D4.4 - Model validation

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2. Introduction

The transportation of hazardous and noxious substances (HNS) on ships has been on the rise in recent years, posing a significant threat to both human health and the environment. The spill of these chemicals can have far-reaching consequences, particularly when dealing with highly volatile substances that can spread rapidly and unpredictably. The MANIFESTS project has been established with the goal of better understanding the behaviour of these substances to improve response capabilities in the event of a spill. Through research and analysis, the project aims to improve already existing models for predicting the behaviour of HNS in various environments, and to validate these models through a series of experiments and real-world scenarios.

Models are essential tools to understand and predict the behaviour of HNS in the event of a spill. However, they are not perfect and have limitations in terms of accuracy, which must be considered by the users. During the MANIFESTS project, the models CHEMMAP, OpenDrift, OSERIT, and MOHID, have been utilized and compared against separate sets of data. These models will be introduced briefly in the next section.

This report consists of three validation sections. The first section compares a small-scale laboratory experiment that visualizes the competition between evaporation, dissolution, and volatilization, and assesses the model's ability to simulate these processes. The second section investigates the impact of wind on the evaporation rate and provides as much environmental data as possible to the model, using a wind tunnel. The two last section of this report compares the models' simulation with the sea trials that took place at the end of May 2022. These sections compare both the drift in the water and the air dispersion against field data. By analysing these different experiments, we can understand the capabilities and limitations of the models used in this project.

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3. Model description

3.1. OSERIT

OSERIT is a multipurpose Lagrangian particles model able to simulate the trajectory of floating objects adrift at sea as well as the drift, fate, and behaviour of acute marine pollution events by oil and other harmful and noxious substances (HNS) **(Dulière et al., 2012; Legrand et al., 2017)**. The model employs external forcing from various sources to simulate drift and atmospheric dispersion and considers several parameters, such as wind, wave, current, and temperature. Lagrangian particles move in a 3D space and are influenced by the value of the parameters at their location. For instance, airborne particles are affected solely by wind, while those at the surface are impacted by wind, current, and waves. In contrast, particles in the water column are only affected by current and waves. Additionally, there are many more factors at play, including turbulent kinetic diffusion and buoyancy (only for particles in the water).

To compute the fate, the pollutant volume is equally divided between the different Lagrangian particles; the pollutant volume being itself subdivided at the level of a particle as a function of the chemical compound (or pseudo-compound). Each of the chemical compounds in the particle can be in several states: liquid (slick or droplets), emulsified, evaporated, dissolved, and degraded. The model is also able to simulate mixture, when they are non-azeotropic and there is no chemical reaction: each component of the mixture is treated as separated compounds. To track accurately the change of state of chemicals, the weathering module of OSERIT have been improved in the framework of the MANIFESTS project (Lepers and Legrand, 2022). It includes among other, evaporation, dissolution, and volatilization. Finally, because the state of chemical compounds influences the drift behaviour of a Lagrangian particle, the pollutant mass is periodically redistributed between neighbouring particles to minimize the number of different states active in each particle. This also assures the conservation of mass of the pollutant during the entire simulation.

The tree main processes that have a significant impact on the atmospheric concentration of volatile HNS when spilled at sea are evaporation, dissolution, and volatilization. For that reason, they will be explained more in depth in this section. The evaporation rate will be a central focus, and it is calculated using an equation derived from **(Brighton, 1985)**:

$$E_{(i)} = C_{s(i)} \, U_* \, \overline{j_{c(i)}}$$

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The evaporative mass flux $E_{(i)}$ (kg/m²s) for the compound i is estimated from several parameters. The friction velocity of the air U_* (m/s) is proportional to the wind speed and vary with the atmospheric stability class, the chemical's vapor-phase saturation concentration $C_{s(i)}$ (kg/m³) is proportional to the vapor pressure and the molar mass of the chemical. The mass transfer coefficient $\overline{j_{c(i)}}$ is a non-dimensional kinematic parameter, function of the physico-chemical properties of the HNS and with the properties of the environment. To have an estimation of the mass flux on the entire slick, the result needs to be multiplied by the slick area.

The dissolution rate is estimated following (Hines and Maddox, 1985; Legrand et al., 2017; MacKay and Leinonen, 1977):

$$D_{(i)} = K \left(x_i C_i^S - C_i^w \right)$$

Dissolution rate $D_{(i)}$ (mol/m²s) of the compound i depend on several parameters. The solubility C_i^S (mol/m³) and the molar fraction x_i of the compound are increasing the dissolution rate and the concentration of the compounds in the water C_i^w (mol/m³) decrease it. This means the dissolution rate decreases when a large amount of compound is already dissolved. The mass transfer coefficient K (m/s) depends on several other variable such as the viscosity of water, the current speed, and the physico-chemical properties of the HNS. The slick area is needed to compute the flux on the entire slick.

The volatilization is the transfer of HNS from the dissolved phase to the evaporated phase and is also important to assess the amount in the atmosphere. The volatilization rate is estimated from (Lyman et al., 1990):

$$N_{(i)} = K_{L(i)} \left(C_{(i)} - \frac{P_{(i)}}{H_{(i)}} \right)$$

The flux $N_{(i)}$ (g/cm²s) of the chemical i from the dissolved phase to the evaporated one depends on the difference between the concentration of the chemical in the water $C_{(i)}$ (g/cm³) and the vapor pressure of the compound already in the atmosphere $P_{(i)}$ (atm) divided by the henry law constant $H_{(i)}$ (atm cm³/g). A kinetic parameter $K_{L(i)}$ (cm/s) depending on other parameters such as the windspeed and the physico-chemical properties of the HNS is also needed. The result needs to be multiplied by the area to get the rate on the entire slick.

In open sea with enough wind, the partial pressure of the chemical is very low and the $P_{(i)}$ can be neglected ($P_{(i)} \cong 0$). This assumption is invalid in closed environments.

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Evaporation, dissolution, and volatilization happen at the same time, given an interesting competing kinetic which will be compared in a following section. This kinetic is heavily impacted by the parameters $\overline{j_{c(i)}}$, $K_{L(i)}$ and K, defining each the mass flux rates of the different processes.

3.2. MOHID

MOHID chemical spill model (Fernandes, 2014; Soares et al., 2020) is integrated in the Lagrangian component of MOHID model (a public-domain / open-source water modelling system – www.mohid.com). MOHID is a three-dimensional water modelling system, developed by MARETEC (Marine and Environmental Technology Research Center) at Instituto Superior Técnico (IST) which belongs to University of Lisbon. This modelling system allows the adoption of an integrated modelling philosophy, not only of processes (physical and biogeochemical), but also of different scales (allowing the use of nested models) and systems (estuaries, watersheds, open-sea, rivers), due to the adoption of an object-oriented programming philosophy. MOHID has been applied to different study cases, such as coastal and estuarine areas, as well as oceanic processes and reservoirs, and it has showed its ability to simulate complex features of the flows.

MOHID Lagrangian transport module uses the concept of tracer, assuming that the spilled contaminant can be represented as an amount of several different small tracers / spillets, and tracked as they move in three-dimensional space over time. This software is used in several different studies, as oil and HNS spills, floating containers, dispersion of plumes in submarine outfalls, sediments transport, etc. MOHID Lagrangian module can be run simultaneously with the hydrodynamic model (currents, water temperature, salinity, etc.), or in "offline" mode. In both modes, this model is able to digest currents, water properties, wave parameters and atmosphere properties from different model providers. Additionally, MOHID Lagrangian module allows backtracking / modelling, as well as a multi-solution approach (Fernandes et al., 2013) (generating computational grid on-the-fly and using the available information from the multiple metocean forecasting solutions available).

The spilled mass is tracked through phase changes and transport, with all reaction products assumed to move together – chemical reactions are not specifically addressed in the model. The loss of chemical by reaction to some other form no longer of concern is included in degradation, which is estimated assuming a constant rate of "decay" specific to the environment where the mass exists (i.e., atmosphere, water columns, or sediment). The model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column, in the sediments and at the bottom. The model tracks separately surface floating chemical, entrained droplets or suspended particles of pure chemical, chemical adsorbed to suspended particulates,

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and dissolved chemical. The phase changes are computed independently for each particle every time step, and the probabilities of one particle change from one phase to another (e.g., entrained to dissolved) is (pseudo-)randomly obtained, based on the algorithms that quantify the mass balances in the different processes. Therefore, a correct modelling using this kind of approach obviously requires a great number of particles in the simulation, in order to properly reproduce phase changes when slow processes / small mass transfers are involved.

Chemical mass is transported in three-dimensional space and time. The horizontal movement is controlled by currents, wave-induced velocity (Stokes Drift), wind-drift velocity in the surface layer (for floating substances), spreading, and horizontal turbulence. The vertical movement is estimated by vertical advection from currents, rising velocity, sinking velocity, and turbulent dispersion. More details about the model can be found in (Fernandes, 2014) and (Soares et al., 2020).

3.3.   **OpenDrift**

OpenDrift is a generic framework for trajectory simulations (Dagestad et al., 2018), with dedicated modules for specific applications such as oil spills, search and rescue etc. A new, very basic module for HNS has been developed within the MANIFESTS project, starting from the existing and well validated oil drift module OpenOil (Röhrs et al., 2018), and adding weathering processes for chemicals as described in Legrand et al. (2017). As such, the OpenDrift HNS module is expected to provide fairly similar results to the OSERIT model, however as learned within this project, the actual implementation of given algorithms and processes does have a significant impact, e.g., the order at which weathering, and entrainment processes are executed.

Particles can be in one of several states: liquid (slick or droplets), emulsified, evaporated and dissolved, with transfer based on parameterizations as described for the OSERIT model above.

Particles in air are advected with the wind velocity, with an optional horizontal diffusivity as may be specified by the user.

Particles at the ocean surface (slick) are advected with surface current, Stokes drift, as well as 2% of the surface wind, as found empirically in many experiments (e.g., Brekke et al. (2021)). If surface Stokes drift is not available from a wave model, the wind drift factor can be increased from 2% to about 3.5%, providing very similar results in most cases. In addition to this horizontal advection, a constant horizontal diffusivity can be specified, providing spreading through random walk processes.

The wind drift factor is only applied to particles at the surface, and the Stokes drift is decreasing with depth as described in Breivik et al. (2016).

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Surface particles/chemicals are entrained at the rate/probability at which breaking waves occur at the surface, proportional to wind speed over wave period, but with no entrainment for winds below 5 m/s. After entrainment, droplets are mixed vertically with a diffusivity obtained from ocean model or parameterized from wind if not available. This is performed in an inner loop also taking buoyancy into account, with schemas described in Nordam et al. (2019).

3.4. CHEMMAP

CHEMMAP is a HNS drift, behavior and fate model solution developed and marketed by RPS : https://www.rpsgroup.com/services/oceans-and-coastal/modelling/products/chemmap/. Widely considered as the reference model on the market, CHEMMAP is a chemical discharge modelling and response system that predicts the transport, fate, and biological impacts of a wide variety of chemical substances in the marine environment and atmosphere. The model is applied worldwide for emergency response, risk assessment, contingency planning- including worst-case scenario, natural resource damage assessment, drills and education as well as cost-benefit analysis.

CHEMMAP computes 3D chemical transport and fate in water and air and integrates algorithms for dissolution, evaporation, volatilization, sediment interaction, adsorption and shore-line interactions. Operated by Cedre, CHEMMAP is the only commercial solution used in this validation exercise.

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4. Validation of evaporation, dissolution, and volatilization processes with laboratory experiments

4.1. Experimental setup

To obtain data for validating the model's evaporation, dissolution and volatilization parametrization processes, CEDRE conducted small-scale experiments in a nearly closed fume hood, with the extractor fan turned off. A small container was placed on a scale, containing either salt water or no water, and HNS was then spilled either on the water surface or at the container's bottom. The mass on the scale has been monitored throughout the experiment, as it decreased due to HNS evaporation. While these experiments yielded useful data, they were limited as they did not record the HNS concentration in the fume hood air or the wind speed within it.

4.2. OSERIT validation for the evaporation parametrization

With the setup described in the previous section, several experiments with multiple volatile chemicals have been performed by CEDRE. The compounds chosen are cyclohexane (evaporator), vinyl acetate (evaporator-dissolver) and acrylonitrile (dissolver-evaporator).

Table 1: Properties of the chemical used, from the HNS database. The Henry's constant is obtained by the ratio of the saturation vapor pressure and the solubility

Name	Saturation vapor pressure [Pa] at 20°C	Solubility [mol/m^3] at 20°C	Henry's constant [(Pa m^3)/mol] at 20°C	Density [kg/m^3]
Cyclohexane	10265	0.653	15707	778.1
Vinyl acetate	12000	232.3	51.6	930
Acrylonitrile	11500	1488.8	7.7	810

A windspeed was needed as model input, a value of 0.1 m/s has been chosen. This is an arbitrary value because there is no data available on the true windspeed during this experiment and the slowness of the air movement challenge the assumption that there are no residual vapor of the chemical decreasing the volatilization rate (because there is not a good evacuation of the vapor). In the simulation, the partial pressure of any compound is nevertheless at 0 Pa unless specified otherwise. The surface of the container is not the same in all the experiments, thus the rate of the processes should not be compared between multiple figures.

Table 2: Conditions of each experiment with free chemical, the temperature is the temperature in the hood at the start of the experiment

Figure	HNS	HNS volume [ml]	Area [cm^2]	Temperature [°C]
Figure 1	Cyclohexane	10.24	75.43	21.65
Figure 2	Vinyl acetate	10.072	75.43	19.75
Figure 3	Acrylonitrile	10.247	75.43	21.6
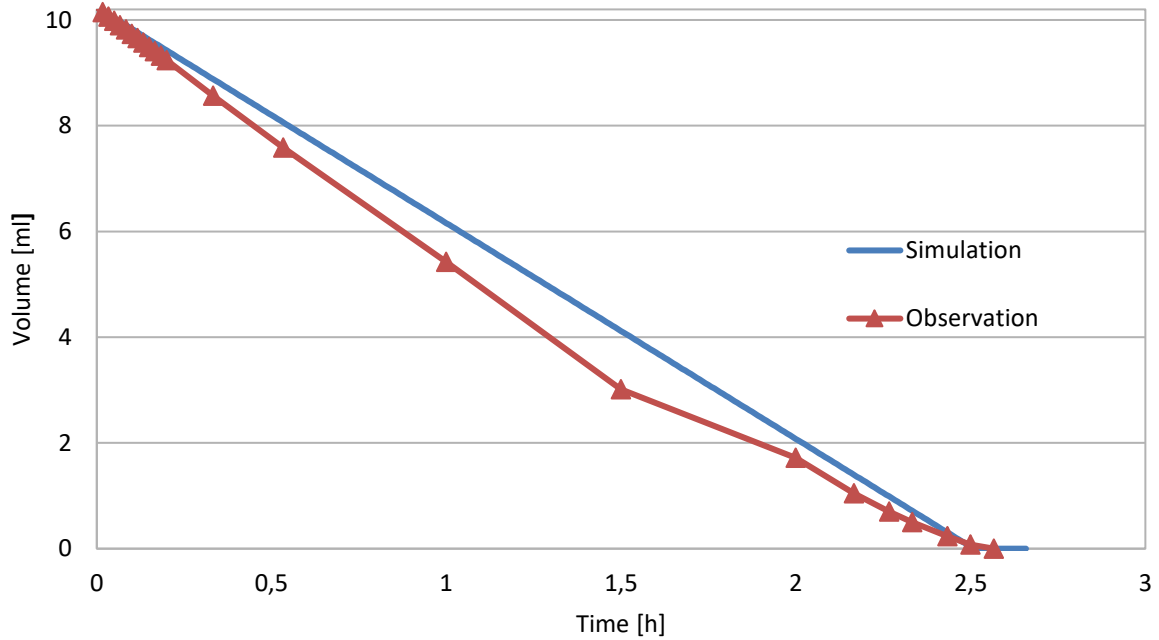
Figure 1: Free cyclohexane (evaporator) volume remaining in the container trough time. Each triangle is an observation, and the blue line is the simulation from the model

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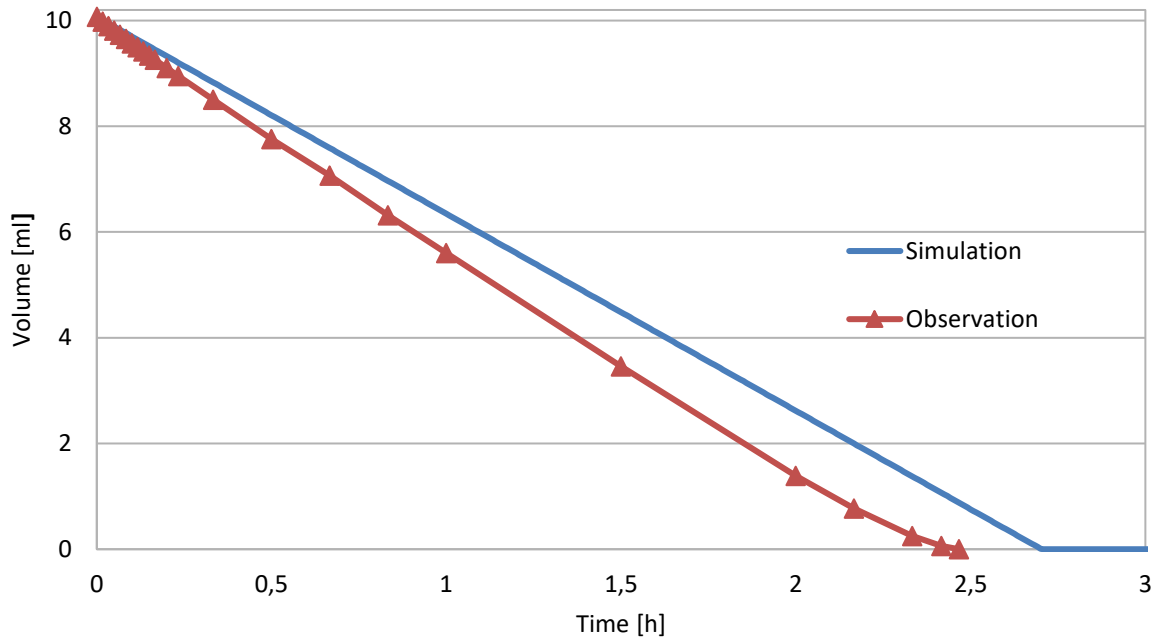
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Figure 2: Free vinyl acetate (evaporator-dissolver) volume remaining in the container trough time. Each triangle is an observation, and the blue line is the simulation from the model
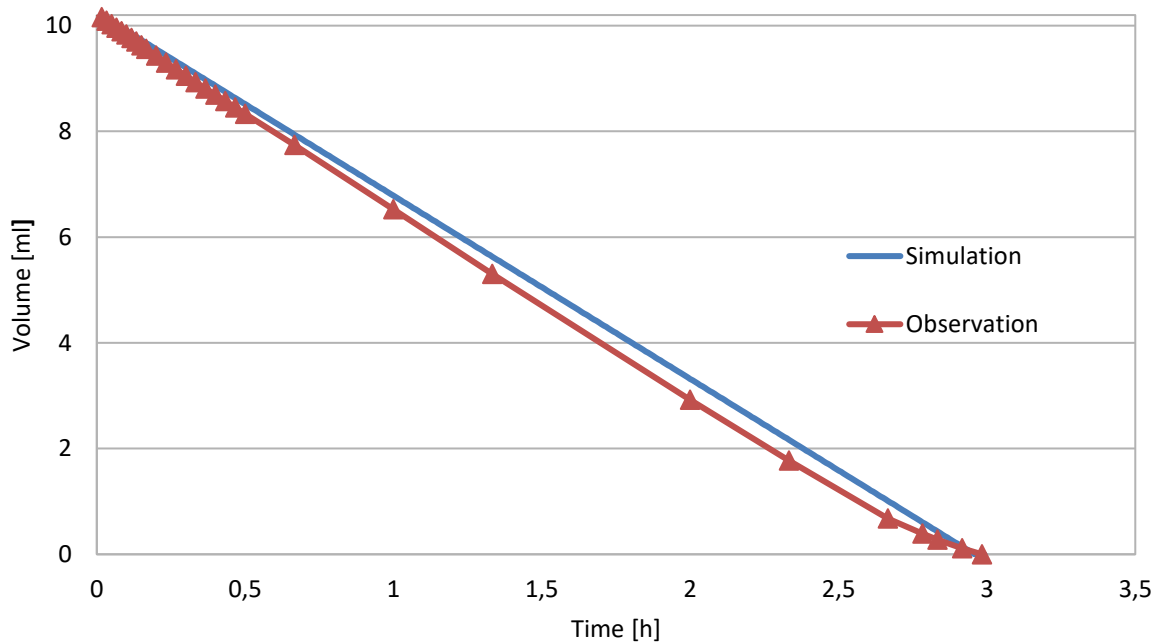

Figure 3: Free acrylonitrile (dissolver-evaporator) volume remaining in the container trough time. Each triangle is an observation, and the blue line is the simulation from the model

In all experiments involving free chemicals (as seen in Figure 1, Figure 2, and Figure 3), only evaporation occurred since no water was present to enable dissolution. Since the evaporation rate was constant, the amount evaporated exhibited a linear progression until all the chemicals had evaporated. The model and experimental data both demonstrated this behaviour, indicating that the parameterization is capable of accurately simulating the evaporation rate.

Table 3: Evaporation rate of free HNS compared to the model simulations, the lasts points are not considered for the rate of the observation

Name	Evaporation rate [kg/ (m^2 s)]		$\frac{\sqrt{(simulation - observation)^2}}{observation}$ %
	Simulation	Observation	
Cyclohexane	1.170E-04	1.389E-04	15.8
Vinyl acetate	1.276E-04	1.498E-04	14.8
Acrylonitrile	1.033E-04	1.091E-04	5.5

The error between the simulation and the observations can be seen in the Table 3, ranging between 5.5 and 15.8%. This confirms what is said just above, the model can simulate the evaporation rate.

4.3. Validation of the competition between dissolution, evaporation, and volatilization in OSERIT

A second set of experiment has been performed with the same chemicals put at the surface of salt water. The goal was to highlight the competition between the evaporation, dissolution and volatilization processes, and the ability of the model to predict it.

Table 4: Conditions of each experiment with chemical put on salt water, the temperature is the temperature in the hood at the start of the experiment

Figure	HNS	Salt-water volume [ml]	HNS volume [ml]	Area [cm^2]	Temperature [°C]
Figure 4	Cyclohexane	196.63	10.2	59.44	21.2
Figure 5	Vinyl acetate	491.69	9.9	98.52	20.75
Figure 6	Acrylonitrile	194.3	10.2	59.44	21.2

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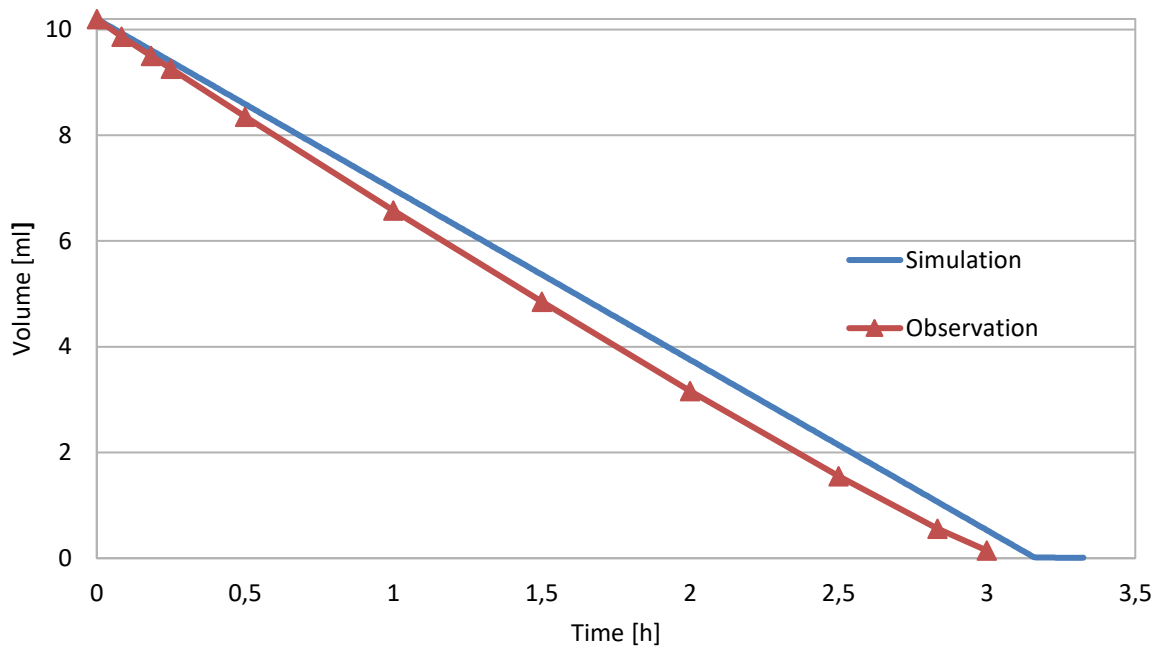Co-funded by the European Union Civil Protection

Figure 4: Cyclohexane (evaporator) volume remaining in the container trough time at the surface of salt water. Each triangle is an observation, and the blue line is the simulation from the model

The cyclohexane is an evaporator and not a dissolver. In Figure 4, when poured on the surface of salt water, its evaporation rate is like that when it is free. The model's behaviour is consistent with the observed dynamic, indicating that the model accurately predicts this behaviour.
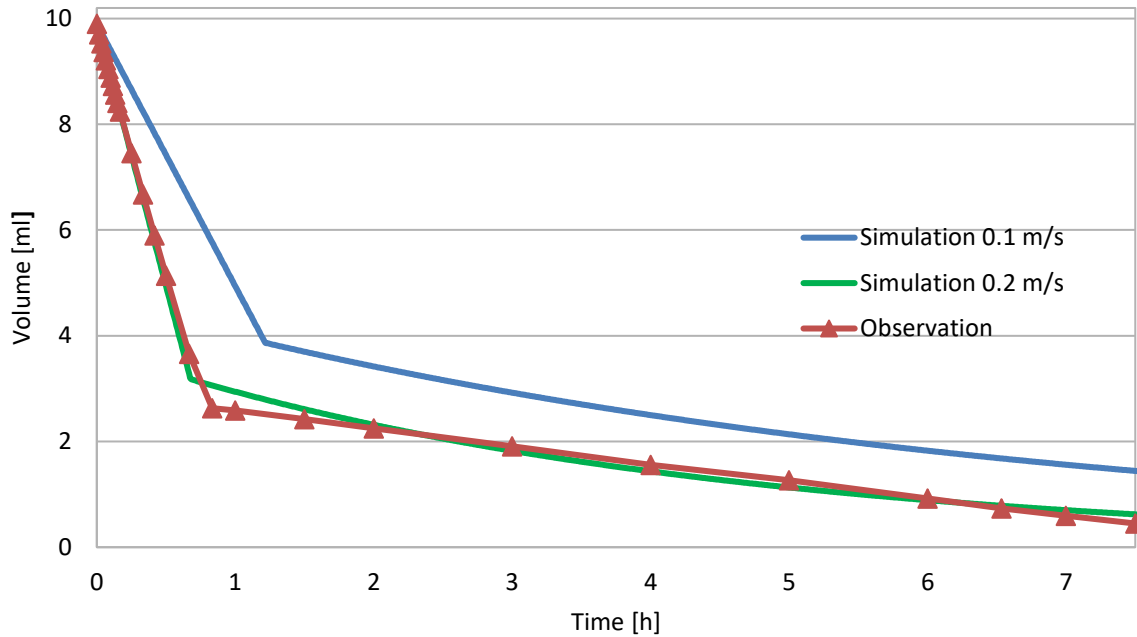
Figure 5: Vinyl acetate (evaporator-dissolver) volume remaining in the container trough time at the surface of salt water. Each triangle is an observation, and the blue line is the simulation from the model with a wind speed of 0.1 m/s, in green it is the same simulation but with a wind speed of 0.2 m/s.

The behaviour of vinyl acetate at the surface of salt water (as seen in Figure 5) is distinct and demonstrates two stages. Initially, the chemical evaporates and dissolves, with the model underestimating both the evaporation rate and amount. Once all the slick has dissolved and evaporated, the chemical only volatilizes (at a slower rate than the evaporation), like what the model predicts (albeit slightly faster). The model accurately represents this inflection point that separates these two behaviours, indicating that competition between evaporation and dissolution is a key factor in predicting the HNS rate that goes to the atmosphere. A second simulation was conducted with a windspeed of 0.2 m/s instead of 0.1 m/s (these are arbitrary values because there was no windspeed recorded), and the simulation closely followed the model.

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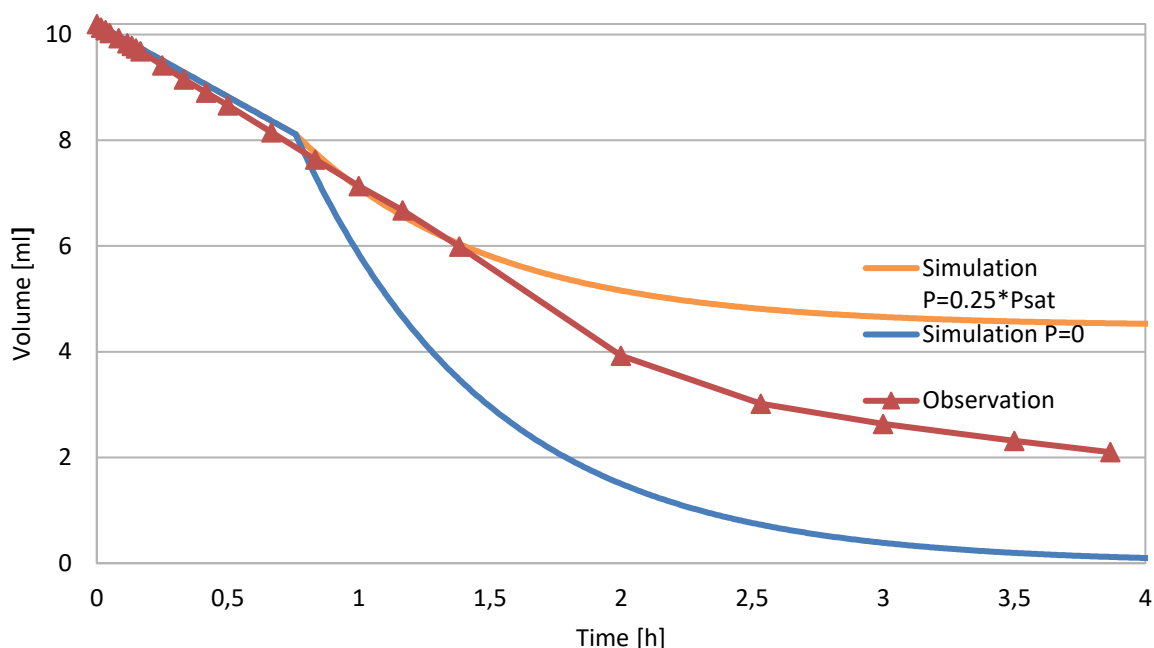Co-funded by the European Union Civil
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Figure 6: Acrylonitrile (dissolver-evaporator) volume remaining in the container trough time at the surface of salt water. Each triangle is an observation, and the blue line is the simulation from the model, with no acrylonitrile in the air for the volatilization. The orange line is a simulation with a fixed amount of 25% of the saturation vapor pressure of acrylonitrile

For the acrylonitrile in the water (Figure 6), the evaporation is similar between the model and the observation. When all the compound is dissolved and evaporated, the volatilization process begins. It goes a lot faster in the model compared to the observation. If a constraint of 25% of partial pressure (compared to the saturation vapor pressure) is artificially added in the model, the rate changes dramatically and the simulation underestimates the volatilization process. This suggest that some HNS concentration could have started to build up in the experiment during the evaporation dissolution phase, causing a slowing of the volatilization. The inflexion point is less visible for this chemical, but there are still two different stages, first a fast linear one (evaporation and dissolution) and then a slower one (volatilization).

Table 5: Evaporation rate, computed on the firsts points, before any inflexion

Name	Evaporation rate [kg/ (m^2 s)]		$\frac{\sqrt{(simulation - observation)^2}}{observation}$ %
	Simulation	Observation	
Cyclohexane	1.172E-04	1.277E-04	8.2
Vinyl acetate	1.301E-04	2.504E-04	48.05
Acrylonitrile	1.041E-04	1.156E-04	9.21

The model predicts the evaporation rate of the cyclohexane and the vinyl acetate with a similar accuracy with or without water. This suggest that during the first phase of the competition between dissolution and evaporation the evaporation rate is very similar to the evaporation without water

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(which is an assumption of the model). For the vinyl acetate, there is a huge underestimation, but it is the value of the simulation at 0.1m/s of windspeed which is shown here. As visible in the Figure 5, the simulation with a windspeed of 0.2 m/s is very close to the evaporation rate of the observations.

4.4. Conclusion

OSERIT can simulate the processes impacting the slick such as evaporation, dissolution and volatilization, the error of the evaporation rate is between 5% and 16% for all the chemicals and both the observation and the model have a linear slope when there is no water.

When water is added, the evaporator-dissolver and dissolver-evaporator start to behave in a more complex manner. First, the chemical evaporates and dissolve, and the scale measure a similar evaporation rate as the chemicals free (for cyclohexane and acrylonitrile). Then, all the chemical is either evaporated or dissolved and a second phase start; the remaining dissolved chemical begin to volatilize from the water to the atmosphere. The rate of this process is slower than the evaporation of the free chemical. This suggest that an accurate modelling of the competition between the evaporation, dissolution and volatilization is necessary. In this set of experiment, the concentration of the chemical in air trough time have not been measured, but this can have a huge impact such as demonstrated in the Figure 6. Because the fume hood was closed and turned off, it is possible than an accumulation of chemical has slowed the volatilization.

These results suggest the evaporation parametrization from (Lyman et al., 1990) can describe the volatilization and the parametrization of (Brighton, 1985) can estimate the evaporation rate. However, they are sensitive to the windspeed and the vapor accumulation, and a new set of experiment has been performed by CEDRE using a wind tunnel with the aims to control these factors. This is described in the next section.

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5. Validation of evaporation with the wind tunnel

5.1. Description of the experimental setup

With the help of ARMINES, CEDRE has built a device allowing them to monitor the evaporation rate and control the wind speed at the same time. It is composed of a centrifugal fan positioned on one side of a tunnel made of wood, with some structure to reduce the turbulence of the air flow. Near the other side, a petri dish is positioned on a scale, with thermocouples and an anemometer to have a precise windspeed estimation. All of this is illustrated in the Figure 7.
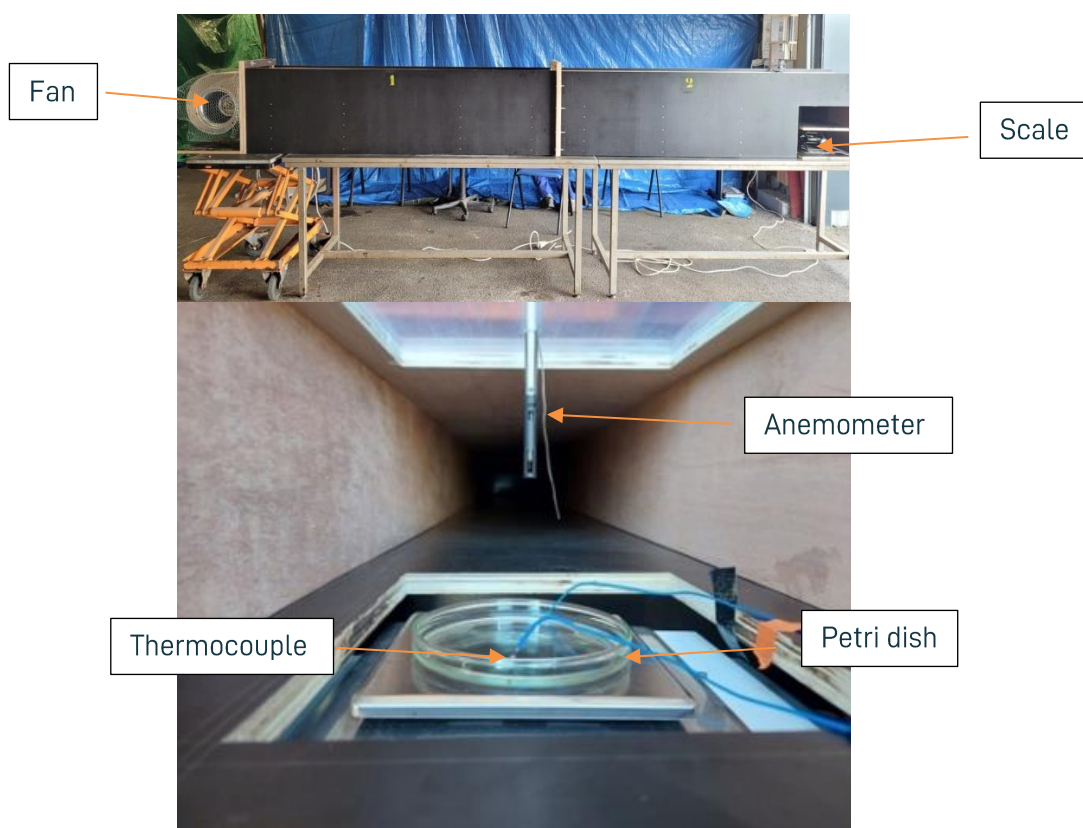
Figure 7: Pictures of the wind tunnels (copyright CEDRE)

To begin the experiment, approximately 10 ml of the selected chemical – cyclohexane, acrylonitrile, or vinyl acetate – is poured into a petri dish. As the liquid evaporates, the quantity decreases, and its weight is closely monitored. Simultaneously, the temperature of both the air and the liquid, as well as the wind speed, are measured and recorded to generate several time-series datasets.

The same chemicals used in the initial laboratory experiments are utilized in this study.

5.2.   Comparison with the model

The observation and recording of experiment parameters allow for a thorough comparison of the collected data with the OSERIT outputs, while ensuring that its inputs closely match the experimental conditions. Cyclohexane (Figure 10 and Figure 11) and acrylonitrile (Figure 8 and Figure 9) have both been tested at various wind speeds, and the experiments reveal that as it increases, so does the rate of evaporation. However, the effect diminishes as the wind speed increases further. A qualitative analysis of the initial results indicates that the model accurately predicts this evolution for both chemicals.
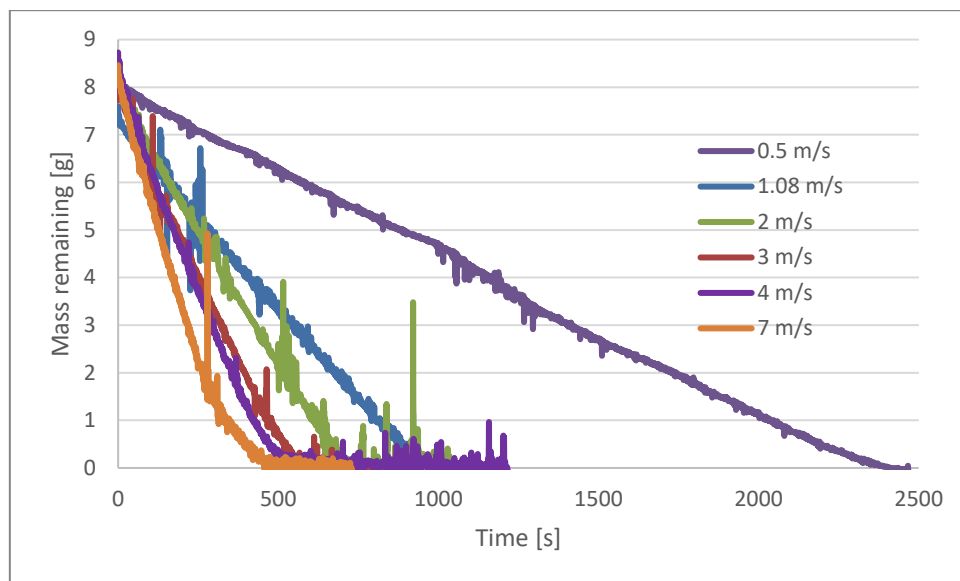

Figure 8: Mass of acrylonitrile remaining in the petri dish in the wind tunnel as a function of time for several windspeed
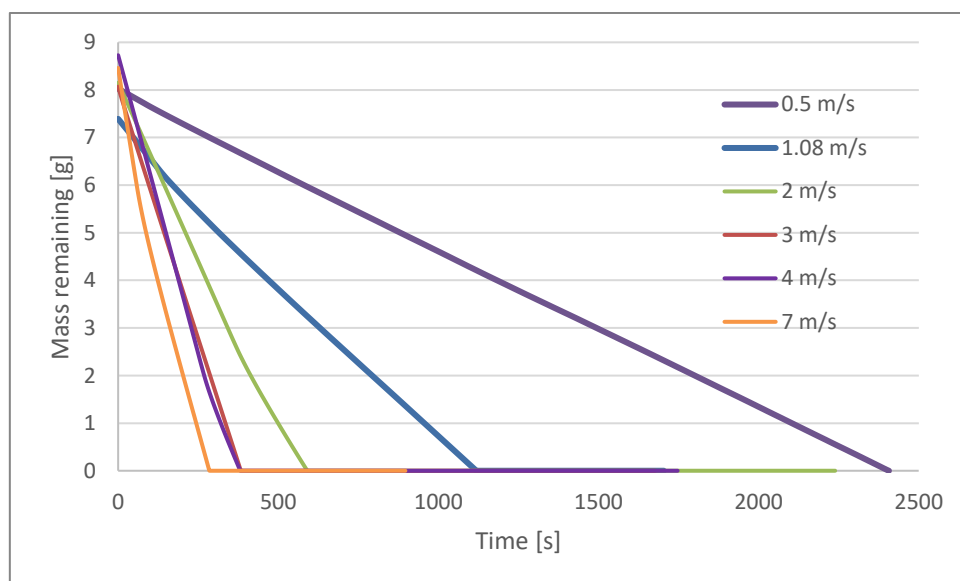

Figure 9: Simulation of the mass of acrylonitrile remaining a function of time for several windspeed
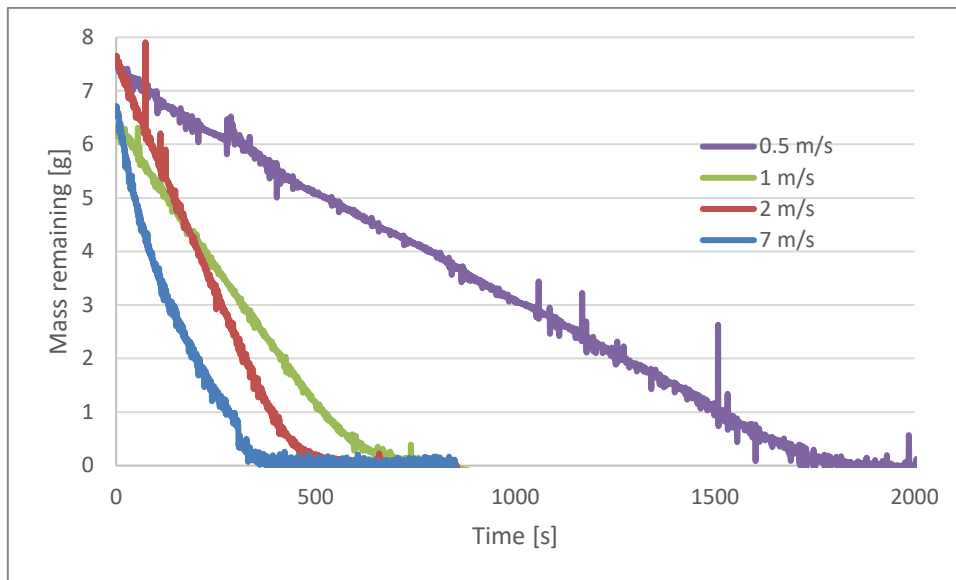
Figure 10: Mass of cyclohexane remaining in the petri dish in the wind tunnel as a function of time for several windspeed
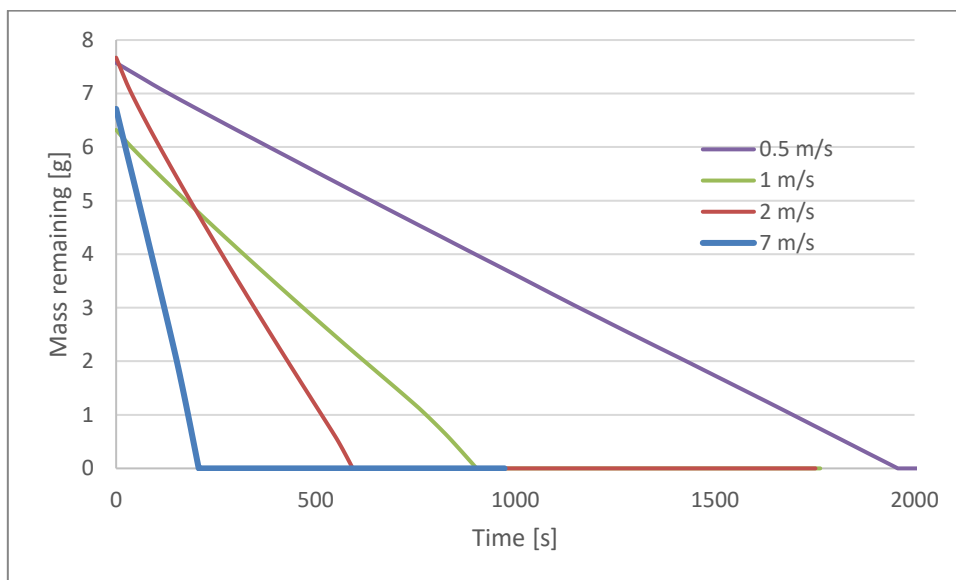

Figure 11: Simulation of the mass of cyclohexane remaining a function of time for several windspeed

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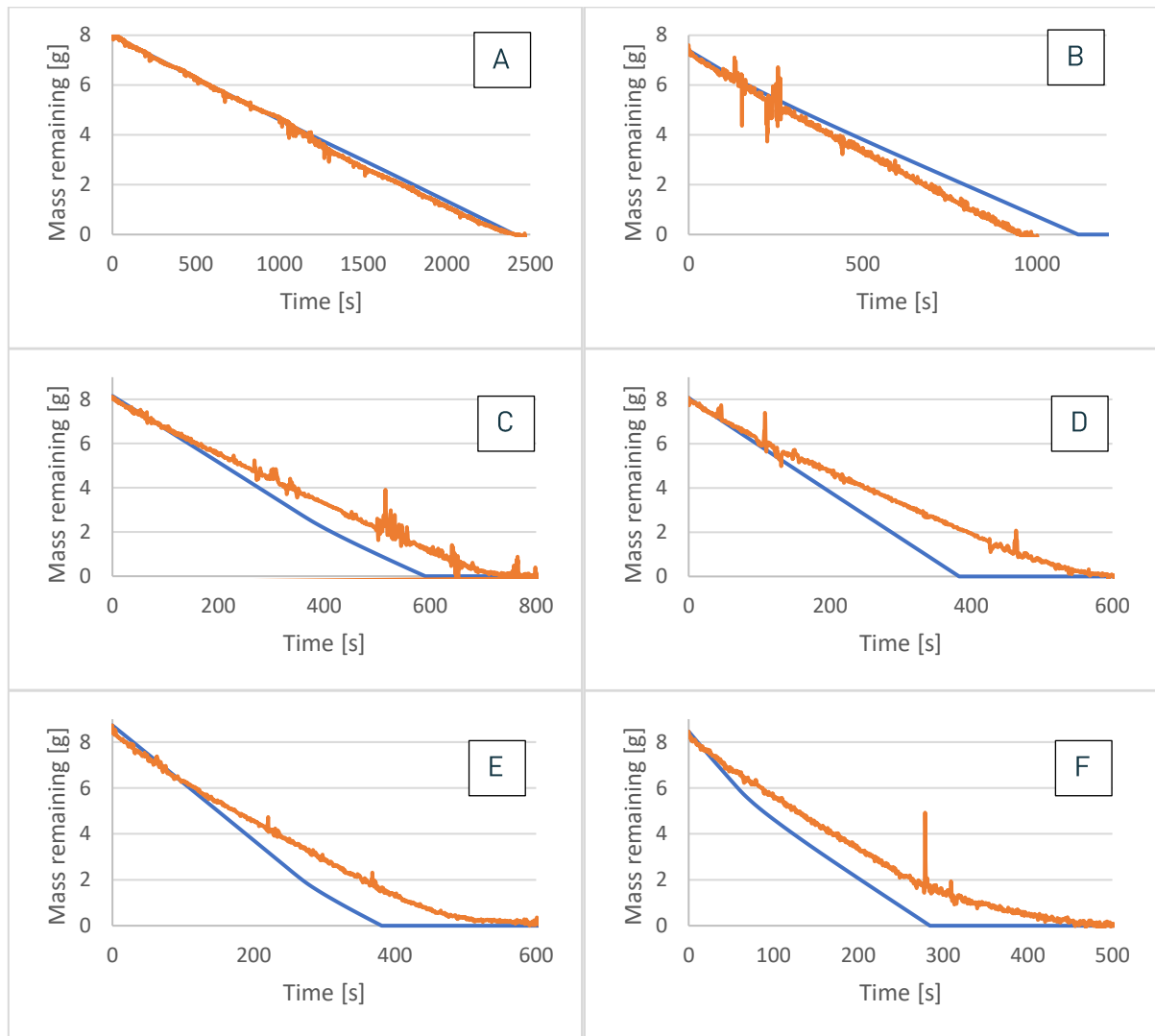Protection

Figure 12: Comparison of the evaporation rate between simulation (blue line) and observation (orange line) for acrylonitrile at several windspeed (A:0.5 m/s, B:1.08 m/s, C:2m/s, D:3m/s, E:4m/s, F:7m/s)

When looking more specifically at the evaporation rate for acrylonitrile at each wind speed (Figure 12), the accuracy of the model's prediction decreases as the wind speed increases. In most case, there is also a decrease in the evaporation rate when almost all the chemical is evaporated, this does not appear in the model. This could be due to a diminution of the slick area when almost all the HNS has evaporated, which not accounted for in the model. This also appears for all the other chemicals

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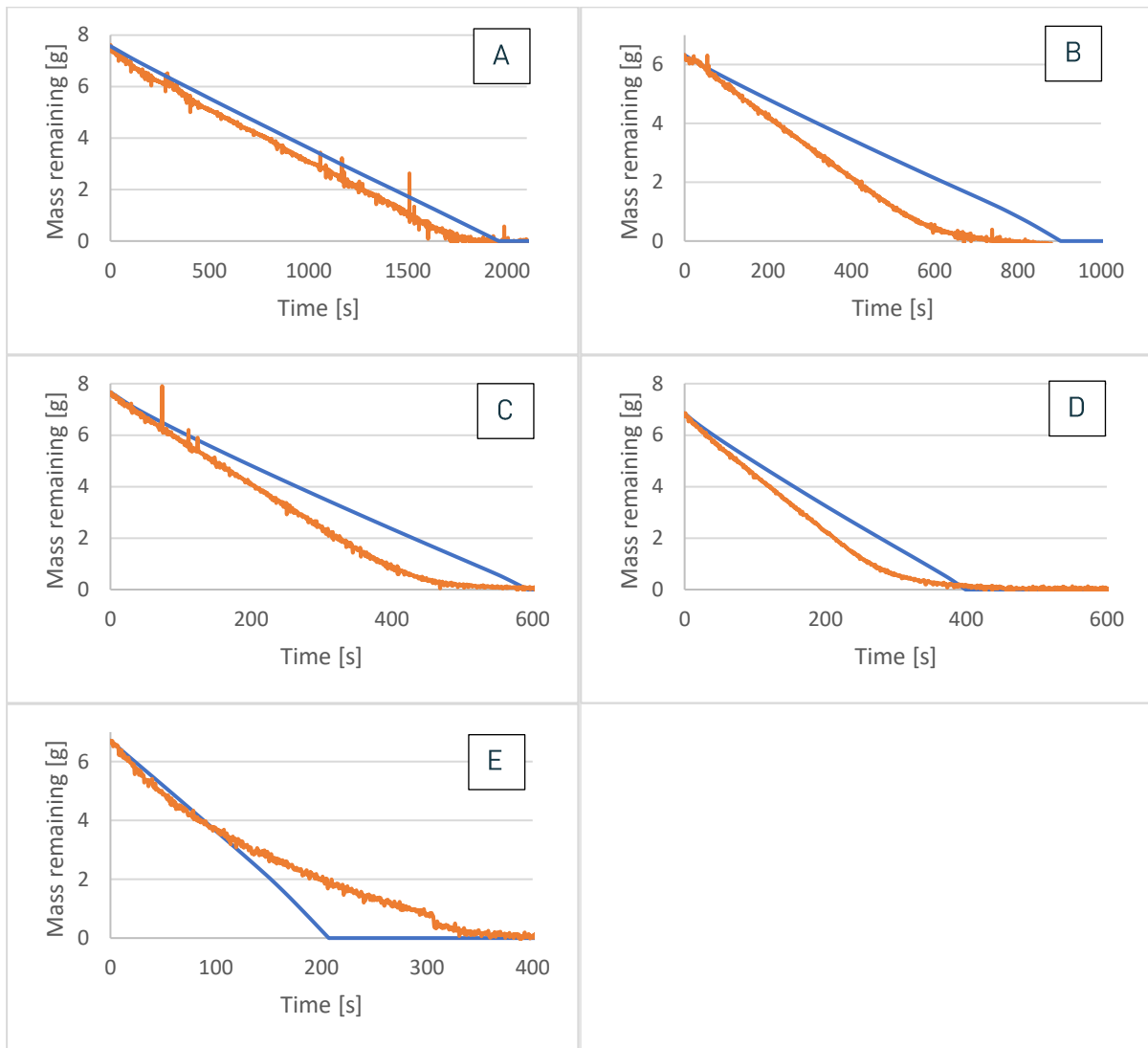
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Figure 13: Comparison of the evaporation rate between simulation (blue line) and observation (orange line) for cyclohexane at several windspeed (A:0.5 m/s, B:1.08 m/s, C:2m/s, D:3m/s, E:7m/s)

A similar observation can be made for cyclohexane (Figure 13), although the impact of wind speed on the difference between the model and observations is comparatively lower.
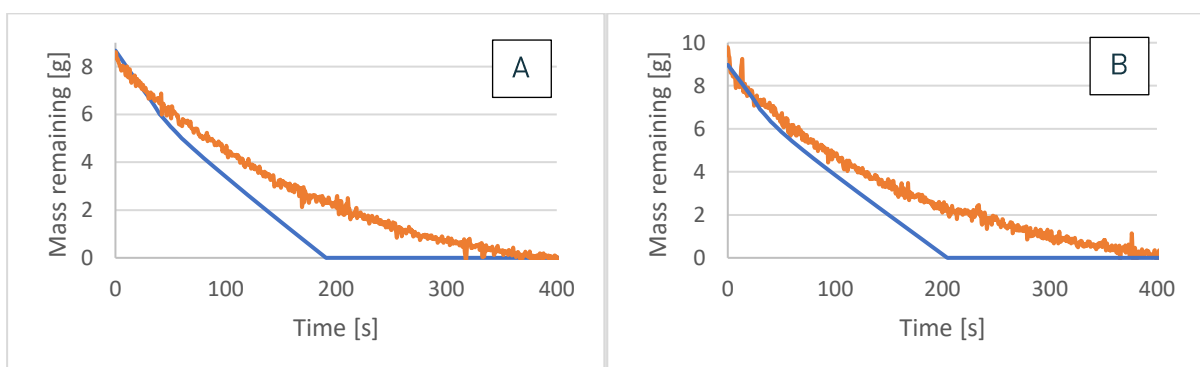
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For the vinyl acetate, only two repetitions of one experiment are compared here. Like cyclohexane and acrylonitrile, there is a decrease in the rate of evaporation when most of the chemical has evaporated. Overall, the two repetitions yield highly similar results in both the observations and the model outputs (Figure 14).

5.3. Conclusion

The OSERIT model is capable of accurately predicting the evaporation rates of acrylonitrile, cyclohexane, and vinyl acetate in the wind tunnel, although differences between the model and observations are still present. However, it is likely that these differences fall within the uncertainty of wind speed estimates derived from meteorological forcings in cases of sea interventions.

As the chemical evaporates and the amount remaining in the dish decreases, it no longer covers the entire surface and forms droplets. This may explain the decrease in the evaporation rate at this stage, as the surface area decreases, which is not accounted for in the model.

It is possible that the effect of the petri dish on turbulences increases as the wind speed increases, which could explain the increasing difference between model and observation. Additionally, because the slick is small and evaporates quickly, the true temperature at the surface may be lower than the one measured by the thermocouples. In fact, it was observed during the experiment the appearance of cyclohexane ice at the highest wind speed. To mitigate this issue, a new experiment could be performed with the chemical poured on the surface of saltwater. This would help maintain a more constant temperature for the slick through thermal exchange with the water and allow for further testing of the competition between evaporation, dissolution, and volatilization.

6. Validation against MANIFESTS sea trials

6.1. Description of the sea trials

6.1.1. Introduction

Responding to a spill at sea is always challenging, especially when the products involved are liquids with high vapour pressure (i.e., > 3 kPa) or liquefied gases. The slicks formed will rapidly evaporate and potentially form toxic, flammable, or even explosive gas clouds. It is therefore essential to

characterise the risks issued from the evaporation of such substances in order to adapt the response and guarantee safety of first responders.

To this end, CEPPOL (French Navy) and Cedre have been jointly organising experiments involving real spills of oil and HNS at sea for over 20 years. These trials enable pollution response authorities and first responders to improve their knowledge of both the behaviour of pollutants discharged in the natural conditions and the response means to be deployed to handle any accidental release at sea.

Such sea trials are performed in compliance with international regulations in force, especially the international convention for the prevention of pollution from ships 1973[1]. Indeed article 2 of MARPOL Convention reminds that **"discharge" does not include release of harmful substances for purposes of legitimate scientific research into pollution abatement or control**. Concerning experimental conditions, a specific area, far from the shoreline is chosen by the French Navy to prevent any marine activity or population from being exposed to a toxic or flammable gas cloud. Cedre also selects chemicals excluding those that could present significate damage for the environment (e.g., classified as marine pollutants as per IMDG code). In these legal and experimental frameworks, an operation order is established and granted by the French Navy to lead sea trials.

In the case of HNS, recent sea trials, enabled to successfully assess the detection capacity of various on board and airborne infrared sensors for the remote detection of volatile chemical slicks and the associated gas cloud.

6.1.2. Objective of the Sea trials

Last observations made during the MANIFESTS sea trials have been achieved thanks to sea trials spaced out during the last two years. In 2021 the IPOMAC sea trial organised with the support of French Navy allowed to perform sea trial involving national resources, with main objectives to validate the discharge system, test sensors and offer proposer coordination and safe conditions for the aerial manoeuvre. In 2022, the framework of the MANIFESTS project offered the opportunity to scale up the sea trial at international level with objectives to discharge new chemicals, test new sensors and collect observation data in the field to validate models.

The main objective of the MANIFESTS sea trial was to allow the testing and the calibration of sensors currently used for maritime survey and of sensors under development that may offer an added value for the detection of gaseous or volatile HNS. Thanks to the experience of the IPOMAC sea trial, different surveillance aircrafts with sensors used in routine (French customs and Belgian coastguard – RBINS) were involved. Due to the relevant results obtained by the multispectral

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[1] https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/ConferencesMeetings/Documents/MARPOL%201973%20-%20Final%20Act%20and%20Convention.pdf

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camera during the IPOMAC sea trial, it has been deemed promising to implement such camera both on board vessel and airborne in a plane. This way, this would ensure a combined detection of both the slick and the gas cloud. To this end, an open-sea trial under the responsibility of the French Navy (Maritime Prefecture of Atlantic, Brest) and in conjunction with the CEPPOL and CEDRE was carried out. This trial consisted of the release of 8 HNS (MARPOL Annex II) that were selected according to the results collected through the desktop study (task 3.1) performed in the MANIFESTS project, ii) their theoretical behaviour based on the SEBC, iii) their volumes transported at sea and iv) their hazards. Second objective of the MANIFESTS sea trial was to validate forecast drifting models thanks to the discharge of a persistent floater product.

6.1.3. Sea trial location

The MANIFESTS Sea trial was authorised by the French Navy that granted an operation order to perform experimentations. The discharge location was in the Atlantic Ocean, off the island of Sein from the 30th of May to the 1st of June 2022. The discharge of chemicals was performed in an area of less than 3 nautical miles around the geographical point 47°20'30''N,005°05W. Weather conditions during the trial were particularly calm: clear skies, light breezes and flat seas (Less than Beaufort 2 during the first 2 days).

6.1.4. Selection of chemicals

In collaboration with CEPPOL (French Navy), some chemicals of interest were identified (Table 6), taking into account their SEBC behaviour, their intrinsic hazard(s) and risks in case of human approach after an accidental release and their frequency of transport in bulk (ECHA).Chemicals with the short-term behaviour F (floating) and E (evaporating), based on behaviours of the SEBC classification were preferred. Acetone was selected to calibrate ONERA's SIMAGAZ sensor (multispectral detection).

Table 6: names of chemicals for the MANIFESTS sea trial, type of conditioning, volume discharged and CAS number

Name of chemical (SEBC)	Type of conditioning	Volume (m^2)	CAS number
Butyl acetate	IBC RSX electrostatic	2	123-86-4
Acetone	IBC RSX electrostatic	3	67-64-1
N-propyl acetate	IBC RSX electrostatic	2	09-60-4
Isopropyl acetate	IBC STAINLESS STEEL solvent	2	108-21-4
Methyl Ter Butyl Ether (MTBE)	IBC STAINLESS STEEL solvent	2	1634-04-4
Toluene	IBC RSX electrostatic	1	108-88-3
Xylenes	IBC RSX electrostatic	2	1330-20-7 90989-38-1

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Soybean oil	IBC RSX electrostatic	3	67701-30-8

The soybean oil was kindly offered by the BUNGE Company in order to improve the response at sea in case of spillage of vegetable oil. Acetone and toluene required a declaration of final destination, in accordance with the European regulations in force.

6.2.   Validation of the drift

During the sea trials, several drifters were released into the sea and their trajectory was monitored for 14 days. The location data from the drifters is highly valuable for validating models, as the drift of the drifters can be simulated using the models. Among the drifters, one, whose trajectory closely resembled the others, was chosen and compared against the simulations of four models (OSERIT, MOHID, OpenDrift and CHEMMAP). The models used different input forcing, which can also explain some of the variability obtained in the model results (Table 7).

Table 7: Forcings providers for the different models

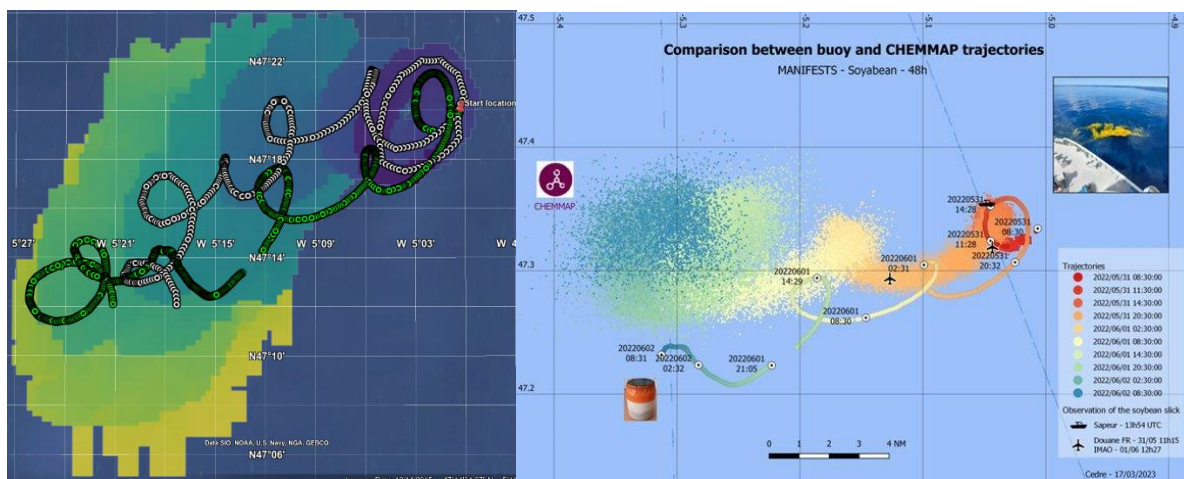| Model name	Hydrodynamic forcing	Wind forcing
OSERIT	CMEMS NWS	ECMWF
MOHID	CMEMS NWS	ECMWF
OpenDrift	CMEMS NWS	NCEP
CHEMMAP	CMEMS NWS	AROME

Figure 15: comparison of the drift from a drifter released at sea during the sea trials and simulations of OSERIT (left image, 72h) and CHEMMAP (right image, 48h) of the soybean slick. The drifter trajectory is the green line for the left picture and the coloured line for the right picture. The footprint of the pollution predicted by the models is showed as the coloured

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In the Figure 15, the trajectory of the drifter is compared to the simulation footprint. For CHEMMAP, the drifter remains near the predicted footprint, while in OSERIT, the drifter stays within the bounds of the simulation footprint. In subsequent plots, only the center of mass will be taken into consideration, although this information remains relevant.

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By conducting a new simulation every day, with the buoy's location as the starting point for the simulation, it was possible to compare multiple simulations to the buoy's trajectory. Each simulation lasted for three days and began at approximately midnight. The comparison between the buoy drifter and the model simulations are presented from Figure 16 to Figure 24.

For the first two days (Figure 16) the met-ocean conditions were characterized by a North-North-East light breeze. This explains the steady South-Westwards drift superposed on the tidal signal observed both at sea and the models.

Days 3 to 5 are dominated by the passage of a low pressure system in the area with winds of over 40 km/h and a shift of the wind direction from North to West. The comparison between drifters and trajectories (Figure 16 to Figure 20) suggests the meteorological models forecasted the passage of the low pressure system at least 6 hours in advanced and a few 10th of kilometres too southwards. This explains why the simulated trajectories were systematically in advanced during this period with respect to the observed trajectory. During this period, the spread between modelled trajectories also increased. This is explained by the fact the different models associate different on the waves-induced Stokes drift.

Days 6 to 10 are characterized by moderate but quite variable West winds, explaining the general Eastward drift patterns of Figure 21-Figure 23. Finally, from days 10 to 14, wind increased turned to North explaining the Southward patterns of the drift trajectory Figure 23 - Figure 24.
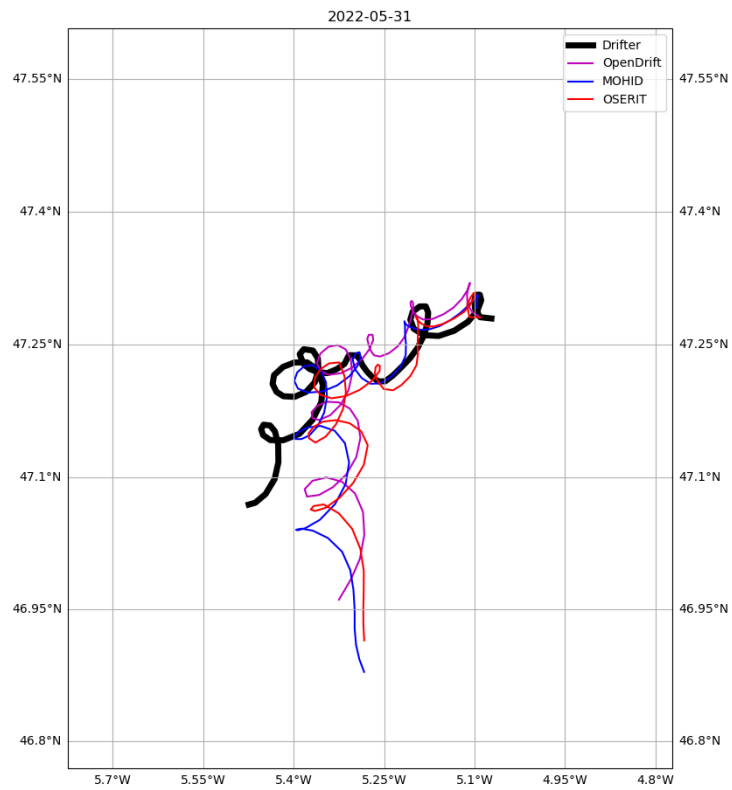
Figure 16 of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-05-31 and finishing on 2022-06-02
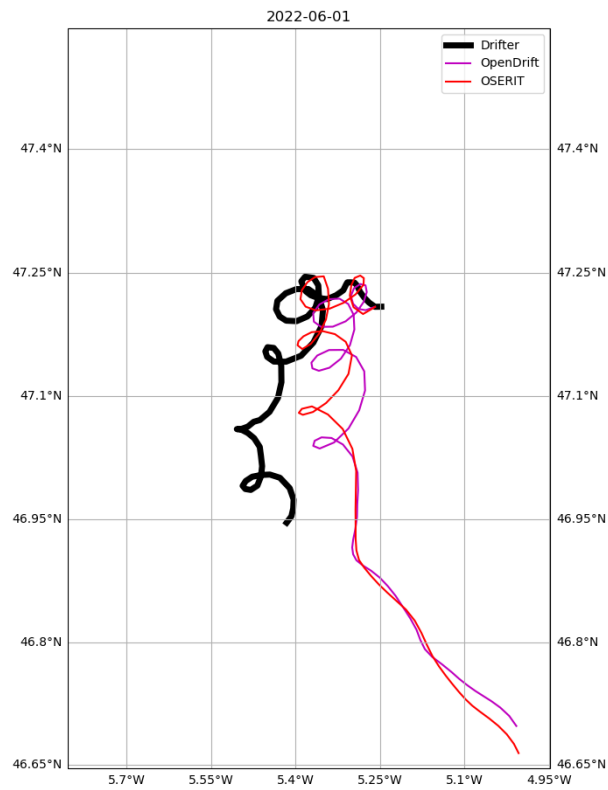
Figure 17: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-01 and finishing on 2022-06-03
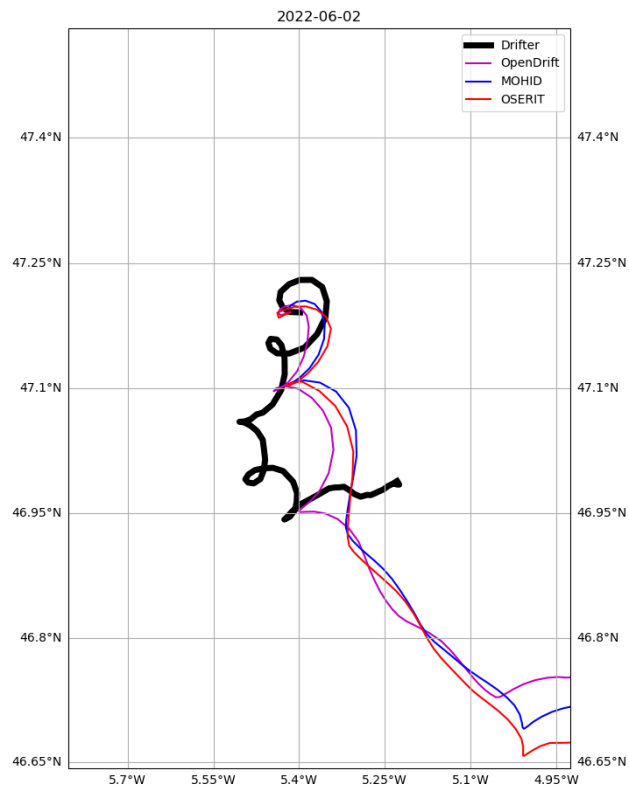
Figure 18: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-02 and finishing on 2022-06-04
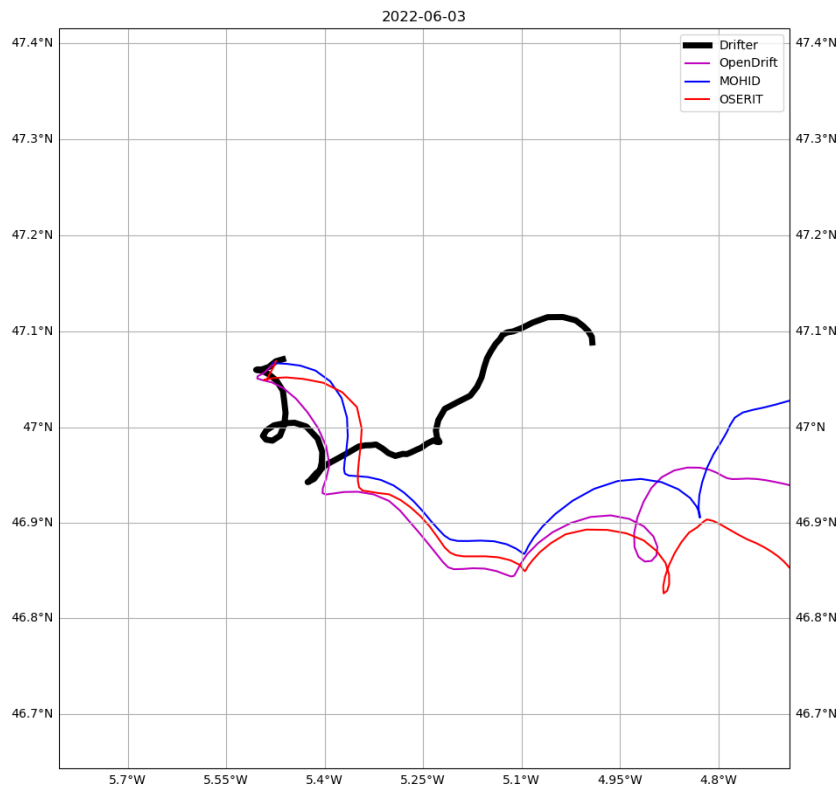
Figure 19: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-03 and finishing on 2022-06-05
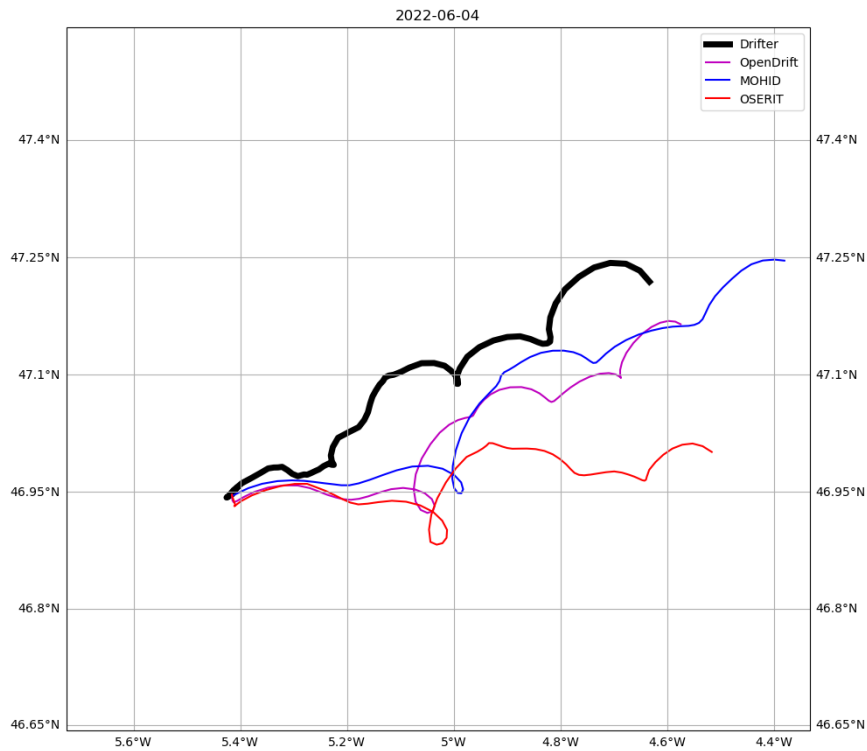
Figure 20: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-04 and finishing on 2022-06-06

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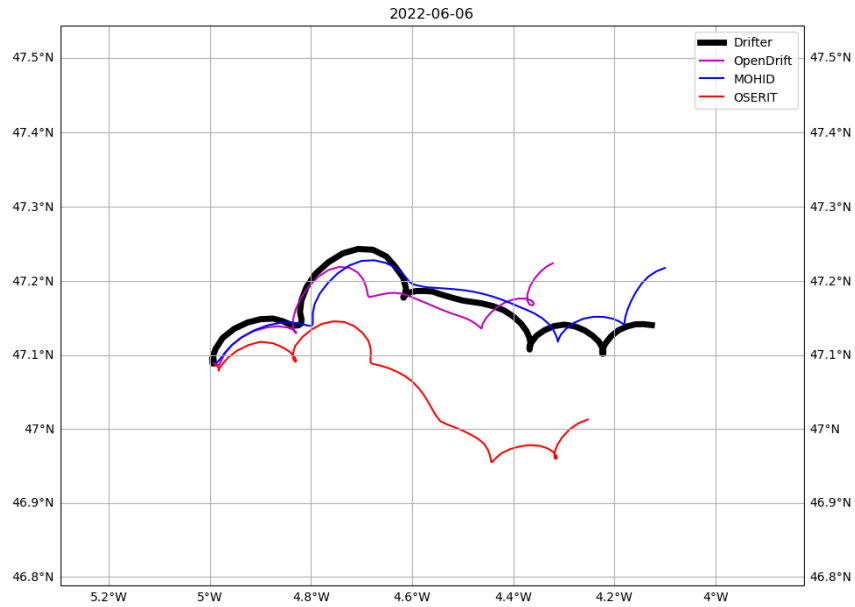Co-funded by the European Union Civil
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Figure 21: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-06 and finishing on 2022-06-08
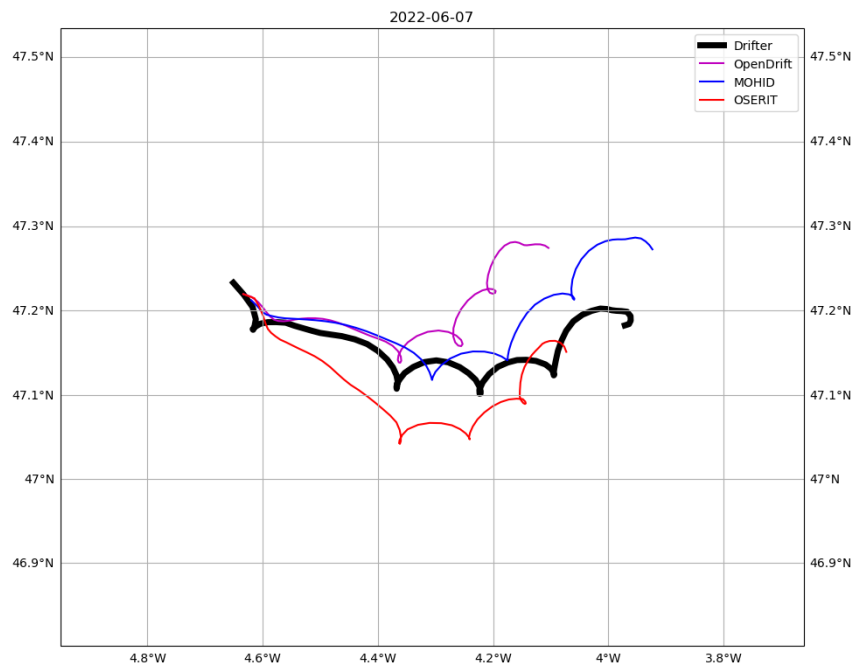
Figure 22: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-07 and finishing on 2022-06-09

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Figure 23: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-08 and finishing on 2022-06-10
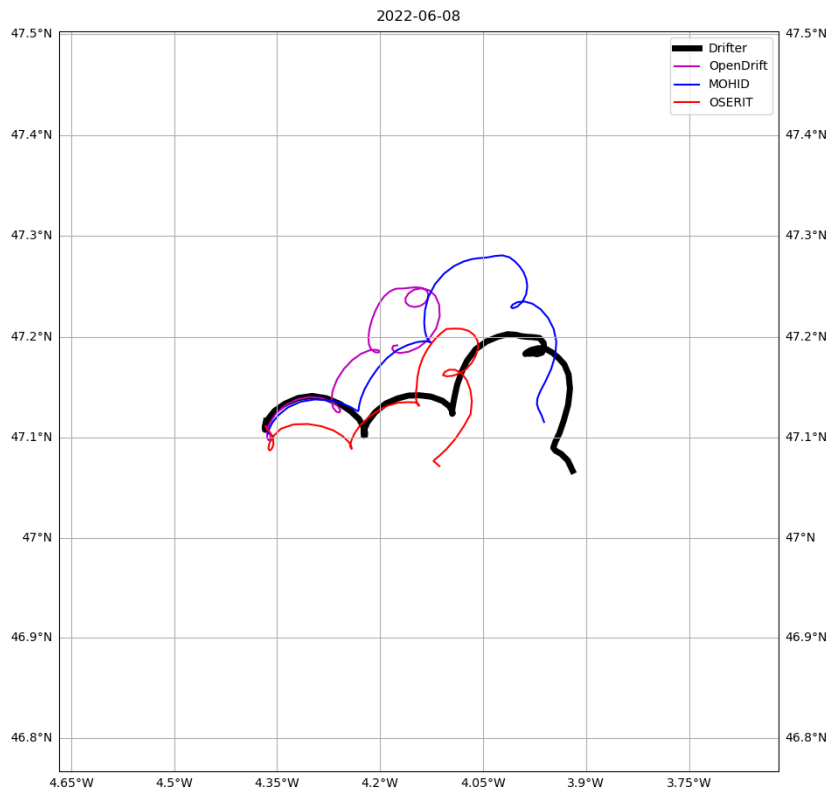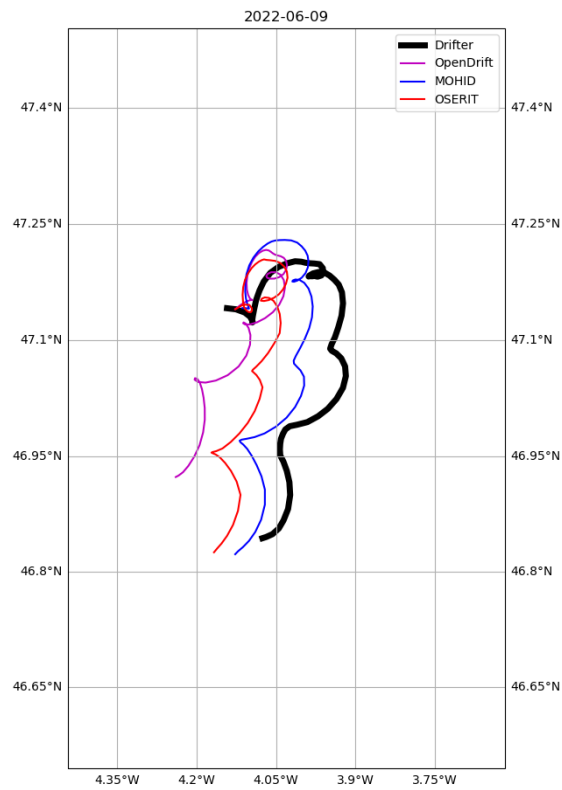
Figure 24: Comparison of the drift between the drifter released at sea during the sea trials and simulation from OpenDrift, MOHID, OSERIT starting on 2022-06-09 and finishing on 2022-06-11
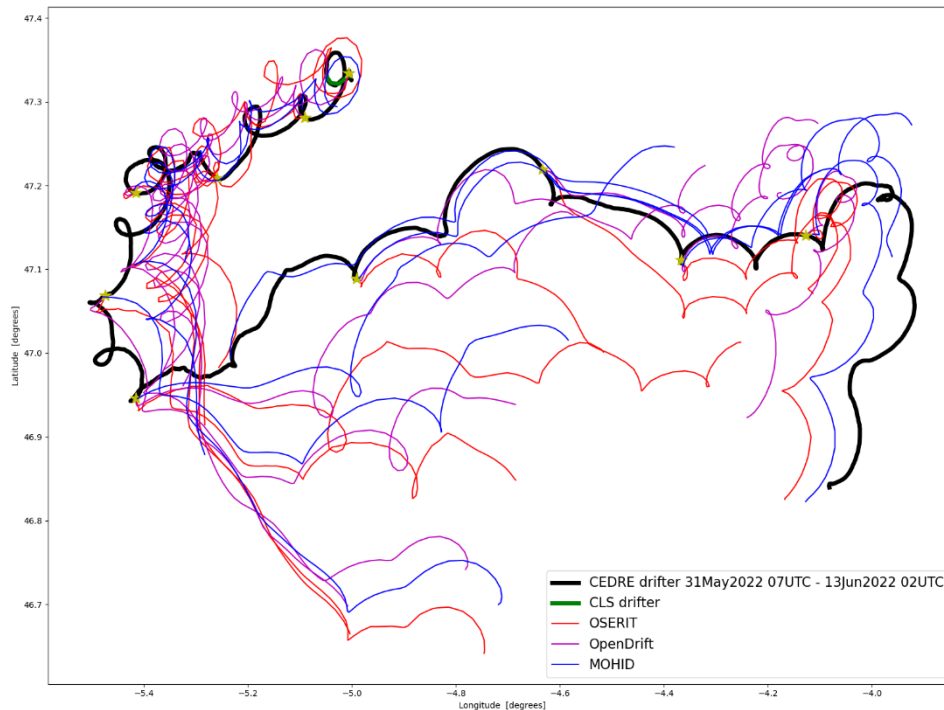
Figure 25: The black trajectory shows the 14 days drift of one of the three CEDRE drifters deployed during the sea trials on 31 May 2022. Trajectories are simulated with three models (OSERIT, MOHID and OpenDrift) starting every day at midnight (indicated with yellow stars) and lasting for 72 hours (3 days).

The Figure 25 shows the complete trajectory of the drifter along with all the associated simulations. To measure the accuracy of the model predictions, the distance between the drifter position and the model prediction was computed for each simulation and referred to as "error". Since multiple simulations were performed, the errors were averaged over the elapsed time since the start of each simulation for MOHID, OSERIT, and OpenDrift (as shown in Figure 26). This approach enables a comprehensive comparison of the models' accuracy over time.

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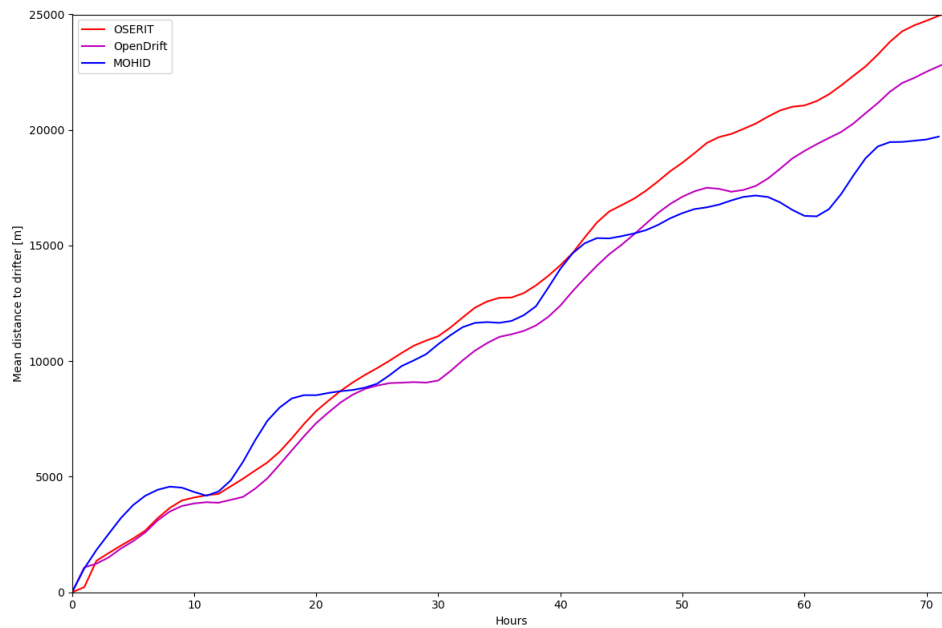Co-funded by the European Union Civil Protection

Figure 26: The mean distance between the simulated and observed trajectories (Figure 25) for each of the three models (OSERIT, MOHID, OpenDrift) as a function of time from the start of each simulated segment.

All three models behaved similarly, with an average error of 350 meters per hour. This provides an estimate of the confidence that a user can have in the models' predictions, even though the error may vary under different met-ocean conditions. The linear increase of the error indicates that users can expect a steady increase over time, but no sudden spike in average error. This information can help users choose a suitable period for their predictions to keep the error under a certain threshold.

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6.3. Validation of the atmospheric dispersion with the sea trials

During the sea trials of MANIFESTS, several spills of volatile HNS occurred at sea. Various instruments were utilized to monitor the evolution of these events. Although the formation of a gas cloud was observed (for instance on the Figure 27), accurately quantifying it to validate models proved to be a significant challenge.
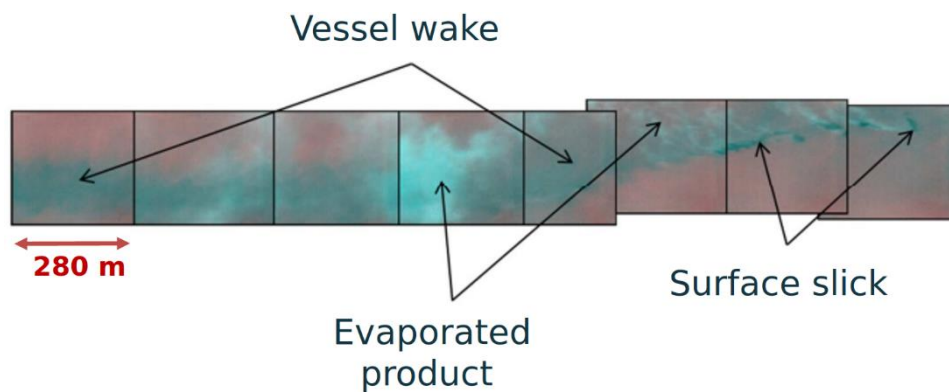

Figure 27: Pictures of the spill and gas cloud of butyl acetate at 300m of altitude (false color) 45 minutes after the start of the release

The models CHEMMAP, OpenDrift, OSERIT and MOHID have simulated the release of the butyl acetate with a focus on the gas cloud (Figure 28).
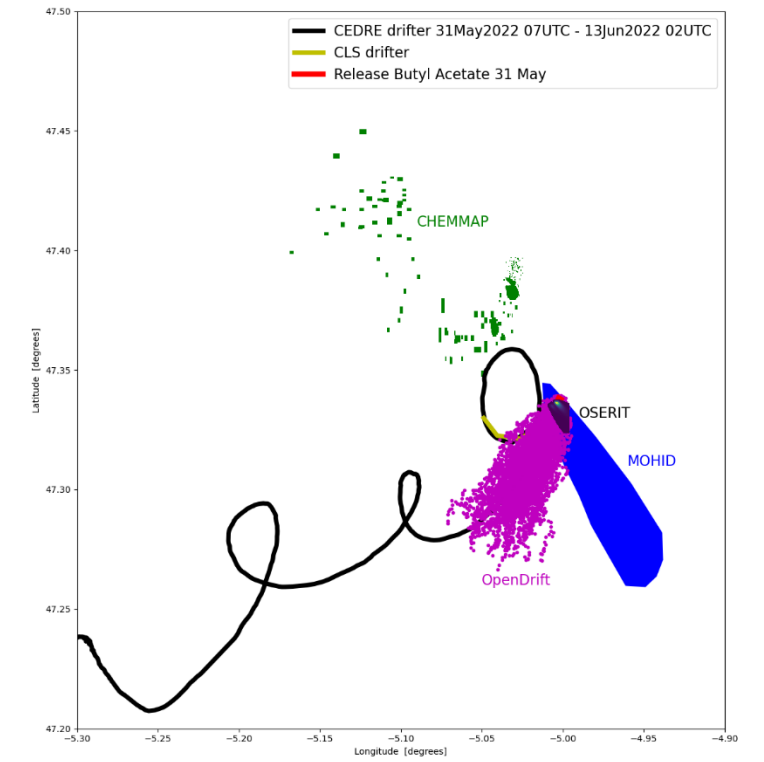
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Figure 28: Atmospheric dispersion of evaporated Butyl Acetate ("gas cloud") for the sea trial after 1 hour of simulation with the four models: OSERIT (black/green), MOHID (blue), OpenDrift (purple) and CHEMMAP (green). As a reference, the trajectories of ocean surface drifters are shown as black lines (CEDRE drifter) and yellow lines (CLS drifter). The chemical was released along the segment indicated by the short red line.

There is a large variation in the predictions made by the models, except for OSERIT and MOHID, which showed similar results. This discrepancy could be attributed to the extremely low wind conditions on that day, leading to a high degree of uncertainty in wind direction. Additionally, the models employed different wind providers, except for OSERIT and MOHID, which could further explain the differences. Nevertheless, all models predicted a similar distance travelled by the HNS within the given period. Figure 27 images were taken 45 minutes after the HNS spill, directly above the spill location on the ship. The models had predicted a farther distance for the HNS from the slick. This highlights the high uncertainty of wind direction for low wind speed.

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7. Conclusion

The validation process carried out in the MANIFESTS project provided valuable insights into the capabilities and limitations of the models used to simulate the behaviour of HNS at sea. Through the comparison of four models (CHEMMAP, OpenDrift, OSERIT, and MOHID) with separate sets of data, it was possible to quantify the accuracy and range of validity of their predictions. This allowed for a better understanding of the complex processes involved in HNS spills, such as evaporation, dissolution, and volatilization.

The validation experiments, ranging from small lab-scale simulations to large-scale laboratory experiments and sea trials, demonstrated the model's ability to estimate the drift of HNS in water and air dispersion. However, it was also evident that wind speed and direction estimation is critical for accurate simulation results, and the uncertainty associated with these parameters is often greater than that of the models themselves.

These models are all able to produce outputs of similar accuracy that can be used to help responders take decision in case of an accidental spill, or to prepare the response to take in case of a spill to mitigate the impact of HNS on the human population and on the environment. The simulation results must still be interpreted by a trained user for all the models.

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