Understanding HNS behaviour in the marine environment

DG-ECHO civil protection funding mechanism
2014 Call for Prevention and Preparedness

Co-funded by the European Commission, DG-ECHO

Ecole des Mines d'Ales

French University in south of France

Ecole des Mines d'Ales

Industrial Risk and Safety Laboratory

Experimental and numerical study of industrial accident

Methodology and support tools for crisis management

Static and dynamic modelisation of vulnerability

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Industrial Risk and Safety Laboratory

Experimental and numerical study of industrial accident

Methodology and support tools for crisis management

Static and dynamic modelisation of vulnerability

Ecole des Mines d’Ales

Industrial Risk and Safety Laboratory

- **Field and laboratory tests**
  - Fire
  - Explosion
  - Atmospheric dispersion
  - Maritime pollution
  - Fragments effects

Understanding HNS behaviour in the marine environment

Context: Physico-chemical properties are usually evaluated in standard conditions (at laboratory scale and equilibrium state)

- Non representative of chemical release in marine environment

Objectives is to understand the behavior of HNS in marine environment

- Calculation of the source term (flow rate and liquid velocity at breach level)
- Characterization of the temporal evolution of the competition between the different processes that act simultaneously (solubilisation, evaporation,…)
- Characterization of the droplet size and velocity distribution clearly represents the chemical behaviour in the water column

Understanding HNS behaviour in the marine environment

1. HNS release at sea surface
   1. Liquid jet velocity
   2. Volumic flow rate at breach level

2. HNS release in the water column
   1. Volumic flow rate at breach level
   2. Droplet velocity in the water column
   3. HNS solubilisation in the water column

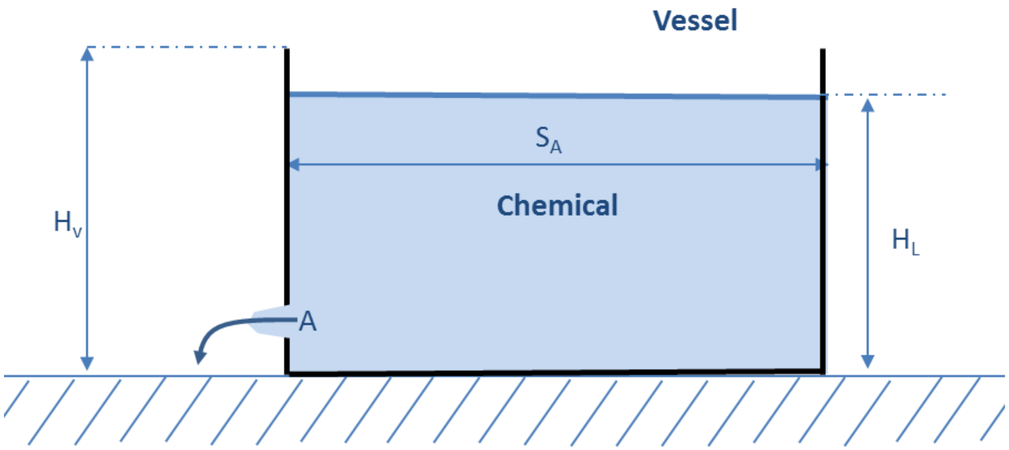
Understanding HNS behaviour in the marine environment

HNS release at sea surface

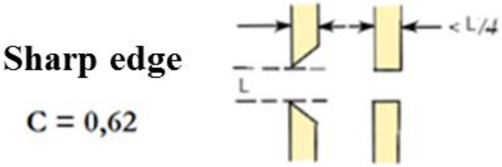
HNS draining for floating vessel

- Draining vessel is calculated with the Torricelli law derived from the Bernoulli equation

$$Q = C\sqrt{2gH_L}$$



Q: volumic flow rate [$m^3.s^{-1}$]
H_L: liquid level in the tank [m]
C: discharge coefficient (C=0.62 for circular orifice)

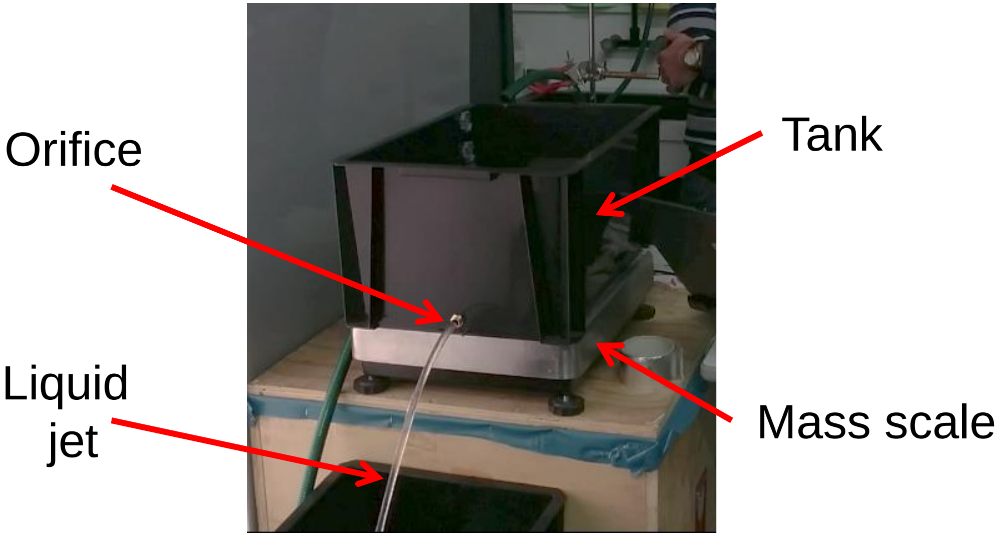


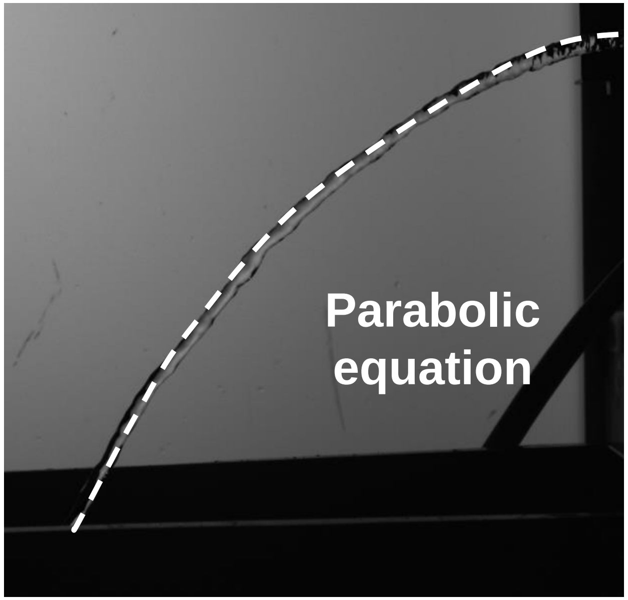
HNS release at sea surface

HNS draining for floating vessel

- **Experimental setup**
  - 45L tank with circular orifice of 8mm of diameter
  - Mass scale
  - High definition video camera (1280x800 px-60 fps)

- **Objectives**：Verify the Torricelli theory at the orifice (liquid velocity and draining time)

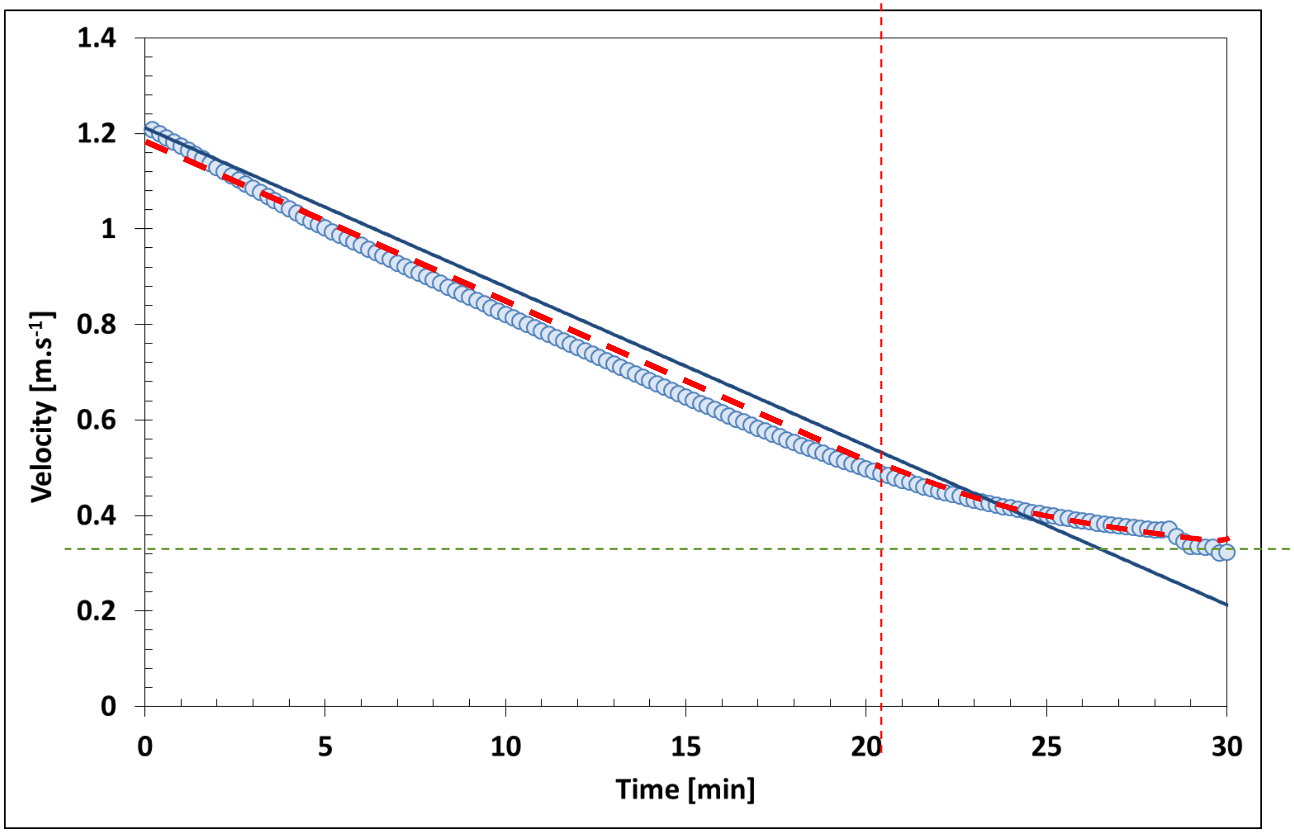




HNS release at sea surface

HNS draining for floating vessel

- **Results : Liquid velocity at the exit**
  - Linear variation for liquid velocity at the breach level
  - Good agreement between model and experiments for linear variation (discrepancy<10%)
  - Non linear variation at the end of test due to non submerged orifice

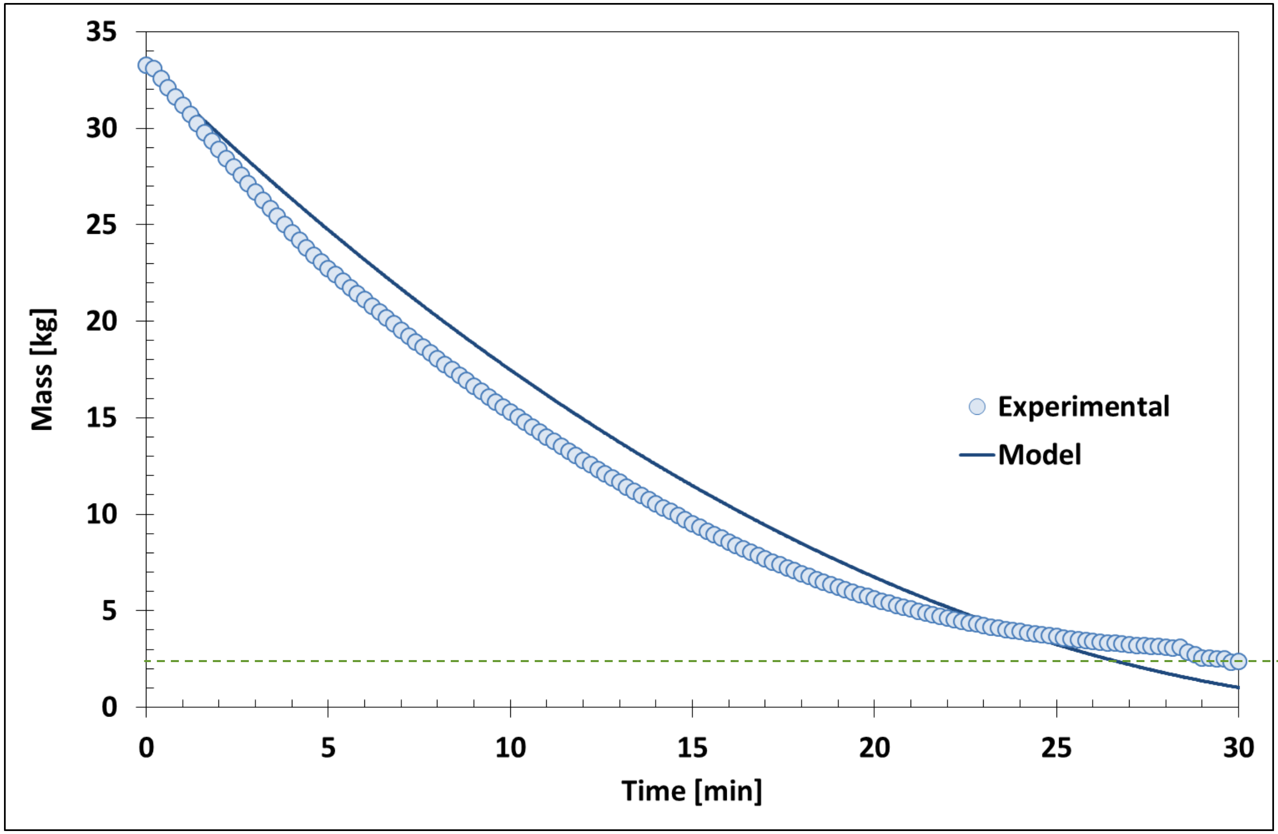


Remaining liquid in the tank

HNS release at sea surface

HNS draining for floating vessel

- **Results : Tank draining**
  - Quadratic equation for mass variation during tank draining
  - Good agreement between model and experiments
    - Total draining is modelled in 26min40s instead of 30min



Remaining liquid in the tank

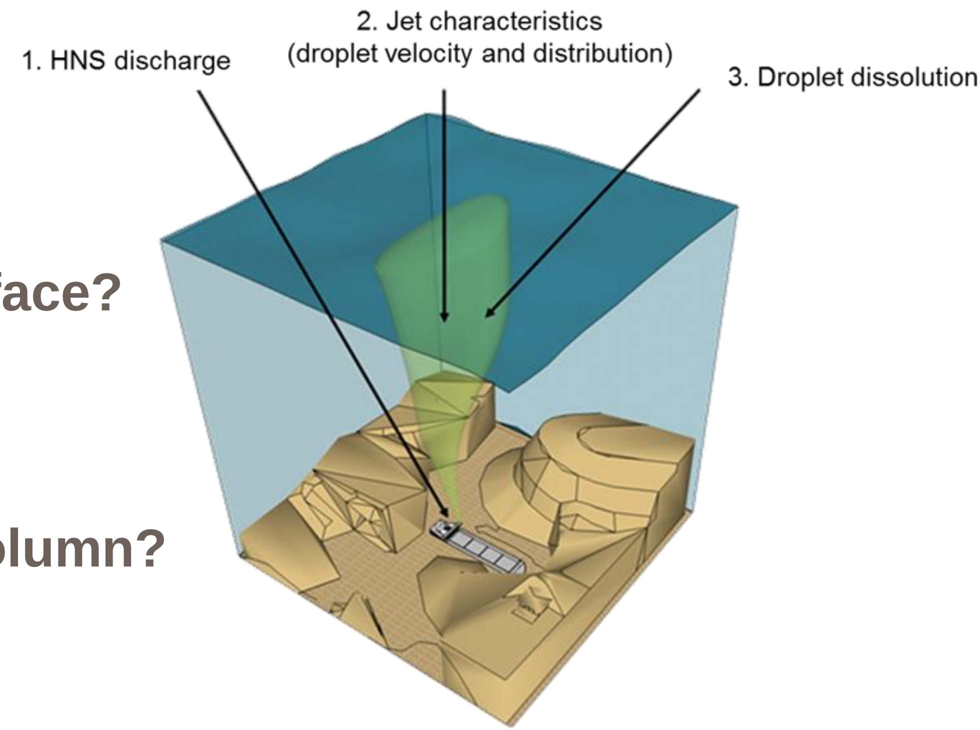
Understanding HNS behaviour in the marine environment

1. HNS release at sea surface
    1. Liquid jet velocity
    2. Volumic flow rate at breach level

2. HNS release in the water column
    1. Volumic flow rate at breach level
    2. Droplet velocity in the water column
    3. HNS solubilisation in the water column

HNS release in the water column

- How long is the draining time
- Chemical slick at the sea surface?
- If so, when and how much ?
- What happens in the water column?



Calculation of chemical behavior in marine environment

Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

1. Case of single hole with floating chemical

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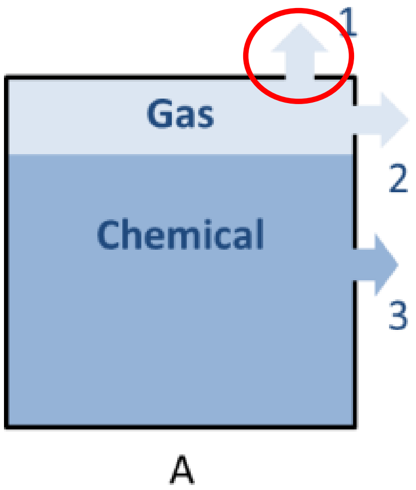
Characterization of the influence of orifice position

1. Case of single hole with floating chemical

The breach is located at a top position (arrow 1)



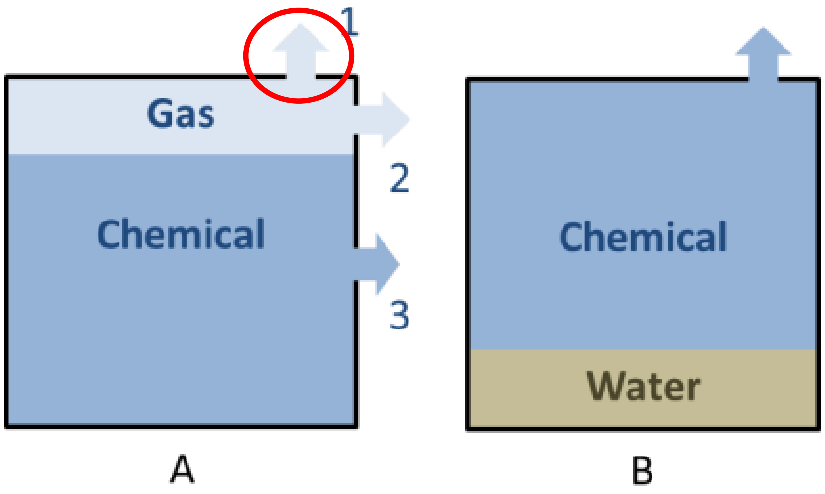
Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

1. **Case of single hole with floating chemical**

The breach is located at a top position (arrow 1)

- Gas is entirely released and replaced with water creating a layer under the chemical (case B).
- The whole quantity of chemical is released

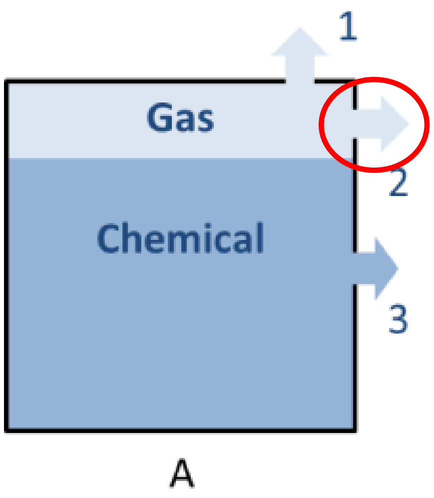


Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

1. **Case of single hole with floating chemical**

The breach is located below the top but still at gas level (arrow 2)



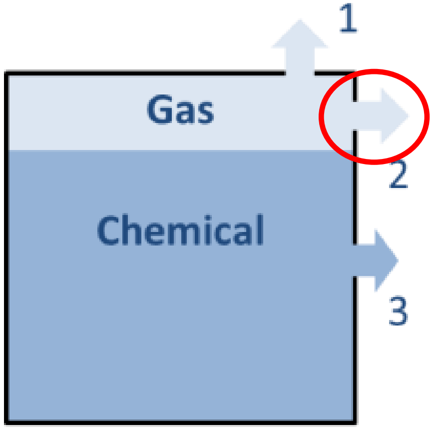
Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

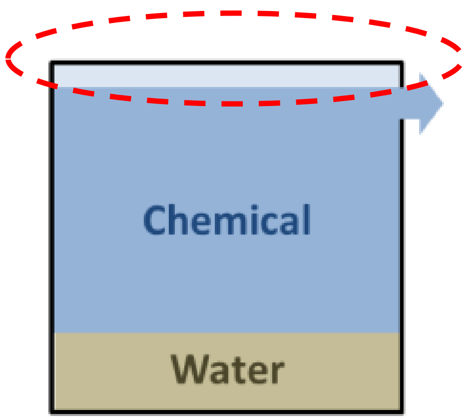
1. **Case of single hole with floating chemical**

The breach is located below the top but still at gas level (arrow 2)

- All the chemical is ejected and replaced by an equivalent volume of water.
- Some gas will be trapped in a cavity (dead space) and is excluded from the study of discharge **(case C)**



A



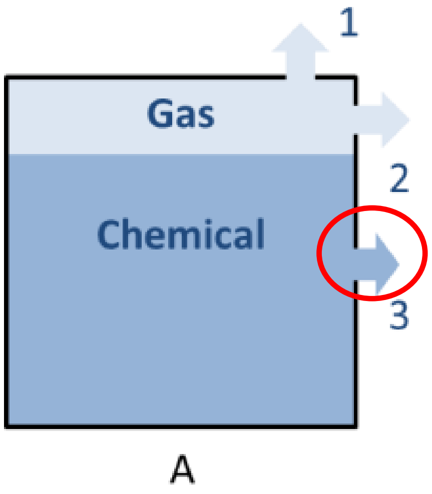
C

Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

1. Case of single hole with floating chemical

The breach is located at the chemical level (arrow 3)



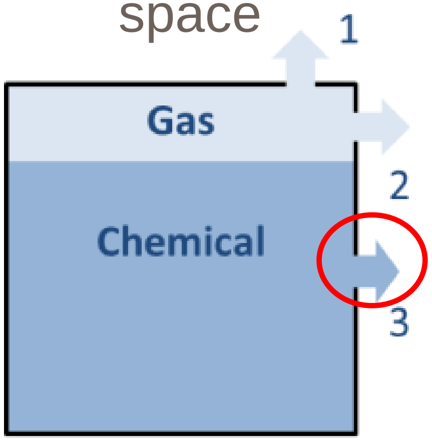
Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

1. **Case of single hole with floating chemical**

The breach is located at the chemical level (arrow 3)

- The ejected volume is replaced by an equivalent volume of water.
- This situation will continue until the position D is reached.
- Both gas and chemical will remain trapped in the tank in a dead space



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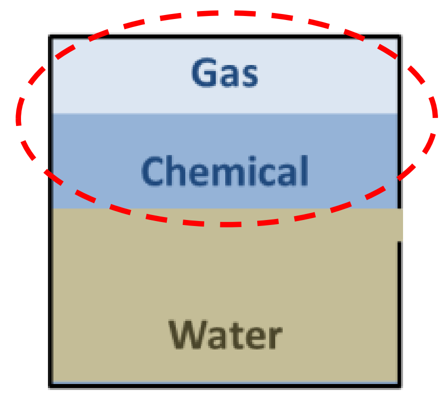


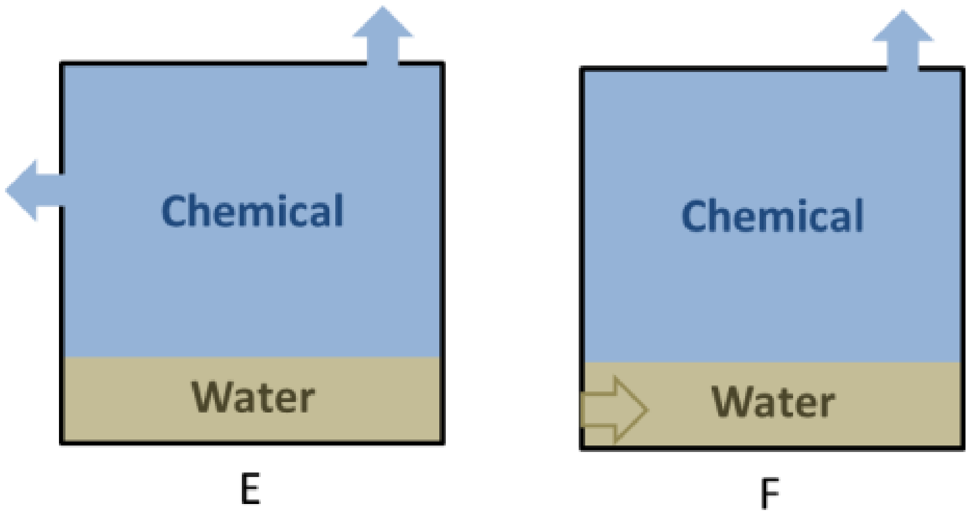
D

Understanding HNS behaviour in the marine environment

Characterization of the influence of orifice position

2. **Case of double hole with floating chemical**

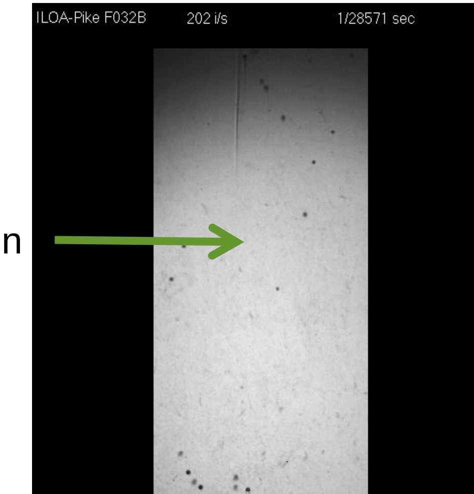
- **Same behaviours are observed but draining time is faster than single hole**
- **In bot case the leak will stop when the water level reaches the upper orifice**



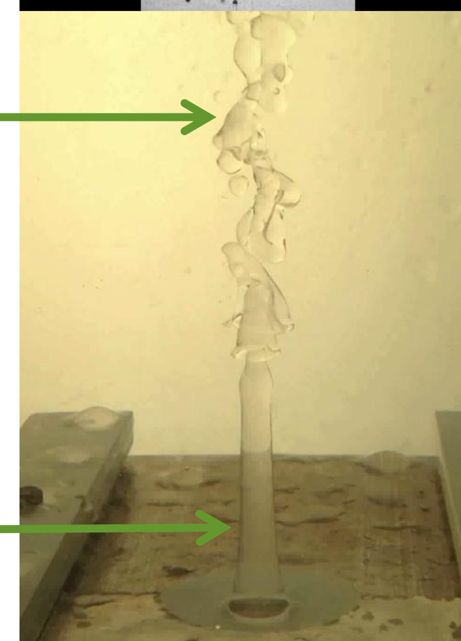
Understanding HNS behaviour in the marine environment

Source : Marine Nationale
Ievoli Sun leak (2000)

3. Droplet dissolution



2. Jet characteristics (droplet velocity and distribution)



1. HNS draining

Understanding HNS behaviour in the marine environment

1. HNS release at sea surface
    1. Liquid jet velocity
    2. Volumic flow rate at breach level

2. HNS release in the water column
    1. **Volumic flow rate at breach level**
    2. Droplet velocity in the water column
    3. HNS solubilisation in the water column

Flow rate modelling

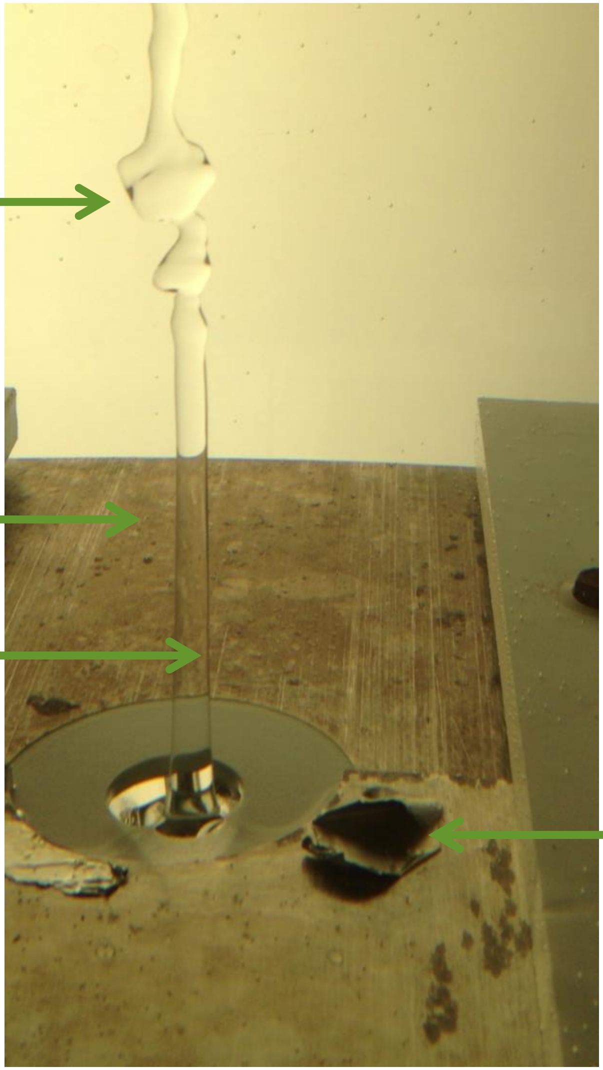
Draining theory

Chemical droplets

Chemical liquid jet

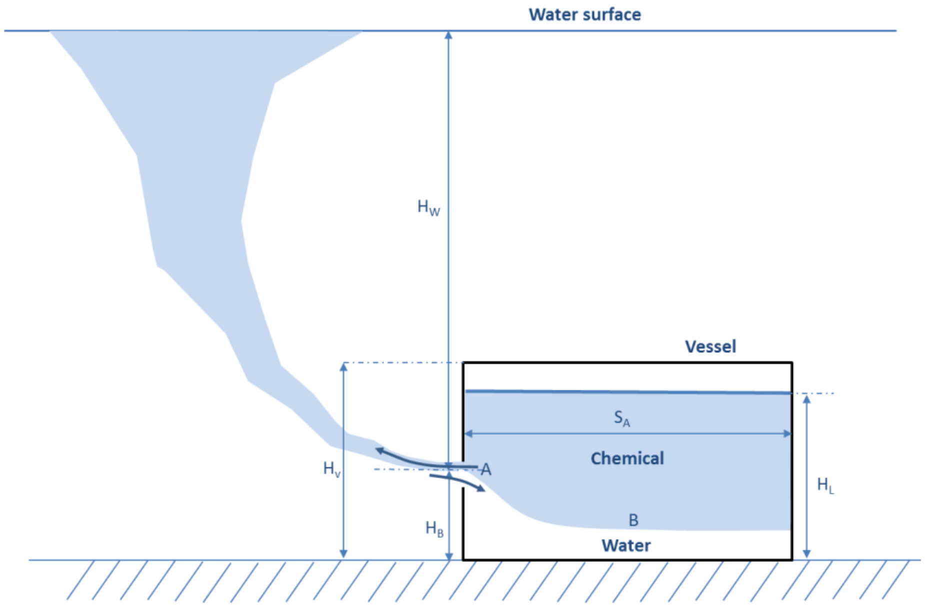
Water liquid jet

Water/chemical interface



Flow rate modelling

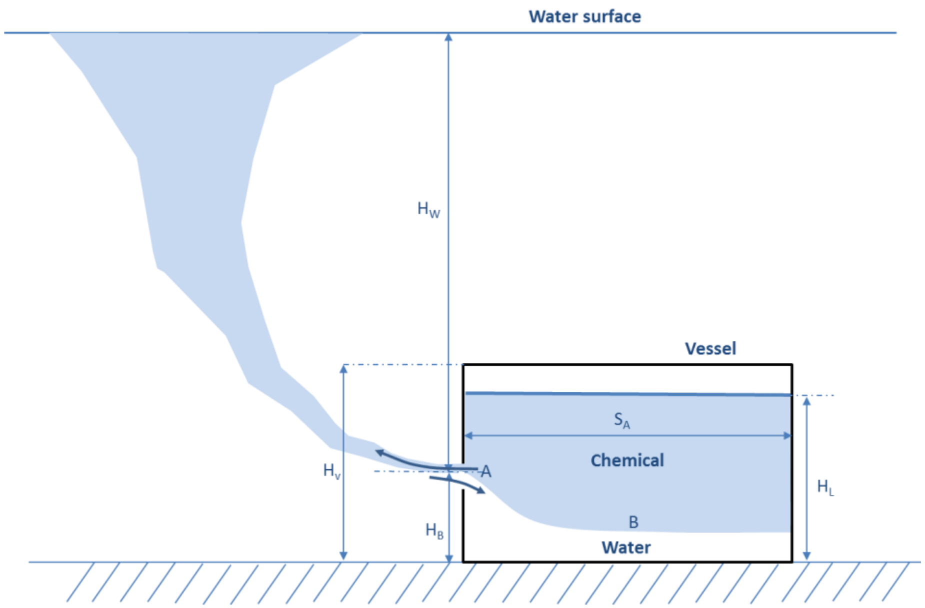
Draining theory



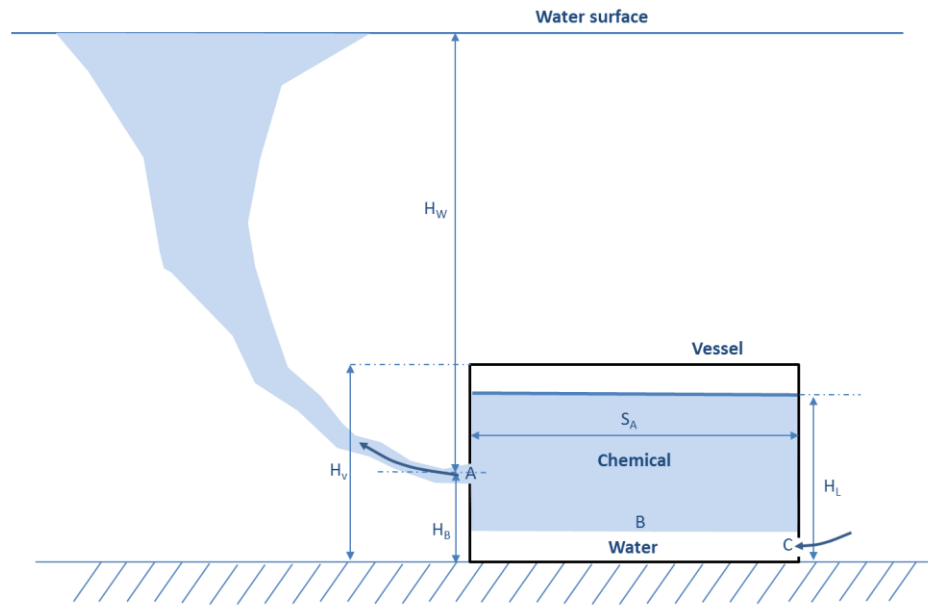
Floating chemical – 1 holes

Flow rate modelling

Draining theory



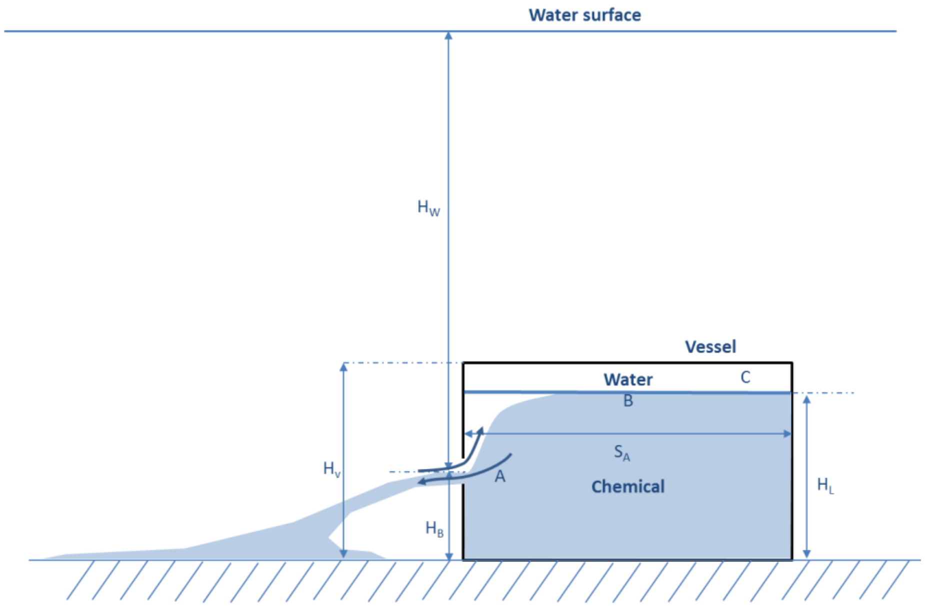
Floating chemical – 1 holes



Floating chemical – 2 holes

Flow rate modelling

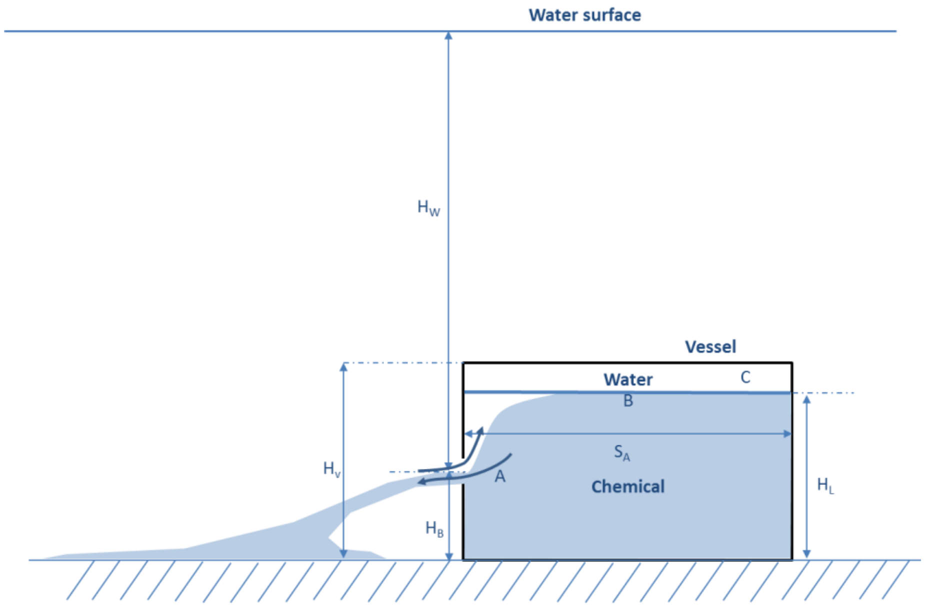
Draining theory



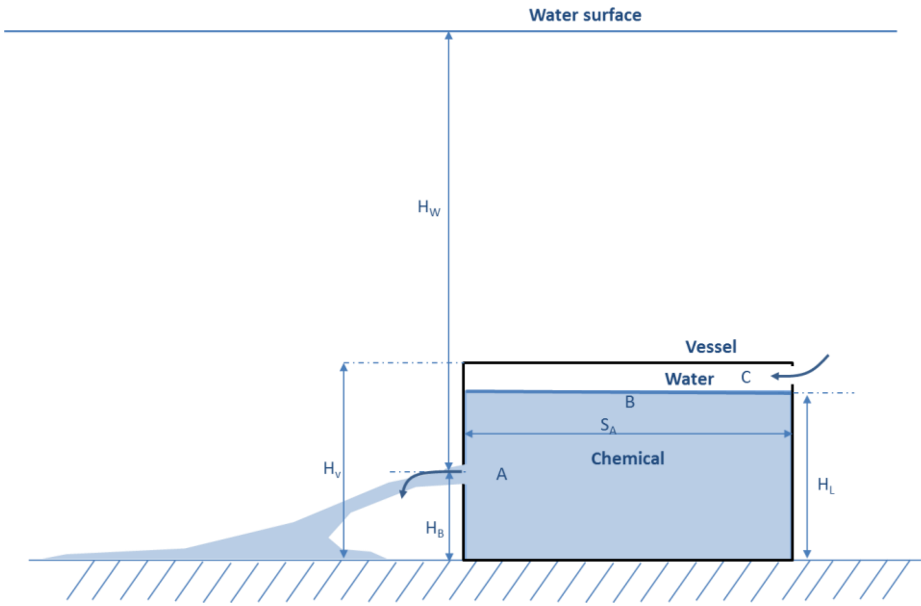
Sinking chemical – 1 holes

Flow rate modelling

Draining theory



Sinking chemical – 1 holes



Sinking chemical – 2 holes

Flow rate modelling

Draining theory

In all cases, the determination of the leakage rate requires an estimation of :

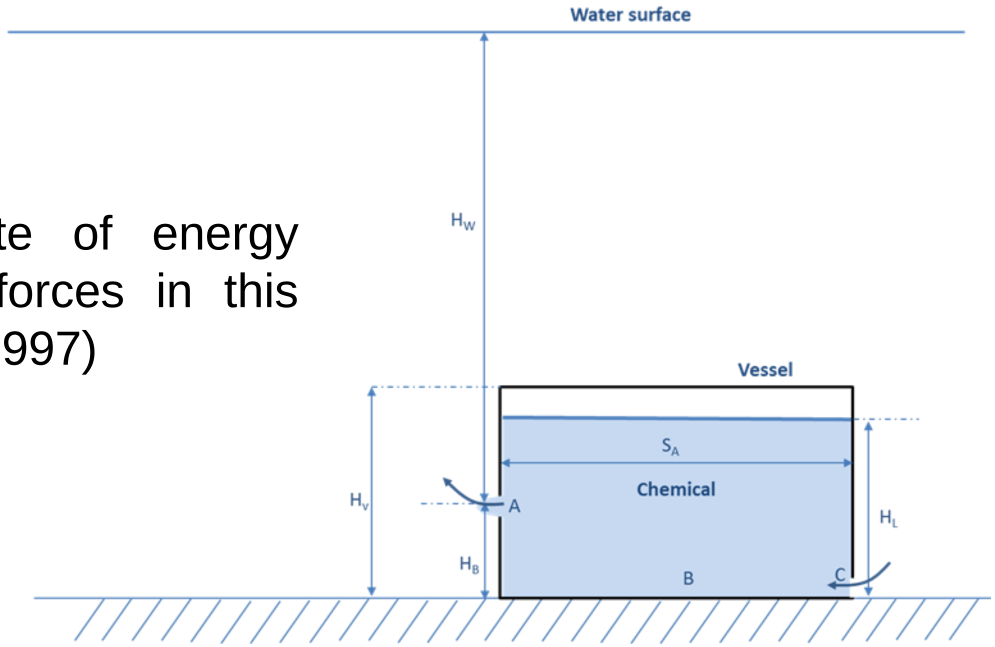
- The orifice(s) location(s)
- The orifice dimensions (diameter, length, width,…)
- The initial volume of chemical inside the vessel
- The vessel size
- The chemical properties

Flow rate modelling

Draining theory

- Draining vessel is calculated with the Bernoulli principle derived from the principle of conservation of energy

$$\frac{1}{2}\rho_d v_A^2 Q - \frac{1}{2}\rho_c v_C^2 Q + P_A Q - P_C Q = \rho_c g(H_V - h_L)Q - \rho_d g h Q - \dot{W}$$



$\dot{W}$ Represents the total rate of energy dissipated by the viscous forces in this system→ Dugdale's model (1997)

$$\dot{W} = p.Q = \frac{C\mu Q^2}{{r_0}^3}$$

Flow rate modelling

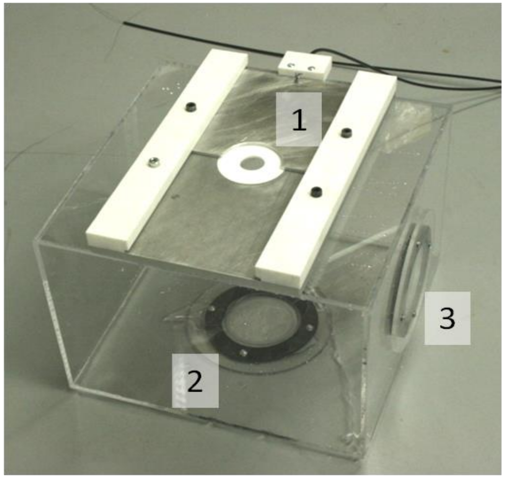
Experimental Setup

- Tests performed in the Cedre Experimental Column
- Stainless steel and glass hexagonal column of :
  - 5m of height
  - 0.8m of diameter
  - 2.8 m^3 of water (fresh or sea water)

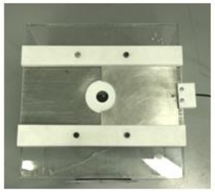
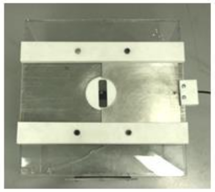
Flow rate modelling

Experimental Setup

- Tests performed in the Cedre Experimental Column
- Release system located at the bottom of column to measure flow rate at breach level
    - Various orifices diameters and shapes



Release Vessel

Orifice diameter (mm)	Shape
6	Round 
13	
20	
30	
40	
50	
60	
10x70	Rectangle 
20x70	

Experimental setup

CEC experiments – Droplets size an velocity distribution

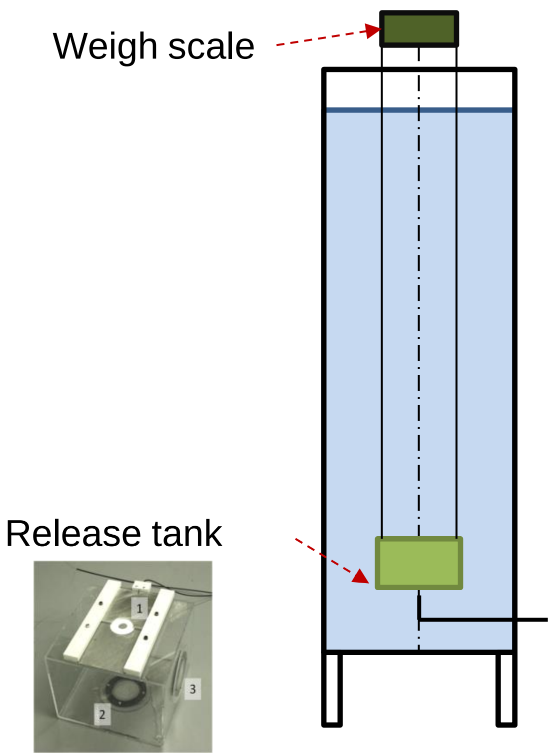
– Tests performed with various chemicals in seawater and fresh water

Chemical (T=20°c)	Density ($kg.m^{-3}$)	Dynamic Vicosity (Pa.s)
Silicon oil (Rhodorsil 47V5)	910	$4.50\ 10^{-3}$
Silicon oil (Rhodorsil 47V20)	950	$19\ 10^{-3}$
Silicon oil (Rhodorsil 47V50)	959	$48\ 10^{-3}$
DEHA (Bis(2-ethylhexyl)adipate	922	$13.2\ 10^{-3}$

Flow rate modelling

Results

- Mass flow rate vs. time for each fluids and configurations



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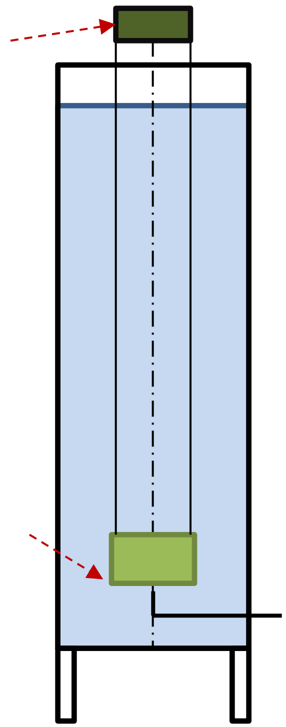
Flow rate modelling

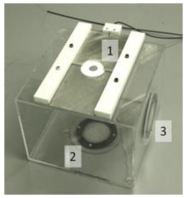
Results

- Mass flow rate vs. time for each fluids and configurations

Weigh scale



Release tank

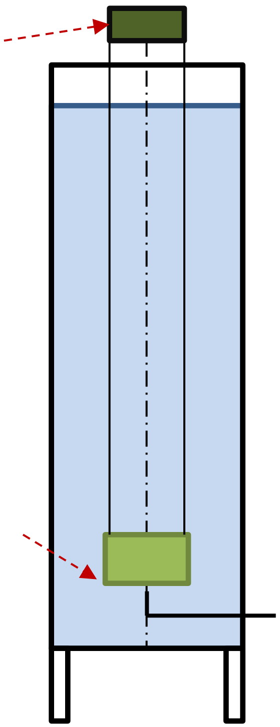


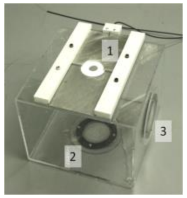
Test #	Top orifice diameter mm	Down orifice diameter mm	Release flow rate $m^3.s^{-1}$
1	40	/	$2,5.10^{-5}$
2	60	/	$9,0.10^{-5}$
3	10x70	/	$5,9.10^{-5}$
4	20x70	/	$3,5.10^{-5}$
5	30x70	/	$5,0.10^{-5}$
6	20	13	$2,9.10^{-5}$
7	30	13	$2,9.10^{-5}$
8	60	13	$1,0.10^{-4}$
9	13	30	$3,5.10^{-5}$
10	40	30	$1,7.10^{-4}$
11	60	30	$1,6.10^{-4}$
12	6	100	$7,1.10^{-6}$
13	20	100	$8,6.10^{-5}$
14	10x70	100	$2,1.10^{-4}$

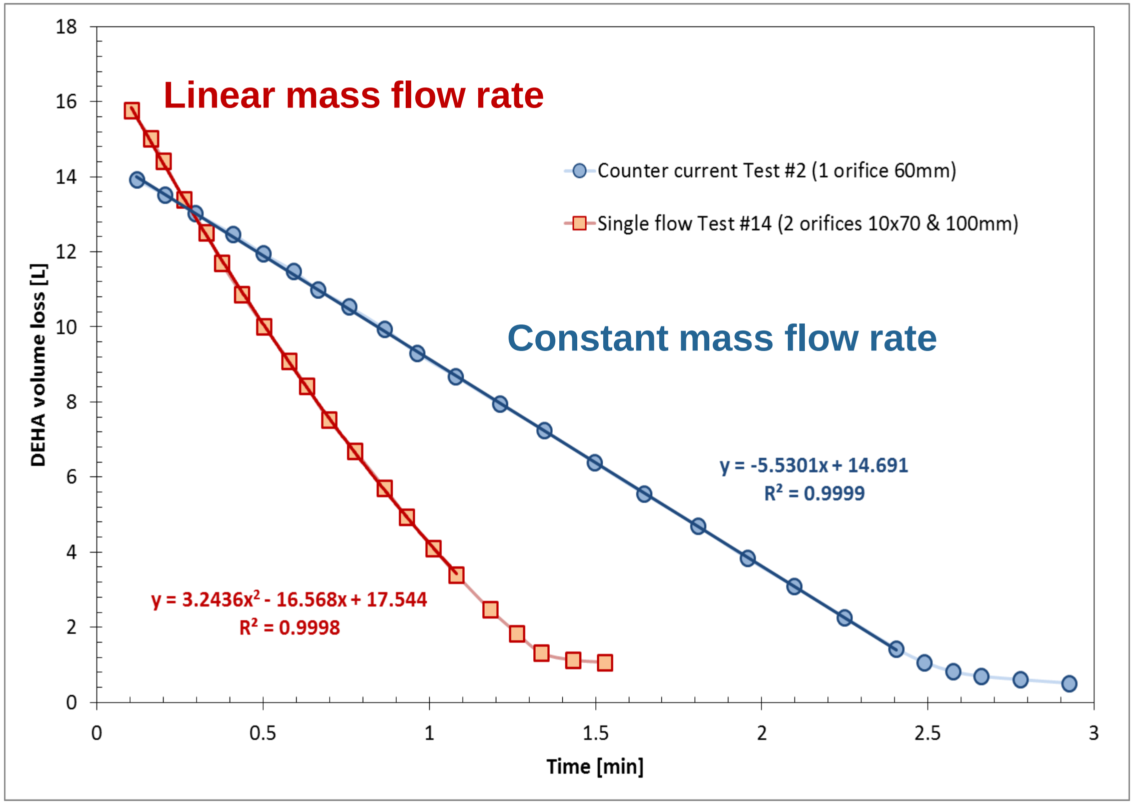
Flow rate modelling

Results

- Mass flow rate vs. time for each fluids and configurations







Flow rate modelling

Results

Dugdale's constant measurements

- Two different behaviours depending on fluid viscosity

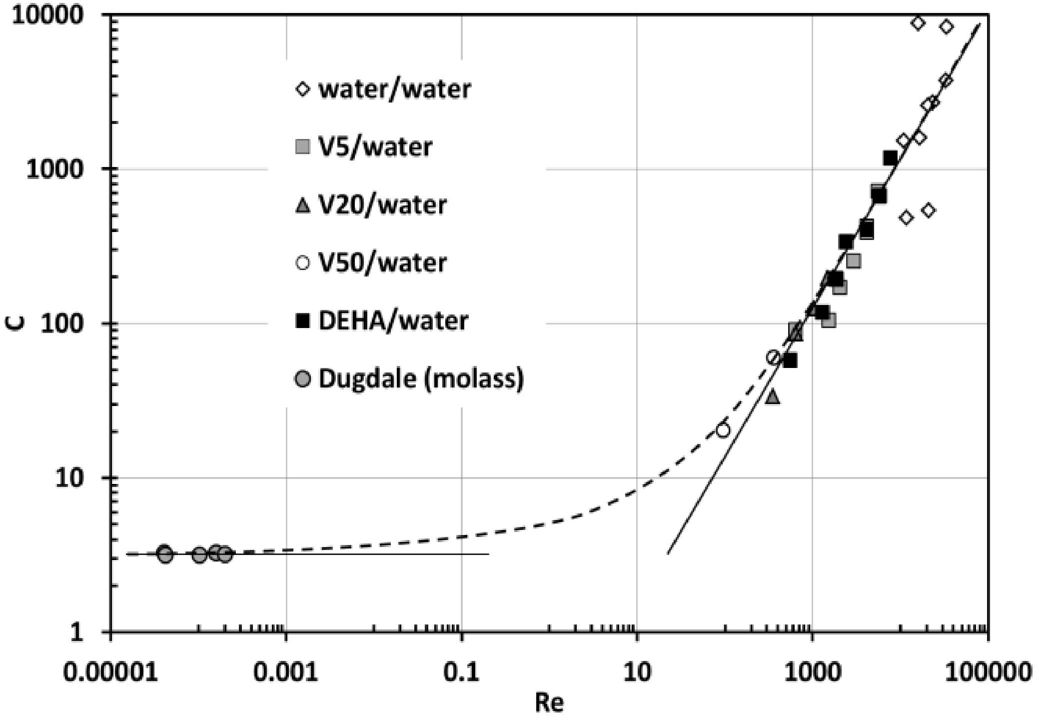
$$\dot{W} = p.Q = \frac{C\mu Q^2}{{r_0}^3}$$

For Re<1

C=3.2

For Re>1

$C=0.14\ Re^{0.95}$

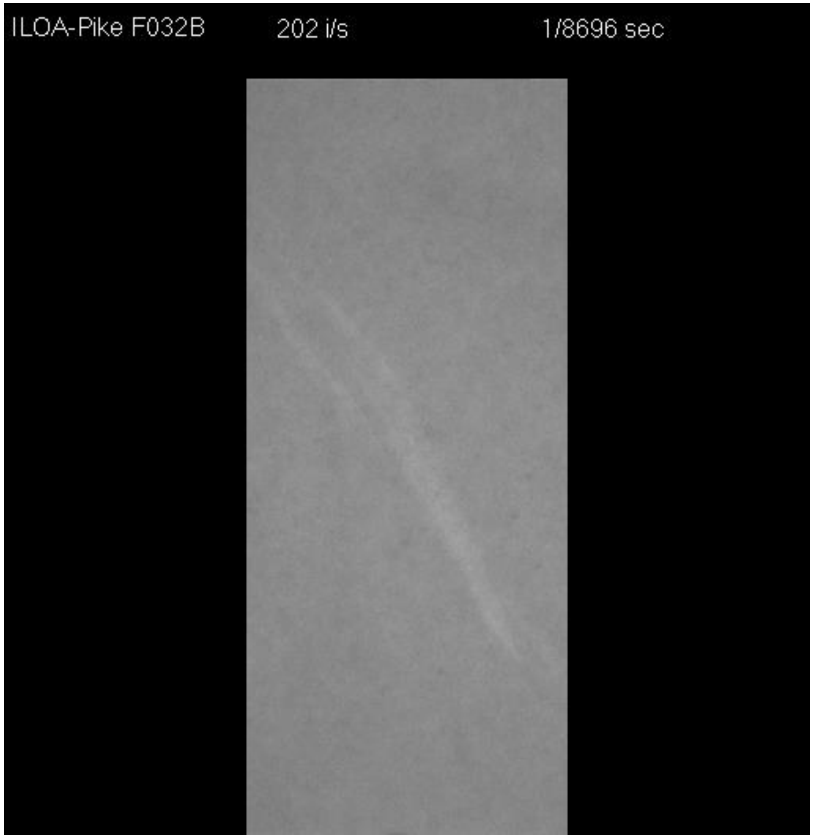


Understanding HNS behaviour in the marine environment

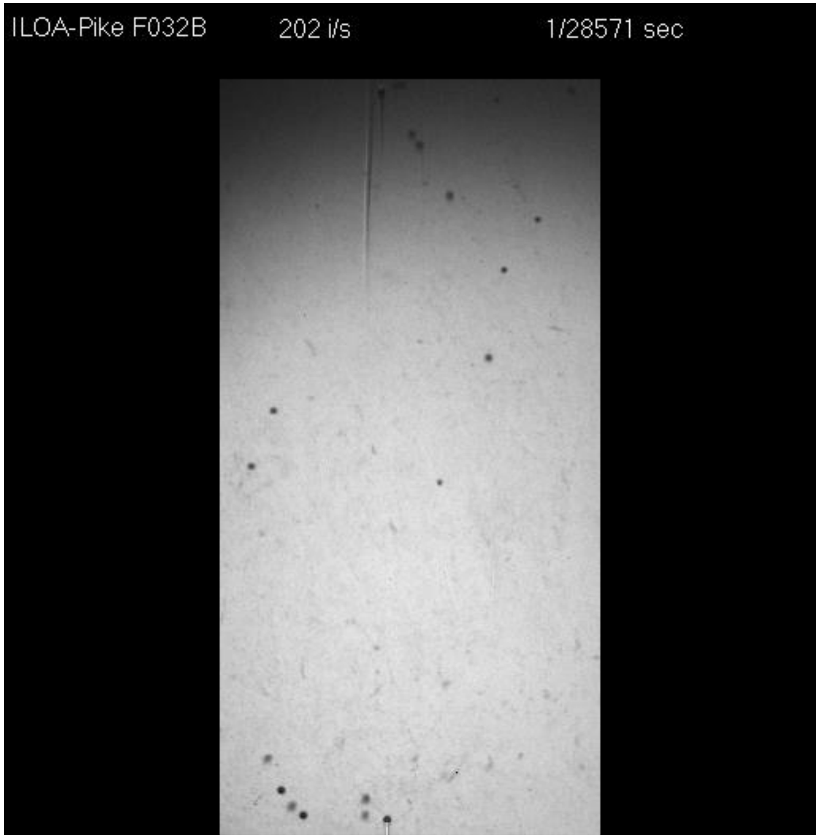
1. HNS release at sea surface
    1. Liquid jet velocity
    2. Volumic flow rate at breach level
2. HNS release in the water column
    1. Volumic flow rate at breach level
    2. **Droplet velocity in the water column**
    3. HNS solubilisation in the water column

Droplet velocity

Droplet behaviour: butanol droplet (1.8mm of diameter and 9cm/s)



Diffuse Light



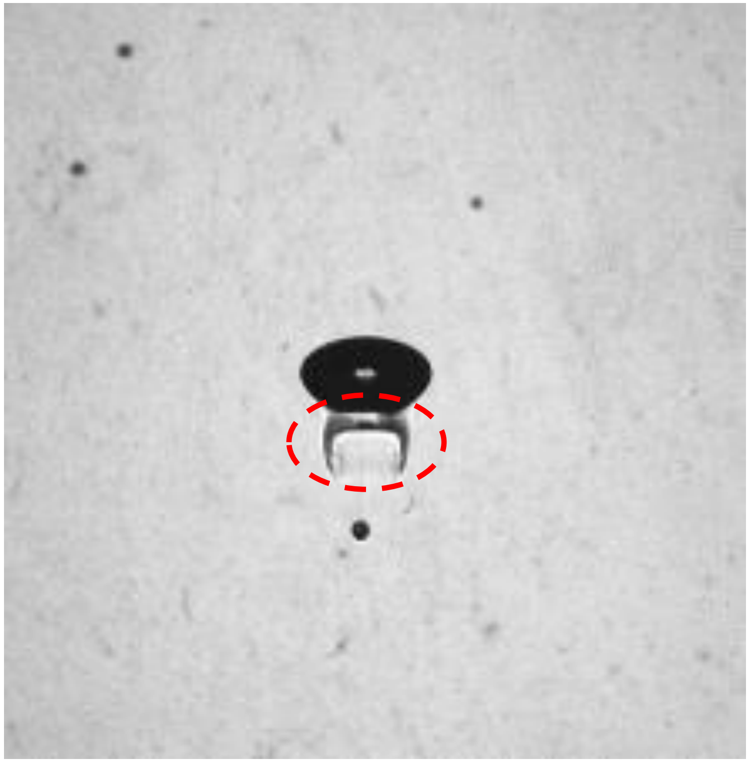
Collimated Light

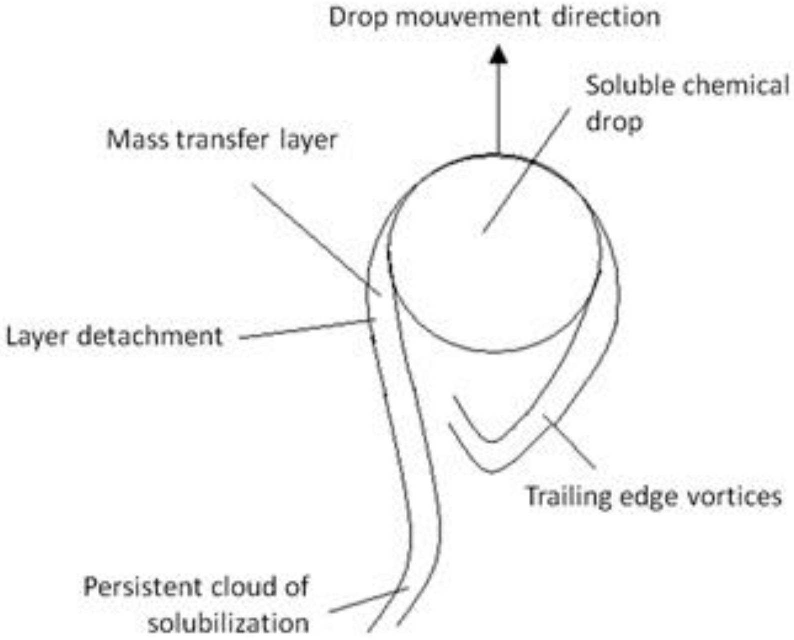
Co-funded by the European Commission, DG-ECHO

Droplet velocity

Droplet behavior

- Visualisation of the solubilisation proccess in the wake of the droplet with a pair of vortices
- Visualization of turbulences and recirculation cells





Droplet velocity

Theory

- Droplet velocity calculated using ellipsoidal shape regime

$$Mo < 10^{-3};\ Eo < 40;\ Re > 0{,}1$$

$$v = \frac{\mu_c}{\rho_c d} Mo^{-0.149}(J - 0{,}857)$$

$$Avec \quad \begin{cases} J = 0{,}94H^{0{,}757} & 2 < H \leq 59{,}3 \\ J = 3{,}42H^{0{,}441} & H > 59{,}3 \end{cases}$$

$$Et \quad H = \frac{4}{3} Eo Mo^{-0.149} \left(\frac{\mu_c}{\mu_w}\right)^{-0{,}14} \qquad avec\ \mu_w = 0{,}9\ mPa.s$$

- μ_c= dynamic viscosity of continue phase
- μ_w= dynamic viscosity of water
- rc= density of continue phase
- Mo = Morton number
- Eo = Eötvos number

Droplet velocity

Experimental setup

- Tests performed in the Cedre Experimental Column
- Small injection system to measure solubilisation process
  - Round nozzle diameter of 5 mm of diameter
  - Volumetric flow rate between 100 – 300 $mL.min^{-1}$

Droplet velocity

Experimental setup

– Tests performed with various chemicals in seawater

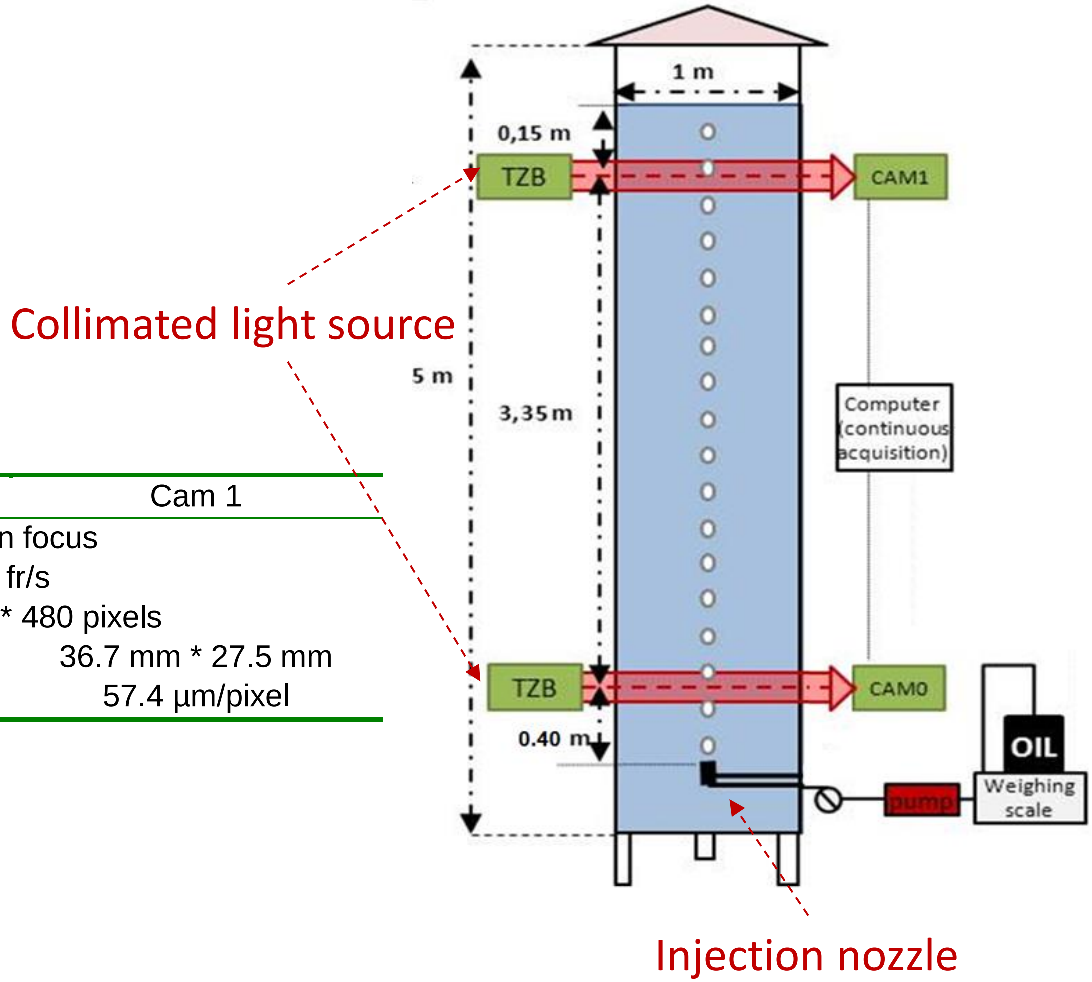
Chemical (T=20°c)	Density ($kg.m^{-3}$)	Dynamic Vicosity (Pa.s)
n-butanol	810	$3.08\ 10^{-3}$
Methyl isobutyl ketone	800	$7.6\ 10^{-4}$
Methyl methacrylate	940	$6\ 10^{-4}$
Ethyl acetate	902	$4.09\ 10^{-4}$
Methyl ter butyl ether	740	4.710^{-4}

Droplet velocity

Experimental setup

- Droplets velocities measured at 2 levels by video camera
- Shadowgraphy technique

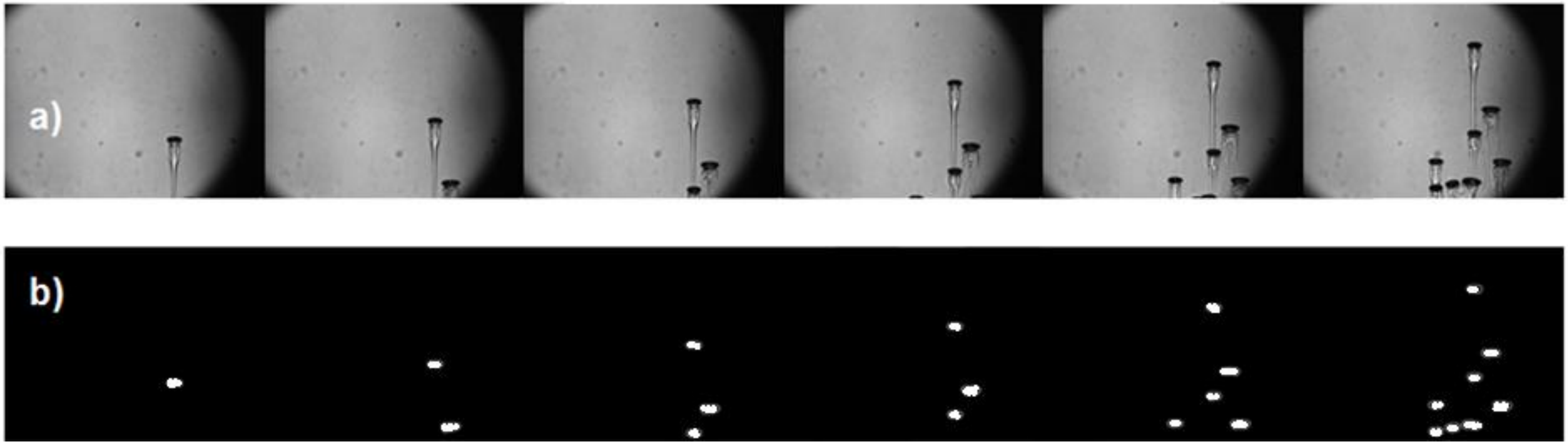
	Cam 0	Cam 1
Video camera	Photon focus	
Frame rate	20 fr/s	
Sensor area	640 pixels * 480 pixels	
Region of interest	40.9 mm * 30.7 mm	36.7 mm * 27.5 mm
Magnification	63.9 µm/pixel	57.4 µm/pixel



Droplet velocity

Experimental setup

- Each test was recorded during about 1 min, and the results are in a sequence of images of the droplets in the seawater
- Each sequence of images is processed to locate and track the droplet (detection of differences of gray level)
- Measurements of droplets mean velocities between bottom to top of the water column



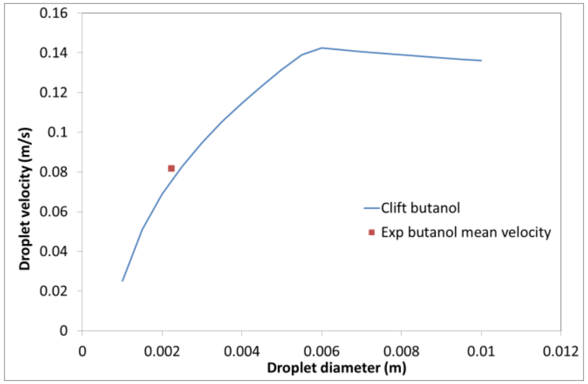
butanol rising droplet in seawater

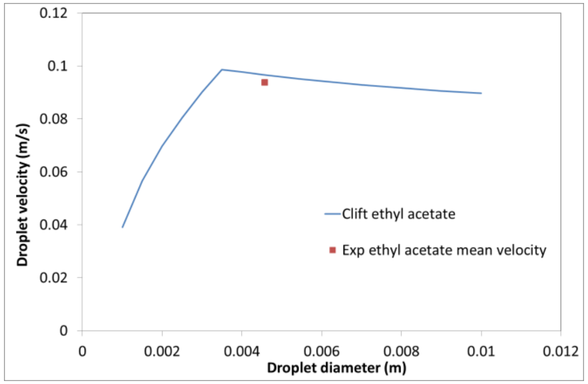
Co-funded by the European Commission, DG-ECHO

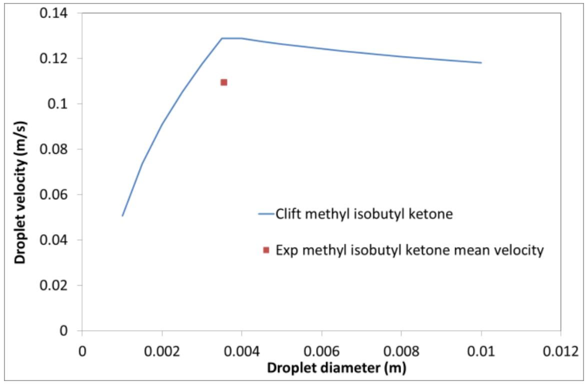
Droplet velocity

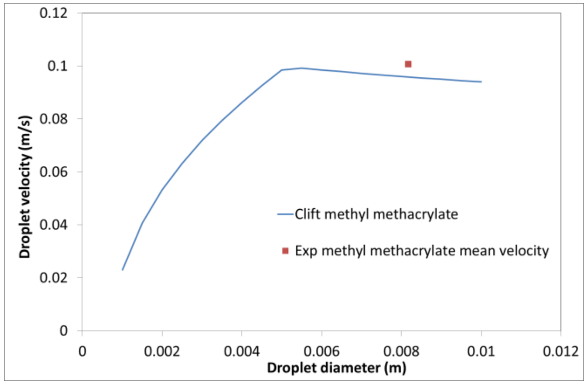
Results

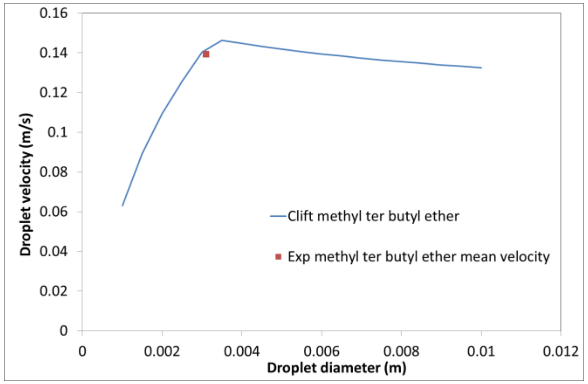
- Good agreement between Clift's model and experiments (<20%)
- Discrepancy due to wobbling droplet during rising and uncertainties on droplet diameter











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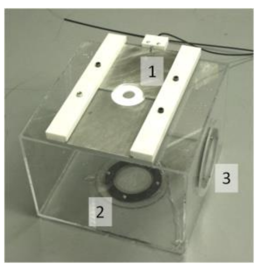
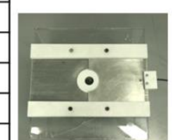
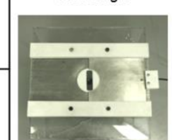
Flow rate modelling

Experimental Setup

- Tests performed in the Cedre Experimental Column
- Stainless steel and glass hexagonal column of :
  - 5m of height
  - 0.8m of diameter
  - 2.8 m^3 of water (fresh or sea water)



Orifice diameter (mm)	Shape
6	Round 
13	
20	
30	
40	
50	
60	
10x70	Rectangle 
20x70	

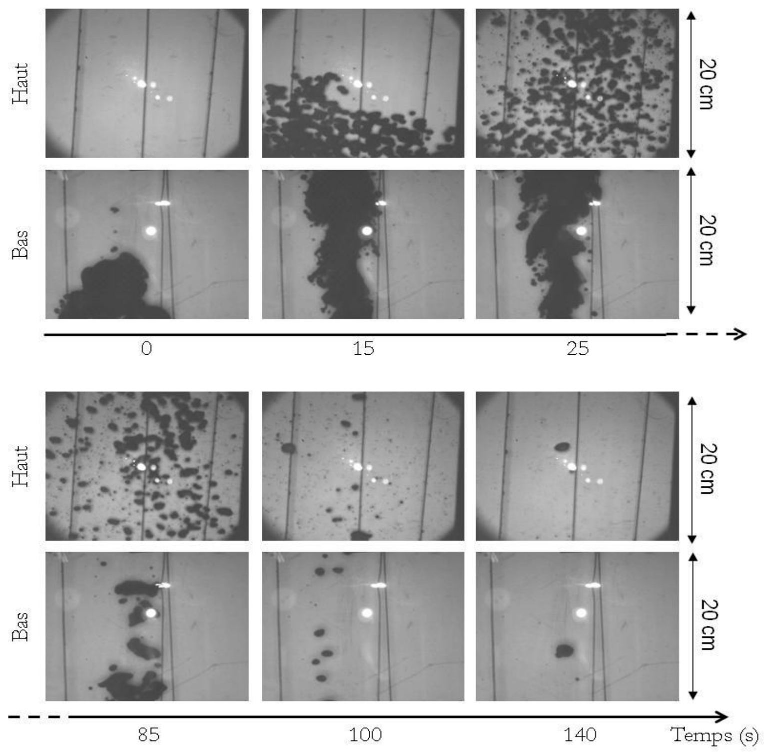
- Tests performed with DEHA

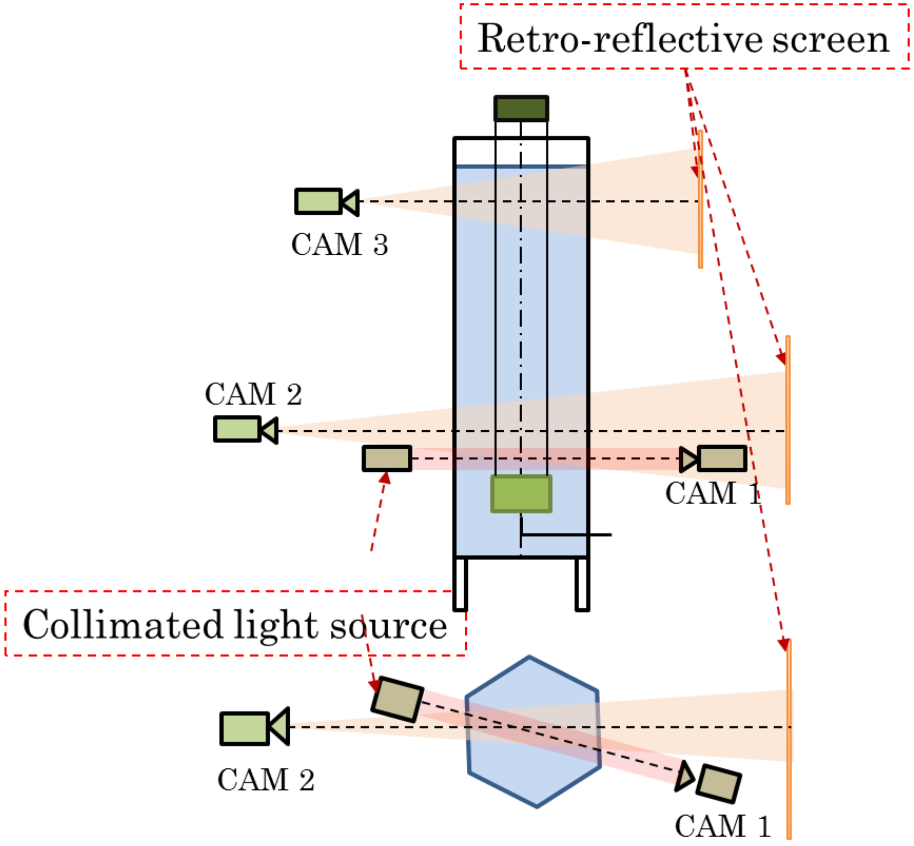
Chemical (T=20°c)	Density (kg.m^{-3})	Dynamic Vicosity (Pa.s)
DEHA (Bis(2-ethylhexyl)adipate	922	13.2 10^{-3}

Droplet velocity

Experimental setup

- Droplets size distribution measured at bottom and top of the column
- "Edgerton" retro-reflective shadowgraphy system





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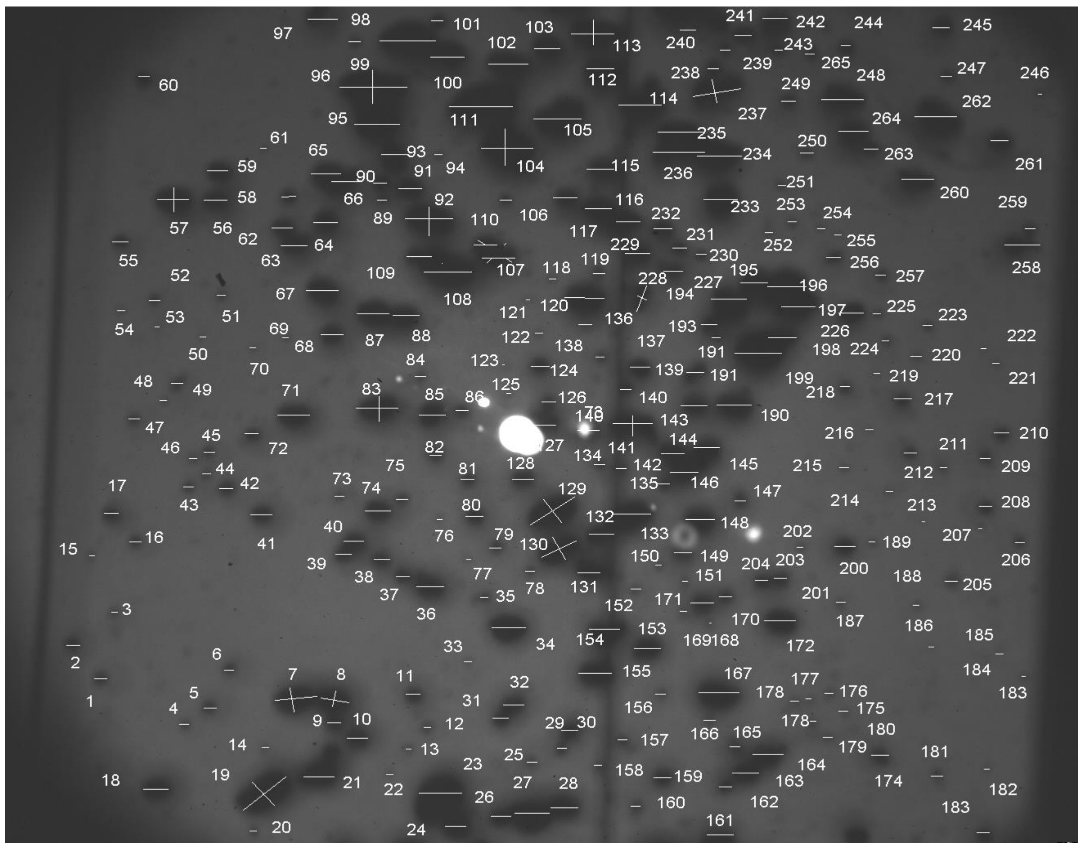
Droplet size distribution

CEC experiments – Droplets size an velocity distribution

- Handmade analysis on 100 uncorrelated images



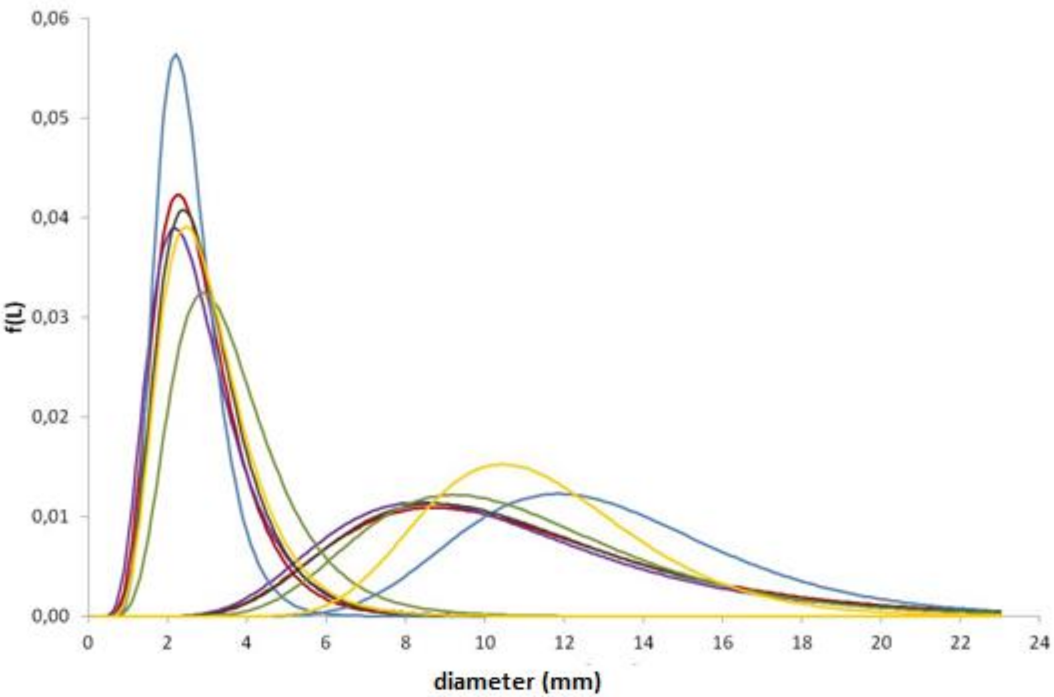
Droplet size distribution

Droplets Diameters

- All tests are characterized by mono modal or bi-modal distributions

$$f(D) = \frac{e^{-\frac{1}{2}\left(\frac{lnD-\mu}{\sigma}\right)^2}}{D\sigma\sqrt{2\pi}}$$

	$Q<10^{-4}\ m^3.s^{-1}$		$Q\geq10^{-4}\ m^3.s^{-1}$
μ	-5.69	-4.51	-5.3
σ	0.561	0.364	0.635

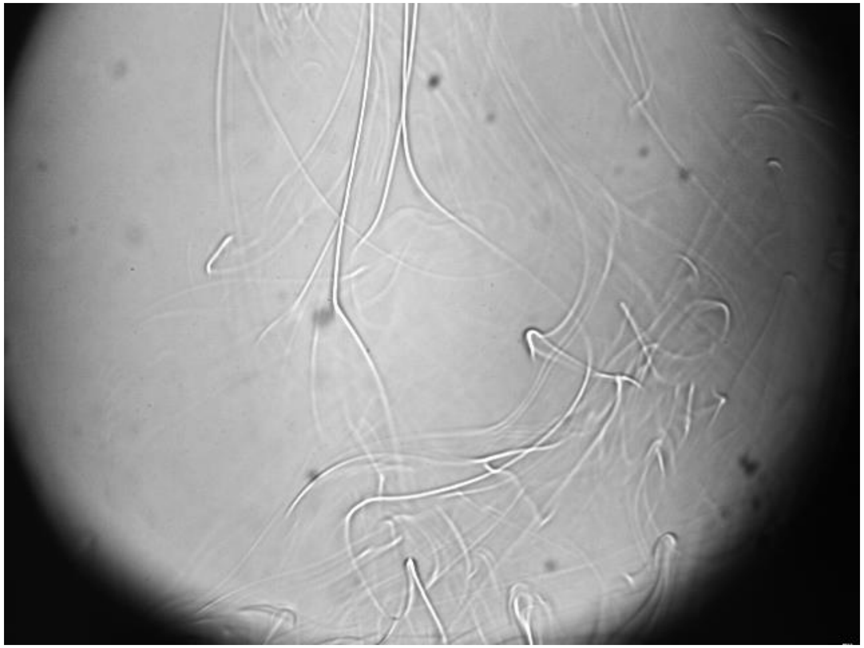


Understanding HNS behaviour in the marine environment

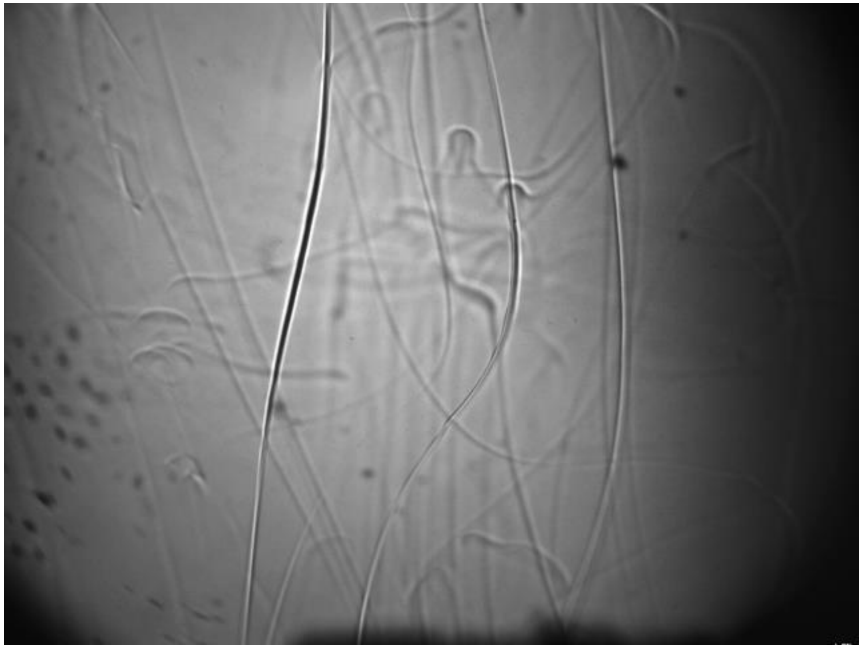
1. HNS release at sea surface
    1. Liquid jet velocity
    2. Volumic flow rate at breach level
2. HNS release in the water column
    1. Volumic flow rate at breach level
    2. Droplet velocity in the water column
    3. **HNS solubilisation in the water column**

Droplet solubilization

Behaviour



N-butanol bottom



N-butanol top

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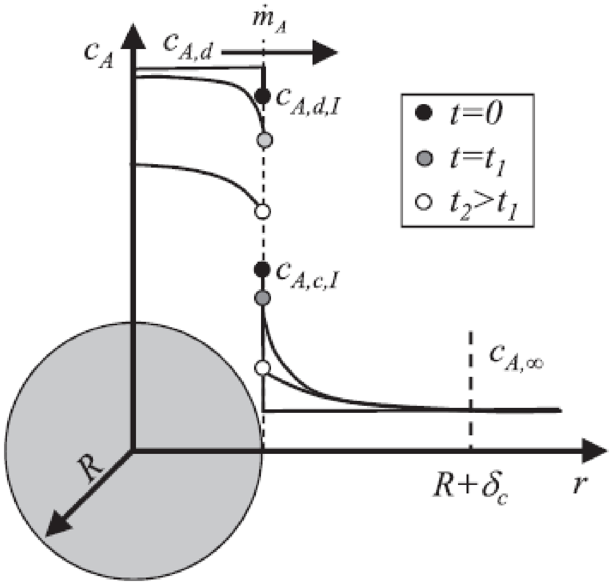
Droplet solubilization

Solubilization theory

- Two film theory (Wegener et al. 2014)

$$\dot{m}_A = k\,(C_{A,I} - C_{Ac,\infty})$$

$$Sh = \frac{kd}{D}$$



- m_A : mass flux, kg.m^{-2}.s-^{1}
- D : molecular diffusivity (m².s^{-1})
- k : mass transfer coefficient (m.s^{-1})
- d: droplet diameter (m)
- $C_{(A,I)}$: concentration of component A at interface (kg.m^{-3})
- $C_{(Ac,\infty)}$: concentration of component A in continuous phase (kg.m^{-3})

Droplet solubilization

Experimental setup

- Tests performed in the Cedre Experimental Column
- Small injection system to measure solubilisation process
  - Round nozzle diameter of 5 mm of diameter
  - Volumetric flow rate between 100 – 300 $mL.min^{-1}$

Droplet velocity

Experimental setup

– Tests performed with various chemicals in seawater

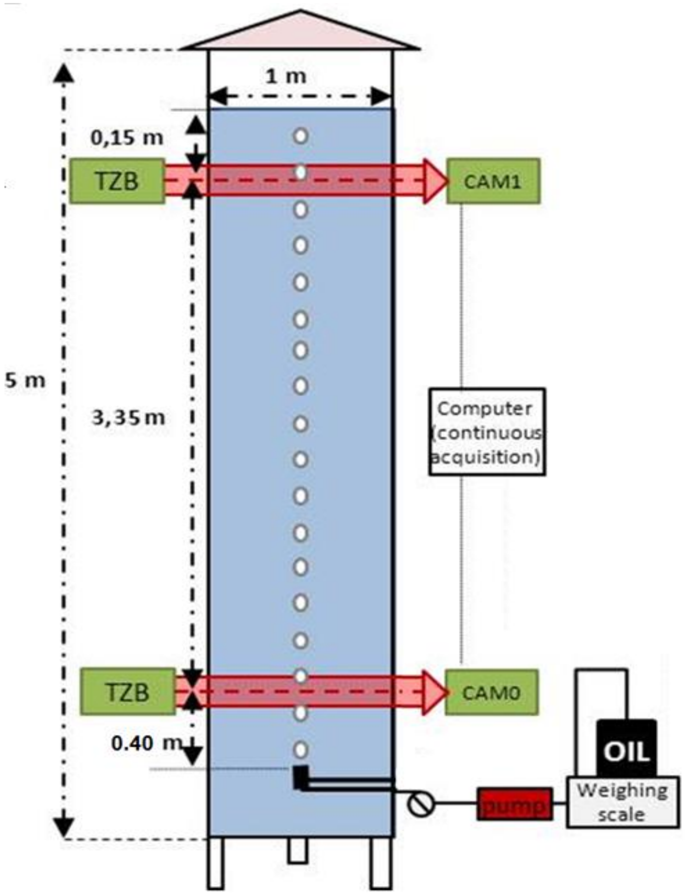
Chemical (T=20°c)	Density ($kg.m^{-3}$)	Dynamic Vicosity (Pa.s)
n-butanol	810	$3.08\ 10^{-3}$
Methyl isobutyl ketone	800	$7.6\ 10^{-4}$
Methyl methacrylate	940	$6\ 10^{-4}$
Ethyl acetate	902	$4.09\ 10^{-4}$
Methyl ter butyl ether	740	4.710^{-4}

Droplet solubilization

Experimental setup

- Same configuration as for droplet velocity
- Droplet diameter is calculated with the Waddel disk diameter d_W,
- Waddel disk diameter is defined as the diameter of the disk with the same area as the particle

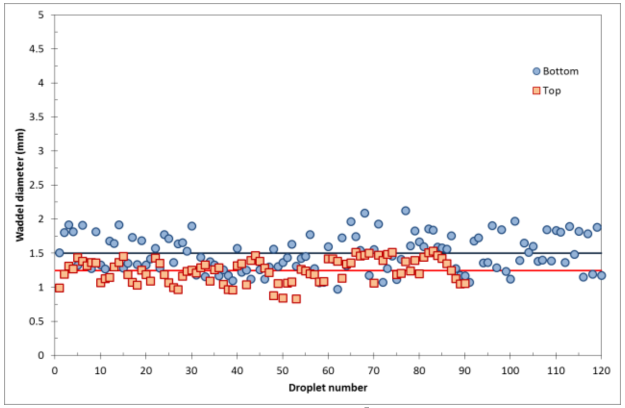
$$d_W = 2.\sqrt{\frac{droplet\ area}{\pi}}$$



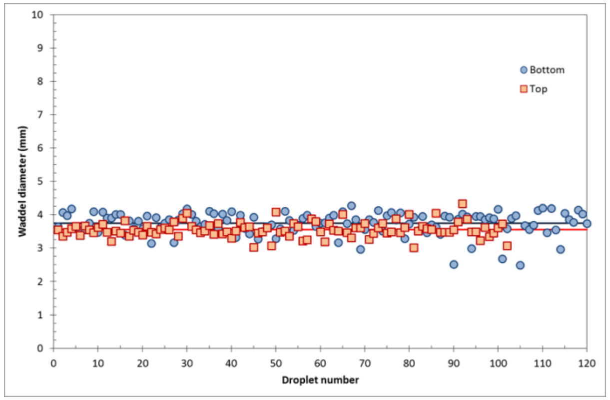
Droplet solubilization

Results

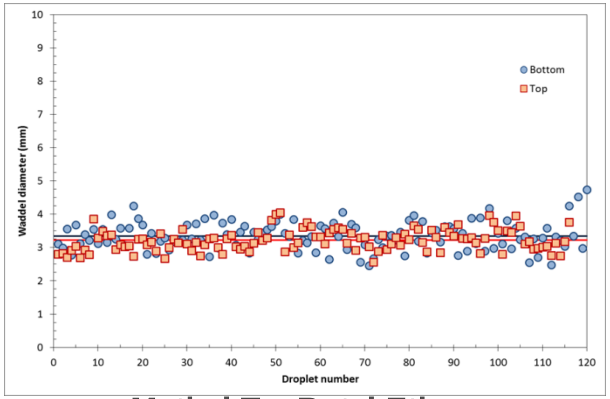
- Decrease of droplets diameters between bottom and top of the column



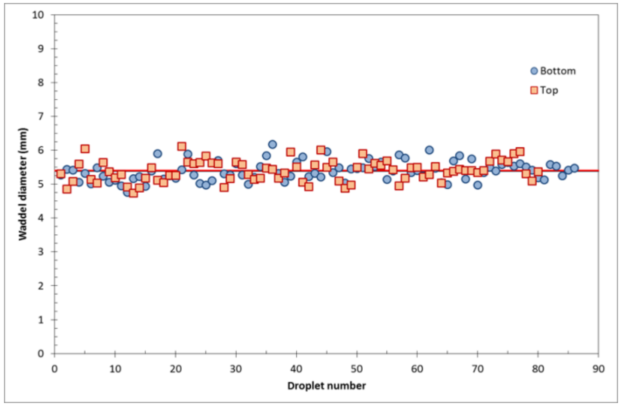
Butanol



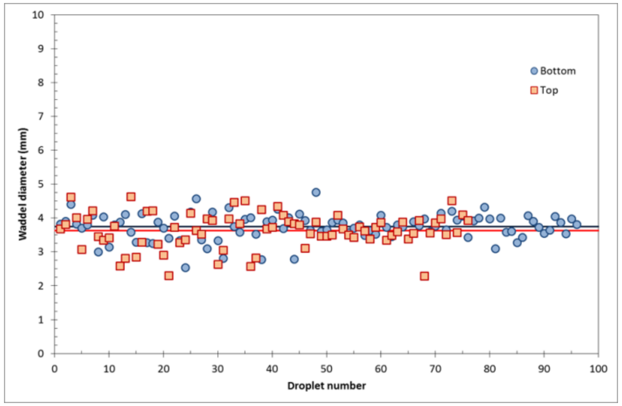
Ethyl acetate



Methyl Ter Butyl Ether



Methyl Metacrylate

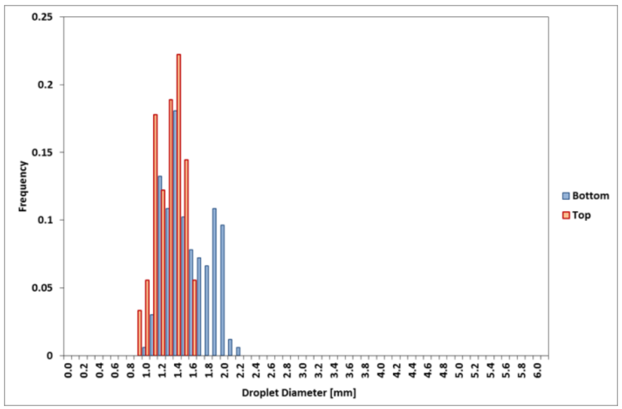


Methyl Isobutyl Ketone

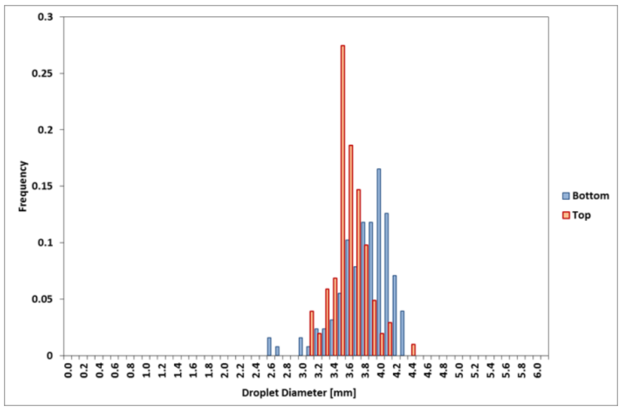
Droplet solubilization

Results

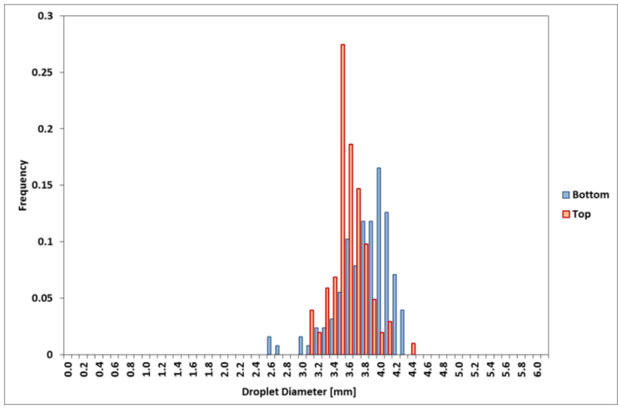
- Decrease of droplets diameters between bottom and top of the column



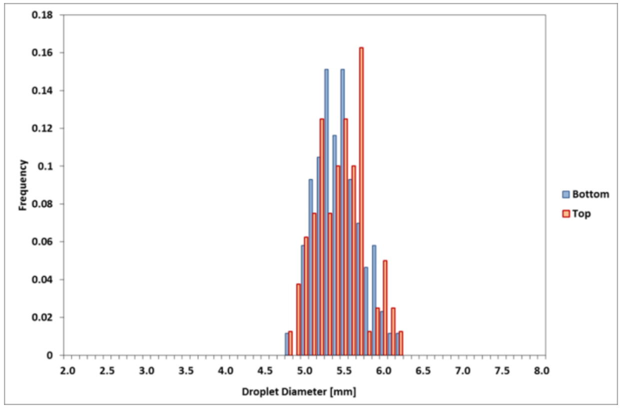
Butanol



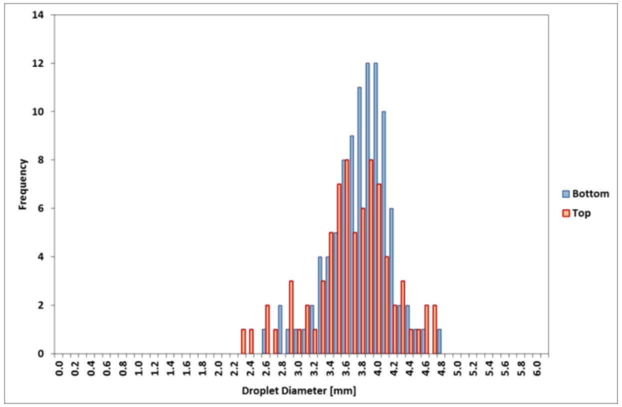
Ethyl acetate



Methyl Ter Butyl Ether



Methyl Metacrylate



Methyl Isobutyl Ketone

Droplet solubilization

Results

- The volume variation is calculated assuming the droplet as a spherical particle.
- The direct comparison with the hydrosolubility value clearly shows no logical link with this parameter
- The values of the solubility measurements from freshwater are not representative of the behavior of chemical in seawater.

Chemical	n-butanol	Ethyl acetate	Methyl Metacrylate	Methyl Isobutyl Ketone	Methyl Ter Butyl Ether
Hydrosolubility at 20°C [$g.L^{-1}$]	77	86	16	18	48
Variation of Waddel diameter along the water column	17.1%	5.1%	0%	2.9%	3.6%
Variation of mean droplet volume along the water column	46%	16%	0%	6%	12%

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Conclusions

- **This study is a contribution to the characterization of chemicals behaviors in seawater due to marine accident.**

- **Experimental tests were performed at large laboratory scale in a seawater column (CEC) to investigate the mass transfer process for various chemical release.**

- **The first part presents the drain of a chemical tank immerged in the CEC and filled with Di ethyl exyl adipate (DEHA).**

- **Two different behaviours were observed corresponding to different scenarios (one or two break in the vessel) and average volumic flow rates were estimated**

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Conclusions

- **The second part of the project focuses on the characterization of the mass transfer process for n-butanol, ethyl acetate, methyl ter butyl ether, methyl methacrylate and methyl isobutyl ketone release in seawater**

- **In comparison with the SEBC method this study is more representative of in-situ release and tends to better estimate the chemical mass reaching the surface**

- **From a global scale, droplets diameters were measured and clearly show a decrease for the majority of the chemical tested**

- **The comparison of measurements with Clift's correlation for droplet rising velocity shows a good agreement for average data**

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Future works

- New experiments with other chemicals to sharply determine the rising velocity and mass transfer rate for massive release,
- Propose adapted mass transfer depending on fluid physico-chemical properties
- Development of a new law of droplet size distribution valid as a function of the interfacial tension
- Development of ne optical method to precisely measure the interfacial tension in seawater

Thank you for your attention

{HNS-MS}

Improving Member States preparedness to face an HNS pollution of the Marine System (HNS-MS)

http://www.hns-ms.eu/

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