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Experimentation to benefit spill response

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Abstract

To respond to an oil spill or another substance, it is essential to know the exact location of the pollution and to anticipate its fate: will it remain at the surface, enter the water column or the atmosphere, or even do all three simultaneously? Over recent years, various modelling software tools designed to predict a substance's fate have entered the marketplace. The results are generated using sophisticated mathematical calculations based on theoretical equations which use physical and chemical constants assessed in the laboratory. Predictions generated by models along with laboratory experiments are not always accurate because uncertainties persist regarding the influence of environmental parameters on the fate of any chemical.

Although the assessment of a substance's physical and chemical constants at laboratory is essential, it is necessary to gain a global understanding of its fate through pilot-scale testing followed by *in situ* validation. On one hand, lab work allows assessing physical and chemical properties of a substance (e.g. viscosity, solubility, etc.) and, on the other hand, pilot-scale testing enables to establish its distribution between the different compartments (e.g. water column, atmosphere) under environmental controlled conditions. The results obtained can then be used to calibrate modelling software that should, wherever possible, undergo a final validation phase involving *in situ* testing in the field. The prediction of a spill's behaviour is essential to define response strategies and the best suited equipment to be deployed.

Here we illustrate this approach by presenting the results obtained at different scales for two volatile HNS (Hazardous and Noxious Substances): heptane (E) and xylenes (FE).

Lab study

In the laboratory, density, viscosity and surface tension of heptane and xylenes were first assessed at various temperatures (5, 10 and 20°C) and, as expected, were found to decrease with increasing temperature. Evaporation kinetics were then determined by following the weight loss fraction method (Okamoto et al. 2010). For heptane and xylenes, a linear mass loss over time was observed with evaporation rates of $\sim 35\% \cdot h^{-1}$ and $\sim 6\% \cdot h^{-1}$, respectively. Full evaporation occurred between 3 and 8h after the beginning of the experiment, respectively.

Pilot-scale studies

Evaporation and dissolution kinetics were then assessed experimentally and simultaneously using the 'Chemistry test bench' designed in Cedre facilities. This system is a compromise between the laboratory and the natural environment as it is designed to recreate the effects of several environmental parameters (water temperature, wind speed, sunshine and surface agitation).

Six environmental conditions were tested: 3 wind velocities (0, 3 and 7 m/s) and 2 water temperatures (10 and 20°C). As soon as the temperature was stabilised in the tank, 150 mL of HNS were gently spilled at the surface to form a slick. For both heptane and xylenes, the evaporation goes faster with stronger wind conditions. As an example, at 20°C and without wind, the spill of heptane disappears 18 min after the spillage. However, with a wind velocity of 7 m/s, the persistence of the spill of heptane is lower than 3 minutes. Still at 20°C and without wind, the slick of xylenes remains 5h following the spillage. However its persistence shortens to 1h lasting for a wind velocity of 7 m/s. Without wind, the vapours of xylenes remain above the slick (higher density than air). This result is thus of major importance for first responders in case of an accident in low ventilated places. Evaporation is also favoured with higher water temperature though to a lesser extent.

The dissolution process is generally much higher with stronger wind conditions. Wind indeed increases surface agitation, which favours contact between the water and the HNS and, hence, the dissolution process. This is the case for xylenes. However for heptane or compounds with a vapour pressure greater than 5 kPa this observation does not seem to apply. For colder temperature, the dissolution is favoured due to a lower evaporation of the HNS. This phenomenon is also explained by the kinetics of the two processes: evaporation is a fast process whereas dissolution has a lower kinetic.

Tests in floating mesocosms were then conducted in order to validate the results obtained with the chemistry test bench. For heptane, seawater temperature was 18°C, air temperature ranged from 14.6 to 26.1°C and wind velocity was 3.7 m/s with gusts of up to 8 m/s. Data collected from PIDs showed that heptane was only detected in the atmosphere for 1h. The spill had fully disappeared 1h after the beginning of the experiment. Heptane was not detected in the water column during the whole experiment. This confirms the observations made using the chemistry test bench.

For xylenes, tests were performed under harsher metocean conditions less favourable to evaporation processes. Air temperature indeed ranged between 3 and 5°C with wind conditions ranging from 3 to 5 m/s and snowfalls occurred. A persistence time of 34 h was observed for xylenes. This longer residence time than previously observed was explained by more important solubilisation processes. The spill of xylenes underwent intense emulsification which led to slower evaporation kinetics and increased transfers to the water column (natural dispersion).

This clearly shows how critical are environmental conditions in the fate of a chemical spill at sea.

Towards an open-sea study

Last but not least, it would be relevant to carry out tests in open sea in order to confirm all these results at a scale as close as possible to an accidental event: what will be the real extent of the slick, how the spreading will be impacted by the environmental conditions, which behaviour will be dominant (e.g. evaporation vs dissolution)? The detection thematic is of high priority to guarantee that no responders will be exposed to toxic vapours. There is a real need to test the response capacity of emerging sensors (hyperspectral cameras) on detecting and monitoring both HNS slicks and the gas cloud.

At the end, all these information must be shared with modellers in order to validate and/or calibrate the models which are essential in the response strategy definition.

Keywords: Experimentation, spill response, HNS, evaporation, gaz cloud
