Summary of key findings from FAMERR

1. How salinity and temperature affect the fate and behaviour of the chemicals?

The project looked at the impacts of temperature and salinity on the fate and behaviour of eight chemicals representing different groups (i.e. floater/dissolver, sinker/dissolver, evaporator/dissolver, dissolver, evaporator). Temperature ranges between 10 - 30°C and salinity range 32 – 40 ppt, both typical of surface seawater variation, were explored. CHEMMAP was used to simulate near shore spills with limited depth and moderate tidal currents. The fate and behaviour of the chemicals for up to four days after the release were investigated.

- **Influence of temperature on behaviour and fate**

In general, rates of evaporation and degradation are enhanced at elevated temperatures. Therefore, notable changes in behaviour are expected with chemicals that evaporate or degrade more readily. As shown in Figure 1, for aniline (Floater/Dissolver), the remaining chemical in the water column four days after the release was four times less when temperature increased from 10°C to 30°C; and the concentration of m-Cresol (Sinker / Dissolver) was only a tenth when the temperature increased from 10°C to 25°C.

For sinkers, their concentrations in the water column shortly after release depends on their solubility in water. Generally, increased water temperature would lead to increased solubility, and higher concentration near the seabed. Nevertheless, the subsequent behaviour largely depends on their intrinsic tendency to evaporate and on degradation. As illustrated in Figure 1, the concentration of trichloroethylene (Sinker/Dissolver) initially increased with the increase of temperature 10 hours after it was spilled, but then decreased due to the enhanced evaporation at elevated temperature.

However, for chemicals with greater tendency to evaporate or degrade, their ultimate fate would not be substantially altered within the temperature range explored. For example, for volatile and moderately volatile chemicals such as acrylonitrile (Dissolver / Evaporator), styrene and m-xylene (Floater/Evaporator), almost 100% of the chemical would evaporate within 90 hours after the release (as shown in Figure 1 and Figure 2), and it is independent of the temperature. Similar fate was predicted for chemicals the degrade readily, such as hypochlorite.

For chemicals with negligible degradation and evaporation within typical sea surface temperature range, temperature alteration would not change their behaviour or fate.

- **Influence of salinity on behaviour and fate**

The influence of salinity on the behaviour and fate of a chemical is generally attributed to the effect on its solubility. For some organic chemicals, the solubility could reduce by 20-30% in seawater (32ppt) than in freshwater. [Xie et al. 1997] However, between the typical variation of ocean salinity around the world, i.e. 32 ppt and 40 ppt, the solubility difference is likely to be very small (in the range of a few percent). For a small number of chemicals, salinity change may affect the degradation rate, such as total residual oxidants produced by chlorine.

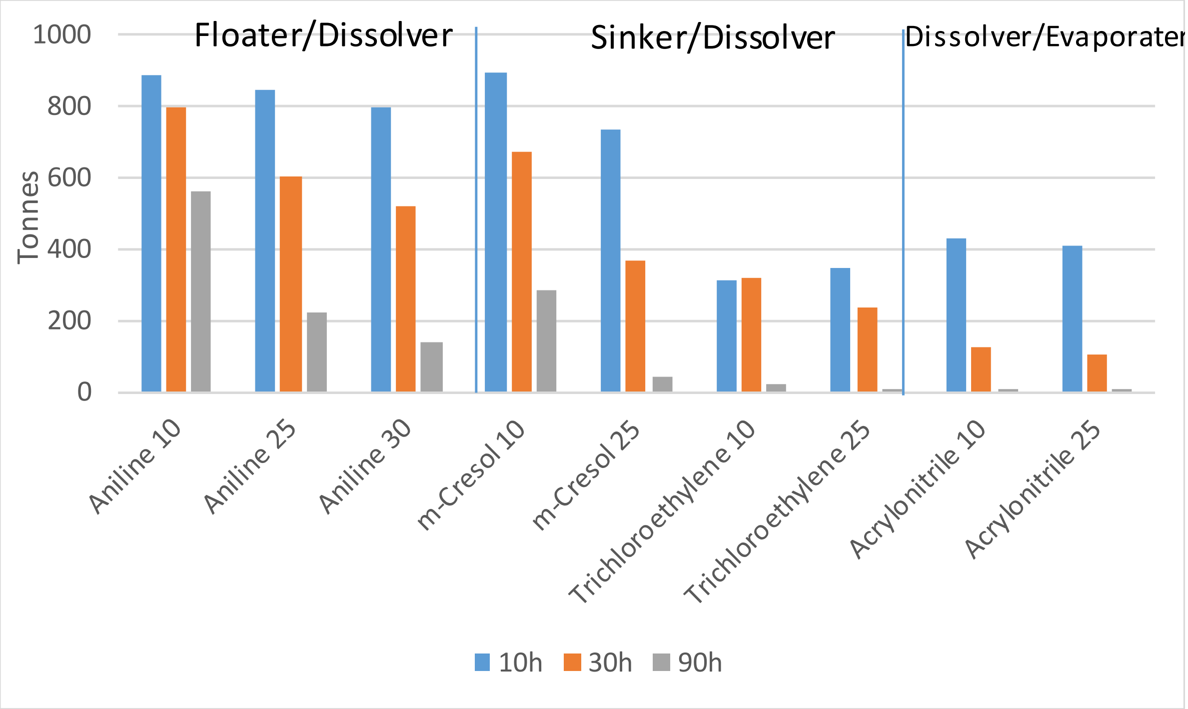

Figure 1. Quantity of different HNS in the water column (tonnes) following a spill of 1000 Tonnes after 10, 30 and 90 hours at temperatures of 10 and 25˚C (also 30˚C for aniline) and salinity of 32 ppt

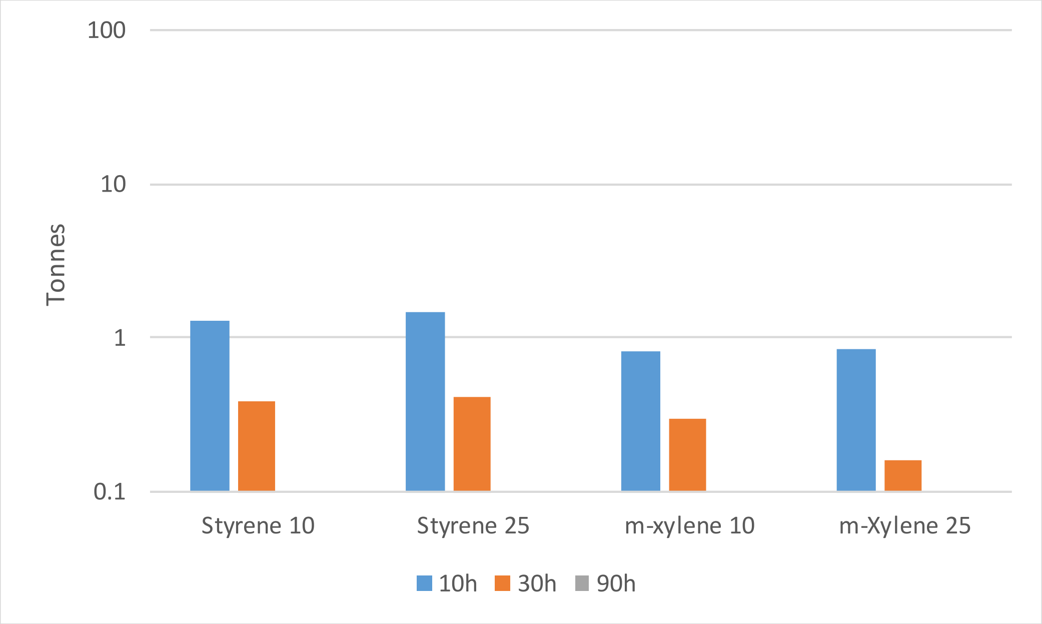

Figure 2. Quantity of floater/evaporator HNS in the water column (tonnes) following a spill of 100 Tonnes after 10, 30 and 90 hours at temperatures of 10 and 25˚C and salinity of 32 ppt

A CHEMMAP simulation of a nearshore spill of 1,000 tonnes aniline with limited depth (10m) and moderate tidal currents (0.3 m/s) was also produced to illustrate the fate of aniline at different temperatures (as shown in Figure 3). It is clear that the concentrations had peaks and troughs even under mild tidal influence. Regardless of the distance from the spill site or water temperature, the near bed concentration gradually reduced to zero over the period of four days under the influence of natural wave mixing energy. However, due to the enhanced evaporation and degradation, the concentration of aniline is considerably lower at elevated temperature (30°C). It is also worth mentioning that stratification is not taken into consideration in this simulation. For a surface spill, stratification would inhibit the mixing to the seabed which would further reduce benthic exposure. Potentially, it would also promote evaporation by retaining a larger portion of the chemical in the surface layer.

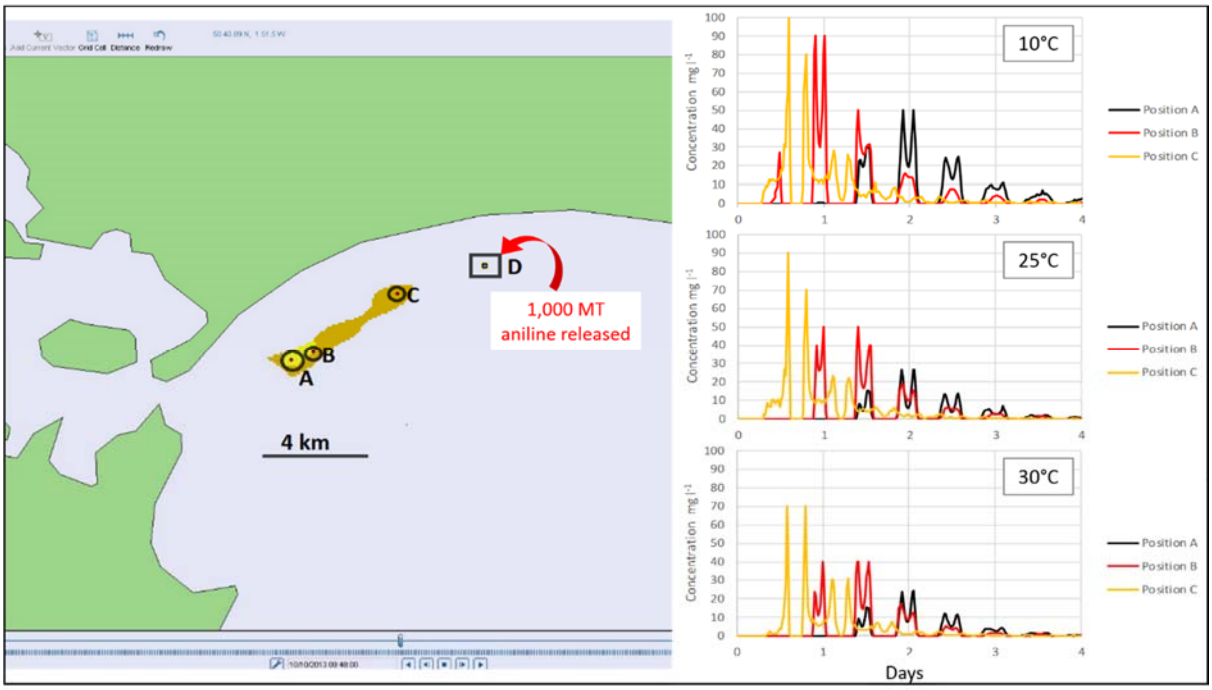

Figure 3. CHEMMAP simulation of near bed concentration change over four days after a nearshore spill of 1,000 tonnes aniline at three temperatures: 10°C, 25°C and 30°C

2. How temperature and salinity affect the toxicity of the chemicals

Six chemicals, i.e. aniline, butyl acrylate, dicamba, zinc sulphate, benzalkonium chloride, and chlorine (total residual oxidants), were tested for their toxicity with the change of temperature and salinity. Again, temperature and salinity ranges characteristic of typical surface seawater were investigated, i.e. 10 - 30 ˚C and 20 - 40 ppt.

Two crustacean species, i.e. copepod *Tisbe battagliai* and amphipod *Corophium volutator*, and two macro algae species, i.e. brown macro algae *Fucus vesiculosus* and the red macro algae *Ceramium tenuicorne*, were used for the toxicity tests. Figure 4 shows the species used for the tests. Three types of toxicity tests, i.e. 48-hour and 96-hour standard exposure, time-based studies, and brief exposure studies, were carried out on the test species. All tests were performed according to stringent quality assurance procedures at Cefas.

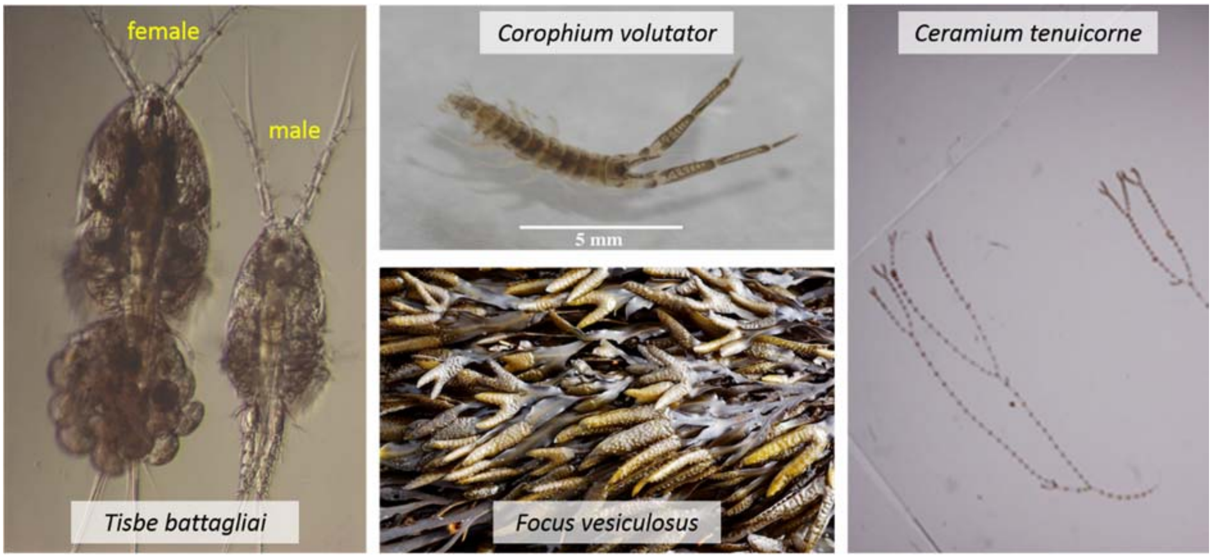

Figure 4. Species used in the toxicity tests

- **Influence of temperature on toxicity**

It has been demonstrated that elevated temperature would lead to increased toxicity for most of the chemicals and species studied in this project. This effect is generally attributed to the enhanced metabolic activities and uptake rates at higher temperature. Most of the aquatic organisms are ectothermic, and their body temperature is the same as the water temperature. It was previously identified that a 10°C temperature change could lead to a twofold change in metabolic rate. Increased metabolic activities and uptake would expose the organism to a larger amount of chemicals in the water column, and subsequently, more noticeable toxic effects. This effect is clearly demonstrated by a series of exposure tests of aniline on *Tisbe battagliai*, as shown in Figure 5. Higher survival rates have been observed at lower temperature (10 °C) at all salinities and at all concentrations tested. Similar trends have been observed with zinc sulphate on *Tisbe battagliai*, total residual oxidant on *Ceramium tenuicorne*.

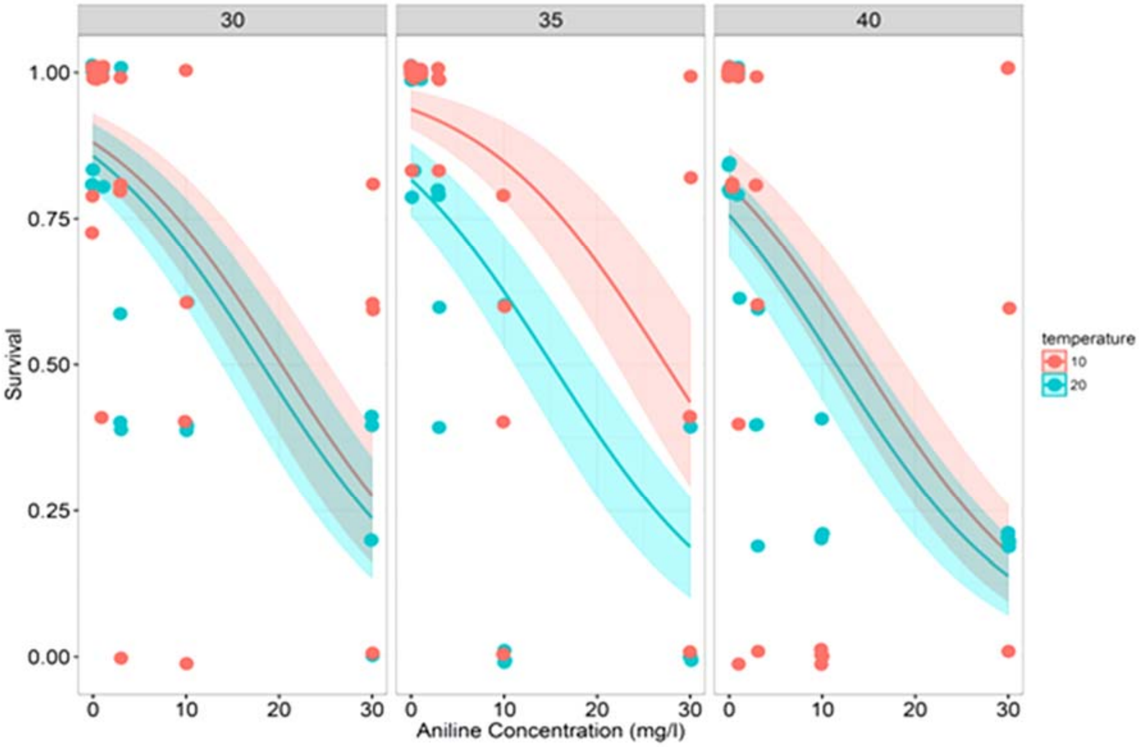

Figure 5: Prediction of the binomial general linear model effect of temperature and 95% confidence level (shaded area) for *T. battagliai* exposed to different concentration of aniline for 48 hours at three different salinities: 30 ppt, 35 ppt and 40 ppt. 40% jittering effect has been applied, so the data points can be clearly presented.

However, it is also worth noting that the influence of temperature on toxicity is primarily determined by the fundamental mechanisms as to how a chemical affects an organism. In the example of benzalkonium chloride, a cationic surfactant typically used as biocide, its toxicity comes from its capacity of binding and disrupting the inner cytoplasmic membranes of the organisms. This rapid mechanism is independent of metabolic and uptake rate. Therefore temperature change is not expected to affect the toxicity of benzalkonium chloride. This point has been demonstrated by a number of experiments carried out in this project, including the 48 hour exposure test on *T. battagliai*, growth inhibition tests on *C. tenuicorne*, and on *F. vesiculosus*, at different salinities. As shown in Figure 6, no significant difference in dose response was observed between 10°C and 20°C, at neither 20 ppt nor 30ppt.

- **Influence of salinity on toxicity**

Compared with data on the influence of temperature, fewer data are available from salinity related toxicity studies. A review carried out by a different research group shows that about 50% of the previous studies demonstrated negative correlation between salinity and toxicity of chemicals, i.e. chemicals show lower toxicity at increased salinity, about 18% of the studies demonstrated positive correlation, and a remaining 32% showed no effect. [Hall and Anderson, 1995]

The results from this project suggest that the effect of salinity is highly chemical and species specific. In addition to the effect of salinity on chemical, the overall impact also depends on the optimal salinity range for the species, as test species are less susceptible to chemical toxicity at their optimum salinity.

For example, results from tests on *T. battagliai* using both aniline and zinc sulphate suggest that significantly lower toxicity was observed at 35 ppt, the optimum salinity for *T. battagliai*. While similar exposure tests of aniline using *Corophium volutator* suggest that toxicity was significantly lower at 40ppt. It was also found out that some species are indifferent to salinity changes.

Overall there is no clear and consistent effect of salinity on toxicity.

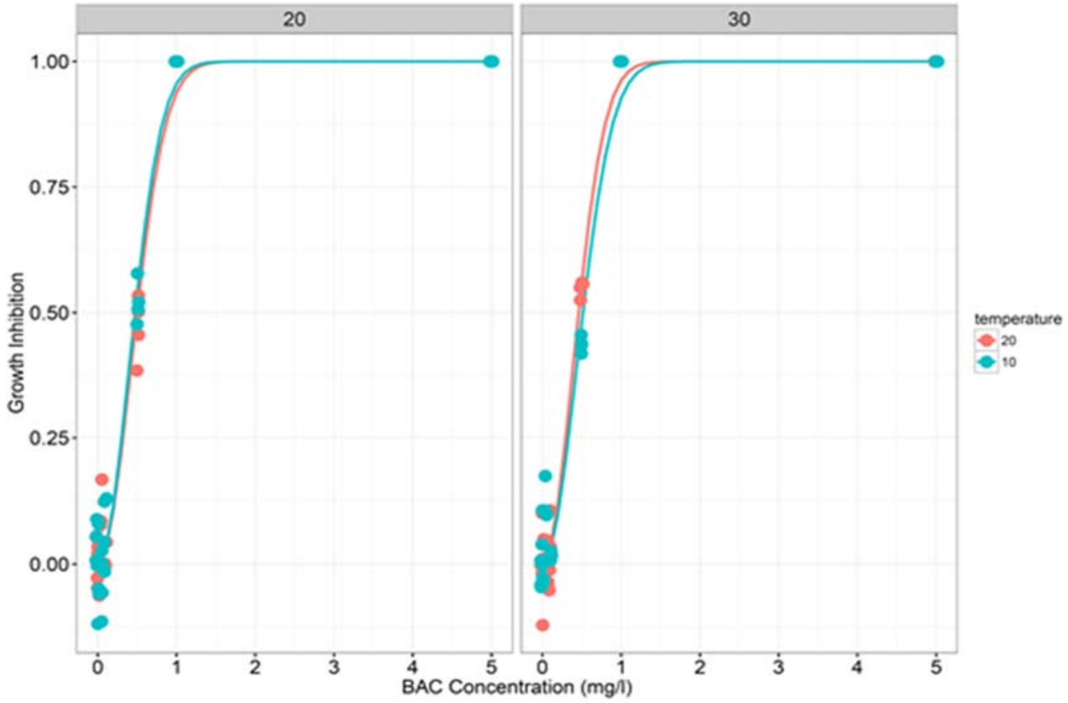

Figure 6. Comparison of dose response curves at 10 and 20°C for salinities 20 and 30 ppt for *F. vesiculosus* exposed to benzalkonium chloride for 96 hours

3. Brief exposure studies

The overall impacts of a chemical on a species are highly specific to the properties of the chemical and the mechanisms it affects in the organisms. This has been demonstrated by a few series of tests during this project. Dicamba, a herbicide, did not cause observable effects on either *Tisbe battagliai* or *Fucus vesiculosus* after 48-hour and 96 hour exposure when tested at 50 mg/L. For aniline, recovery was observed with *Tisbe battagliai* for exposure concentrations up to 300 mg/L for a few hours exposure. In contrast, benzalkonium chloride (a biocide surfactant that disrupt cell membranes) can cause irreversible damage and mortality at concentration as low as 1-5 mg/L, even after 1-hour exposure. Similarly, chlorine (a biocide that cause oxidation reactions within cell cytoplasm) demonstrated significant growth inhibition after 2-hour exposure on *Fucus vesiculosus* and *Ceramium tenuicorne* at a concentration of 2 mg/L.

4. Some general conclusions from this project

Higher salinity is likely to reduce the solubility of chemicals. Therefore, the overall toxicity may be lower when the salinity is in the range of 35-40 ppt, as compared with brackish water. Higher temperature is likely to lead to enhanced evaporation and degradation, and essentially reduce the amount of chemicals in the water column. This effect would be more noticeable for chemicals that remain in the surface layer of the water column (Floaters and Evaporators). For chemicals with higher density (Sinkers), higher temperature may lead to enhanced solubility and improved mixing, which means the chemicals may affect pelagic species as well as benthic species. Higher temperature is likely to increase the metabolism and uptake rate of the organisms, which may lead to more noticeable toxicity effects.

Based on statistics reported in HASREP project, about 50% of the HNS transported in the EU would evaporate or float upon release, as shown in Figure 7. The concentration of these chemicals in the water column are likely to reduce more rapidly at higher water / air temperature. About 25% of the chemicals would dissolve or sink upon release. These chemicals may persist longer in the marine environment, and potentially cause greater concerns. However, the actual impact of each chemical should be assessed individually according to their intrinsic physiochemical properties. Bioconcentration and bioaccumulation are two key factors to consider during such assessments.

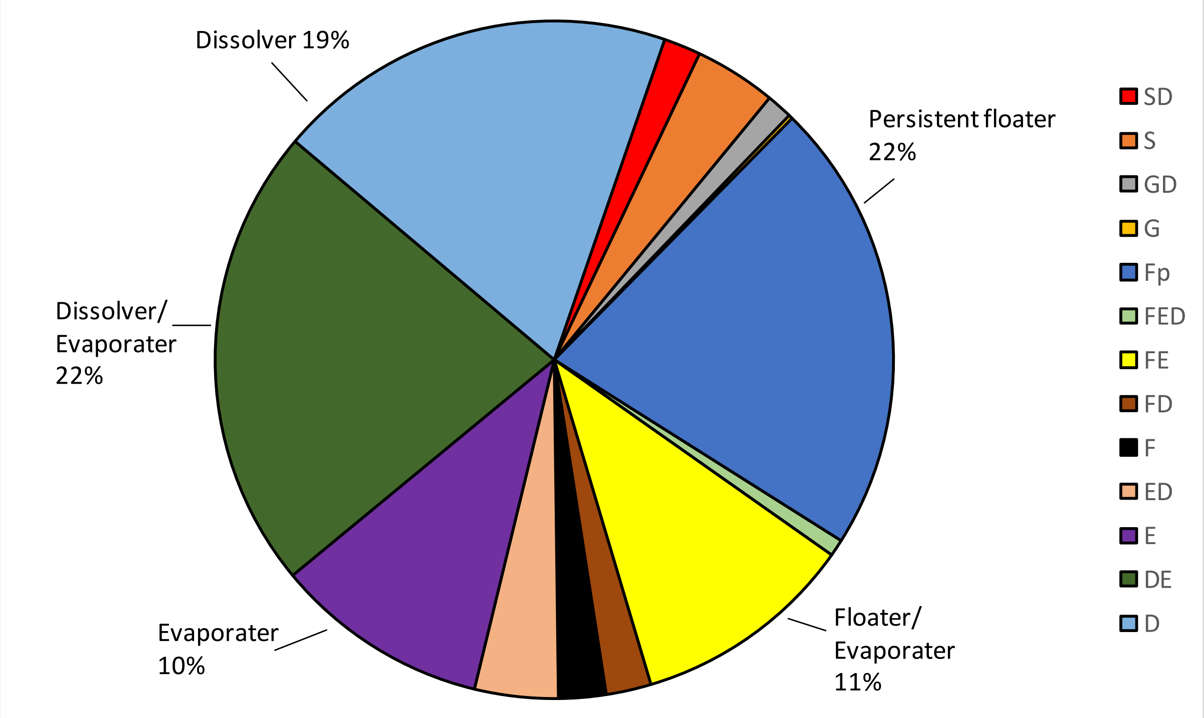

Figure 7 Percentage of top 100 HNS chemicals handled in EU ports based on data reported for 2002 – 2004 [HASREP, 2005]

Due to the tidal influence, local sessile organisms and relatively immobile benthic species may experience a series of concentration peaks and troughs after a nearshore spill. Therefore, the overall toxic effects of a chemical on the species is determined by two factors: how long the chemical remains in local waters and at what concentration; and whether the organism can metabolise and depurate the chemical in between two peak concentrations. Depending on the physiochemical properties of the chemical and the mechanism it affects in an organism, a brief exposure may not cause long term impacts. However, this is highly chemical and species specific and should not be generalised.

Reference

Hall, L. W., & Anderson, R. D. (1995). The influence of salinity on the toxicity of various classes of chemicals to aquatic biota. Critical Reviews in Toxicology, 25(4), 281-346.

HASREP, 2005. Response to harmful Substances spilt at sea. Project co funded by the European commission under the community framework for co-operation in the field of accidental or deliberate marine pollution.

Xie, W-H., Shiu, W-Y and Mackay, D. 1997. A review of the effect of salts on the solubility of organic compounds in seawater. Marine Environmental Research, Vol. 44, No. 4, pp 429-444.