19th Cedre Information Day

Accidental pollution by HNS

Overview of Research on Chemical Substances

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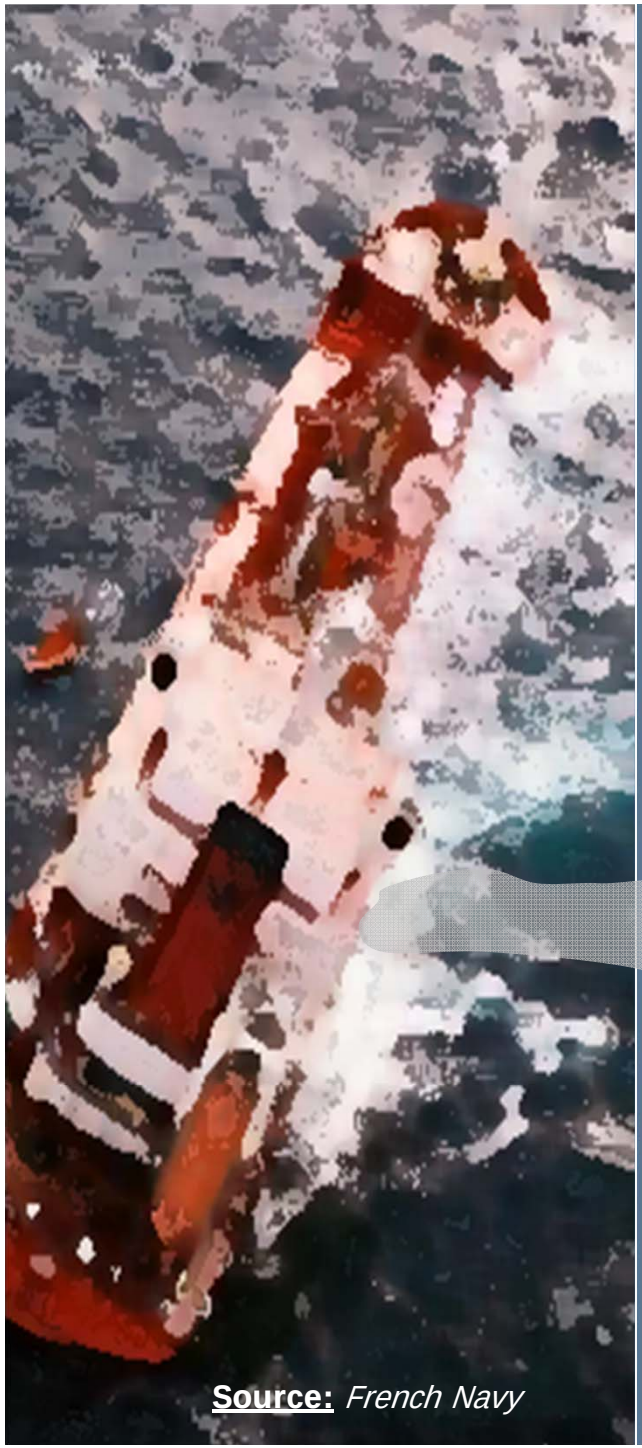


Research interests

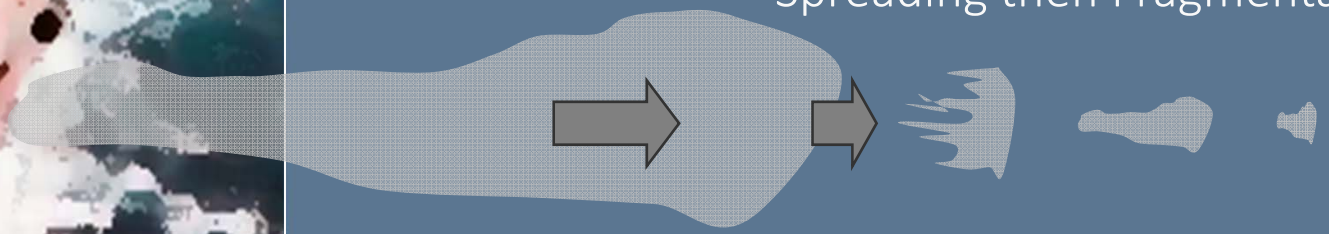
Chemical products in the marine environment:

✓Behaviour (reactivity, transfer)

✓Toxicity

Examples of floating products

Spreading then Fragmentation

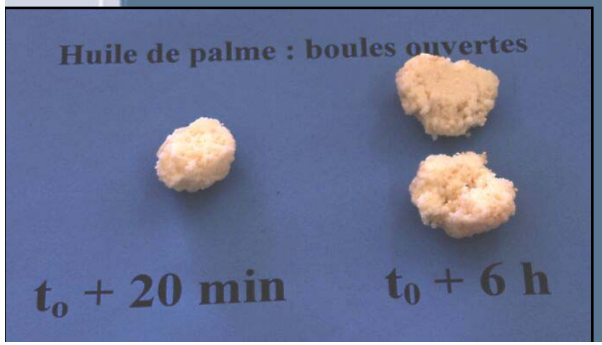


ALLEGRA (1997)

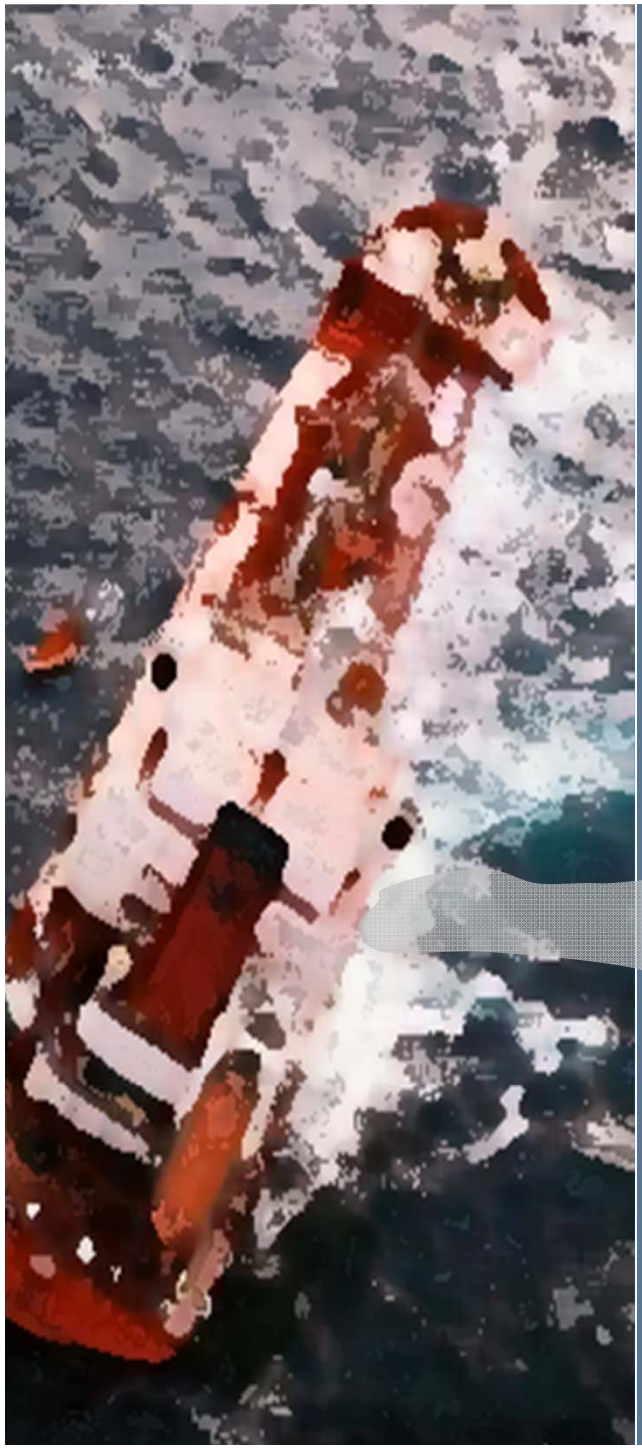
Type of pollutant: Palm kernel oil
Quantity transported: 15,000 tonnes
Quantity spilled: 900 tonnes of palm kernel oil
Quantity recovered: 30 tonnes (manually, trawling)

- Impact on the ecosystem (birds, benthos etc.)
- Diversity of vegetable oils = Fp, F, FD and FE etc.
- Is a response possible (containment and recovery, trawling, dispersant etc.)?

Variety of persistent floating products (viscosity, surface tension etc.) and existence of products that can solidify



Brindisi incident (2002)
MDI (or Diphenyl methane diisocyanate)



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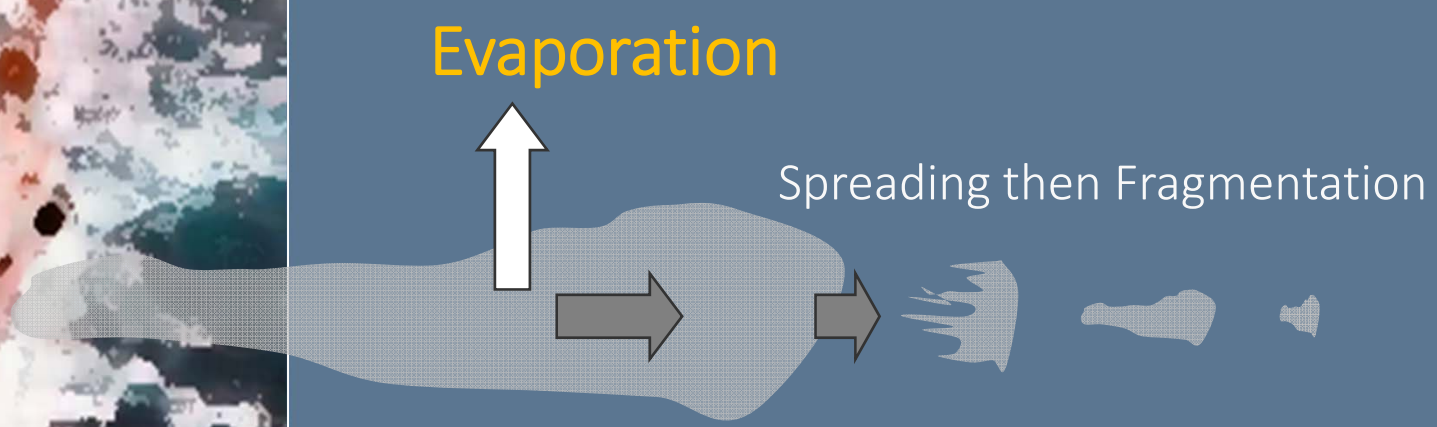

BOW EAGLE (2002)

Source: *French Navy*

A tank containing cyclohexane was breached, the product was gradually released into the sea.

Fate and associated risks?

Density = 0.8 ➡ Solubility = 55 mg/L < 0.1% ➡ Vapour pressure = 12.7 kPa at 20°C > 3 kPa ➡ Vapour density / in air 2.9

Risk associated with a toxic cloud (cyclohexane is neurotoxic)

The French maritime authorities instructed the vessel to moor 5 NM from the port of Dunkirk while the evaporation process finished, the vessel then went on to Rotterdam.

How does a gas cloud form from a slick? What is its fate? How is it influenced by weather conditions?

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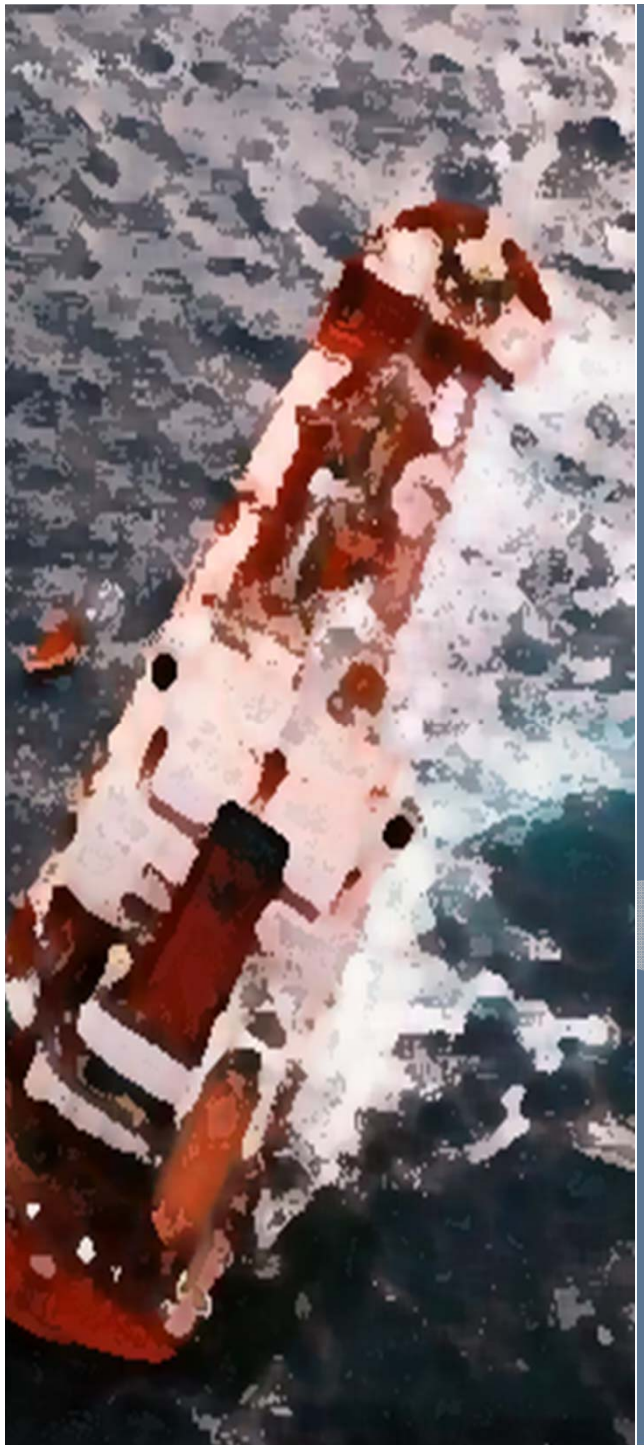

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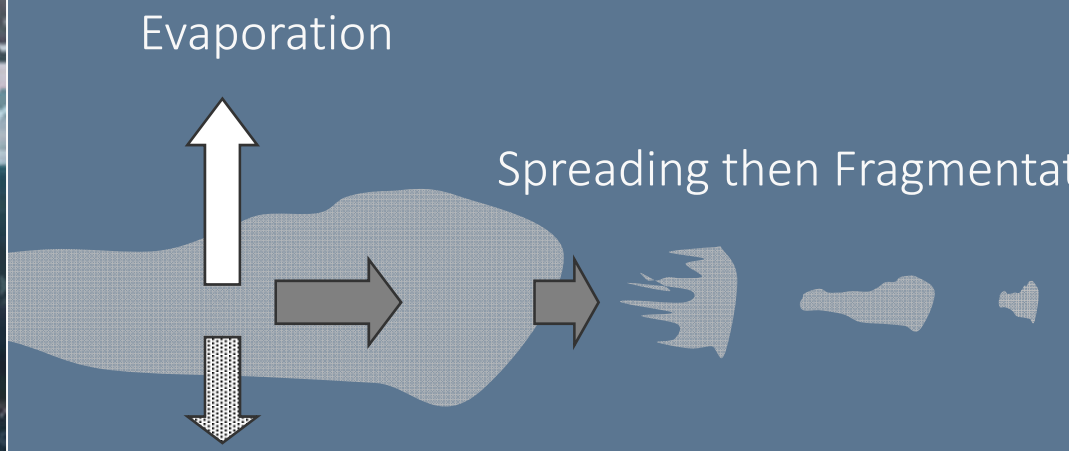


Dissolution

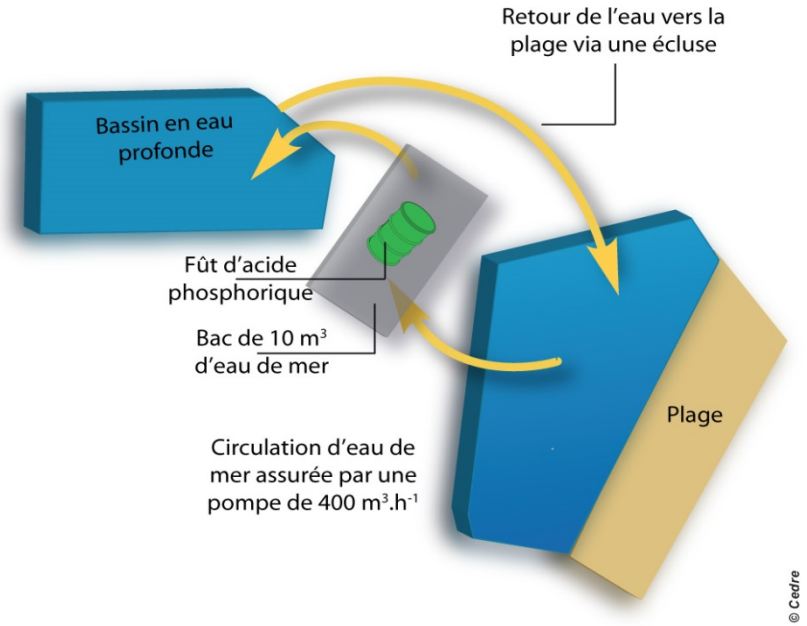
Source: French Navy

ECE (2006)

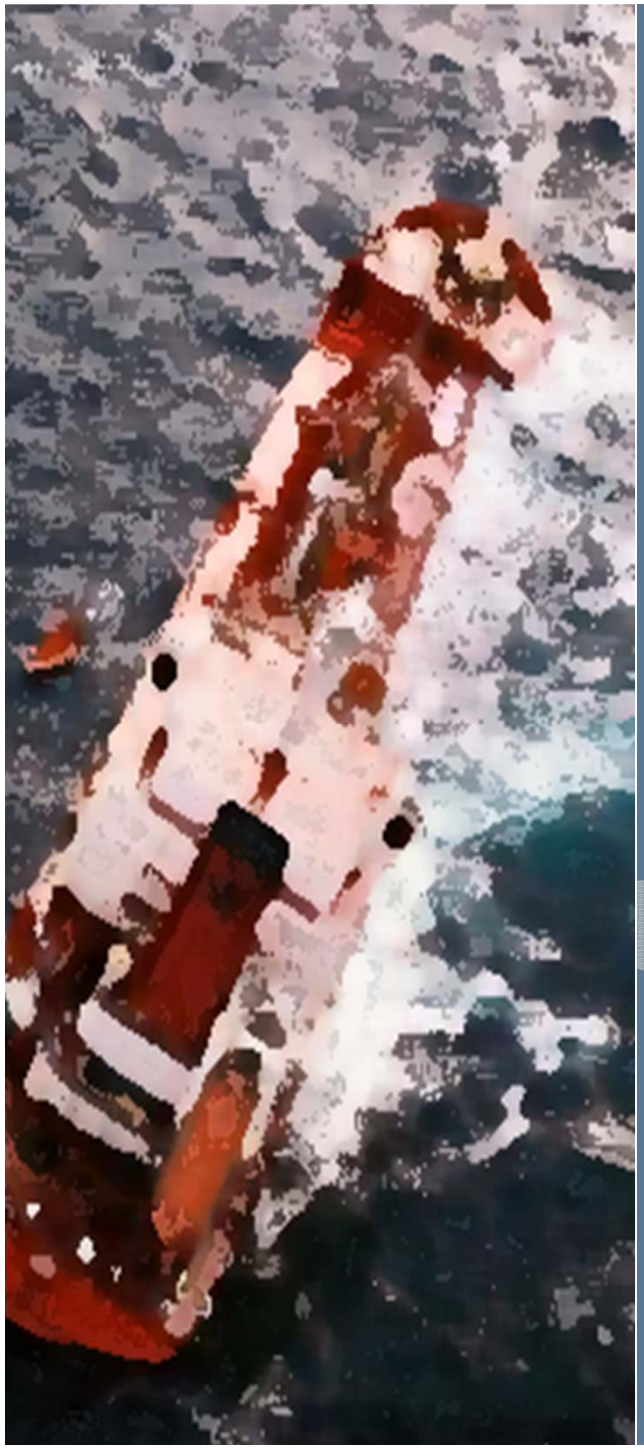
10,000 tonnes of phosphoric acid which, according to the MSDS, is completely hydrosoluble

Solubility was not immediate, required water to be pumped into the bottom of the drum

Issue of the dissolution kinetics of products with a different density to seawater



Methanol which evaporates from the subsurface to form a toxic cloud



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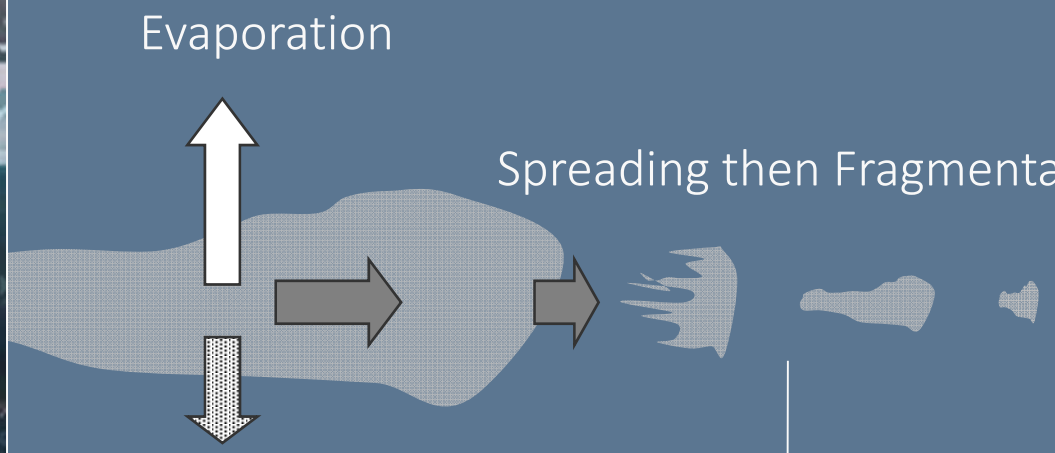
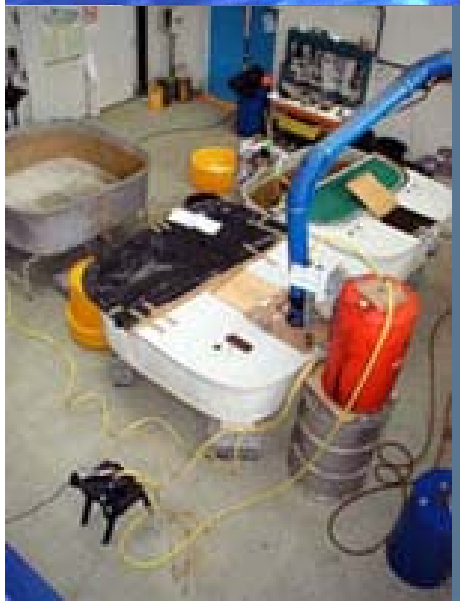
✓Toxicity



Ecotoxicity

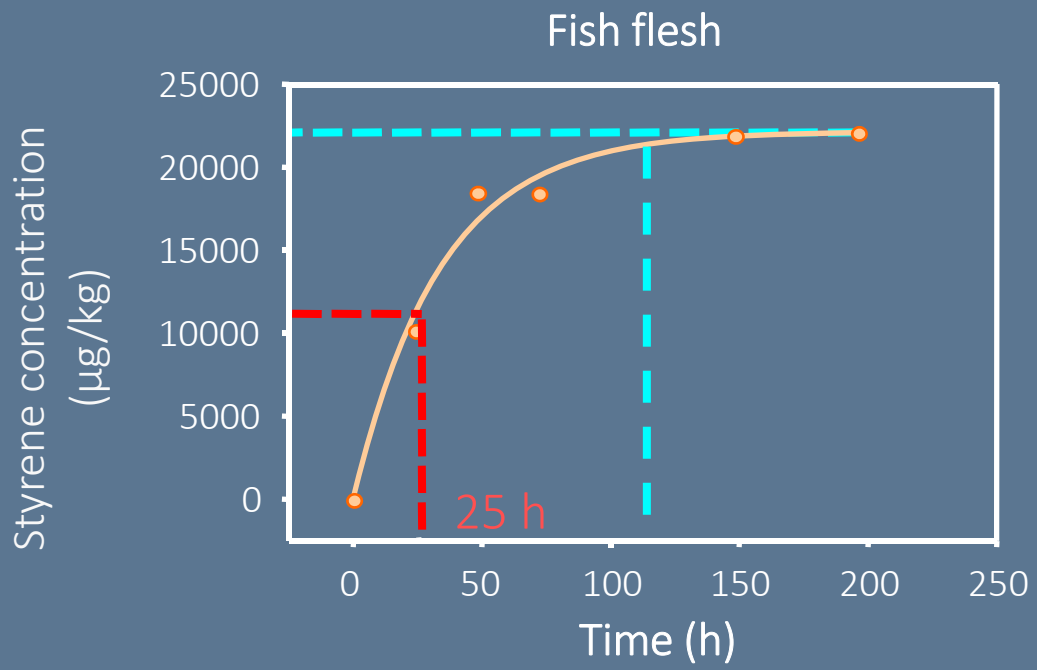
Risk for humans



IEVOLI SUN (2000)

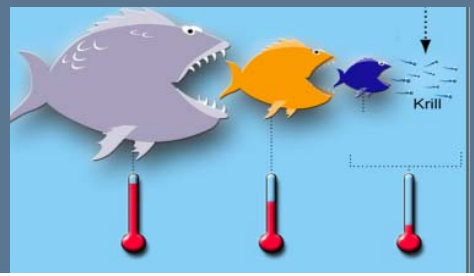
Products and quantity transported

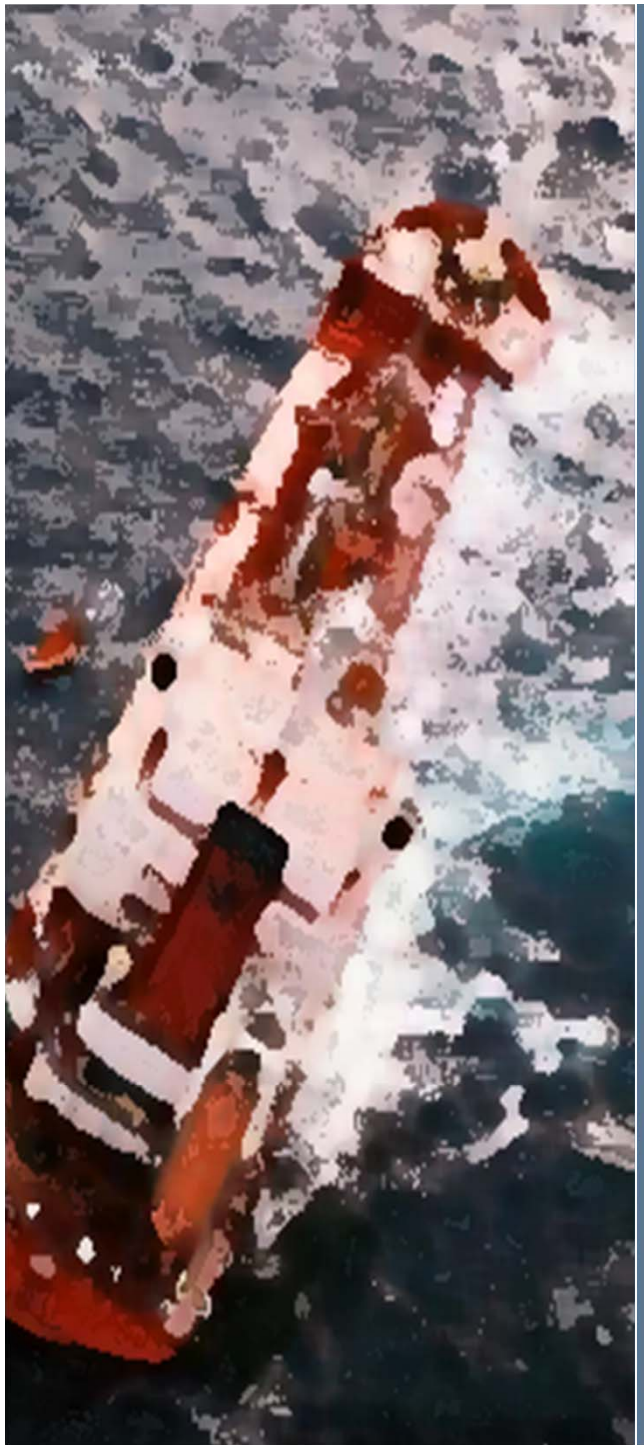
Styrene (3998 t), MEK (1027 t), IPA (996 t)



Two issues

- Fate of the product in the water column
- Food safety





Research areas

Behaviour of chemical products

✓Floating slick

✓Release from a sunken wreck

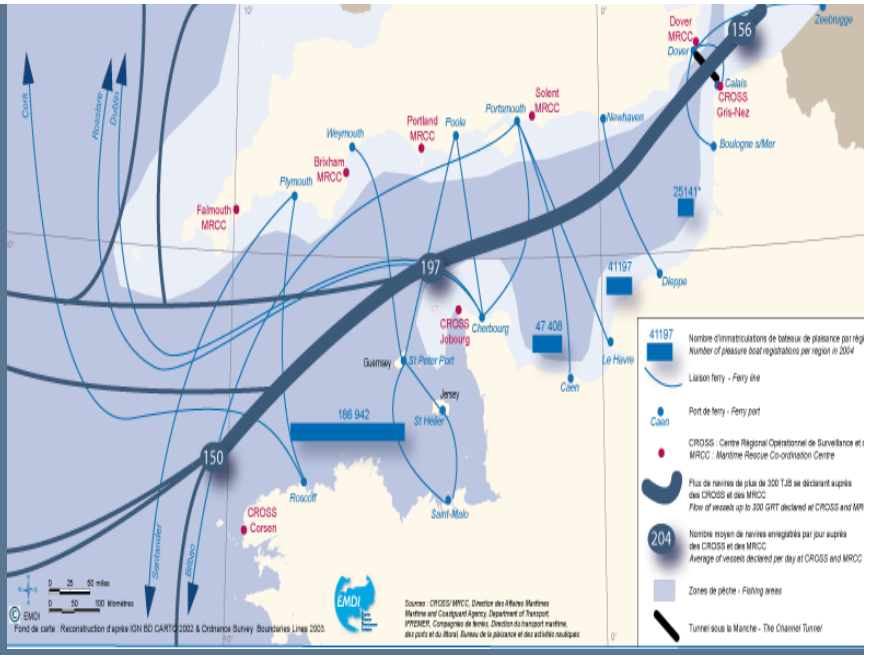
Impact on the environment, Ecotoxicity

✓Acute

✓Sublethal effects

Prior identification of research needs

Which products to work on?



- Traffic (Hasrep, Clara etc.)
- Accident data (White papers e.g. Interspill, technological developments)
- Hazard level (Arcopol)
- Transportation of bulk, liquid and floating products
  - Gesamp (1404 substances)
  - MIDSIS-TROCS/Rempec (672 substances)
  - MAIA
- IMO reports➔ top 10 substances spilled

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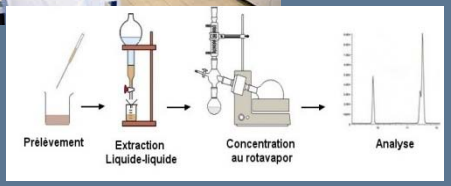
Product fate from a surface slick

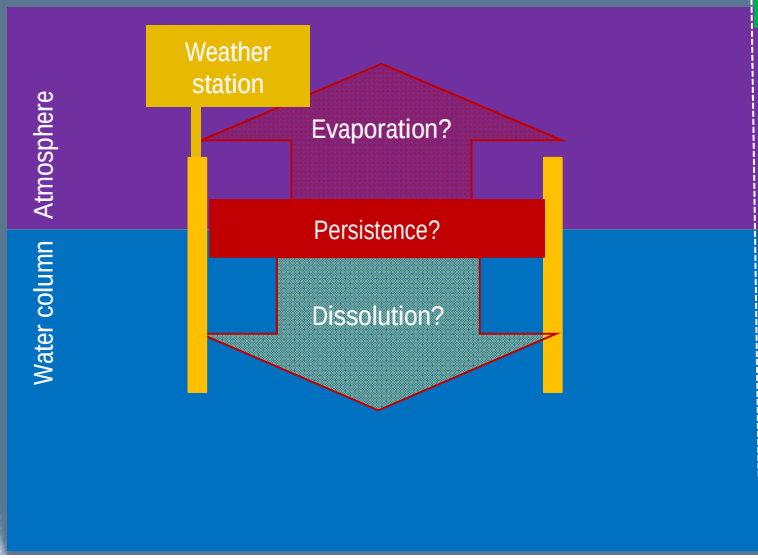
Persistence of the slick, Evaporation, Dissolution, Influence of the weather

Field work ➔ monitored over 5 days

Laboratory work



Floating cells system



System of measures in situ

PID

Continuous

OBSERVATIONS

SF-UV

If detection is possible

Samples

Laboratory analysis

Persistence

- Calibration method
- GC/MS-FID analysis

Characterisation

- Water content
- Viscosity
- Density
- Interfacial tension

Dissolution

- *Sampling at 0.5m, 1m et 2m deep*
- *Sample extraction (SBSE technique, liquid-liquid technique etc.)*
- *GC/MS-FID, GC/MS or HPLC analysis*

Produit	Surface				Eau	Air
	GC-FID	Densité	Teneur en eau	Viscosité	GC-FID	PID
Octanol	16	12	9	17	270	continu
Octane	6	6	6	6	243	continu
Pentanone	16	12	12	6	297	continu

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Produit	N°CAS	Classification SEBC	Conditions météo	Persistance	Observations	Opérations d'intervention
Octane	111-65-9	FE Caractéristiques physico-chimiques: Densité : 0.702 (20°C) Pression de vapeur :	-Vent moyen : 5- 7m.s^{-1} - Vent max : 12m.s^{-1} -Radiation maximale : 150mW/cm² - Mer peu agitée. -Température$_{eau}$: 12°C -Température$_{air}$:9-12°C	**1h-1h20** (pour 16L sur 9m^3)	- Pas d'émulsification ou de solidification - Evaporation forte (moy :50-90ppm ; max:4000ppm) ; ➔Limite VME atteinte ➔Limite d'explosivité non atteinte - Solubilisation faible : Non détectée	➔ Nappe nocive incolore qui s'évapore rapidement si le vent est suffisant (5-7m.s^{-1}). ➔Le nuage de gaz au-dessus de la nappe est toxique et inflammable ➔La durée de demi-vie de la nappe étant de l'ordre de 30 minutes

Produit	N°CAS	Classification SEBC	Conditions météo	Persistance	Observations	Opérations d'intervention
Pentanone	96-22-0	FED Caractéristiques physico-chimiques: Densité : 0,806 (20°C)	- Vent moy. :3-5m.s^{-1}. -Vent max : 10m.s^{-1} -Radiation maximale : 150mW/cm² -Mer peu agitée. -Température$_{eau}$:12°C -Température$_{air}$: 13-17°C.	**50min-1h30** (pour 16L sur 9m^3)	- Pas d'émulsification ou de solidification - Evaporation faible (moy : 25ppm-135ppm ; max :700ppm) ; ➔Limite VME atteinte ➔Limite d'explosivité non atteinte	➔ Nappe nocive incolore qui s'évapore et de dissout rapidement si le vent est suffisant (5-7m.s^{-1}). ➔Le nuage de gaz au-dessus de la nappe est toxique et inflammable

Produit	N°CAS	Classification SEBC	Conditions météo	Persistance	Observations	Opérations d'intervention
Octanol	111-87-5	Fp Caractéristiques physico-chimiques : Densité : 0.827(20°C) Pression de vapeur : 3.2Pa (20°C) Solubilité : 530mg/L (15°C) Viscosité : 12cps mPa.s (13 °C)	- Vent moyen : 5- 7m.s^{-1} - Vent max : 17m.s^{-1} -Radiation maximale 150mW/cm² - Mer peu agitée - Température$_{eau}$: 12°C - Température$_{air}$:9-12°C	**45h-50h** (pour 16L sur 9m^3)	- Pas d'émulsification ou de solidification - Malgré sa classification SEBC Fp, l'octanol a disparu en 45h-50h - **Evaporation** faible (moy : 10ppm ; max : 25ppm) ; ➔Limite VME non atteinte ➔Limite d'explosivité non atteinte - **Solubilisation** faible (moy : <2mg.L^{-1} ; max :5.5mg.L^{-1}) ➔ limites de toxicités connues non atteintes. - CE50 poisson 13mg.L^{-1} - CE50 algue 14mg.L^{-1}	➔ Nappe nocive incolore et odorante qui dérive à la surface poussée par le vent (moins de 5m.s^{-1}). ➔Si des opérations de récupération sont envisagées (fonction des quantités déversées, des conditions météorologiques, de la situation géographique) il possibilité **de confiner et d'utiliser des absorbants inertes**. Tenant compte de la faible viscosité de la nappe, des moyens de pompage peuvent être utilisés, mais nécessité de veiller à ce que les limites d'explosivité ne soient pas atteintes. ⚠ Nappe d'octanol = Nuage de gaz toxique (VME : 30ppm) et inflammable (LIE : 11000ppm ; LSE :80000)

?

MEV = mean exposure value (over 8 hours)

LEL = lower explosive limit

NOTE: in prevailing weather conditions

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Release from a sunken wreck

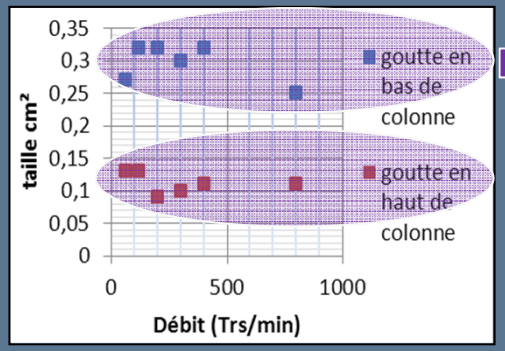
Trial aims

- Study how chemical products rise in the water column
- Risk of a surface slick forming

→Speed of rising droplets

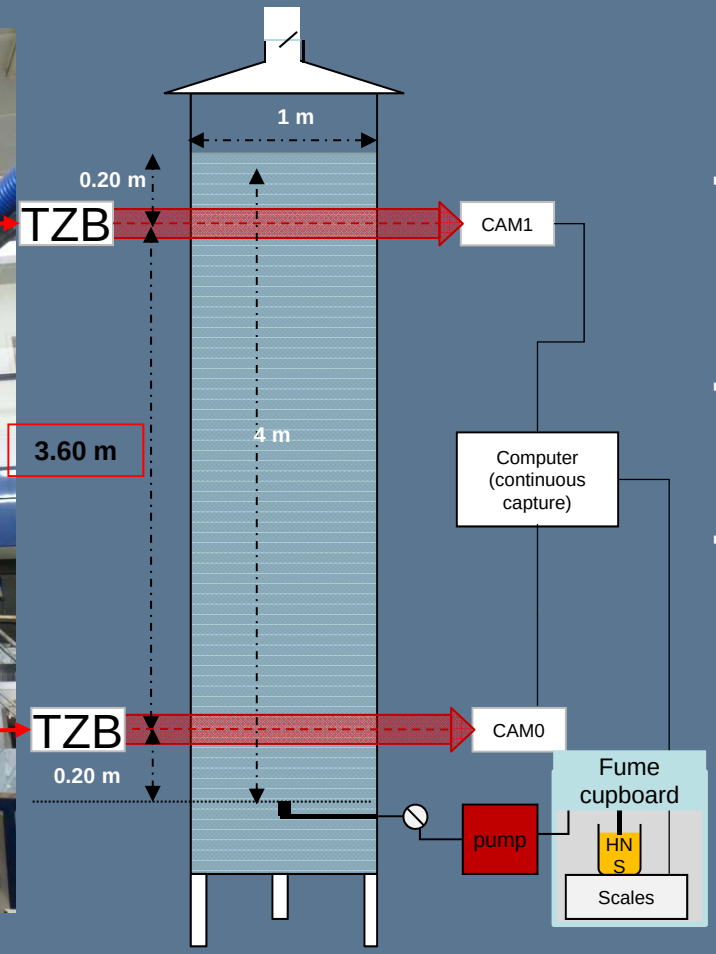
→Dissolution speed

→Droplet size



Loss of volume as droplets rise

Release from a sunken wreck



- 2 high frequency capture cameras positioned 3.60m vertically apart.
- Validation of the technique used: shadowscopy
- Automatic analysis of images (NI Vision Assistant software)

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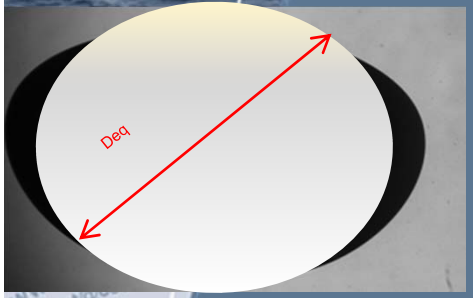
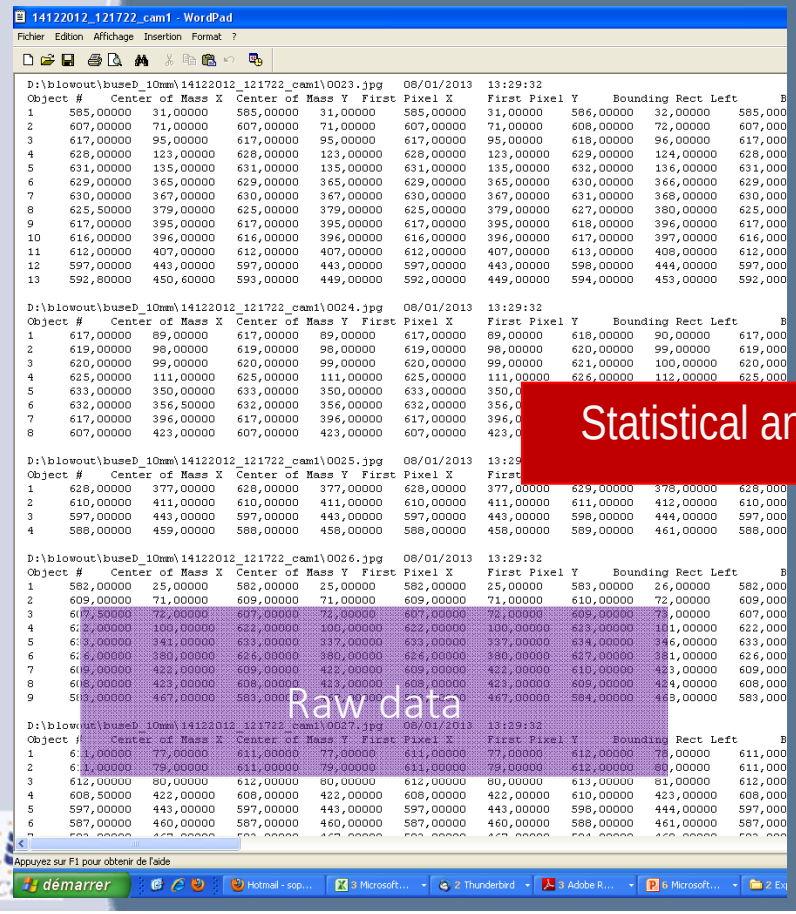


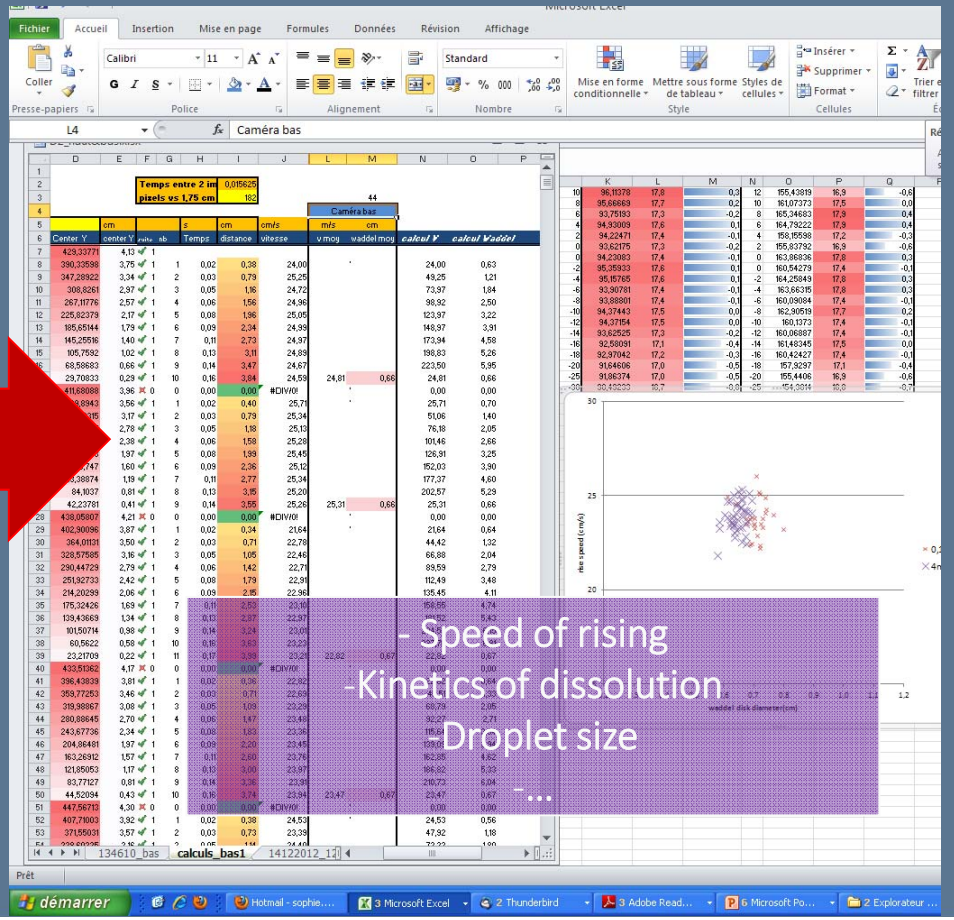
Waddel disk

Study of population of droplets (shape, size etc.) by statistical processing of data

- Calculation of the maximum speed of droplets using their coordinates (X,Y)
- Calculation of the droplet volume at the top and bottom of the column (Waddel disk)



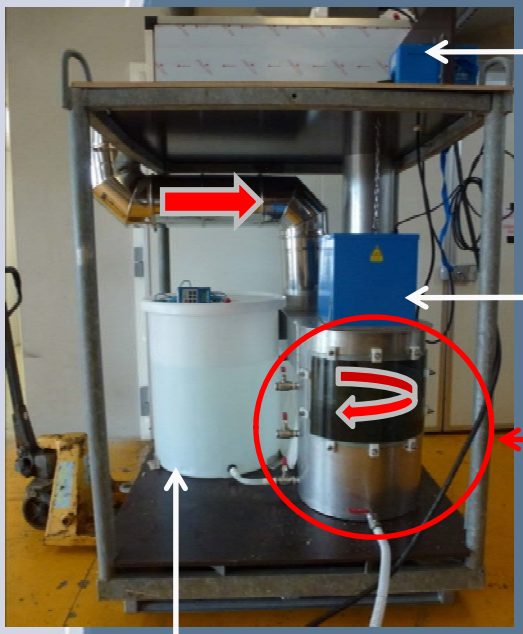
Statistical analysis



- Speed of rising
-Kinetics of dissolution
-Droplet size
- ...

Outlook

Characterise the overall fate (simultaneous processes) by controlling environmental parameters



Wind generator
(0 to 5 $m.s^{-1}$
or
0 to 10 $m.s^{-1}$)

Lamp simulating
solar radiation

test tank

Water reservoir at a controlled temperature
(5 to 10°C)

Monitoring evaporation

Monitoring dissolution

IN ORDER to obtain data to feed databases (MAIA) or forecast models

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Impact on the environment

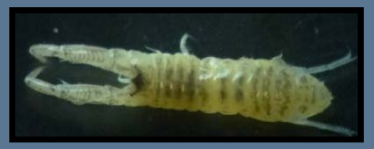
In an incident context, research is very "pragmatic", e.g. *Ievoli Sun*

Non-urgent research, ecotoxicity is often studied within a regulatory framework, i.e. in accordance with OSPAR (LC50)

Marine algae *Skeletonema costatum*
72 hour exposure

Copepods *Acartia tonsa*
48 hour exposure

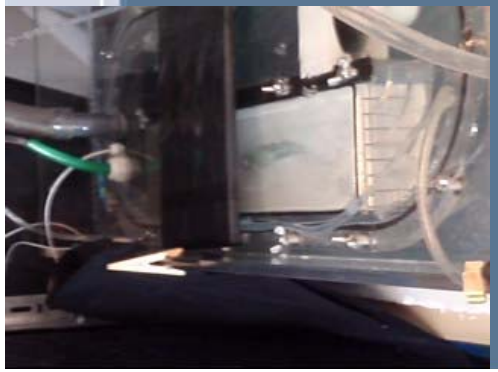
Amphipods *Corophium Volutator*
10 day exposure, bioassay on sediment



Fish *Scophtalmus maximus*
96 hour exposure

Impact on the environment

Research on sublethal effects is carried out via programmes conducted in partnership with the academic world and financed by the EU, ANR or industry.



Cedre is authorised to work on living organisms (accreditation number)
Personnel authorised to carry out tests
Submission of projects to the Ethics Committee

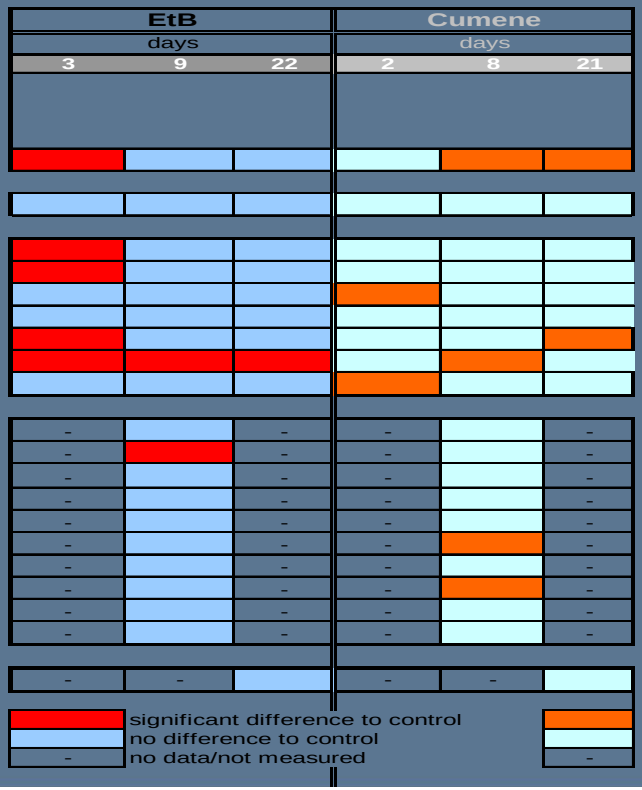
Combination of projects on substance behaviour and toxicity

EXPOSURE EVENTS

OBSERVATIONS PARAMETERS

Exposure	*Body Burden*
General stress	*NRRT (180 min)*
Immune	*Phagocytosis rate*
	Phagocytosis intensity
	Cell count
	ROS production capacity
	ROS activation capacity
	Phenoloxidase
	cell viability
Histology	
digestive gland	*Neutral Lipid*
	Epithelial cell height
	Eosin bodies
gonad	*Development stage*
	ADG
	Atresia
	Apoptosis/Necrosis
	*Parasite **
gill	*Brown cells*
kidney	*Lipofuscin*
General condition	*CI*

** Steinhausia mytilovum*



Conclusion

- Research is aimed towards
  - Characterising the fate of products in the environment as realistically as possible
  - Their potential impact

=> with the final objective being response

- Multi-partner projects (universities, industry etc.)
- Different funding sources (ANR, EU, DEB, MN, Total, Arkema etc.)
- Need for a laboratory equipped with advanced analytical equipment (GC-FID, GC-MS, GC-MS-MS, HPLC etc.) and the possibility of in situ trials

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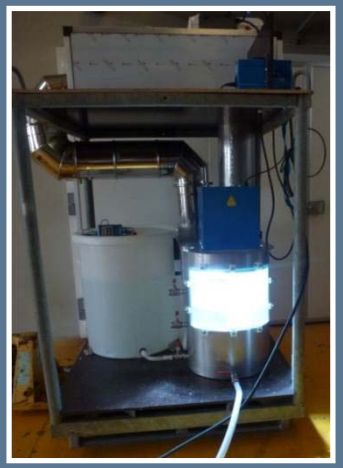

THANK YOU