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Tackling the behaviour of volatile HNS: A key challenge for Marine Pollution response

Laura Cotte¹, William Giraud¹, Laurent Aprin², Paul Harold³, Andrew Kibble³, Raphaël Faschinetti⁴, and Stéphane Le Floch¹

¹ *Cedre, 715 rue Alain Colas, Brest, France*

² *IMT Mines d'Alès, 6 avenue de Clavières, Alès, France*

³ *UK Health Security Agency, Radiation, Chemical and Environmental Hazards Directorate, Cardiff, Wales*

⁴ *CEPPOL, BCRM de Brest, CC79, Brest, France*

Contact: Laura.Cotte@cedre.fr

Abstract

Release of volatile Hazardous and Noxious Substances (HNS) at sea can lead to the formation of toxic, flammable or even explosive gas plumes that can travel large distances and pose risks over a wide area in relatively short timescales.

Evidence-based decisions are thus needed to inform maritime authorities in terms of detection and monitoring, and to protect crews, responders, coastal populations and the environment. Unfortunately current limitations regarding data, decision support tools and proper training and exercise resources challenge response.

When maritime accidents occur, knowledge about any HNS released in open sea (e.g. physical and chemical properties and behaviour in the environment) is essential to predict potential environmental consequences and to adapt first-response. For volatile HNS, other critical parameters that should be systematically predicted and/or assessed are the evaporation and the dissolution kinetics: this would warn first-responders against toxic, flammable and/or explosive gas clouds that might originate from the surface slick.

The theoretical behaviour of a chemical is inferred routinely using the Standard European Behaviour Classification (SEBC) according to its physical and chemical properties. However this method has its limits as it is based on laboratory experiments which do not take into account environmental parameters. The MANIFESTS¹ project aims to address these gaps by providing new experimental data on evaporation and dissolution kinetics of volatile HNS. In addition, new fire and explosion modelling tools will be developed to better assess the gas cloud fate.

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Here we present new experimental data obtained at lab-scale for 5 pure chemicals along with 7 liquid mixtures. The chemicals studied included acrylonitrile, aqueous ammonia (32%), cyclohexane, petroleum benzene and vinyl acetate. They were chosen to reflect key groups of HNS routinely carried at sea or reportedly involved in spills. For the mixtures, liquid samples of 2-5 component systems were then prepared by mixing each chemical in equal volume ratio.

Density, viscosity and surface tension of each chemical were first assessed at various temperatures (5, 10, 15, 20 and 30°C) and, as expected, were found to decrease with increasing temperature.

Evaporation rates of pure chemicals and mixtures were then determined by following the weight loss fraction method (Okamoto et al. 2010). The final objective was to assess mass fluxes at the sea-air interface due to evaporation process and to compare it to analytical models.

All pure chemicals except ammonia showed a linear mass loss over time with a full evaporation observed between 2.5 and 30h after the beginning of the experiment. However, the same chemicals spilled at the surface of seawater generally presented a non-linear mass loss over time, i.e. different and longer evaporation rates. An intermediate behaviour was also observed for mixtures, i.e. either a linear mass loss or not, depending on the composition of the mixture.

Further experiments were then designed in order to test the dissolution of pure chemicals at three different temperatures (15, 20 and 25°C) and salinities (freshwater, 20‰ and 35‰). Samples were analysed by GC-MS with headspace (HS) extraction. Solubility limits were calculated once a plateau of concentrations in water was reached. A mathematical equation was finally generated using Statgraphics in order to relate the solubility of each chemical to water temperature and salinity.

Last but not least, the competition between mass transfer processes was tested for 2 selected HNS; cyclohexane and vinyl acetate using Cedre's chemistry test bench under controlled environmental conditions (air and water temperature, wind velocity, surface agitation). The main feature observed was that evaporation predominates over dissolution. This suggests an increased risk of a toxic gas cloud when a volatile HNS is accidentally spilled at sea. Consequently, these observations should be taken into serious consideration by first-responders in order to ensure their own safety during the intervention.

Given that, these new data could be used to adapt the equations routinely used to model evaporation – especially to address the variations observed for the evaporation rates – and dissolution processes. This would offer crisis management stakeholders more precise information regarding the formation of toxic, flammable or explosive gas clouds (Go/No Go decision).

Keywords: HNS spill, evaporation, solubility limit, gas cloud
