An innovative experimental device to assess the behavior of a chemical under controlled environmental parameters

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Abstract (ID 2017-381)

Knowledge of the behavior of HNS (Hazardous and Noxious Substances) spilled into the aquatic environment is essential to define appropriate response actions; e.g. deployment of efficient equipment and activation of appropriate procedures. As a first approach, the Standard European Behaviour Classification (SEBC) may be used to acquire global knowledge of the short-term behavior of the chemical spilled, taking into account its basic physical and chemical properties (density, solubility and vapor pressure). However, the SEBC presents several limitations. Indeed, the competition between mass transfer processes (evaporation, dissolution,

etc.) is not considered when the behavior of the chemical is theoretically determined from its physical chemical properties alone. Moreover, these measurements are made in standardized conditions (e.g. temperature of 20°C, freshwater) while, depending on its nature, the behavior of a chemical can greatly vary with temperature (e.g. palm oil may be solid under about 25°C) and other environmental parameters (velocity of wind, salinity and suspended matter in the water, etc.).

To tackle these issues, Cedre has developed an experimental device able to rapidly determine the behavior of a chemical under some specific environmental conditions. It is composed of a 80 L tank, specially equipped with a wind generator and a lamp, in order to reproduce some critical environmental parameters: water temperature, velocity of wind and solar radiation. After pouring the chemical onto the surface of the fresh or salt water, under the fixed controlled parameters mentioned above, the concentration of the studied chemical is monitored over time, in both the air and water compartments. These measurements can be used to characterize the short-term behavior of a chemical in specific controlled conditions and thus to compare it to the behavior estimated from the SEBC. Such a tool could be of a considerable interest for responders. In the framework of the preparation of contingency plans, the response to a specific chemical can be optimized by performing experimentations covering a wide range of environmental conditions. In the event of a spill, specific conditions can be immediately reproduced to support responders and authorities who may have to take strategic decisions.

The whole experimental device will be presented, including the tools and procedures to reproduce the environmental conditions. Then, initial results obtained with different chemicals will be presented.

INTRODUCTION

When a spill of a bulk liquid Hazardous and Noxious Substance (HNS) occurs, stakeholders of the emergency response must take strategic decisions that could involve measures to minimize the risk of exposure of surrounding population and the first responders, or to lower the potential impact on the aquatic ecosystem. To be accepted by the actors of the emergency response and the population, the decisional process must be based on a realistic risk assessment. One of the key information to establish a risk assessment is the knowledge of the behavior of the HNS once spilled in water (Cunha, 2013).

In a first approach, the determination of the behavior from to the Standard European Behaviour Classification (SEBC, Bonn Agreement 1994) seems to be the best option. This nomenclature determines the short term behavior of any HNS as long as its physical state (gas, liquid, solid) and basic physico-chemical properties are known at ambient atmosphere and pressure. Density, solubility and vapor pressure are the physico-chemical properties that most influence short term behavior of a spilled HNS. According to their values, HNS are characterized with the main behavior of the chemical: Evaporator (E), Dissolver (D), Floater (F) and Sinker (S). One or two more letters can be added to significate additional behavior(s), but to a lesser extent than the main one. In the case of HNS at liquid state, the SEBC leads to four main behaviors (E, F, D and S) and sub categories with one or two secondary behaviors. As an example a liquid HNS categorized as FED means that the liquid is a floater and it should also evaporate and dissolve when spilled in water.

Though, the SEBC presents some limitations and anyone who will use it must pay attention to its area of validity. First the classification draws upon the physico-chemical

properties determined in laboratory conditions at 20°C in fresh water, while an incidental spill of a HNS can happen in very different conditions. Depending on the exact nature of the product, its physico-chemical properties, or even its physical state can vary with temperature. Secondly the SEBC does not consider the kinetics of the processes of mass transfer such as evaporation or dissolution under different field conditions (e.g. velocity of wind or current).

3D mathematical modelling is a promising way to predict the behavior of an HNS. Different software are already commercialized, or free of use, dedicated to the assessment of the fate in the aquatic compartment, the dispersion in the atmosphere, or aquatic-atmospheric coupled models for an HNS spilled in water. Among the existing software, they may require additional physico-chemical parameters (surface tension, partition coefficient, etc.) compared to the SEBC. They also allow to modify the characteristics of water (salinity, concentration of sediment), and calculations are based on meteorological (or meteo-oceanic) forecasting data. Such modelling software can also theoretically predict the HNS concentration versus time at many points in a targeted zone. Among the possible output data, the area reached by a cumulative contamination exceeding a threshold concentration (e.g. Acute Exposure Guideline Levels or acute ecotoxicity exposure for a biological species) can be visualized. However the exact fate in the environment is very complex to predict due to the huge number of HNS transported, the wide differences of very specific environments and the large number of physical, chemical and biological processes involved.

To be validated and qualified, the modelling software must go through many runs and outputs data should be compared to real situations. Indeed, experimental data can be assimilated by models and they may be necessary to calibrate them. This is the most problematic aspect related to HNS. Accidental spills do not allow to acquire field measurements with networks of

chemical or physical sensors in the atmospheric and aquatic compartments (Cunha, 2015). Aware of this lack of experimental data, Cedre developed floating cells that are regularly deployed to perform *in situ* experimentations in marine environment (Fuhrer, 2012; Le Floch, 2011). Despite of the scientific interest of this type of experimentation, there are still limitations due to reduced number of experimentations and diversity of environmental conditions. Indeed, HNS experimental spillages in natural environment are evidently difficult to be accepted, rare and must be performed in isolated places, distant from populations and ecologically sensitive areas. Cedre decided to pursue in this way and create an innovative tool able to work with near real field conditions with the possibility to apply specific basic environmental conditions: air and water temperature, velocity of wind and sunshine. This paper deals with an innovative experimental device to assess the behavior of an HNS under controlled environmental parameters. First results are presented with Butyl Acrylate at different experimental conditions and the behavior of different HNS is assessed in fixed conditions.

MATERIAL AND METHODS

Chemicals

The seawater used to fill the reactor is collected in the bay of Brest (France). Particles in suspension over 25 µm are filtered and seawater is then treated with UV rays (25 mJ.cm^{-2}). The salinity obtained with a refractometer is 35 kg.m^{-3}.

The characteristics of studied HNS are:

| HNS	Butyl acetate	Butyl acrylate	Toluene	Xylene (isomers o,m,p)
Quality grade	Technical	Synthesis	GLC	Normapur
Supplier	VWR	Merck	Carlo Erba	VWR
Purity	>96%	>99%	>99.5%	Mixture of isomer >98.6%

Table 1: quality, supplier and purity of studied HNS

Chemical reactor

The device is designed at a pilot scale to allow the possibility to reproduce some environmental parameters: water composition and temperature, velocity of wind and solar radiation. It is made with a cylindrical 316L stainless steel reactor with an internal diameter of 50 cm. As shown on **Photo 1**, the stainless steel is partially replaced by a curved hardened glass window to visualize the slick of the HNS during experimentations.

The volume of seawater introduced in the reactor is 80 L. A constant seawater temperature is fixed with the help of a SIEBEC M15 pump (in PP with EPDM joint) connected to a TECO TR20 thermoregulated batch. The setpoint temperature is adjusted in order to obtain an efficient temperature of 10 ± 1 °C or 20 °C ± 1 °C, measured with a thermocouple in the reactor.

A constant velocity of wind is applied with the help of a ventilation unit and an Atlantic IP.65 regulator. Three levels were chosen: 0.4 ± 0.1 m.s^{-1}, 3.00 ± 0.07 m.s^{-1} and 6.9 ± 0.1 m.s^{-1}. The actual velocity of wind is recorded with a multisensory anemometer MiniAir20 (Schiltknecht), the sensitive part being placed at about 5 cm above water surface. Air temperature is regulated with the help of a mobile reversible air-conditioning unit CoolMobile E25. A SOL500 lamp from

HONLE society, reproducing radiations of sunshine and able to shine the surface of water, is fixed above the reactor but was not used for this study.
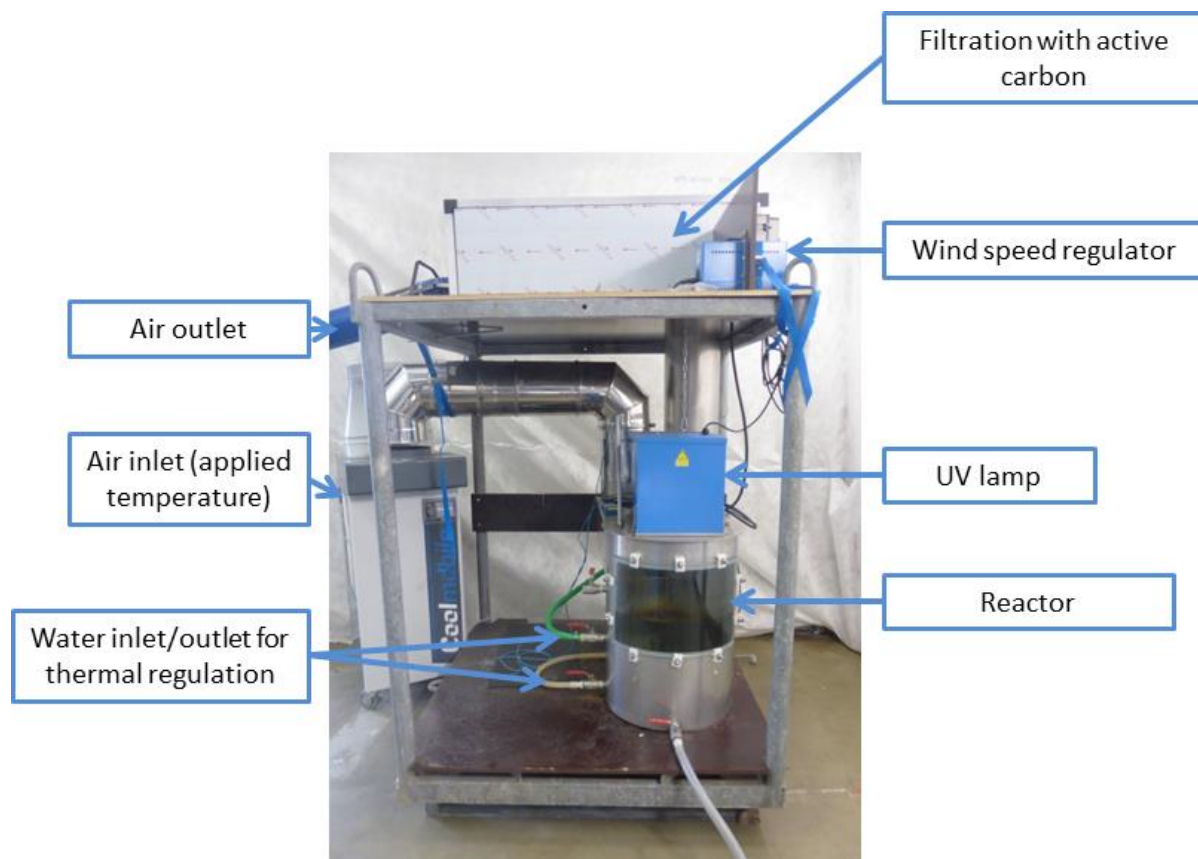
Photo 1: device for assessment of HNS behavior

Air analyses

The concentration of HNS evaporated in the atmosphere above water is measured with a Photo Ionization Detector (PID) MiniRAE 3000 equipped with a lamp of 10,6 eV. The calibration is performed with isobutylene and a factor of correction is applied, correlated with HNS studied.

The air admission tip of PID is placed at 10 cm above surface water and an average measure is recorded every 10 s. In first approximation we consider that HNS slick has disappeared when the signal of PID tends to 0.

Water analyses

Analyses were performed with Agilent technologies 7890A Gas Chromatography (GC) coupled with a Flame Ionization Detector (FID). The GC is equipped with an Agilent technologies HP-5 5% phenyl Methyl Siloxan column (30 m x 250 µm x 0.25 µm). GC experimental conditions are presented in **Table 2**.

HNS	n-Butylacetate*	Toluene and xylenes	n-Butylacrylate
Oven program	40 °C for 2 min then 50 °C.min^{-1} to 250 °C for 14min	40 °C for 5 min then 11 ° C.min^{-1} to 150 °C for 0 min	40° C for 2 min then 7° C.min^{-1} to 100 °C for 0 min then 25 ° C.min^{-1} to 200 for 2 min
Carrier gas	H$_2$	He	He
Flow	7.8566 mL.min^{-1}	1 mL.min^{-1}	1 mL.min^{-1}
Inlet temperature	300 °C	225 °C	250 °C
Injection volume	1 µL	1 µL	1 µL
Ion targeted/dwell (select ion monitoring)	FID detection	(91;150) (92;150) (100;150)	(55;100) (70;100) (71;100) (73;100) (84;100)
Internal standard	Pentyl acetate	Toluene D8	Hexyl acrylate
Concentration of internal standard	2 mg.mL^{-1}	0.1 mg.mL^{-1}	0.050 mg.mL^{-1}

Table 2: GC experimental conditions

*: addition of 1mL ethanol to facilitate extraction

Sampling and preparation

For each HNS studied, a preliminary assessment of solubility in seawater is done to check that the dissolved concentration during the experiment remains substantially below it. T_0 corresponds to the pouring of 150 mL of the HNS at surface water when water and air temperatures are stabilized. A volume of 10 mL is sampled at 1 cm under the water surface for analysis at different times: 1 h, 3 h, 5 h, 7 h and 8h30.

For each sample, a liquid-liquid extraction is performed with 2 mL of hexane in which the internal standard is dissolved. A 30 s manual stirring is done before separation on GC.

RESULTS AND DISCUSSION

Study of n-Butylacetate at different experimental conditions

The effect of temperature and velocities of wind is studied with n-Butyl acetate. This HNS is categorized as FED with SEBC. Results are presented in **Figure 1**. We can notice that each plot has the same overall shape. The concentration in the air is maximum at the beginning of the experiment. This maximum seems to be correlated with the setpoint temperature of the system. Indeed, initial concentrations are gathered between 400 and 600 ppm at 20 °C, while at 10 °C they are gathered around 200 and 400 ppm. This predictable information is essential as, whatever the velocity of wind, the higher the temperature, the higher the maximum concentration in the air will be. The thermal energy brought by water surface increases the process of evaporation.
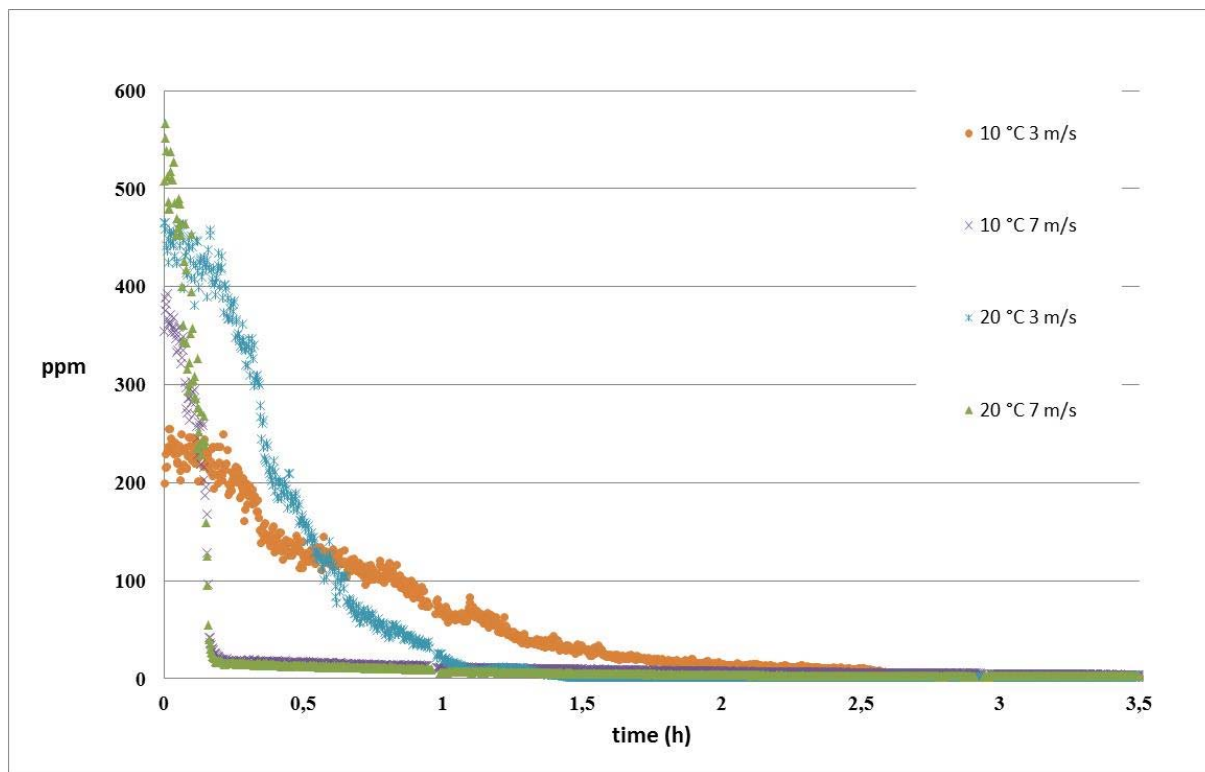
Figure 1: concentration of n-Butyl acetate in the air for different temperatures and velocities of wind

Rapidly, air concentration decreases to go through an inflexion point before reaching zero. This is less clear for the 3 m.s^{-1} velocity of wind as the drop seems to oscillate for both studied temperatures. The drop of the concentration is higher with high temperature, excepted for the highest velocity of wind (results non to improve visibility) for which plots have the same slope whatever temperature. The process of evaporation is thus directly increased with temperature and more strongly influenced with forced convection of wind.

The material balance can be normalized and expressed versus time. An extrapolation of the plot of PID measurements, assimilated to a straight line, allows determining the time when the slick is supposed to have totally disappeared. From that point, the amount of product evaporated is

deducted from the total initial amount of product minus the amount dissolved in water, the latter being calculated with the concentration of the dissolved fraction in seawater. The results obtained from this calculation are presented in **Figure 2**. On these results, it can be noticed that the concentration of the dissolved part always go through a maximum. This shows that the process occurring in the reactor can be divided in two phases. At the beginning of the experimentation, the chemical is progressively and simultaneously dissolved in seawater and evaporated in the atmosphere. This part is interesting as it reflects the competition between mass transfer processes of dissolution versus evaporation. Then, when the gradient of concentration between chemical dissolved in seawater and the surface is reversed (absence of slick), the dissolved fraction can diffuse to the surface and evaporate. It can also be noticed that, at fixed temperature, the minimum amount of chemical dissolved in seawater corresponds to the 3 $m.s^{-1}$ velocity of wind. At a higher velocity of wind, surface agitation promotes dissolution during first hour.
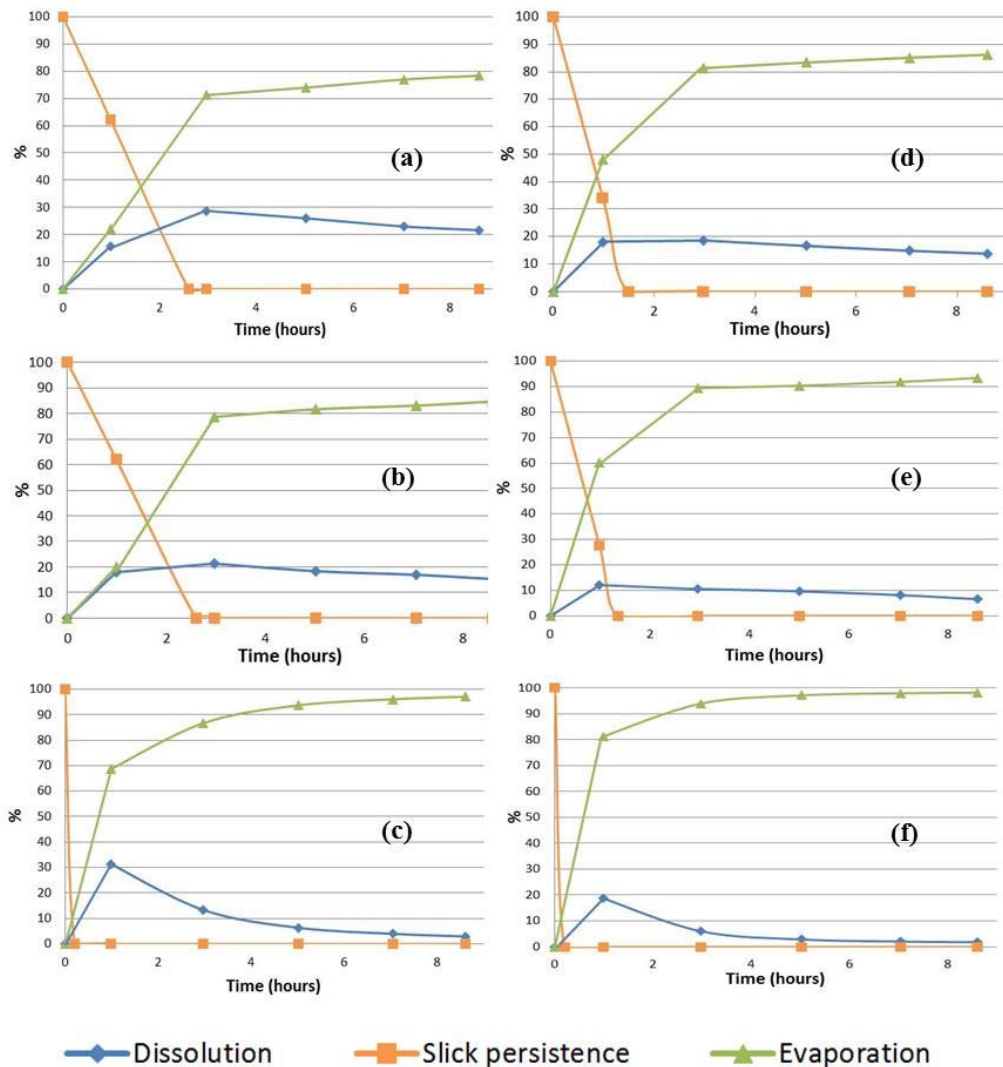
Figure 2: normalized material balance of n-Butyl acetate dissolved in seawater, remaining in the slick or evaporated at velocities of wind of 0, 3 and 7 m.s^{-1}, at 10 °C (a, b, c) and 20°C (d, e, f).

The theoretical SEBC category of n-Butylacetate is FED and this study confirms the predominance of evaporation versus dissolution. The results obtained also allow to roughly quantify the performance and evolution versus time of each process depending on the experimental conditions. Thus, during the first minutes or hours after HNS is spilled, temperature

regulates the maximum amount of product evaporated, higher at 20 °C, while the velocity of wind promotes directly the kinetic of evaporation.

Comparison of n-Butylacetate, Butyl-acrylate, Toluene and Xylene

In addition to n-Butylacetate, similar experimentations were performed with n-Butylacrylate, Toluene and Xylenes. Their theoretical SEBC categories and theoretical vapor pressure are summarized in **Table 3**. Vapor pressure, used to determine the SEBC category, is an indication of a liquid's evaporation rate.

HNS	SEBC category	Vapor pressure (kPa)
n-Butylacetate	FED	1.33 (20°C)[1]
n-Butylacrylate	FED	0.53 (20°C) [1]
Toluene	E	2.67 (18.3°C) [1]
o-Xylene		0.65 (20°C) [2]
m-Xylene	FE	0.83 (20°C) [2]
p-Xylene		0.84 (20°)[2]

Table 3: SEBC categories (assessed from physico-chemical properties) and vapor pressure data

(sources: CAMEO[1], National Institute of Standards and Technology[2])

With the same approach than for n-Butylacetate, normalized material balances are presented in **Figure 3**.

The evaporated fraction is 100% for Toluene and Xylenes, whatever the temperature, but the kinetics is faster for the first one. This result is in accordance with SEBC categories, respectively E and FE.

The total evaporated fractions of n-Butylacetate and n-Butylacrylate, 8 h after spillage are similar, about 85-90 % at 10 °C, and about 90-95 % at 20 °C. The identical SEBC category (FED) is coherent with the obtained results for the two products. However we can notice that the kinetics of evaporation of n-Butylacetate is much higher compared to n-Butylacrylate, 80 % versus 50 % after 3 h. Despite of the differences of the vapor pressure values of the two products, at 20 °C, it seems that vapor pressure, a thermodynamic value, has a stronger influence on the kinetic aspect but not tremendously on the final evaporated fraction. This information might be of importance for the modelling software developers.
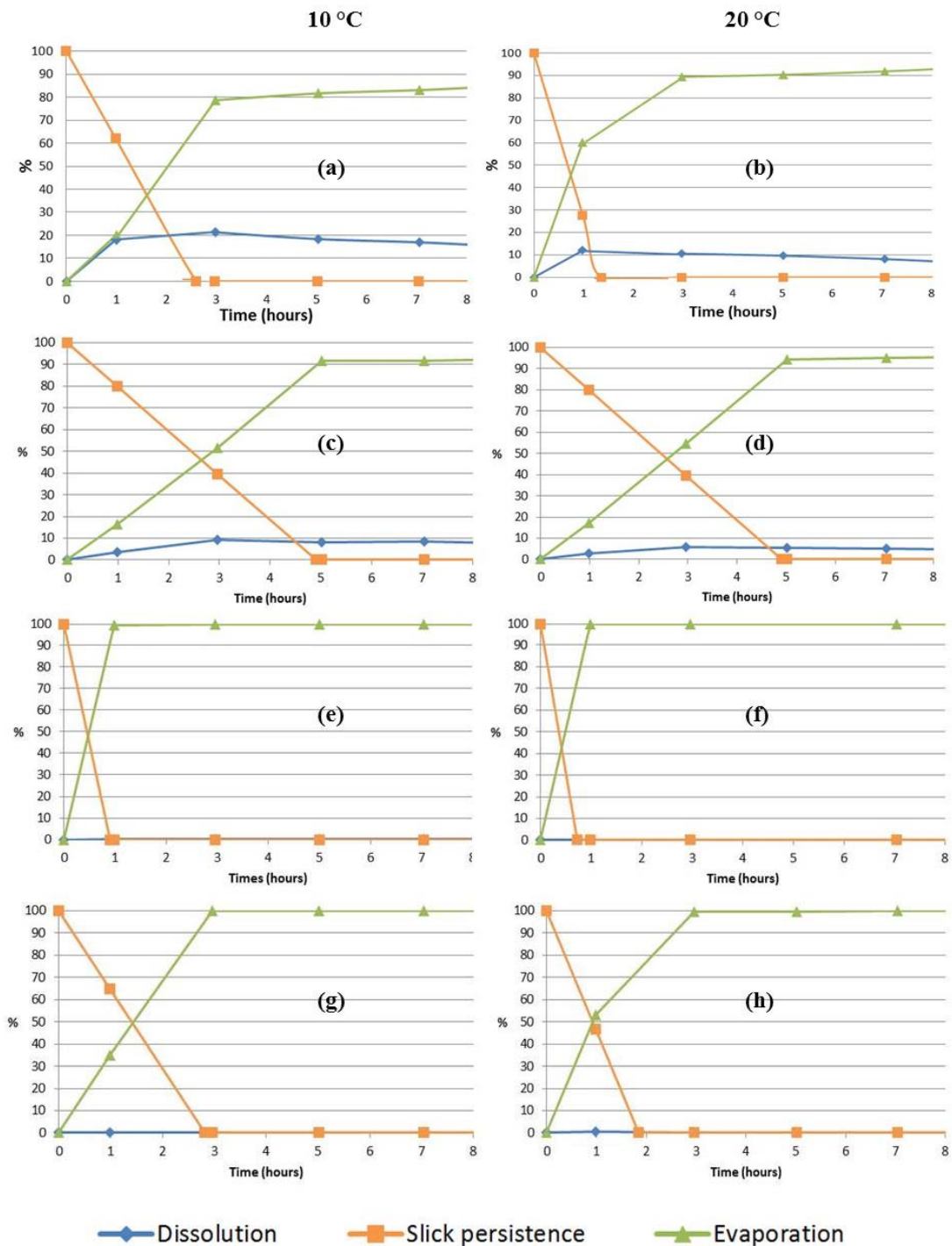
Figure 3: normalized material balance of fractions dissolved in seawater, remaining in the slick or evaporated at velocity of wind of 3 m.s^{-1}, at 10 °C and 20°C, respectively for n-Butyl acetate (a, b), Butyl-acrylate (c, d), Toluene (e, f) and Xylene (g, h).

CONCLUSION

For the first time at our knowledge, an original tool is proposed to establish simultaneously a competition between the two processes of evaporation and dissolution. This innovation is very promising as first experimental results obtained are mainly in accordance with theory. Our results will allow developers to assimilate the essential experimental data required to validate modelling software. Moreover, in case of HNS incidental spill, Cedre is able to determine rapidly the effective behavior of a product, taking into account the real environmental conditions, especially wind and temperature. The possibility to provide such information is a real advantage for stakeholders of emergency response to protect population and to assess potential risk exposure for first responders. Further experimentations will be performed with more complex environmental parameters, including new influencing parameters such as solar radiation simulation.

ACKNOWLEDGEMENTS

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