



19th Cedre Information Day

Accidental pollution by HNS

Overview of Research on Chemical Substances

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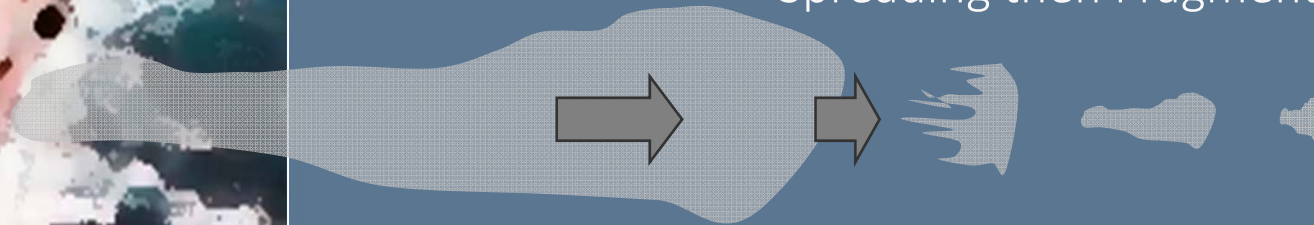
Research interests

Chemical products in the marine environment:

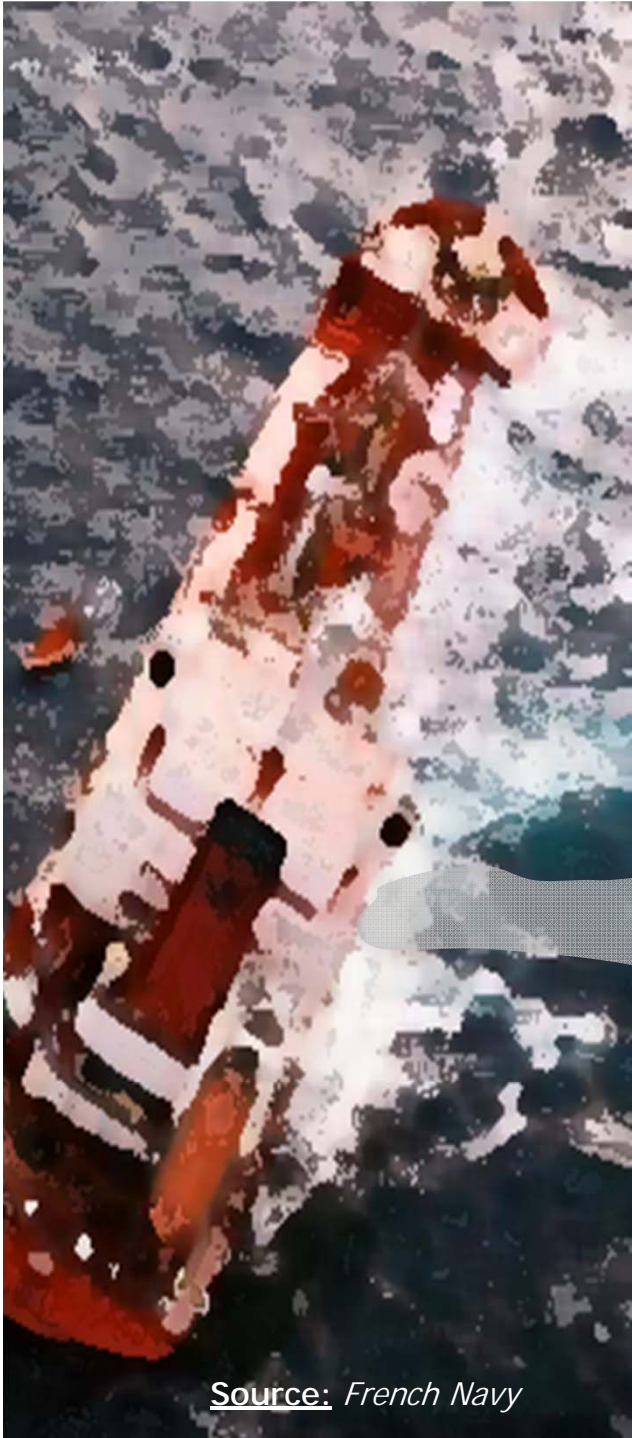
- ✓ Behaviour (reactivity, **transfer**)
- ✓ Toxicity

Examples of floating products

Spreading then Fragmentation



Source: *French Navy*



ALLEGRA (1997)



Type of pollutant: Palm kernel oil

Quantity transported: 15,000 tonnes

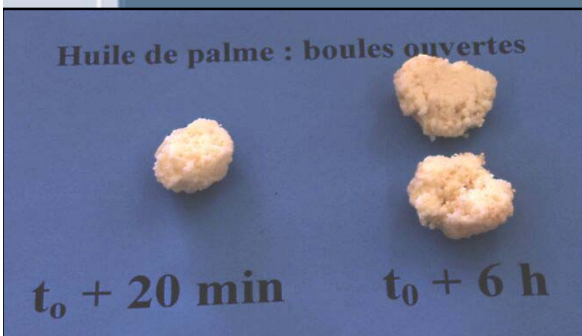
Quantity spilled: 900 tonnes of palm kernel oil

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)



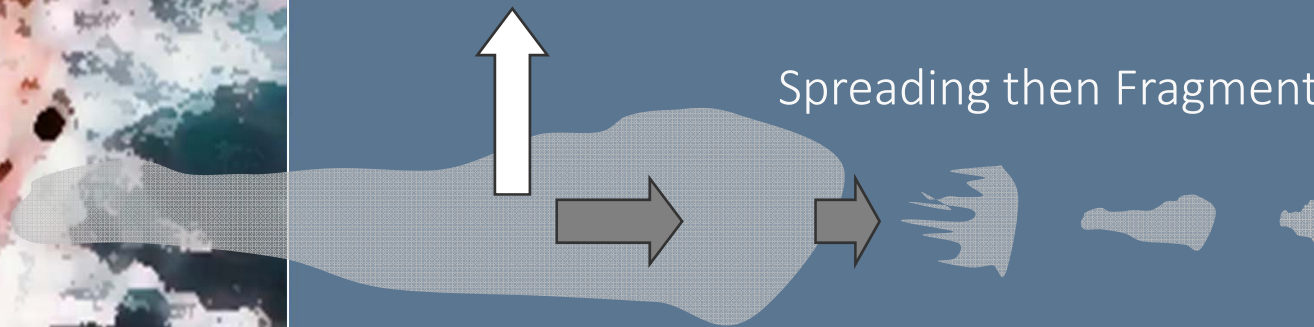
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Chemical products in the marine environment:

- ✓ Behaviour (reactivity, transfer)
- ✓ Toxicity

Evaporation

Spreading then Fragmentation





BOW EAGLE (2002)



Source: French Navy

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

Fate and associated risks?

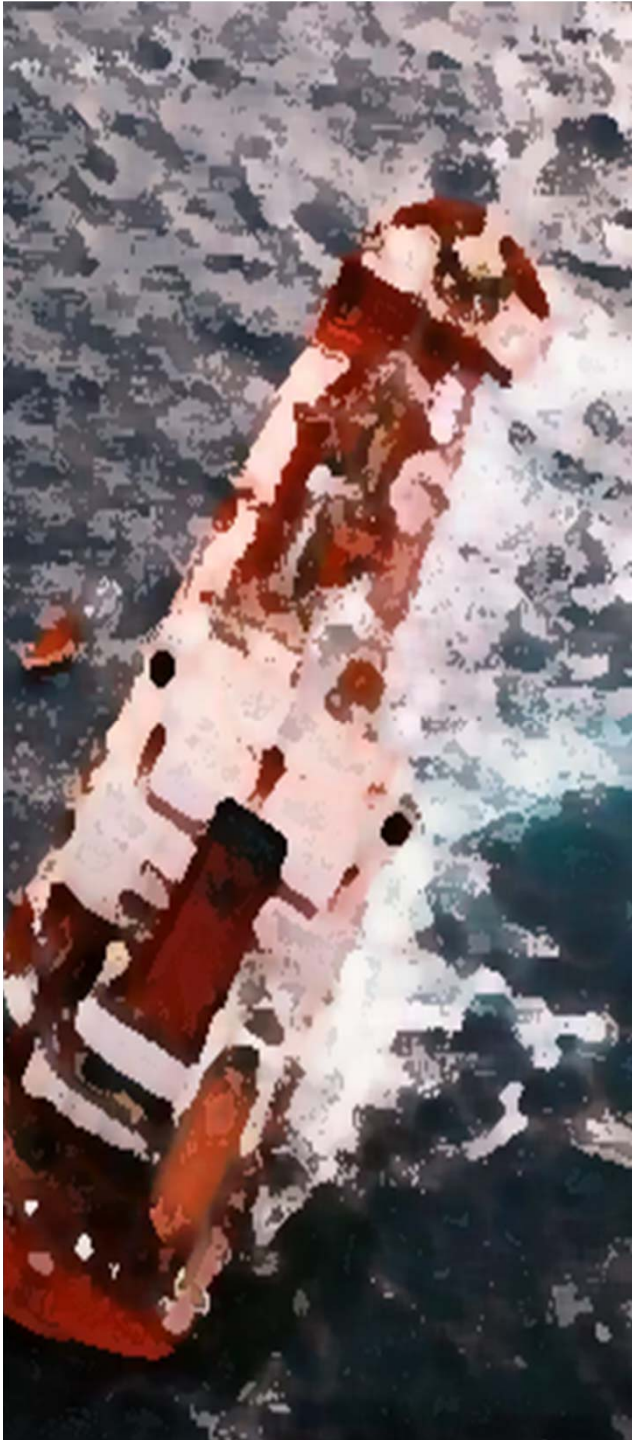
Density = 0.8 \Rightarrow Solubility = 55 mg/L \Rightarrow Vapour pressure = 12.7 kPa \Rightarrow Vapour density / in air
 $< 0.1\%$ at 20°C > 3 kPa 2.9

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?

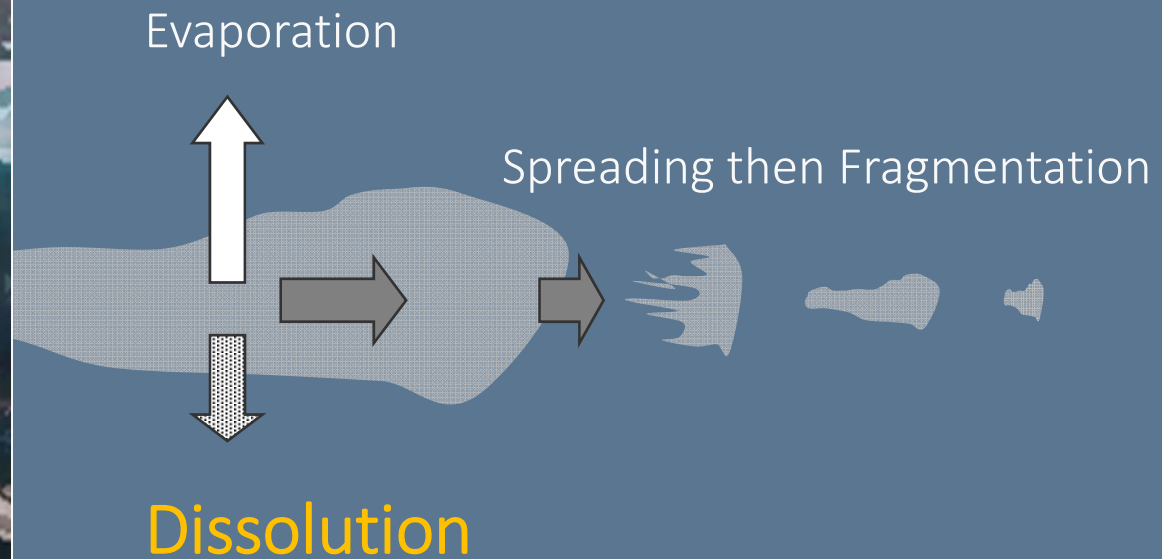




Research interests

Chemical products in the marine environment:

- ✓ Behaviour (reactivity, transfer)
- ✓ Toxicity



ECE (2006)

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



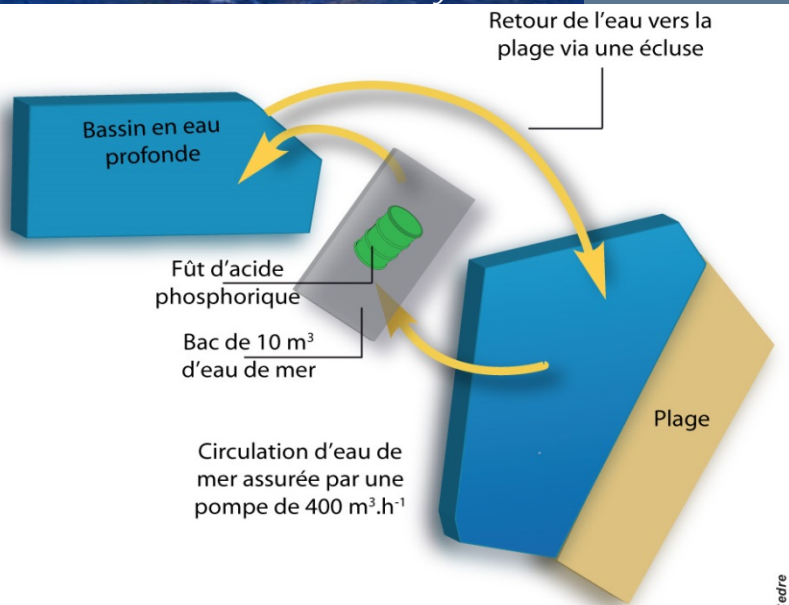
Source: French Navy

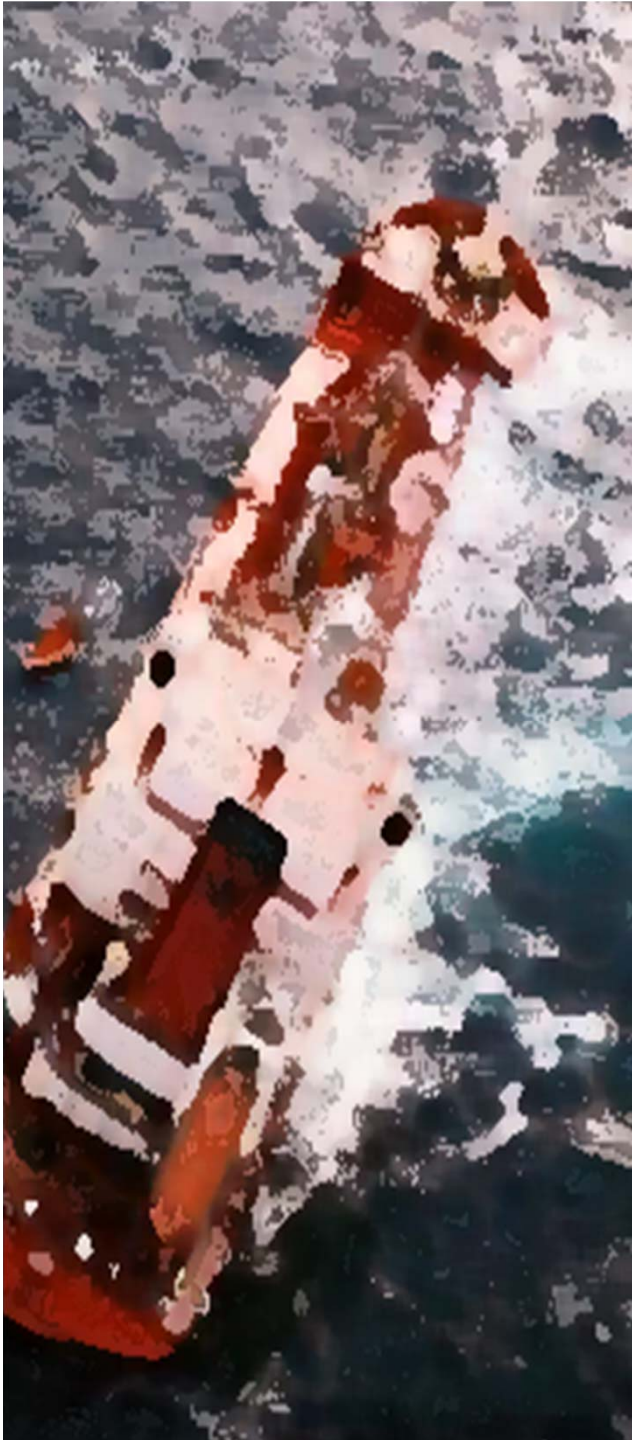


Solubility was not immediate, required water to be pumped into the bottom of the drum

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

Methanol which evaporates from the subsurface to form a toxic cloud

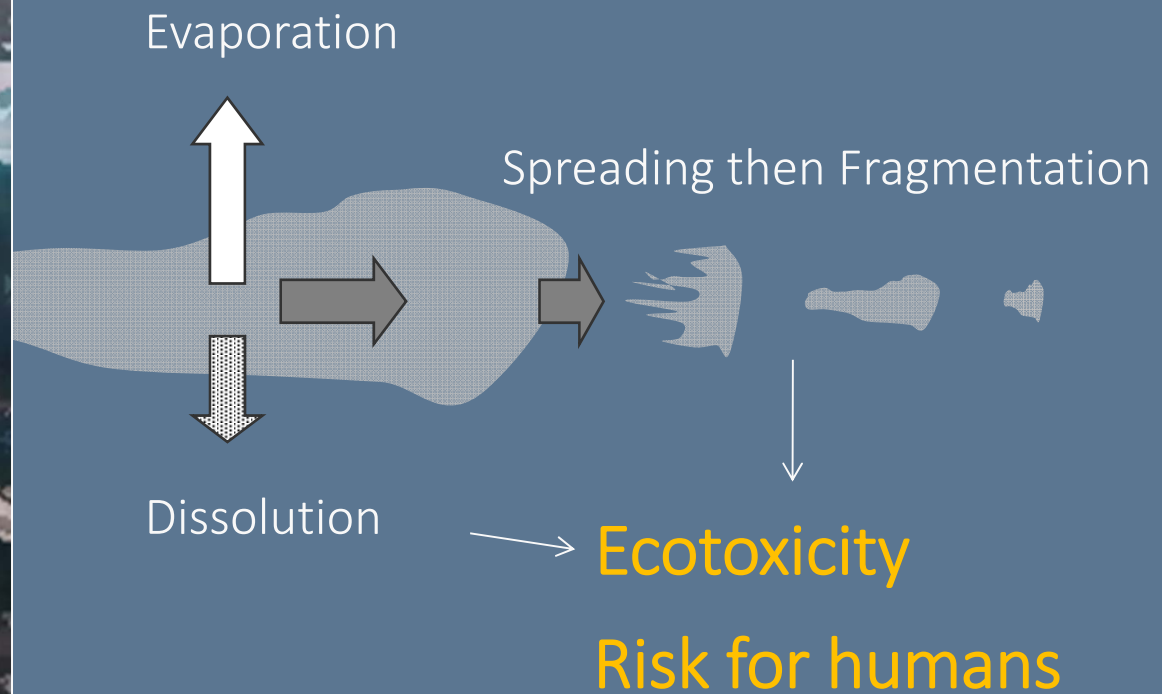




Research interests

Chemical products in the marine environment:

- ✓ Behaviour (reactivity, transfer)
- ✓ Toxicity



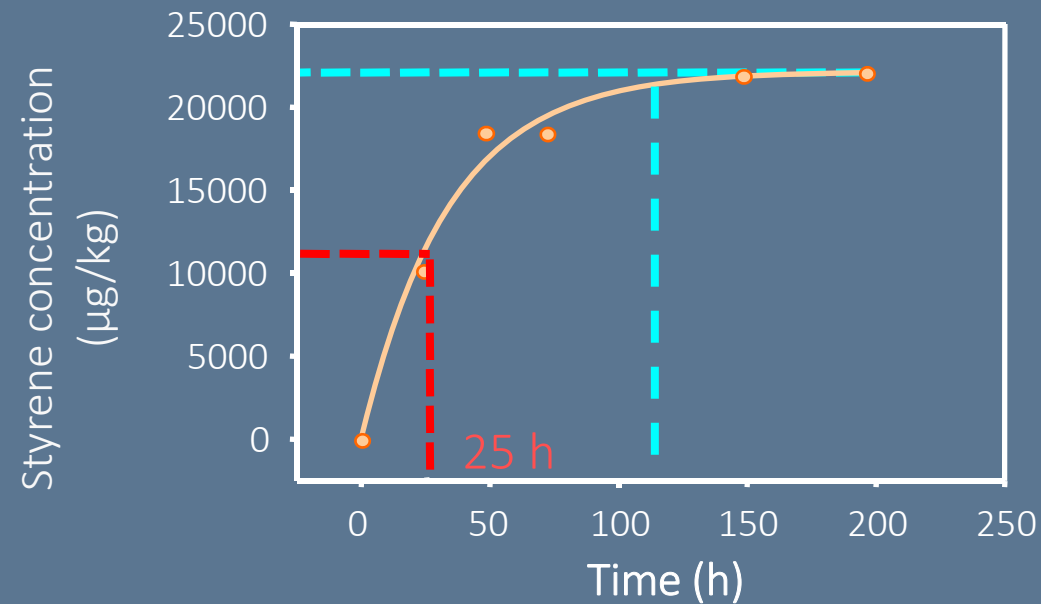


IEVOLI SUN (2000)

Products and quantity transported
Styrene (3998 t), MEK (1027 t), IPA (996 t)

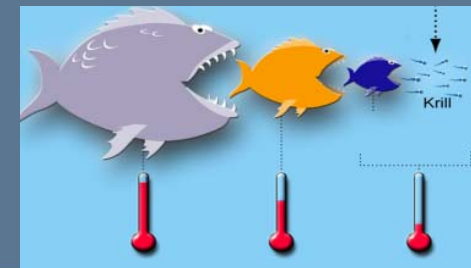


Fish flesh



Two issues

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



Research areas

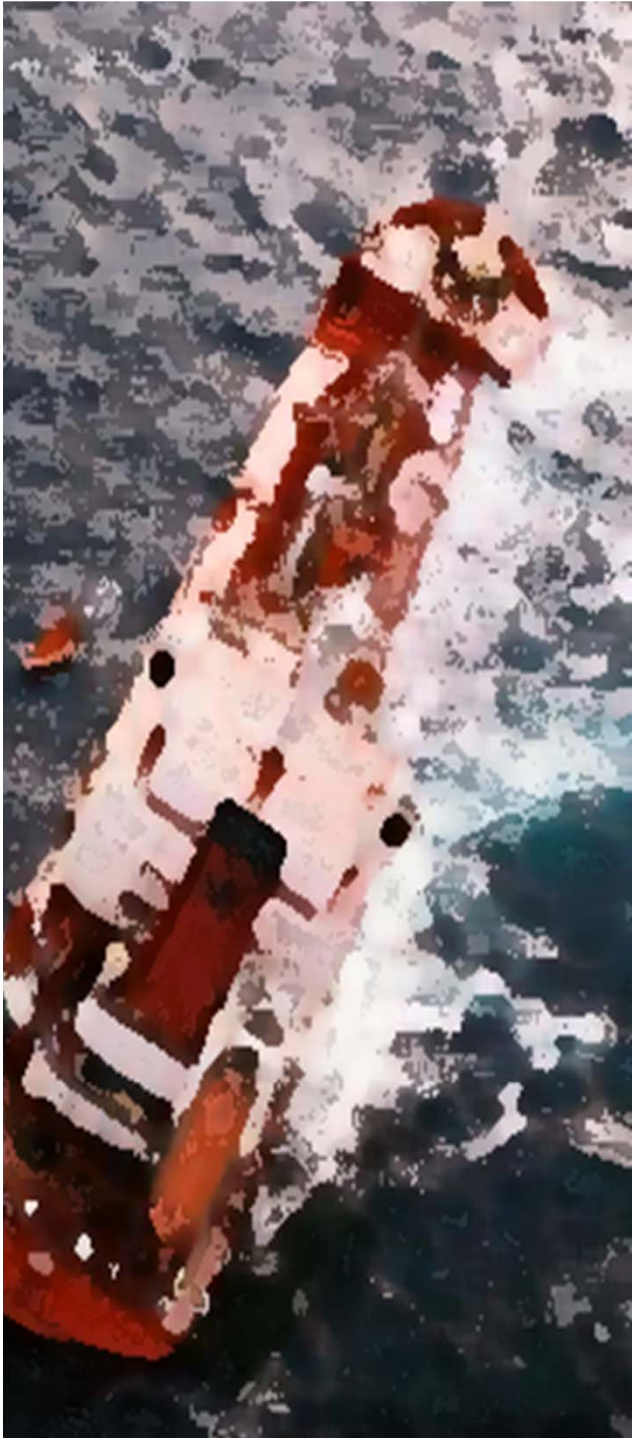
Behaviour of chemical products

- ✓ Floating slick
- ✓ Release from a sunken wreck



Impact on the environment,
Ecotoxicity

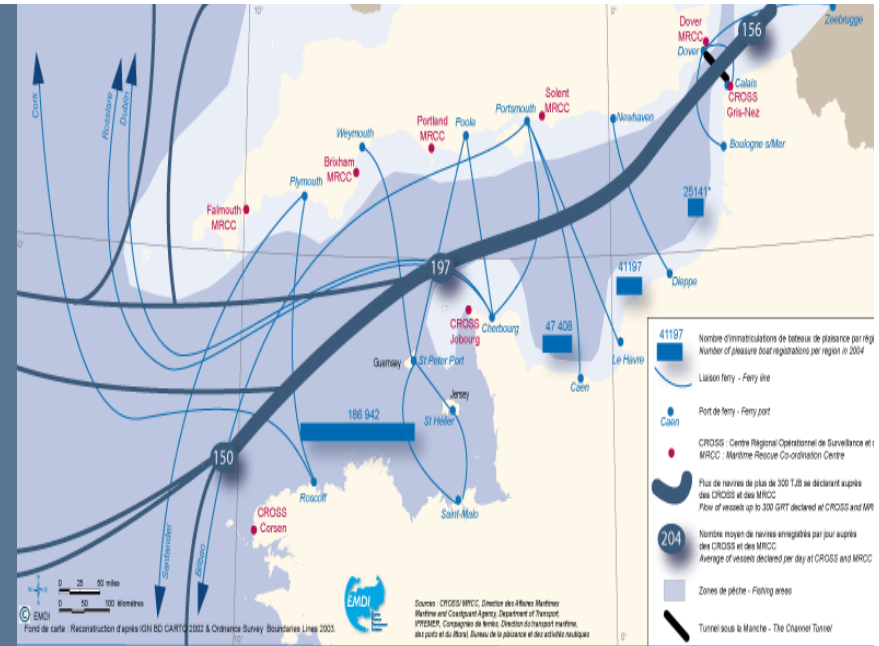
- ✓ Acute
- ✓ Sublethal effects



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

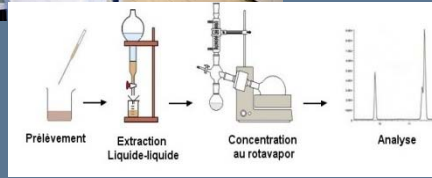
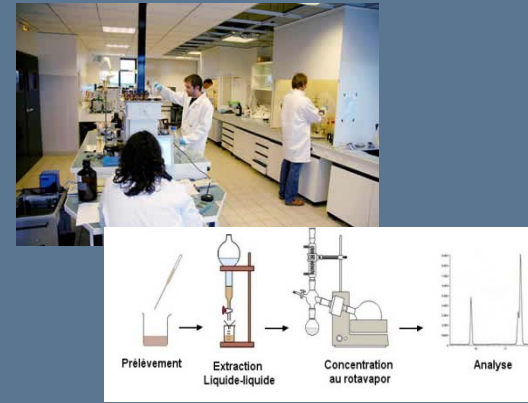
Persistence of the slick, Evaporation, Dissolution, Influence of the weather



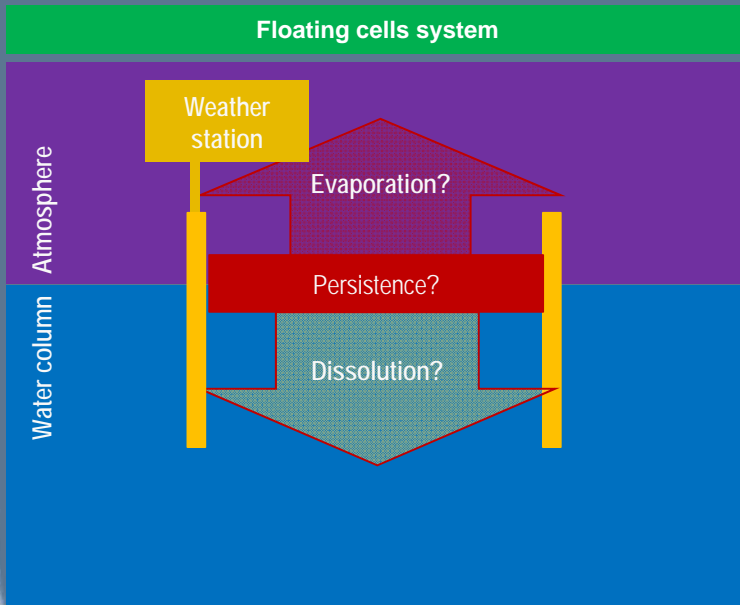
Field work → monitored over 5 days



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		
Octanol	16	12	9	17	270	continu
Octane	6	6	6	6	243	continu
Pentanone	16	12	12	6	297	continu

Produit	N°CAS	Classification SEBC	Conditions météo	Persistance	Observations	Opérations d'intervention
Octane	111-65-9	FE	-Vent moyen : 5- 7m.s ⁻¹ - Vent max : 12m.s ⁻¹ -Radiation maximale : 150mW/cm ² - 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:400ppm) ; → 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

MEV = mean exposure value (over 8 hours)
LEL = lower explosive limit

Produit	N°CAS	Classification SEBC	Conditions météo	Persistance	Observations	Opérations d'intervention
Pentanone	96-22-0	FED	- Vent moy. :3-5m.s ⁻¹ . -Vent max : 10m.s ⁻¹ -Radiation maximale : 150mW/cm ² -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	- Vent moyen : 5- 7m.s ⁻¹ - Vent max : 17m.s ⁻¹ -Radiation maximale : 150mW/cm ² - 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 est possible 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)

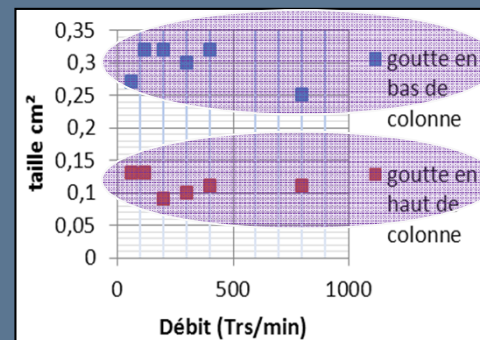
NOTE: in prevailing weather conditions

Release from a sunken wreck



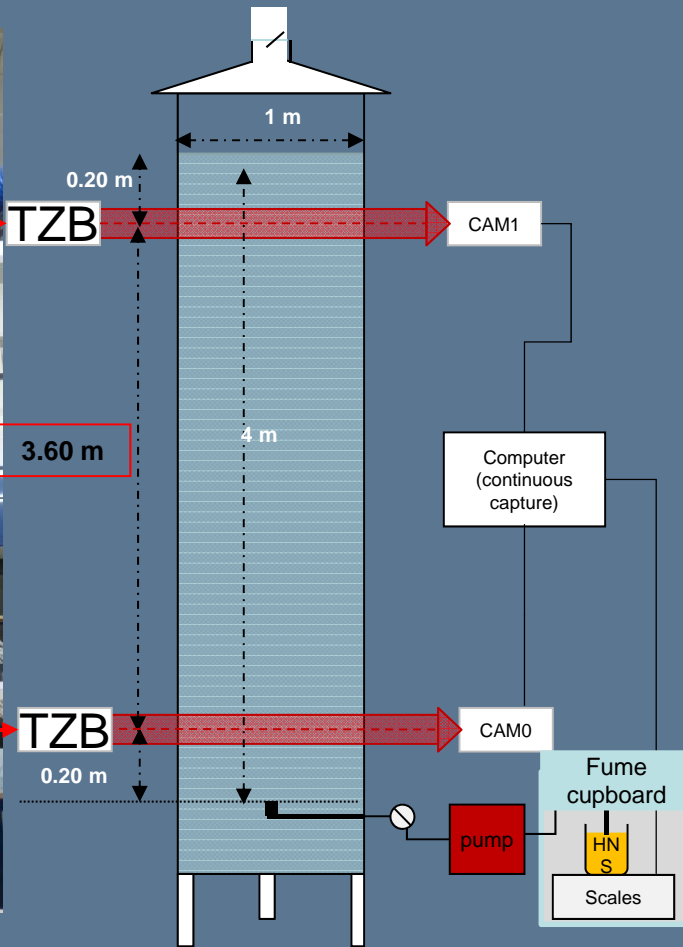
Trial aims

- Study how chemical products rise in the water column
 - Risk of a surface slick forming
- Speed of rising droplets
- Dissolution speed
- Droplet size

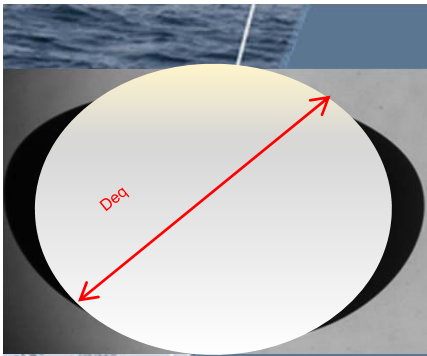


Loss
of volume
as droplets
rise

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)



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)



14122012_121722_cam1 - WordPad

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Object #	Center of Mass X	Center of Mass Y	First Pixel X	First Pixel Y	Bounding Rect Left	B
1	585,00000	31,00000	585,00000	31,00000	585,00000	31,00000
2	607,00000	71,00000	607,00000	71,00000	607,00000	71,00000
3	617,00000	95,00000	617,00000	95,00000	617,00000	95,00000
4	628,00000	123,00000	628,00000	123,00000	628,00000	123,00000
5	631,00000	135,00000	631,00000	135,00000	631,00000	135,00000
6	629,00000	365,00000	629,00000	365,00000	629,00000	365,00000
7	630,00000	367,00000	630,00000	367,00000	630,00000	367,00000
8	625,50000	379,00000	625,00000	379,00000	625,00000	379,00000
9	617,00000	395,00000	617,00000	395,00000	617,00000	395,00000
10	616,00000	396,00000	616,00000	396,00000	616,00000	396,00000
11	612,00000	407,00000	612,00000	407,00000	612,00000	407,00000
12	597,00000	443,00000	597,00000	443,00000	597,00000	443,00000
13	592,80000	450,60000	593,00000	449,00000	592,00000	449,00000

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Object #	Center of Mass X	Center of Mass Y	First Pixel X	First Pixel Y	Bounding Rect Left	B
1	617,00000	89,00000	617,00000	89,00000	617,00000	89,00000
2	619,00000	96,00000	619,00000	96,00000	619,00000	96,00000
3	620,00000	99,00000	620,00000	99,00000	620,00000	99,00000
4	625,00000	111,00000	625,00000	111,00000	625,00000	111,00000
5	633,00000	350,00000	633,00000	350,00000	633,00000	350,00000
6	632,00000	356,50000	632,00000	356,00000	632,00000	356,00000
7	617,00000	396,00000	617,00000	396,00000	617,00000	396,00000
8	607,00000	423,00000	607,00000	423,00000	607,00000	423,00000

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Object #	Center of Mass X	Center of Mass Y	First Pixel X	First Pixel Y	Bounding Rect Left	B
1	628,00000	377,00000	628,00000	377,00000	628,00000	377,00000
2	610,00000	411,00000	610,00000	411,00000	610,00000	411,00000
3	597,00000	443,00000	597,00000	443,00000	597,00000	443,00000
4	588,00000	459,00000	588,00000	458,00000	588,00000	458,00000

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Object #	Center of Mass X	Center of Mass Y	First Pixel X	First Pixel Y	Bounding Rect Left	B
1	582,00000	25,00000	582,00000	25,00000	582,00000	25,00000
2	609,00000	71,00000	609,00000	71,00000	609,00000	71,00000
3	617,80000	72,00000	617,00000	72,00000	617,00000	72,00000
4	612,00000	100,00000	612,00000	100,00000	612,00000	100,00000
5	613,00000	341,00000	613,00000	337,00000	613,00000	337,00000
6	616,00000	380,00000	616,00000	380,00000	616,00000	380,00000
7	619,00000	423,00000	619,00000	422,00000	619,00000	422,00000
8	616,00000	423,00000	616,00000	423,00000	616,00000	423,00000
9	516,00000	467,00000	583,00000	467,00000	584,00000	467,00000

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Object #	Center of Mass X	Center of Mass Y	First Pixel X	First Pixel Y	Bounding Rect Left	B
1	611,00000	77,00000	611,00000	77,00000	611,00000	77,00000
2	611,00000	79,00000	611,00000	79,00000	611,00000	79,00000
3	612,00000	80,00000	612,00000	80,00000	612,00000	80,00000
4	609,00000	422,00000	608,00000	422,00000	610,00000	423,00000
5	597,00000	443,00000	597,00000	443,00000	598,00000	444,00000
6	587,00000	460,00000	587,00000	460,00000	588,00000	461,00000
7	583,00000	462,00000	583,00000	462,00000	584,00000	462,00000

Raw data

Statistical analysis

Microsoft Excel

Calculs_bas1

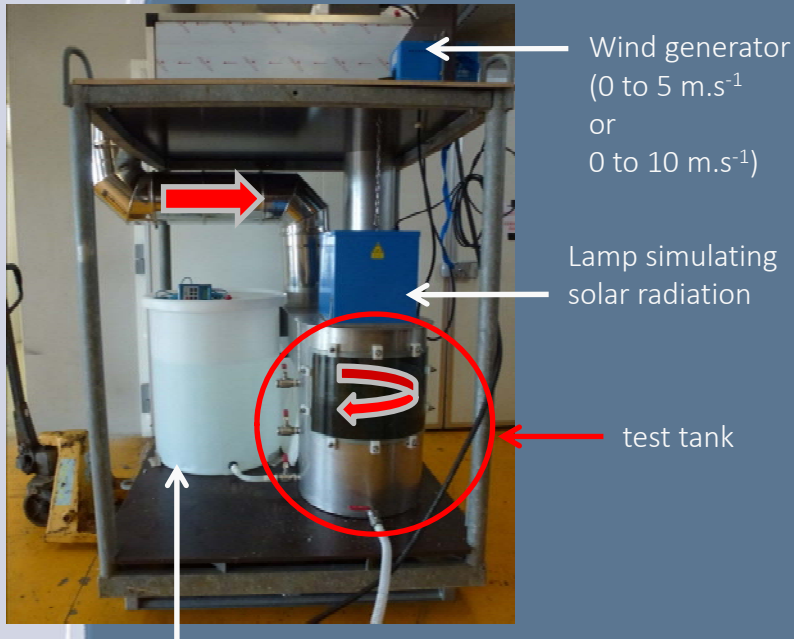
Center Y	center Y	cm	cm	cm	cm/s	m/s	cm	cm	calcul Y	calcul Waddel
428,3377	413	1	0,02	0,38	24,00				24,00	0,63
390,3598	375	1	0,03	0,78	25,28				48,25	1,21
397,2092	334	1	0,03	1,16	24,72				73,87	1,84
308,8261	297	1	0,05	1,56	24,86				98,92	2,50
287,1176	257	1	0,06	1,96	25,06				123,97	3,22
225,8278	217	1	0,08	2,34	24,99				148,37	3,91
195,6044	179	1	0,10	2,72	24,91				173,94	4,56
165,2536	140	1	0,11	3,11	24,83				198,83	5,28
105,7582	102	1	0,13	3,47	24,87				223,50	5,95
88,8863	66	1	0,14	3,84	24,81				248,18	6,68
23,70833	2,9	1	0,18	4,18	24,81	24,81	0,68		0,00	0,00
418,8088	3,96	0	0,00	0,00	NDIV00				0,00	0,00
369,6843	3,96	1	0,02	0,40	25,71				25,71	0,70
315	3,17	1	0,03	0,79	25,34				50,6	1,40
278	2,78	1	0,05	1,18	25,13				76,18	2,05
238	2,38	1	0,06	1,59	25,28				101,46	2,68
197	1,97	1	0,08	1,99	25,45				126,31	3,25
147	1,47	1	0,09	2,38	25,13				151,03	3,90
3,8974	1,19	1	0,11	2,77	25,34				177,37	4,60
84,937	0,81	1	0,13	3,15	25,20				202,57	5,28
42,23761	0,41	1	0,14	3,55	25,26	25,31	0,68		25,31	0,68
438,6007	4,21	0	0,00	0,00	NDIV00				0,00	0,00
402,9098	3,97	1	0,02	0,24	21,64				21,64	0,64
364,0133	3,50	1	0,03	0,71	22,78				44,42	1,22
328,87588	3,16	1	0,05	1,05	22,46				66,88	2,04
290,4729	2,79	1	0,06	1,42	22,71				89,59	2,78
251,92793	2,42	1	0,08	1,79	22,91				112,49	3,48
214,0028	2,06	1	0,09	2,16	22,92				135,45	4,11
175,2426	1,69	1	0,11	2,53	23,05				158,45	4,74
134,3663	1,34	1	0,13	2,87	22,87				181,45	5,43
101,9074	0,98	1	0,14	3,24	23,00				204,45	6,12
69,8622	0,59	1	0,16	3,63	22,97				227,45	6,81
39,23709	0,22	1	0,17	3,99	22,92	22,82	0,67		250,45	7,50
4328,8182	417	0	0,00	0,00	NDIV00				0,00	0,00
398,4338	3,81	1	0,02	0,30	22,82				22,82	0,64
393,7225	3,46	1	0,03	0,71	22,89				45,64	1,22
398,9897	3,09	1	0,05	1,09	22,79				68,78	1,84
290,8845	2,70	1	0,06	1,47	23,16				91,97	2,71
243,67738	2,34	1	0,08	1,83	23,49				115,19	3,14
204,86481	1,97	1	0,09	2,20	23,45				138,41	3,72
163,26932	1,57	1	0,11	2,60	23,79				161,63	4,31
121,69603	1,17	1	0,13	2,99	23,97				184,85	4,90
83,7272	0,81	1	0,14	3,38	24,21				208,07	5,49
44,52994	0,43	1	0,16	3,74	23,94	23,47	0,67		231,27	6,07
447,56718	4,30	0	0,00	0,00	NDIV00				0,00	0,00
407,7903	3,92	1	0,02	0,38	24,53				24,53	0,66
370,5508	3,57	1	0,03	0,73	23,38				47,82	1,28
340,69996	3,16	1	0,04	1,11	24,41				70,63	1,90

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Speed of rising
Kinetics of dissolution
Droplet size

Outlook

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



Monitoring evaporation

Monitoring dissolution

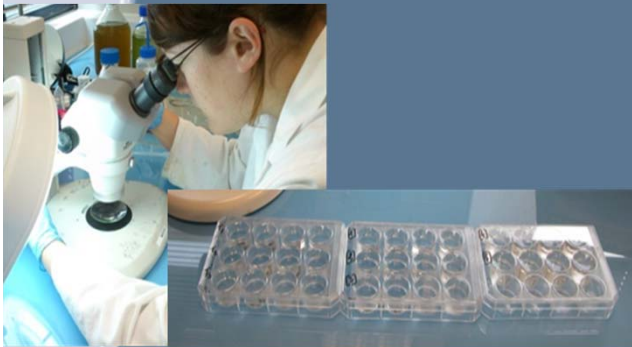
IN ORDER to obtain data to feed databases (MAIA)
or forecast models



Impact on the environment

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

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



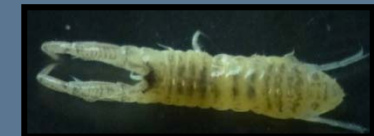
Marine algae *Skeletonema costatum*
72 hour exposure



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

General condition *CI*

* *Steinhausia mytilovum*

EtB			Cumene		
days			days		
3	9	22	2	8	21
Red	Blue	Blue	Light Blue	Orange	Orange
Blue	Blue	Blue	Light Blue	Light Blue	Light Blue
Red	Blue	Blue	Light Blue	Light Blue	Light Blue
Red	Blue	Blue	Orange	Light Blue	Light Blue
Red	Blue	Blue	Light Blue	Light Blue	Light Blue
Red	Red	Red	Light Blue	Orange	Light Blue
Blue	Blue	Blue	Orange	Light Blue	Light Blue
-	Blue	-	-	Light Blue	-
-	Red	-	-	Light Blue	-
-	Blue	-	-	Light Blue	-
-	Blue	-	-	Light Blue	-
-	Blue	-	-	Orange	-
-	Blue	-	-	Light Blue	-
-	Blue	-	-	Orange	-
-	Blue	-	-	Light Blue	-
-	Blue	-	-	Light Blue	-
-	-	Blue	-	-	Light Blue

significant difference to control

no difference to control

no data/not measured



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

