waterborne frameworks, b) The hanging thanks to a crane-truck c) The launch of the floating cells and d) The tow until the experimental zone with a ship and a rubber dinghy.**

In Figure 4 a) a picture of the three floating cells used in order to mimic HNS spills in marine medium and in Figure 4 b) the scheme of a floating cell is presented. Each cell consisted of a 3 x 3 m rigid aluminum 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 sea water inside the skirt of each floating cell was approximately 18 m<sup>3</sup>. As the floating cell enclosures were independent of each other, triplicate experiments could be conducted simultaneously. The release of each chemical was performed closest to the sea surface.

Concerning the instrumentation and the analyses of the chemical substance releases, *i.e.* styrene and vinyl acetate, *in situ* measurements were performed and the sampling was analyzed at the laboratory. The on site experimental procedure is presented Figure 5.



**Figure 3 : a) Localization of the experimental area in the Brest roads and b) scheme of the arrangement of the floating cells.**



**Figure 4 : a) Picture of the three floating cells and b) scheme of a floating cell.**

The atmospheric compartment was characterized with a Photo-Ionization Detectors (PID MiniRAE 2000) which allow the monitoring of Volatile Organic Compounds (VOC) and a meteorological station (Serpe-Iesm). Both tooled up the waterborne frameworks. The aqueous compartment was characterized through *in situ* fluorescence measurements coupled to sampling. The monitoring of the natural dispersion of the products in the water column was carried out thanks to a spectrofluorometer (10AU Field Fluorometer from Turner Designs). The measurements were performed at the middle of each floating cell at 3 depths 1.5, 1 and 0.50 meter (Figure 4 b).

The *in situ* measurements and the common sampling techniques were used concomitantly to improve data processing on natural samples. The taken water samples, stored in amber bottles in a freezer, were analysed some later time in the laboratory. At the laboratory, the water column samples were analysed with a Gas Chromatography – Mass Spectrometry (GC-MS Agilent Technologies 5975C). These samples were used to correct data obtained by fluorescence measurements (Katz, 1987).



**Figure 5 : On site experimental procedure: operator on the boat is pumping samples, PID at the right corner of the floating cell and the meteorological station.**

### **3 Results and Discussion**

#### **3.1 Styrene**

The styrene is considered as a noxious substance. The main chemico-physical characteristics of the styrene are  $V_p = 0.667$  kPa at  $20^\circ\text{C}$ , density of 0.906 and solubility of  $0.3 \text{ g}\cdot\text{L}^{-1}$  (Mackay *et al.* 2006a). The Standard European Behavior Classification (SEBC) indicates that the styrene is considered as a Floater/Evaporator (FE) with a very low solubility.

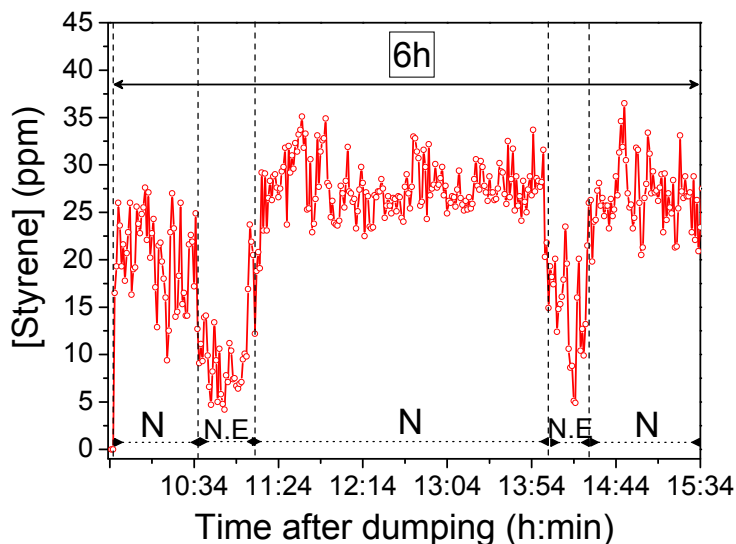
##### **3.1.1 Experimental Conditions and Observations**

The experimental tests were performed in the Brest roads from the 11/22/2010 to 11/24/2010. The release of 25 L of styrene was triplicated in each floating cell. The sea temperature was  $12^\circ\text{C}$  and the average of the air temperature was  $7.7^\circ\text{C}$  with a range from  $4.8^\circ\text{C}$  to  $9.9^\circ\text{C}$ . A prevailing wind oriented north at force 2 on the Beaufort scale ( $11 \text{ km}\cdot\text{h}^{-1}$ ) with a gusty wind at force 4 on the Beaufort scale ( $25 \text{ km}\cdot\text{h}^{-1}$ ) was recorded. The north wind was regularly oriented north-eastern. Concerning the radiant energy an average of  $27 \text{ mW}/\text{cm}^2$  was calculated with a local maximum of  $40\text{-}50 \text{ mW}/\text{cm}^2$ . A minimum of  $0 \text{ mW}/\text{cm}^2$  for the light intensity was recorded from 4:15 pm (GMT) until 8:00 am (GMT) the next day.

Immediately after the dumping of the styrene, a sprawl at the sea surface as continuous large slicks of the chemicals was observed. Four hours after the spill, disparate slicks of emulsion were obtained. One day after the dumping, iridescents at the sea surface were observed. Two days later, localized iridescents were displayed at the sea surface.

### 3.1.2 Atmospheric Compartment

The local gaseous cloud at the sea water surface was characterized thanks to a Photo-Ionization Detectors (PID). The air monitoring of Volatile Organic Compounds (VOC) during the six first hours after the release is presented Figure 6.



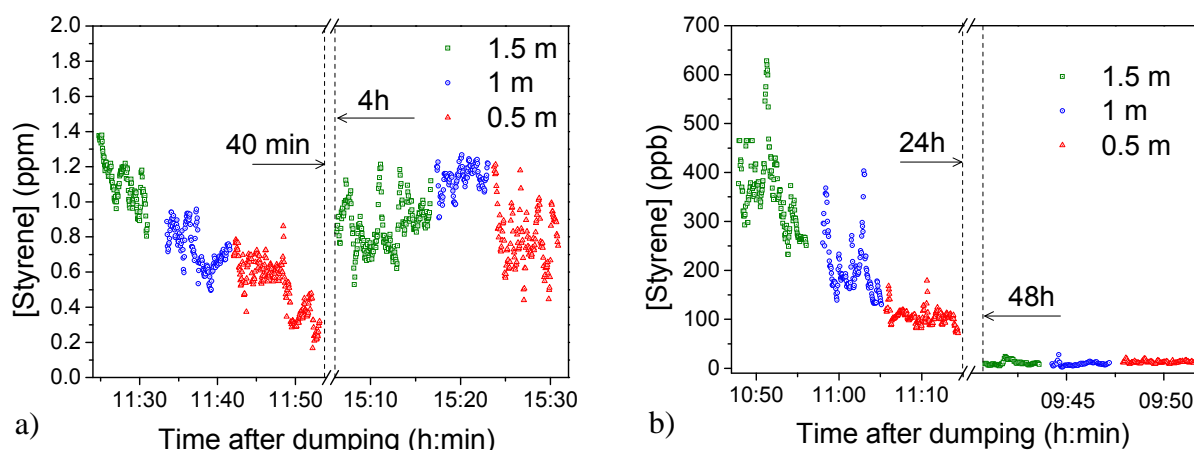
**Figure 6 : PID measurements during the first day.**

At the beginning of the experiment, the wind was oriented north. Few seconds after the spill of styrene, the recorded concentration in the atmosphere was reached 20-25 ppm. Less than one hour after the styrene dumping, the measured concentration was fallen to 5 ppm. Such a decrease of the styrene concentration in the air can be explained through the new wind orientation (north-eastern) during 45 minutes. The PID, stationary placed in a corner of the floating cell, was not well positioned to record the monitoring of the gaseous cloud. The concentration was raised to 35 ppm and stabilized at 28 ppm during 3 hours when the wind was reoriented north. The same phenomenon was occurred for the next decrease and increase of the styrene concentration in the air. During these six first hours, the force of the wind was constant (force 2) and the average light radiation recorded was 20 mW/cm<sup>2</sup> with a local maximum of 26 mW/cm<sup>2</sup> and a minimum of 14 mW/cm<sup>2</sup> at the end of the afternoon. This latter parameter did not seem to affect the styrene evaporation. Any conclusion cannot be conducted onto the effect of the wind force on the styrene evaporation.

### 3.1.3 Aqueous Compartment

The monitoring of the natural dispersion of the products in the water column was carried out thanks to *in situ* fluorescence measurements. These *in situ* measurements were coupled to a sampling which was carried out at 40 minutes, 4 h, 24 h and 48 h after the dumping of the styrene. For each time interval, the samples were taken from most to least deep (1.5; 1 and 0.5 meter). The Figure 7 a) and b) present the monitoring of the water column respectively in the floating cell 1 (40 minutes and 4 h after the spill) and the floating cell 2 (24 h and 48 h after the spill).

40 minutes after the styrene dumping, the higher recorded concentrations (1.4 ppm) were obtained at 1.5 meter of depth. A decrease of the styrene concentration was observed when the measurements were done close to the surface (*i.e.* 0.2 ppm at 0.5 meter). Less than one hour after the spill, the solubilized part of styrene in the water column dived instead of stayed close to the surface; styrene being considered as FE.



**Figure 7 : Concentration of styrene at 3 different depths (1.5, 1 and 0.5 m) with regard to the time after dumping a) floating cell 1 and b) floating cell 2.**

4 h after the release the higher recorded concentrations (1.2 ppm) were lightly lower than the ones obtained 40 minutes after the styrene dumping. The styrene concentration measured at 1.5 meter was decreased in favor of the one at 1 meter (average of ~1.1 ppm) and 0.5 meter (average of ~0.8 ppm) of depth. In comparison, the concentrations recorded 40 minutes after the release at 1 meter (average of ~0.7 ppm) and 0.5 meter (average of ~0.5 ppm) were lower than the ones obtained 4 h after the release.

24 h after the styrene dumping, the chemical was always in the water column, signature of a very low kinetic of solubilization of the styrene. As example, at 1.5 meter of depth the styrene concentration was 600 ppb.

48 h after the still, the styrene concentration was close to zero at the three studied depths. The dumped styrene was quasi non-existent in the marine medium two days after the spill.

The characterization of the aqueous compartment highlights that the styrene was weakly concentrated in the marine medium after a spill; a maximum concentration of 1.4 ppm was recorded while the threshold solubility is considered as  $0.3 \text{ g.L}^{-1}$  (300 ppm) in fresh water at  $20^\circ\text{C}$ . Moreover, the Lethal Dose 50 ( $\text{LD}_{50}$ , 96 h) for fish (*Pimephales promelas*) is  $4.02 \text{ mg.L}^{-1}$  (~ 4 ppm) (Cedre, 2004). In addition, the very low kinetic of solubilization of the styrene was notified with a concentration, 24 h after the spill, only half as the maximum concentration recorded.

### 3.2 Vinyl Acetate

The vinyl acetate is considered a flammable substance. The main chemico-physical characteristics of the vinyl acetate are  $V_p = 11.7 \text{ kPa}$  at  $20^\circ\text{C}$ , density of 0.931 and solubility of  $20 \text{ g.L}^{-1}$  (Mackay *et al.*, 2006b). The Standard European Behavior Classification (SEBC) indicates that vinyl acetate is considered as an Evaporator/Dissolver (ED).

#### 3.2.1 Experimental Conditions and Observations

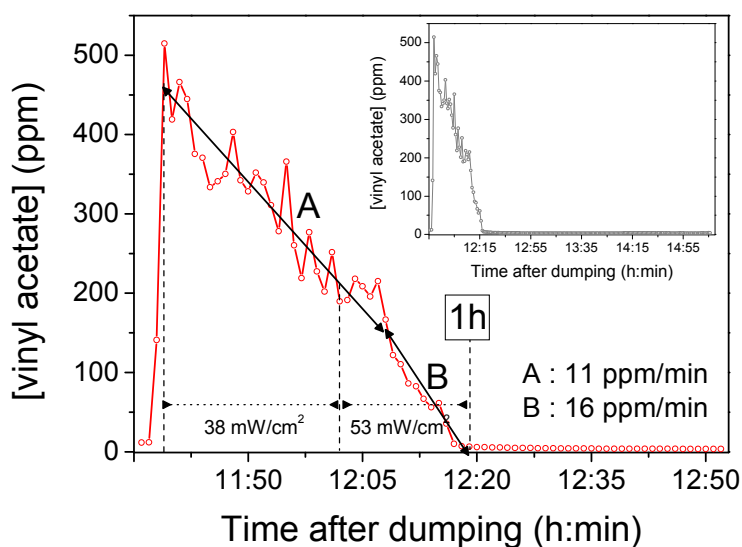
The experimental tests were performed in the Brest roads the 11/29/2010. The release of 20 L of vinyl acetate was triplicated in each floating cell. The sea temperature was  $11.5^\circ\text{C}$  and the average of the air temperature was  $4^\circ\text{C}$  with a range from  $2.8^\circ\text{C}$  to  $4.7^\circ\text{C}$ . A prevailing wind oriented east at force 4 on the Beaufort scale ( $27 \text{ km.h}^{-1}$ ) with a gusty wind at force 5 on the Beaufort scale ( $38 \text{ km.h}^{-1}$ ) was recorded. Concerning the radiant energy an

average of  $30 \text{ mW/cm}^2$  was calculated with a local maximum of  $50\text{-}60 \text{ mW/cm}^2$ . A minimum of  $9 \text{ mW/cm}^2$  for the light intensity was recorded from 3:15 pm (GMT).

Immediately after the dumping of the vinyl acetate, emulsions were observed instead of a continuous large slick of the chemical. Less than two hours after the spill, spherical solid particles were observed at the sea surface. The particles, with a diameter around the centimeter dimension, disappeared during the day.

### 3.2.2 Atmospheric Compartment

The local gaseous cloud at the sea water surface was characterized thanks to a Photo-Ionization Detectors (PID). The air monitoring of Volatile Organic Compounds (VOC) after the release is presented Figure 8.



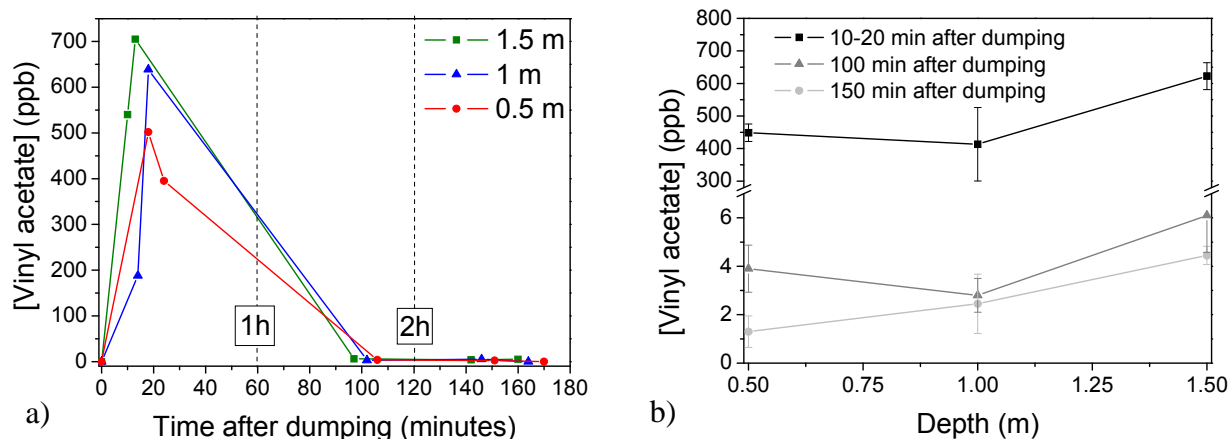
**Figure 8 : PID measurements after the dumping. In inset, the total measurement.**

The vapor pressure of the vinyl acetate is very high ( $V_p = 11.7 \text{ kPa}$  at  $20^\circ\text{C}$ ) and the detected average concentration during the first ten minutes was  $380 \text{ ppm}$ . One hour after the spill, the quasi totality of the substance was evaporated. Moreover, the wind conditions (force 4-5) during the experiments could affect the evaporation rate and increase it. Two segments (A and B) were defined on the recorded measurements. An evaporation rate of  $11 \text{ ppm}$  and one of  $16 \text{ ppm}$  were found respectively for the segment A and B. This variation of the evaporation rate was correlated to the solar radiation. An increase of the radiant energy was measured from  $38$  to  $53 \text{ mW/cm}^2$ .

### 3.2.3 Aqueous Compartment

Only the taken samples analysed at the laboratory with the Gas Chromatography – Mass Spectrometry (GC-MS) techniques were gathered Figure 9; the *in situ* measurements recorded thanks to the SF-UV spectrofluorometer were not consistent. The Figure 9 a) presents the evolution of the vinyl acetate concentration into the three cells at three different depths (1.5, 1 and 0.5 meter) with regard to the time after dumping. The Figure 9 b) shows the average of the vinyl acetate concentration into the three cells at three different times after dumping with regard to the depth.





**Figure 9 : a) Vinyl acetate concentration into the 3 cells at 3 different depths (1.5, 1 and 0.5 m) with regard to the time after dumping. b) Average of the vinyl acetate concentration into the 3 cells at 3 different times after dumping with regard to the depth.**

The solubility of the vinyl acetate is quite high ( $S = 25 \text{ g.L}^{-1}$  or 25000 ppm) then, the first samplings were done less than half an hour after the spill. The average concentrations of vinyl acetate, recorded between 10 and 20 minutes after the spill, were 622, 413 and 448 ppb at respectively 1.5, 1 and 0.5 meter of depth (Figure 9 b). We can consider that the natural dispersion of the vinyl acetate in the water column was homogeneous.

100 minutes after the spill, the analysed concentrations were 4, 3 and 6 ppb at respectively 0.5, 1 and 1.5 meter of depth.

150 minutes after the release, the recorded concentrations were 1.3, 2.4 and 4.4 ppb at respectively 0.5, 1 and 1.5 meter of depth.

The limit of solubility is 25 0000 ppm in fresh water and the high average concentration recorded in the water column was 622 ppb.

Such results confirm the ones obtained during the monitoring of the gaseous cloud of the vinyl acetate slick. The evaporation phenomenon was predominant *versus* the solubilization phenomenon with these meteorological conditions.

#### 4 Conclusions

The results obtained during a series of trials in these floating cells were presented. The aim of such experiments was to characterize the behavior of two chemicals, styrene and vinyl acetate. These results highlight the need to study *in situ* the behavior of chemicals to complete the theoretical classification based only on laboratory data.

The behavior of a styrene slick was established considering the meteorological conditions and it was in adequacy with the SEBC code which considers styrene as a Floater/Evaporator (FE) with a very low solubility. Indeed, a low concentration of styrene was found in the water column and an atmospheric average concentration of 30 ppm was detected.

However, the behavior of a vinyl acetate slick was mainly induced by the evaporation phenomenon in these meteorological conditions. The vinyl acetate was classed Evaporator/Dissolver (ED) in the SEBC code and the concentration analyzed in the water column was very low. In these experimental conditions, the vinyl acetate behaved only as Evaporator (E). Such results were obtained without the consideration of the lateral movement induced by waves and the mixing in the water mass below the chemical layer which induce strong chemical dispersion and dilution into the water column.

Such experiments on the behavior of HNS releases in sea water allow: (i) Adding further information to the chemical emergency response guides; the vinyl acetate which is

considered as an Evaporator/Dissolver (ED) behaves as an E substance. In a case of emergency response in the same weather conditions, the atmospheric compartment has to be especially considered by the intervention team which has, firstly, to protect itself *versus* the gaseous cloud. (ii) Giving experimental data base for the use of a forecast software. According to environmental weathering conditions and behaviors of chemical substances spilled at sea water, a template of HNS behavior can be established.

## 5 Acknowledgements

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