



D4.2 Improving the prediction of HNS concentration in the atmosphere

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1. Introduction

Responding to maritime accidents can be extremely challenging when involving HNS that behave as evaporators. Due to their potential to form toxic or combustible clouds, evidence-based decisions are needed to protect the crew, responders, the coastal population and the environment. However, when an emergency is declared, key information is not always available for all the needs of responders. A case in point is the lack of knowledge and data to assess the risks that responders or rescue teams could take when intervening, or those that could impact coastal communities when allowing a shipping casualty to dock at a place of refuge.

The MANIFESTS project aims to address these uncertainties and improve response and training capacities through the development of an operational decision-support system (DSS) for volatile HNS spills. Besides management and communication, the project includes four other work packages: WP2 on collecting new data on evaporators, WP3 on table top exercises and field training, WP4 on improving modelling tools and WP5 on the development of the DSS. Key expected outcomes include:

- Operational guidance;
- Desktop and field exercises;
- In situ training;
- Experimental data on gas cloud fate;
- A brand-new fire and explosion modelling module;
- Improved HNS database with new experimental data on evaporation/dissolution kinetics.

This report presents the developments realized in the framework of the task 4.2. This task gave the opportunity to the MANIFESTS consortium to improve one or several features of their models allowing to better simulate the HNS concentration in the atmosphere. Only RBINS seized this opportunity and has implemented in OSERIT some improvements in order to better simulate the HNS concentration at the sea surface, evaporation processes and finally has implemented a new atmosphere transport and dispersion model.

OSERIT (Oil Spill Evaluation and Response Integrated Tool) is a model which describes the drift of a pollutant at sea using Lagrangian particle. It can be used in case of an accident with release of oil or chemical, to obtain an estimation of the pollution trajectory as well as some basic information about its behavior and fate at sea.

In the framework of the MANIFESTS project, a new atmospheric dispersion module fully coupled to OSERIT has been developed and several marine processes have been improved. In this report, the improved processes are described and their actual implementation in OSERIT is explained.

2. Model description

In order to start a simulation, data about the chemical and physical properties of the pollutant must be provided with along with the forcing (wind, waves, current...). This is used to simulate the drift and the weathering of the pollutant. These processes will be explained in this section.

2.1. Drift

The drift is all the processes responsible for the movement of the pollutant. The pollutant will drift under the influence of currents, waves, and wind when at the sea surface. A fraction of the pollutant can go into the water column forming droplets or bubbles. There they are advected by sub-surface currents and waves, can be dispersed under the action of turbulence, can resurface or go deeper. Pollutant can also be dissolved. If the pollutant reaches the seabed, it will stay still (unless it dissolves). Similarly, if a pollutant reaches a shore it can beach on it. The vertical speed of the pollutant is impacted by the density difference with the water along with the size and shape of the droplets of pollutant (depending on the properties of the pollutant and of the environment). The weathering processes described later will also modify the drift of the pollutant, by changing the properties of it. Furthermore, when a pollutant is fully dissolved it will not have any buoyancy. Evaporated pollutant will only be advected by wind. Evaporated pollutant will also be progressively dispersed during its aerial drift, an effect that is represented by a gaussian distribution whose the standard deviation increases as a function of the distance travelled in the atmosphere and of the atmospheric conditions.

2.2. Weathering

The pollutant is distributed in multiple "fraction", such as the evaporated fraction (pollutant in the air), the dissolved fraction or the fresh fraction (pollutant at the surface of the water). Several processes (named "weathering") will modify the pollutant properties. In order to estimate the rate of these processes, several parametrizations are used and are described here. They always describe the amount of chemical transferred from a fraction to another one (for instance, evaporation is the transfer from the fresh fraction to the evaporated fraction).

2.2.1. Evaporation

Two parametrizations are available in OSERIT for the evaporation process. The Schmidt number Sc is used in both parametrization and is computed as follows:

$$Sc = \frac{\nu}{\kappa_c} \quad (1)$$

ν : Molecular kinematic viscosity of air [m^2/s]

κ_c : Molecular diffusivity of pollutant in air [m^2/s]

It can be estimated as (Lehr et al., 2002):

$$Sc = 1.3676 \left(\frac{0.018}{MW_{avg}} \right)^{-1/2} \quad (2)$$

Parametrization derived from (Mackay and Matsugu, 1973)

It must be computed for each i compound.

$$\frac{dV_i}{dt} = \frac{K_i A P_i \bar{V}_i X_i}{RT} \quad (3)$$

V_i : Volume of the compound i evaporated [m^3]

A : Area of the quadtree leaf [m^2]

R : Gas constant [J/mol K]

T : Temperature [K]

K_i : Mass transfer coefficient [m/s]

\bar{V}_i : Molar volume of i [m^3/mol]

P_i : Vapour pressure of i [Pa]

X_i : Mole fraction of i []

$$K_i = 0.0048 U_{wind}^{7/9} X^{-1/9} Sc^{-2/3} \quad (4)$$

X : Downwind length of the oil slick axis [m]

U_{wind} : Wind speed [m/s]

$$X_i = \frac{\frac{V_i}{\bar{V}_i}}{\sum_{j=1}^{i_{max}} \frac{V_j}{\bar{V}_j}} \quad (5)$$

Parametrization derived from (Brighton P.W.M., 1985)

The evaporation mass flux is computed from the following equation:

$$E_{(x,t)} = C_s U_* j_{(x)} \quad (6)$$

$E_{(x,t)}$: Evaporative mass flux depending on distance and time [$\text{kg m}^{-2} \text{s}^{-1}$]

$j_{(x)}$: Mass transfer coefficient []

U_* : friction velocity of the air [m s^{-1}]

C_s : Chemical's vapor-phase saturation concentration [kg m^{-3}]

$$C_s = \frac{M_v P_v}{RT} \quad (7)$$

M_v : Molecular weight of the vapour

P_v : vapor pressure of the puddle [Pa]

Because $j_{(x)}$ depends on the position along the axis oriented parallel to the wind direction, it can be integrated over the whole area.

$$\bar{j} = \frac{1}{D_p} \int_0^{D_p} j_{(x)} dx \quad (8)$$

D_p : Diameter of a uniform circular puddle [m]

The main equation becomes:

$$E_{(t)} = C_s U_* \bar{j}_c \quad (9)$$

For the friction velocity of air:

$$U_* = 0.03U \left(\frac{10}{z}\right)^n \quad (10)$$

U : wind speed [m s^{-1}]

z : height of specified wind speed [m]

n : value depending on the wind speed profile, as in Table 1

Table 1 : Values of n

Pasquill Stability Class	n
A	0.108
B	0.112
C	0.120
D	0.142
E	0.203
F	0.253

The average mass transfer coefficient can be expressed as:

$$\bar{j} \approx \frac{k}{Sc_T} (1 + n) \left[\frac{1}{2} - \frac{1}{\pi} \tan^{-1} \left(\frac{e^\Lambda X_l}{\pi} \right) + \frac{1 - \gamma_e}{\ln^2(e^\Lambda X_l) + \pi^2} + \frac{(1 + (1 - \gamma_e)^2 + \frac{1}{6} \pi^2) \ln(e^\Lambda X_l)}{(\ln^2(e^\Lambda X_l) + \pi^2)^2} \right] \quad (11)$$

γ_e : Euler constant (equals 0.577)

X_l : Dimensionless distance evaluated at the downwind edge []

$$X_l = \frac{nk^2 D_p}{Sc_T z_0 e^{\frac{1}{n}}} \quad (12)$$

z_0 : Surface roughness length [m]

k : von Karman constant (equals 0.4)

Λ : Measure of the ratio of the scalar roughness length of the puddle and the momentum roughness length of the terrain

$$\Lambda = \frac{1}{n} + 1 + 2 \ln(1 + n) - 2\gamma_e + \frac{k}{Sc_T} (1 + n) f_{(Sc)} \quad (13)$$

$$f_{(Sc)} = \begin{cases} \left(3.85 Sc^{\frac{1}{3}} - 1.3\right)^2 + \frac{Sc_T}{k} \ln(0.13 Sc) & \text{for } Re_0 < 0.13 \\ \text{for } 0.13 \leq Re_0 \leq 2 : \text{interpolation between 0.13 and 2} & \\ 7.3 Re_0^{\frac{1}{4}} \sqrt{Sc} - 5Sc_T & \text{for } Re_0 > 2 \end{cases} \quad (14)$$

Sc_T : Turbulent Schmidt number (equals 0.85)

Re_0 : Roughness Reynolds number

$$Re_0 = \frac{U_* z_0}{\nu} \quad (15)$$

ν : Kinematic viscosity of air [$m^2 s^{-1}$]

2.2.2. Dissolution process described in (Hines and Maddox, 1985; Legrand et al., 2017; MacKay and Leinonen, 1977)

The dissolution process describes the transfer from the slick to the aqueous phase.

$$\frac{dn_{i,d}}{dt} = K (x_i C_i^S - C_i^W) A \quad (16)$$

$n_{i,d}$: Number of dissolved moles [mol]

A : Area [m²]

x_i : Mole fraction of component i []

C_i^S : Pure component i solubility [mol m⁻³]

C_i^W : Concentration of component i in water [mol m⁻³]

K : Mass transfer coefficient [m s⁻¹]

Re_L : Reynolds number []

$$Re_L = \frac{C_w L}{\nu_w} \quad (17)$$

ν_w : Kinematic viscosity of water [m s]

C_w : current speed [m s⁻¹]

Sc : Schmidt number in water []

$$Sc = \frac{\nu}{\kappa_c} \quad (18)$$

ν : Molecular kinematic viscosity of water [m² s⁻¹]

κ_c : Molecular diffusivity of pollutant in water [m² s⁻¹]

Sh : Sherwood number []

$$Sh = 0.578 Sc^{1/3} Re_L^{1/2} \quad (19)$$

2.2.3. Volatilization (Lyman et al., 1990)

The volatilization is the process for the transfer of the pollutant from the dissolved fraction to the evaporated one.

1. Henry law constant

$$H = \frac{P_{vp}}{S} \quad (20)$$

H : Henry law constant [atm m³/mol]

P_{vp} : vapor pressure of the compound [atm]

S : solubility [mol m⁻³]

If $H < 3 \times 10^{-7}$, volatilization is ignored.

H' : nondimensional Henry constant:

$$H' = \frac{H}{RT} \quad (21)$$

R : 8.2e-5 [atm m³ mol⁻¹ K⁻¹]

T : temperature [K]

2. Compute the liquid phase exchange coefficient

If $M < 65$ (g/mol)

$$k_l = 20 \sqrt{\frac{44}{M}} \quad (22)$$

M : molar mass [g mol⁻¹]

k_l : liquid phase exchange coefficient [cm h⁻¹]

Else (approximative), if windspeed < 3 m/s:

$$k_l = 2.5$$

if windspeed < 6 m/s

$$k_l = 10$$

if windspeed < 10 m/s

$$k_l = 23$$

if windspeed > 10 m/s

$$k_l = 50$$

3. Compute the gas phase exchange coefficient

If $M < 65$:

$$k_g = 3000 \sqrt{\frac{18}{M}} \quad (23)$$

k_g : gas phase exchange coefficient [cm h⁻¹]

If the molar mass is greater than 65:

$$k_g = 1137.5(V_{wind} + V_{curr}) \sqrt{\frac{18}{M}} \quad (24)$$

V_{wind} : wind speed [m s⁻¹]

V_{curr} : current speed [$m\ s^{-1}$]

4. Compute the overall liquid phase mass transfer coefficient

$$K_L = \frac{H' k_g k_l}{H' k_g + k_l} \quad (25)$$

K_L : mass transfer coefficient [$cm\ hr^{-1}$]

5. Compute the flux

$$N = K_L \left(C - \frac{P}{H} \right) \quad (26)$$

N : flux [$g\ cm^{-2}\ s^{-1}$]

C : concentration [$g\ cm^{-3}$]

P : vapor pressure of the compound [atm]

H : henry law constant [$atm\ cm^3\ g^{-1}$]

2.2.4. Emulsification (Scory, 2005)

Pollutant will go from fresh to emulsified with the following parametrization. It is a parametrization for oil.

$$\frac{dV_w}{dt} = \frac{C_{18}}{1 - C_{18}} \frac{K_{em}}{C_{15}} V_r H_s \quad (27)$$

V_w : Volume of water caught in the emulsion [m^3]

V_r : Oil volume at the surface [m^3]

H_s : Significant wave height [m]

C_{15} : 5×10^7 [m s]

C_{18} : Maximum water content (0.8) []

K_{em} : Ability to form emulsion (0-120) []

The new volume emulsified is computed from the new amount of water ($= \frac{dV_w}{C_{18}} \times (1 - C_{18})$)

2.2.5. Degradation

The degradation process destroys free pollutant with time. It follows a simple half-life process (the amount of pollutant is divided by two for each half-life).

3. Implementation

OSERIT is a Lagrangian model, which means the pollutant is distributed in multiple discrete particles. The number of particles is fixed at the start of the simulation, the volume in each of them will remain the same through all the processes. The pollutant in each particle is then divided into multiple fractions (fresh, emulsified, dissolved, evaporated, degraded).

OSERIT now uses a pseudo-components approach, which means that the pollutant is composed of multiple components. Each component has properties needed for the weathering processes and are treated separately (The goal is to model an oil as a mix of varying proportion of several fractions identical for several oil). In the case of a pure HNS, the pollutant can be represented by only one component with the properties of the HNS.

The particles are drifting with the current and are impacted by wave, wind... They can sink into the water column and resurface afterward or reach the bottom. Once a particle only contains dissolved fraction, it will become buoyancy neutral and if the particle contains only evaporated fraction, it will drift following only the wind. To achieve these states, the weathering processes must be applied to the pollutants but not directly to the particle as explained in the next section.

3.1. Use of quadtree

Several weathering processes need a surface for the slick to estimate the flux, but the particles are points and have no area. Furthermore, only applying weathering processes on individual particles would cause them to all contain a mix of multiple fractions (a particle in this situation will behave as a fresh one). To resolve these issues, a quadtree system is used.

A quadtree is a data structure which is composed of nodes, each having 4 or 0 children. If a node has 0 children, it is a leaf or terminal node. The goal is to subdivide the space in smaller space with a higher density of object of interest (example in Figure 1).

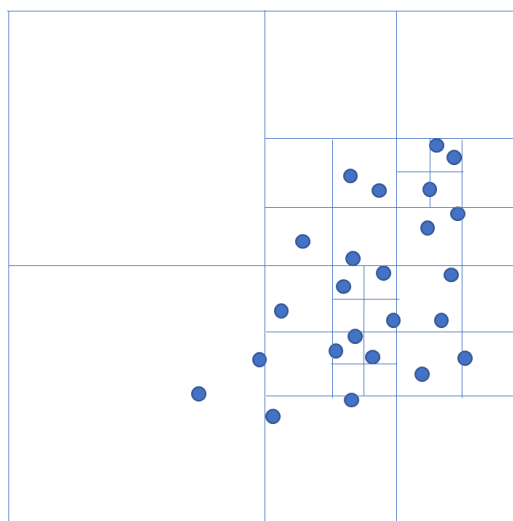


Figure 1: example of quadtree, the particles are represented by the blue dots and the quads of the quadtree by the squares

At each timestep of the model, particles are put into one of the three quadtree implemented. The ones at the surface will be in the "surface quadtree", the one in the water column in the "water column quadtree" and the ones at the seabed in the "bottom quadtree". Not all the particles are put in the quadtrees, only the ones that can be weathered (not the ones already fully dissolved or evaporated, chemically dispersed, out of domain), the ones stranded can be weathered if specified.

The particles in the surface quadtree are attributed to the leaf of the quadtree in which they are located (which have been subdivided to contains only a certain number of particles and be of a certain size). The particles are then "aggregated", which means that the fraction of each particle is added with the fractions of the others ones in the same leaf. All the pollutants are then located only in the leaves of the quadtree. The evaporation process then occurs on the leaves themselves, allowing the model to estimate the surface of the leaves as the surface of the evaporation. After that, the fractions are redistributed in the particles, each receiving the same amount. The model tries to minimize the number of fractions in each particle and to not change the fraction in the particle if possible (A particle with 50% of evaporated fraction in it before the aggregation will receive in priority evaporated fraction compare to one with 30% evaporated fraction, like illustrated in figure 2).

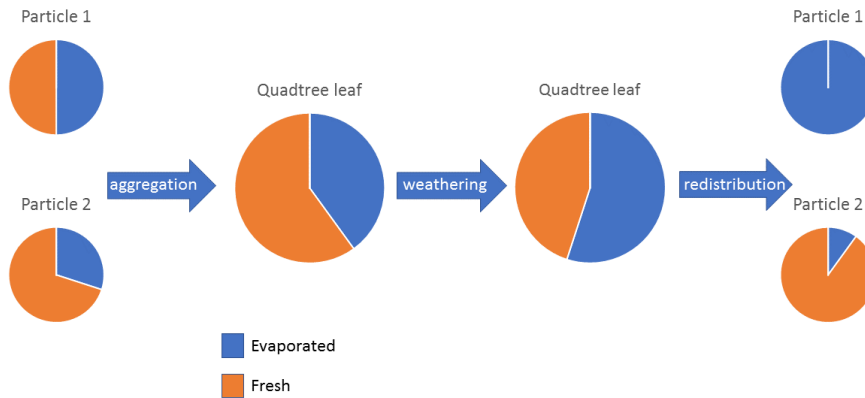


Figure 2: aggregation, weathering and redistribution applied on two particles in the same leaf of the quadtree

The process is the same for volatilization and dissolution. For computing the area of exchange, the area of the leaf is used. For computing the concentration of the pollutant in the water, a fixed height multiplied by the area of the leaf is used to find the volume of water and then the concentration with the amount of dissolved fraction in the leaf.

For the water column quadtree, the area is the sum of the droplet area (find from the droplet radius) and the water volume is the sum of all the water volume attributed to particles. A cylindrical water volume is linked to each particle. To take into account the vertical and horizontal turbulent dispersion of the pollutant in the water column, the water volume of the cylinder increases at each time step as follows (The height and circle area of the cylinder are fixed at the value of the leaf of the quadtree when at the surface):

$$dh = \sqrt{2} \times \left(\sqrt{\frac{t+dt}{K_{z(n)}}} \times (K_{z(n)} - K_{z(n-1)}) + \sqrt{\frac{K_{z(n)}}{t+dt}} \times dt \right) \quad (28)$$

dh : increase of the height of the cylinder during the time interval dt [m]

$K_{z(n)}$: vertical diffusion coefficient at the timestep n [$\text{m}^2 \text{s}^{-1}$]

$K_{z(n-1)}$: vertical diffusion coefficient at the timestep $n-1$ [$\text{m}^2 \text{s}^{-1}$]

t : time since the particle release [s]

dt : duration of a timestep [s]

$$da = 4K_x dt \quad (29)$$

da : increase in the area of the cylinder basis during a time interval dt [m^2]

K_x : horizontal diffusion coefficient [$m^2 s^{-1}$]

The area of the water column quadtree is never used, and is thus never subdivided (there is only one leaf around all the particles in the water column). The processes of degradation and dissolution occur in the water column.

For the bottom quadtree, there is also no subdivision. The concentration of pollutant dissolved is fixed at 0 (the particle stays at the bottom while the water is advected) and the exchange surface for the dissolution process is the surface of the droplet in the particle. It however estimates the surface there not as sphere but as a disc of the same radius. Quadtree are used in the water column and at the bottom, but only with one leaf. This is done to have only one kind of object (quadtree leaf) for applying the weathering processes in all cases.

The degradation does not require surface exchange to work and is applied on each quadtree, the emulsification is only applied on the surface quadtree.

In order to increase the accuracy of the weathering processes for highly volatile or highly soluble pollutants, the weathering time stepping schemes is embedded inside the drift time stepping scheme. The weathering timestep is an integer fraction of the drift timestep. Note that the quadtrees and the redistribution of the pollutant fractions between the Lagrangian particles are only computed once per drift time step. If specified by the user, a fourth quadtree is added for the stranded particles. The evaporation and volatilization processes will be applied on it.

3.2. Droplet impact on the vertical velocity

Within the water column, pollutant droplets are subject to buoyancy. Depending on the difference of density between the pollutant and the seawater, droplets might have upward or downward vertical motion. In the previous version of OSERIT, this vertical velocity was computed from the Stoke's law, assuming that each droplet behaves like a rigid sphere. In this work, this simplified approach has been improved by using Clift's empirical parameterizations (Clift et al., 1978). The empirical equations give the absolute value of the terminal droplet velocity but the upward or downward direction of the displacement is a function of the density difference between the water and pollutant. This terminal velocity is added to the other components of the velocity due to the currents and turbulence.

The Eötvös and Morton number needs to be computed as follows (an absolute value is used for both of them):

$$Eo = \frac{g(\rho_w - \rho_p)d^2}{\sigma} \quad (30)$$

Eo : Eötvös number []

g : 9.81 [m s⁻²]

ρ_w : water density [kg m⁻³]

ρ_p : density of the pollutant [kg m⁻³]

σ : interfacial tension [N m⁻¹]

d : particle diameter [m]

$$M = \frac{g(\rho_w - \rho_p)\mu_w}{\rho_w^2\sigma^3} \quad (31)$$

M : Morton number []

μ_w : water viscosity [Pa s]

3.2.1. Rigid spherical droplet

If the diameter of the droplets associated to a particle is smaller than 1mm, the droplets are considered spherical and rigid. The particle speed depends on the droplet diameter, the Reynolds number and a drag coefficient. This leads to the non-linear problem (32) - (41). This problem is iteratively solved, assuming a first guess speed of 1 m/s.

$$Re = \frac{S_d\rho_w d}{\mu_w} \quad (32)$$

Re : Reynolds number []

S_d : speed of the particle

ρ_w : water density [kg m⁻³]

d : particle diameter [m]

μ_w : water viscosity [Pa s]

For a Reynolds number smaller than 1:

$$S_d = \frac{gd^2(\rho_w - \rho_p)}{18 \mu_w} \quad (33)$$

ρ_p : density of the pollutant [kg m⁻³]

g : 9.81 [m s⁻²]

For a Reynolds number between 750 and 350000:

$$S_d = 1.73 \sqrt{\frac{gd(\rho_w - \rho_p)}{\rho_w}} \quad (34)$$

If the Reynolds number is not comprised in the previous intervals, the speed is computed from the drag coefficient:

$$S_d = \sqrt{\frac{4gd(\rho_w - \rho_p)}{3\rho_w C_D}} \quad (35)$$

C_D : drag coefficient []

The drag coefficient is estimated from the Reynolds number in one of the following equations:

Reynolds number under 20:

$$C_D = \frac{24}{Re} (1 + 0.1315 Re^{0.82-0.05 \log_{10} Re}) \quad (36)$$

Reynolds number under 260:

$$C_D = \frac{24}{Re} (1 + 0.1935 Re^{0.6305}) \quad (37)$$

Reynolds number under 1500:

$$C_D = 10^{1.6435-1.1242 \log_{10} Re + 0.1558 (\log_{10} Re)^2} \quad (38)$$

Reynolds number under 400000:

$$C_D = 29.78 - 5.3 \log_{10} Re \quad (39)$$

Reynolds number under 1000000:

$$C_D = 0.1 \log_{10} Re - 0.49 \quad (40)$$

For the Reynolds number higher than 1000000:

$$C_D = 0.19 - \frac{800000}{Re} \quad (41)$$

3.2.2. Ellipsoidal droplet

If a particle is composed of droplets between 1 and 15 mm in diameter, with an Eötvös number under 40 and a Morton number under 0.001, its velocity is computed with the following equations (for ellipsoidal droplet):

$$H = \frac{4}{3} EoM^{-0.149} \left(\frac{\mu_w}{0.009} \right)^{-0.14} \quad (42)$$

If H is bigger than 59.3:

$$J = 3.42H^{0.441} \quad (43)$$

If H is smaller than 59.3 but higher than 2:

$$J = 0.94H^{0.757} \quad (44)$$

If H is smaller than 2, the droplet will follow a spherical cap regime described in the next section. Otherwise, the speed is computed as follow:

$$S_d = \frac{\mu_w}{d\rho_p} M^{-0.149} (J - 0.857) \quad (45)$$

3.2.3. Spherical cap droplet

When a particle is composed of droplets too big to follow a rigid sphere regime and does not fit the requirement for an ellipsoidal regime, it will follow the spherical cap regime.

$$S_d = 0.711 \sqrt{\frac{g(\rho_w - \rho_p)d^2}{\rho_w}} \quad (46)$$

3.3. Pollutant properties

To run the weathering and the drift, the physical and chemical properties of the pollutant must be provided. Some properties can be inferred from other properties, mainly for oil, but it is always better to provide data obtained from experiment and literature.

3.3.1. Initial volume

In cubic meter, the initial volume needs to be provided for each of the components of the mix.

3.3.2. Boiling temperature

The boiling temperature in Kelvin is useful for estimating other properties, for instance the vapor pressure. It can be estimated from the density if the pollutant is oil. (Mishra and Kumar, 2015)

$$T_{eb} = 532.98 - 3.125 \left(\frac{141367}{\rho_{15}} - 131.5 \right) \quad (47)$$

T_{eb} : ebullition temperature [K]

ρ_{15} : density at 15°C [kg m⁻³]

3.3.3. Molar mass

The molar mass is useful to estimate some other properties and for conversion. It can be estimated for hydrocarbon from the boiling temperature. (Jones, 1997)

$$MW = \frac{0.04132 - 1.985 \times 10^{-4} T_{eb} + 10^{-9} T_{eb}^2}{1000} \quad (48)$$

MW : molar mass [kg mol⁻¹]

3.3.4. Vapor pressure

The vapor pressure, in pascal, is useful in weathering processes, like evaporation and volatilization. Due to the relation of the vapor pressure with the temperature, it can be estimated using Clausius Clapeyron:

$$P_v = P_{v0} \exp \left(\frac{\Delta H_v \times MW}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right) \quad (49)$$

P_v : vapor pressure [Pa] at the temperature T [K]

P_{v0} : vapor pressure [Pa] at the reference temperature T_0 [K]

ΔH_v : vaporization enthalpy [J kg⁻¹]

R : 8.314, perfect gas constant [J mol⁻¹ K⁻¹]

If the vapor pressure at a reference temperature is not available, the following estimation is used (Lyman et al., 1990):

$$P_v = 101325 \times \exp\left(\frac{\Delta S_{vb} (T_{eb} - C_2)^2}{0.97 R_{old} T_{eb}} \left(\frac{1}{T_{eb} - C_2} - \frac{1}{T - C_2}\right)\right) \quad (50)$$

$$\Delta S_{vb} = K_F (8.75 + R_{old} \ln T_{eb}) \quad (51)$$

$$C_2 = -18 + 0.19 T_{eb} \quad (52)$$

K_F : constant depending on the dipole moment of the molecule, supposed to be 1.06 []

R_{old} : 1.987, perfect gas constant in [cal mol⁻¹ K⁻¹]

3.3.5. Molar volume

The molar volume of the pollutant (when liquid) is used for conversion purpose and in some parameterization. It is estimated as the division of the molar mass of the pollutant by the density of the pollutant. If they are not available, the following estimation can be used (for hydrocarbon, based on alkanes between 3 and 20 carbon):

$$\bar{V} = 7 \times 10^{-5} - (2.102 \times 10^{-7} T_{eb}) + (10^{-9} \times T_{eb}^2) \quad (53)$$

\bar{V} : molar volume [m³ mol⁻¹]

3.3.6. Vaporization enthalpy

The vaporization enthalpy [J/kg] can be estimated with Clausius Clapeyron and the boiling temperature, if the vaporization enthalpy is supposed to be constant with the temperature. This is a very rough estimating method.

$$\Delta H_v = \frac{-R \ln \left(\frac{P_v}{P_a} \right)}{MW \left(\frac{1}{T_{eb}} - \frac{1}{T} \right)} \quad (54)$$

P_a : atmospheric pressure [Pa] (101325)

3.3.7. Air diffusivity

Air diffusivity of the pollutant is used in the evaporation parametrization. It can be estimated from the Graham law:

$$D_1 = D_2 \sqrt{\frac{MW_2}{MW_1}} \quad (55)$$

D_1 : diffusivity of the chemical [$\text{m}^2 \text{s}^{-1}$]

D_2 : diffusivity of a reference chemical [$\text{m}^2 \text{s}^{-1}$]

MW_1 : molar mass of the chemical [kg mol^{-1}]

MW_2 : molar mass of the reference chemical [kg mol^{-1}]

The water molecule can be used as a reference, with an air diffusivity of $2.39 \times 10^{-5} \text{ m}^2/\text{s}$ and a molar mass of 0.018 kg/mol.

3.3.8. Water diffusivity

The water diffusivity coefficient is the diffusivity of the pollutant in water, useful for the dissolution process. It can be estimated at 25°C from the following parametrization (Lyman et al., 1990):

$$D_c = \frac{13.26 \times 10^{-9}}{(\mu_w \times 10^3)^{1.14} (\bar{V} \times 10^6)^{0.589}} \quad (56)$$

D_c : water diffusivity coefficient [m^2/s]

μ_w : dynamic viscosity of water [Pa s]

3.3.9. Half-life

The half-life is the time needed for half the chemical to be degraded.

3.3.10. Density

The density is used in multiple processes, and should be provided. For the oil, it can be estimated from the ebullition temperature however (Mishra and Kumar, 2015):

$$\rho_{15} = \frac{1}{\frac{532.98 - T_{eb}}{441772} + 9.3 \times 10^{-4}} \quad (57)$$

ρ_{15} : density at 15°C [kg m⁻³]

3.3.11. Solubility

The solubility [mol/m³] is used for the dissolution process. There are no estimation methods for this parameter implemented. Dissolution can therefore only be simulated for chemicals whose solubility has been measured in lab.

3.3.12. Kemls

The Kemls [] is the constant used for the emulsion.

4. Atmospheric dispersion module

OSERIT Lagrangian particles module computes the advection of the evaporated pollutant in the atmosphere, i.e. it computes the aerial trajectory of each Lagrangian particle under the only influence of the wind at 10 meters. To compute the dispersion process along this aerial trajectory, a classic gaussian atmospheric dispersion model has been implemented. This model associates to each "aerial" Lagrangian particle, a 3D gaussian distribution of the pollutant mass. This distribution is centered on the position of the Lagrangian particle and is advected with it.

In this section, we present the gaussian distribution, first and then the different options we have taken to present the results of this model.

4.1. Gaussian distribution of the pollutant concentration

The classic formulation of a gaussian atmospheric advection-diffusion model with a steady wind can be written as : (Turner, 1970):

$$C_{(x,y,z)} = \sum_{i=1}^n \left(\frac{m_i}{(2\pi)^{3/2} \sigma_{x_i} \sigma_{y_i} \sigma_{z_i}} \right) \times \exp \left(-\frac{[x - x_0 - u(t - t_i)]^2}{2\sigma_{x_i}^2} \right) \\ \times \exp \left(-\frac{[y - y_0 - v(t - t_i)]^2}{2\sigma_{y_i}^2} \right) \times \exp \left(-\frac{(z - z_0)^2 + (z + z_0)^2}{2\sigma_{z_i}^2} \right) \quad (58)$$

With:

$C_{(x,y,z)}$: the concentration at the point of coordinate x, y, z [kg/m^3]

m_i : the mass released in the particle i [kg]

$\sigma_{x_i}, \sigma_{y_i}, \sigma_{z_i}$: the standard deviation in the x, y and z axis [m]

x, y, z : position where the concentration is looked at [m]

x_0, y_0, z_0 : starting position for the particle [m]

u, v : 10m- wind speed in the x and y direction [m/s]

t : time[s]

t_i : time of release of the particle i

To adapt this equation to OSERIT, several changes have been made:

- The $[x - x_0 - u(t - t_i)]^2$ and $[y - y_0 - v(t - t_i)]^2$ is replaced by the distance between the point of coordinate x, y, z and the position of the particle at this timestep.
- z_0 is supposed to be 0 (the particle comes from the sea surface and stays at the sea surface)
- The 3 exponentials are put into a single one to gain computation time
- $\sigma_{x_i} = \sigma_{y_i} = \sigma_i$

$$C_{(x,y,z)} = \sum_{i=1}^n \left(\frac{m_i}{(2\pi)^{3/2} \sigma_i^2 \sigma_{z_i}} \right) \times 2 \times \exp \left(-\frac{dx^2 + dy^2}{2\sigma_i^2} - \frac{z^2}{2\sigma_{z_i}^2} \right) \quad (59)$$

dx : difference between x and the particle x coordinate [m]

dy : difference between y and the particle y coordinate [m]

The standard deviation is derived from this equation (Turner, 1970):

$$\sigma = ax^b + c \quad (60)$$

σ : standard deviation [km]

x : distance from the source [km]

With the coefficient described in the table 2 or in the table 3, for horizontal and vertical standard deviation, respectively.

Table 2: coefficient for horizontal standard deviation

Atmospheric stability (Pasquill)	a	b	c
A	0.215	0.858	0
B	0.155	0.889	
C	0.105	0.903	

D	0.068	0.908	
E	0.05	0.914	
F	0.034	0.908	

Table 3: coefficient for vertical standard deviation

Atmospheric stability (Pasquill)	a	b	c
A	0.467	1.89	0.01
B	0.103	1.11	0
C	0.066	0.915	0
D	0.0315	0.822	0
E (x < 1km)	0.0232	0.745	0
E (x > 1km)	0.148	0.15	-0.126
F (x < 1km)	0.0144	0.727	0
F (x > 1km)	0.0312	0.306	-0.017

Because the conditions may vary during the simulation, the standard deviation is evaluated by incrementing the standard deviation at the previous timestep:

$$\sigma_n = \sigma_{n-1} + \int_{x_{n-1}}^{x_n} \frac{d\sigma}{dx} dx \tag{61}$$

$$\sigma_n = \sigma_{n-1} + a((x_{n-1} + \Delta x)^b - x_{n-1}^b)$$

σ_n : standard deviation at the timestep of interest

σ_{n-1} : standard deviation at the previous timestep

x_{n-1} : total distance travelled by the particle at the previous timestep [km]

Δx : distance travelled by the particle between the duration of the timestep [km]

4.2. Plotting results for atmospheric dispersion

The postprocessing aims to give estimation of the dispersion of the pollutant of each particle. The repartition of the pollutant from the particle coordinate is assumed to follow a gaussian distribution. To represent this graphically, two plots series are realized, one which describes the time-evolution of the aerial pollution footprint (i.e. the localization of the areas impacted by the pollutant) and another one showing the time-evolution of the pollutant aerial concentration. This second approach is extremely computationally intensive and is therefore only applied around the release area. using a grid with a concentration in each cell. In order to realize these plots, each particle receive a horizontal standard deviation and a vertical one when they become fully evaporated. All the following steps are started only after the simulation with the drift and the transfer to the atmosphere have been successfully finished.

The postprocessing generates a list of the standard deviation of each of the evaporated particle for each timestep. The timestep can be shorter than the OSERIT timestep, to have a better representation of the evolution of the cloud.

The following figures are from a test case, and are there as example of the information provided by the model. They are not from real world condition.

4.2.1. Aerial pollution footprint

The first way to plot the data is to use directly the sigma to draw a disk (Figure 3 and 4). Using the normal law, it is possible to specify a certain amount that should be enclosed by a circle of a certain radius. For instance, it is possible to take a radius of 3σ in which there will be the majority of the pollutant. The last step is to draw the circle, with as center the coordinate of the particle and as radius 3σ .

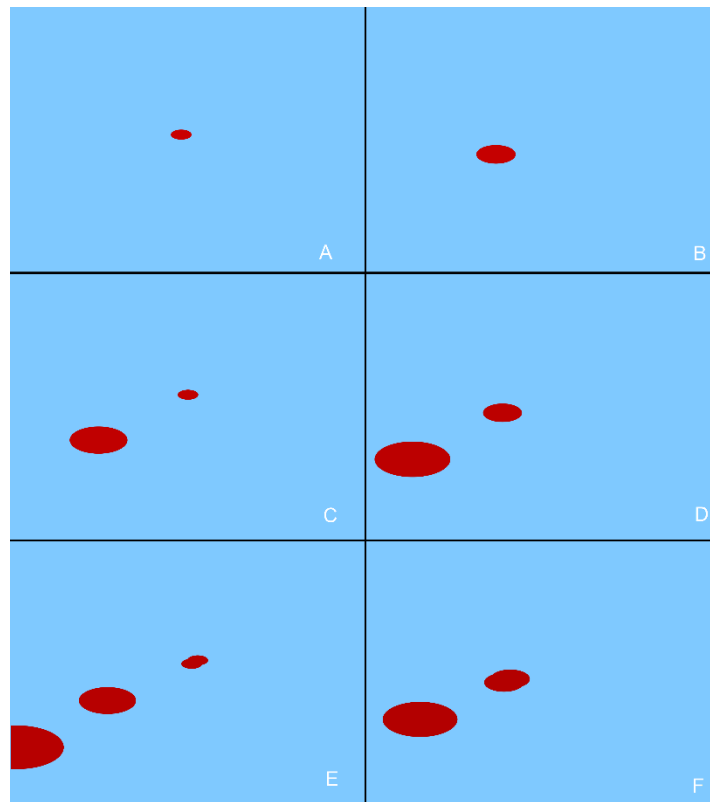


Figure 3: instantaneous localization of most of the pollutant evaporated (from A to F chronologically)

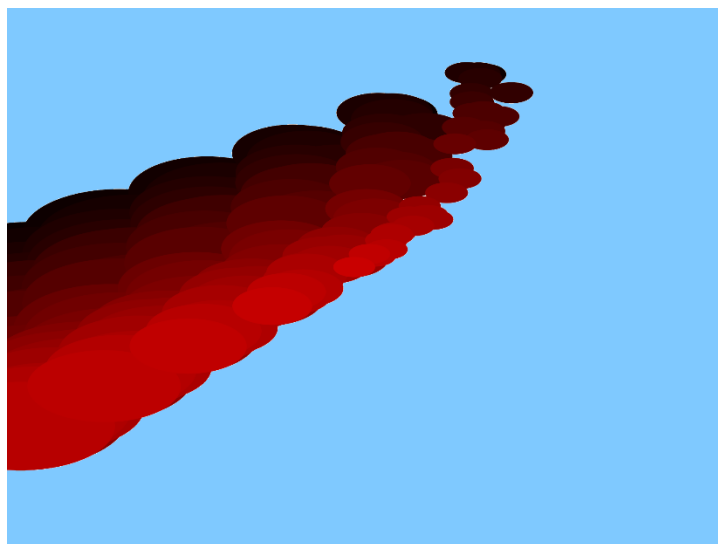


Figure 4 : compilation of all of the instantaneous plots on the same plot. A disk lighter than another one means it has been plotted in an instantaneous plot from earlier

4.2.2. Concentration

As seen previously, the standard deviation has already been computed for all the particle at all timestep needed, a grid is then created. The model adds the contribution of each particle to each

cell of the grid for each timestep. This process is very slow, in order to optimize it the model look a particle at a timestep and then compute the concentration at the grid cell at which the particle is located. Then the model does it again for the 8 neighboring cells, and for the neighbors of these ones. This continue and stop when the concentration added is considered to be too small to be meaningful. The model repeats this algorithm for each particle, and for each timestep and then plot the grid as a result.

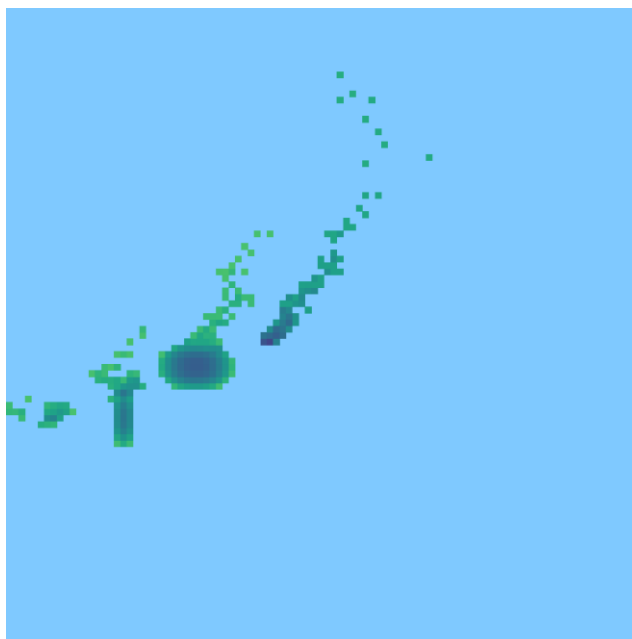


Figure 5: maximum concentration at each square of the grid

4.2.3. Mass balance

The model generates several plots. In this section the ones about the evaporation will be described, with example plots. A simple timeseries of the repartition of the volume of pollutant in the fraction is showed in the Figure 6.

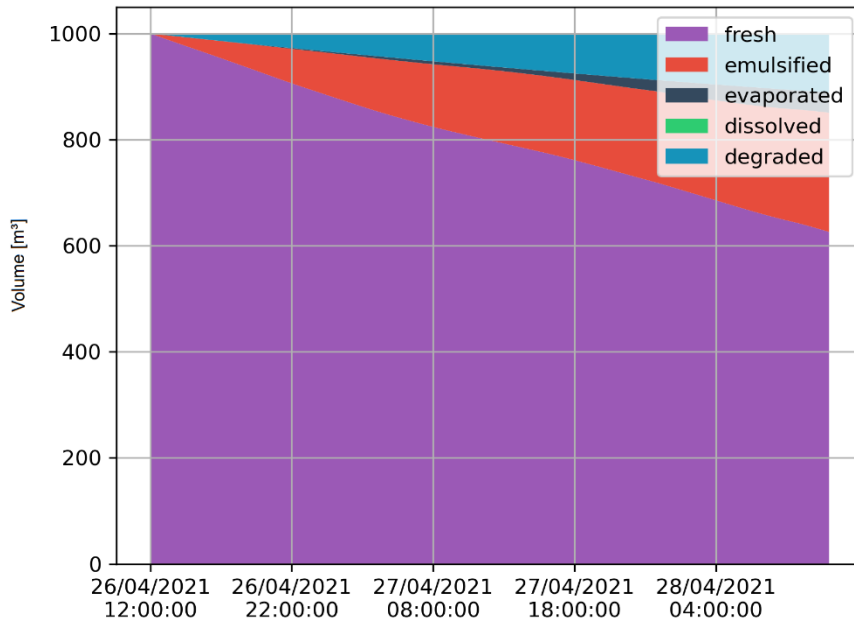


Figure 6 : repartition of the volume of the pollutant as a function of the time

5. Conclusion

A new module for OSERIT has been developed in the framework of the MANIFESTS project. The model is now able to estimate the concentration and localization of an HNS which have evaporated in the atmosphere. To achieve this goal, a new method for estimating the slick surface has been implemented along with a gaussian spreading of the HNS when drifting in the atmosphere. New visualization tools are now available to help understand the predictions quickly.

Several others improvements have been done to improve the prediction of the fate of HNS and oil spilled at sea, such as multiple weathering processes and a pseudocomponents approach of the pollutant. A better description of the velocity in the water column relative to the shape and size of the droplet has also been developed.

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7. Annexes

7.1. States and driftstates

All the particles in OSERIT have a state and a driftstate, updated at each timestep of the model. The driftstate describes if the particle is active or not, the value it can take are described below:

- 0. Particle has stopped to drift and will not be weathered anymore
- 1. Particle is not released yet
- 2. Particle is drifting

The state is about the location of the particle, it can be at the following value:

- 0. Particle at the sea surface
- 1. Particle in the water column
- 2. Particle chemically dispersed (in the water column, cannot sink at the seabed or resurface)
- 3. Particle stranded
- 4. Particle on the seabed
- 5. Particle out of domain
- 6. Particle contains only evaporated fraction and drift with the wind in the atmosphere
- 7. Particle contains only dissolved fraction

The interaction between the state and driftstate and their implications are described in the Figure 7.

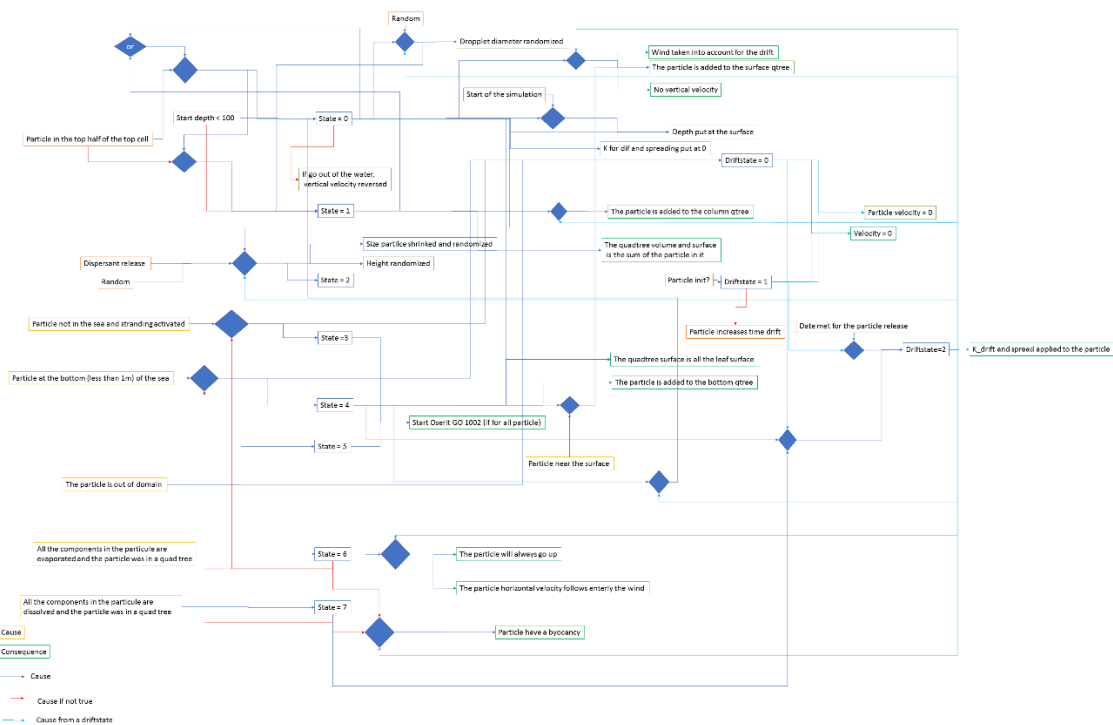


Figure 7 : Interaction of state and driftstates