Session 2
Characterising HNS

CEDRE
Stéphane Le Floch
Sophie Chataing-Pariaud

Co-funded by the European Commission, DG-ECHO

Few words on

- Need of a **database adapted** to the HNS-MS project (specific gravity, viscosity, evaporation / vapour pressure and solubility)

- Selection of HNS (the most relevant)
  - Criteria
  - List of HNS (120)

- Laboratory characterisation
  - Selection of HNS (19)
  - Physical and chemical properties tested
  - Results

Selection of HNS – Criteria

- Transport at sea in the Bonn Agreement area
- Representativeness in the SEBC (E, F, D and S)
- Toxicity for Humans and impact on the marine environment

- Gas not taken into account

Co-funded by the European Commission, DG-ECHO

Selection of HNS – Criteria

→ Cross-check of HNS lists issued from :

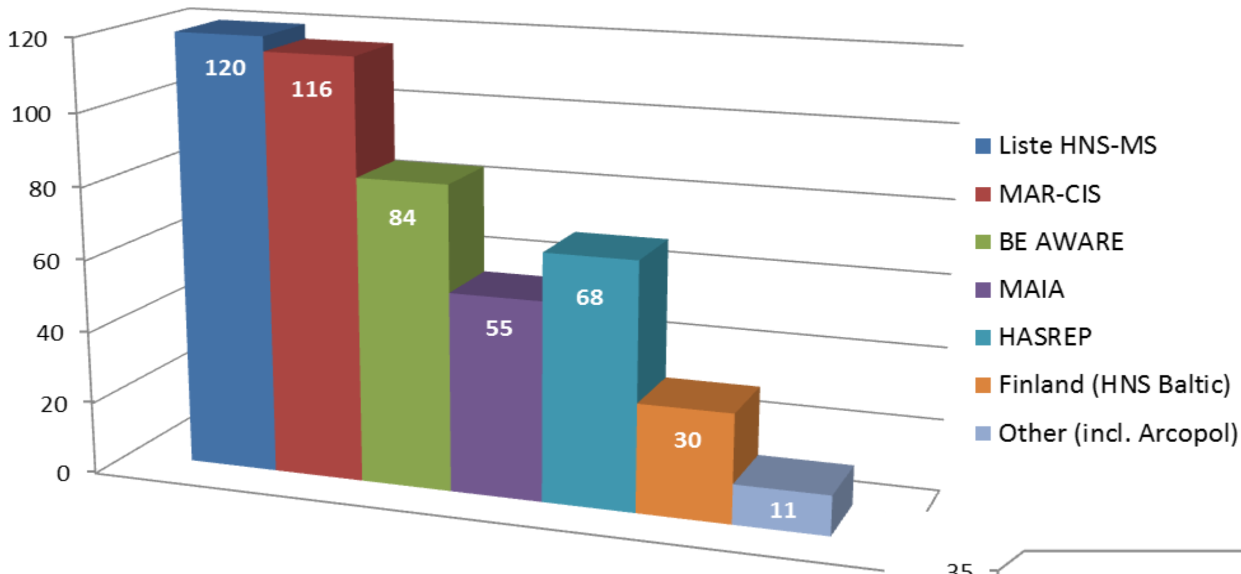
- HASREP - Mar-CIS - GESAMP / EHS
- Be Aware - ARCOPOL
- And “fresh” data from French and Finnish harbours

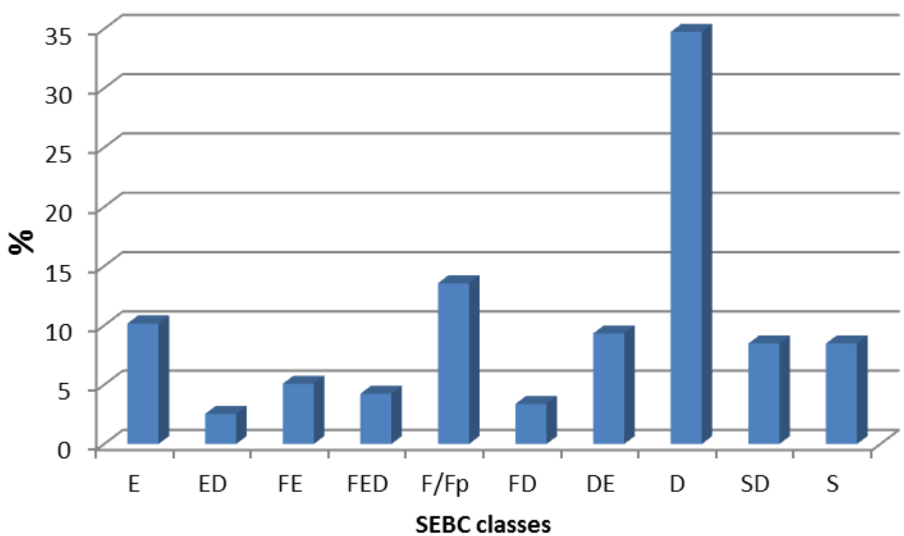
→ Selection of the HNS classified by repetition

→ Mainly pure chemical substances but also some blended substances

Co-funded by the European Commission, DG-ECHO

Selection of 120 HNS – List





Laboratory characterisation – selection of 19 HNS

Part of the 100+ HNS listing

HNS	CAS number	SEBC code
2,2,4-Trimethyl-1,3-Pentanediol-1-Isobutyrate	25265-77-4	F
2-Ethylhexanoic acid	149-57-5	FD
2-Ethylhexyl acrylate	103-11-7	F
2-propanol	67-63-0	D
Acétone	67-64-1	DE
Butyl acrylate	141-32-2	E
Ethyl acetate	141-78-6	DE
Heptane	142-82-5	E
Hydrochloric acid	7647-01-0	DE
Methanol	67-56-1	DE
Methyl isobutyl ketone	108-10-1	FED
Methyl methacrylate	80-62-6	FED
Methyl tert butyl ether	1634-04-4	ED
n-Butyl acetate	123-86-4	FED
n-Butyl alcohol	71-36-3	D
n-Hexane	110-54-3	E
Nonyl alcohol (all isomers)	2430-22-0	F
Pentane	109-66-0	E
Toluene	108-88-3	E
Xylenes	1330-20-7	FE

Laboratory characterisation – Properties tested

- Specific gravity
- Viscosity
- Surface tension

At 5 / 10 / 20 °C

- Interfacial tension (HNS/seawater)

- Evaporation kinetics: pure HNS and a “slick” of HNS on seawater

- Dissolution kinetics: 20 °C
  freshwater, 5‰ and 35 ‰

Laboratory characterisation – Results

- Specific gravity

HNS	5 °C	10 °C	20 °C
1-Nonanol	0,8383	0,8348	0,8291
2,2,4-Trimethyl-1,3-Pentanediol-1-Isobutyrate	0,9577	0,9542	0,9477
2-Ethylhexanoic acid	0,9173	0,9142	0,9061
2-Ethylhexyl acrylate	0,897	0,8918	0,8861
2-Propanol	0,7875	0,7946	0,7946
Acetone	0,807	0,8018	0,7918
Butyl acrylate	0,9131	0,9085	0,9001
Ethyl acetate	0,9181	0,9119	0,902
Heptane	0,6971	0,6938	0,6853
Methanol	0,8055	0,8013	0,7932
Methyl isobutyl ketone	0,8145	0,8102	0,8031
Methyl methacrylate	0,9574	0,9534	0,9438
Methyl tert-butyl ether	0,7574	0,7527	0,7531
n-Butyl acetate	0,896	0,8916	0,881
n-Butyl alcohol	0,8213	0,8179	0,8116
n-Hexane	0,6753	0,6696	0,6613
Pentane	0,6429	0,6384	0,6278
Toluene	0,8809	0,8757	0,8683
Xylenes	0,879	0,8743	0,8677

- Experimental data at 20 °C are in accordance with literature data (less than 2% of gaps).

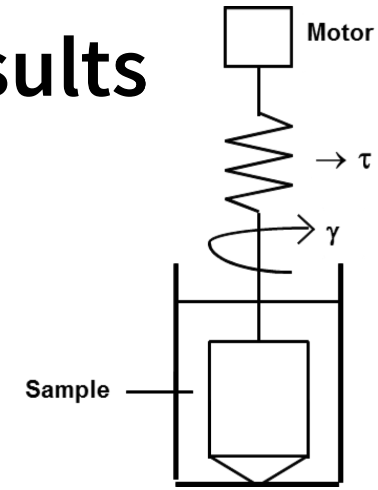
- Decrease in temperature results in an increase of specific gravity: difference of 1 to 2 % between 5 and 20 °C.

Co-funded by the European Commission, DG-ECHO

Specific gravity

- Floatability (floater, sinker versus Temperature)
- For different experimental conditions (closed to the natural environment), gaps are less than 2%
- Possible to accept this gap in the modelling tool,
- **No need to maintain our efforts on this parameter**

Laboratory characterisation – Results



- Viscosity

HNS	Viscosity (mPa.s)		
	5°C	10°C	20°C
1-Nonanol	15,25	18,77	12,39
2,2,4-Trimethyl-1,3-Pentanediol-1-Isobutyrate	45,52	33,37	18,95
2-Ethylhexanoic acid	16,43	12,83	8,41
2-Ethylhexyl acrylate	3,99	3,73	5,55
2-Propanol	4,44	3,63	3,51
Acetone	1,28	1,16	1,36
Butyl acrylate	2,58	2,5	2,36
Ethyl acetate	1,63	1,63	1,59
Heptane	1,42	1,38	1,33
Methanol	1,95	1,79	1,6
Methyl isobutyl ketone	1,9	2,31	1,78
Methyl methacrylate	2,11	2,03	1,82
Methyl tert-butyl ether	1,33	1,32	1,14
n-Butyl acetate	2,42	2,25	2,06
n-Butyl alcohol	4,78	9,79	3,88
n-Hexane	1,21	1,04	1,12
Pentane	0,86	0,85	0,62
Toluene	1,98	1,81	1,81
Xylenes	2,1	2,03	1,91

- Experimental data at 20 °C are in accordance with literature data for HNS with viscosity > 3 mPa.s

- Difficulties of measurements for viscosities < 3 mPa.s

- Usually, decrease in T° results in an increase of viscosity.

Co-funded by the European Commission, DG-ECHO

Viscosity

- Spreading (size of the slick versus Temperature)
- For viscosity higher than 8 mPa.s at 20°C, the viscosity at 5°C increases by a factor of 2 (at least!)
- Uncertainties for a viscosity less than 3 mPa.s at 20°C, need to adapt the experimental protocol
- **Need to maintain our efforts on this parameter**

Laboratory characterisation – Results

- Surface tension

HNS	Surface tension ($mN.m^{-1}$)		
	5°C	10°C	20°C
1-Nonanol	28,91	28,02	27,8
2,2,4-Trimethyl-1,3-Pentanediol-1-Isobutyrate	29,46	28,73	28,12
2-Ethylhexanoic acid	28,42	27,62	26,86
2-Ethylhexyl acrylate	27,91	27,68	26,82
2-Propanol	21,44	21	20,79
Acetone	24,9	24,14	23,44
Butyl acrylate	26,77	26,56	25,63
Ethyl acetate	25,08	24,39	23,82
Heptane	21,6	21,08	20,32
Methanol	23,88	23,06	22,67
Methyl isobutyl ketone	24,47	23,73	23,61
Methyl methacrylate	27,77	27,1	25,99
Methyl tert-butyl ether	20,04	19,07	18,06
n-Butyl acetate	25,8	25,02	24,83
n-Butyl alcohol	25,71	24,9	24,25
n-Hexane	19,92	19,09	18,6
Pentane	17,55	16,77	16,43
Toluene	29,8	28,66	28,01
Xylenes	29,04	27,88	26,96

- Experimental data at 20 °C are in accordance with literature data.

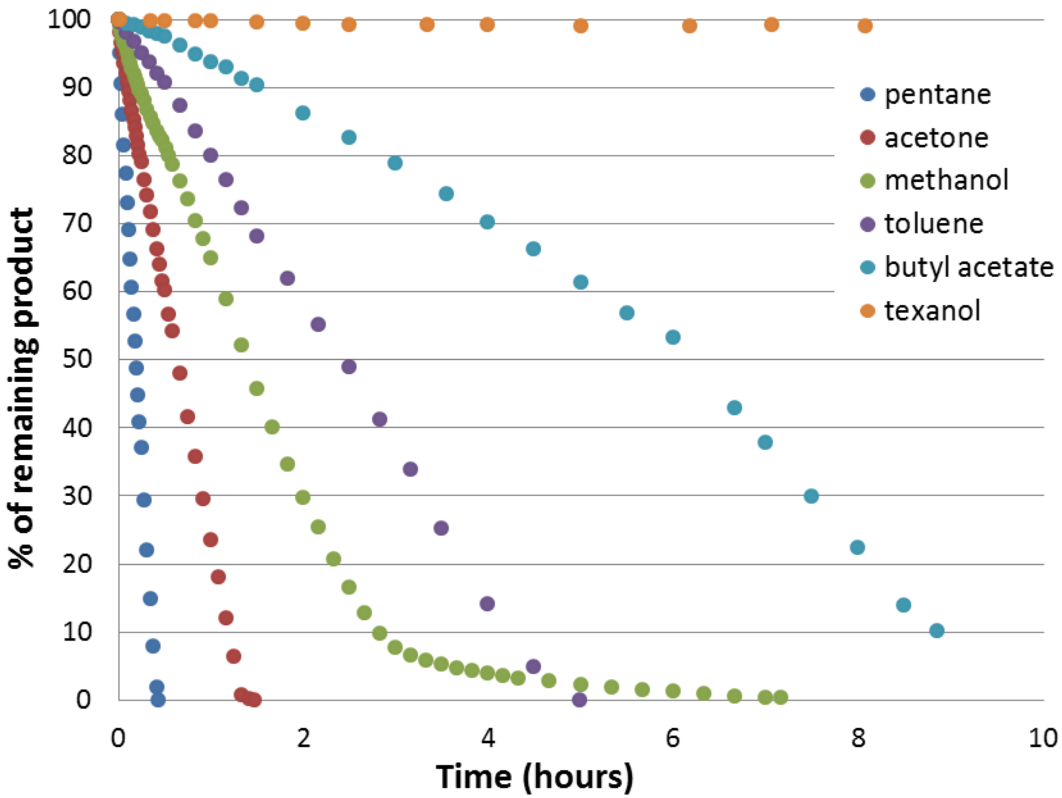
- Decrease in temperature results in an increase of surface tension: difference of 3 to 10 % between 5 and 20 °C.

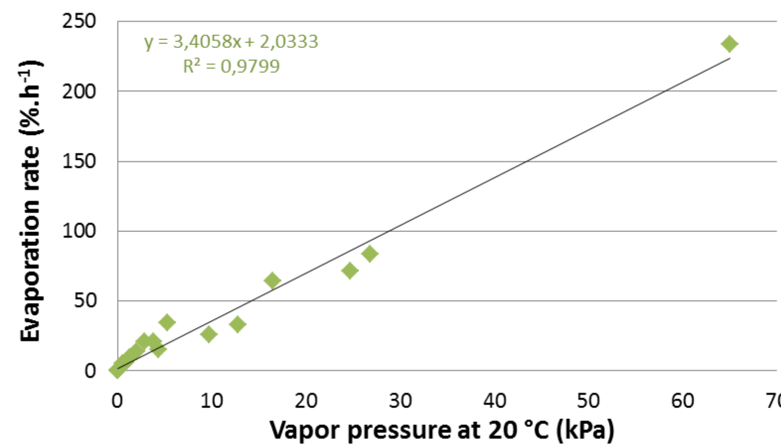
- Interfacial tension data are being processed.

Co-funded by the European Commission, DG-ECHO

Laboratory characterisation – Results

- Evaporation kinetics – HNS (weight loss measurement / 7 mL at T0)



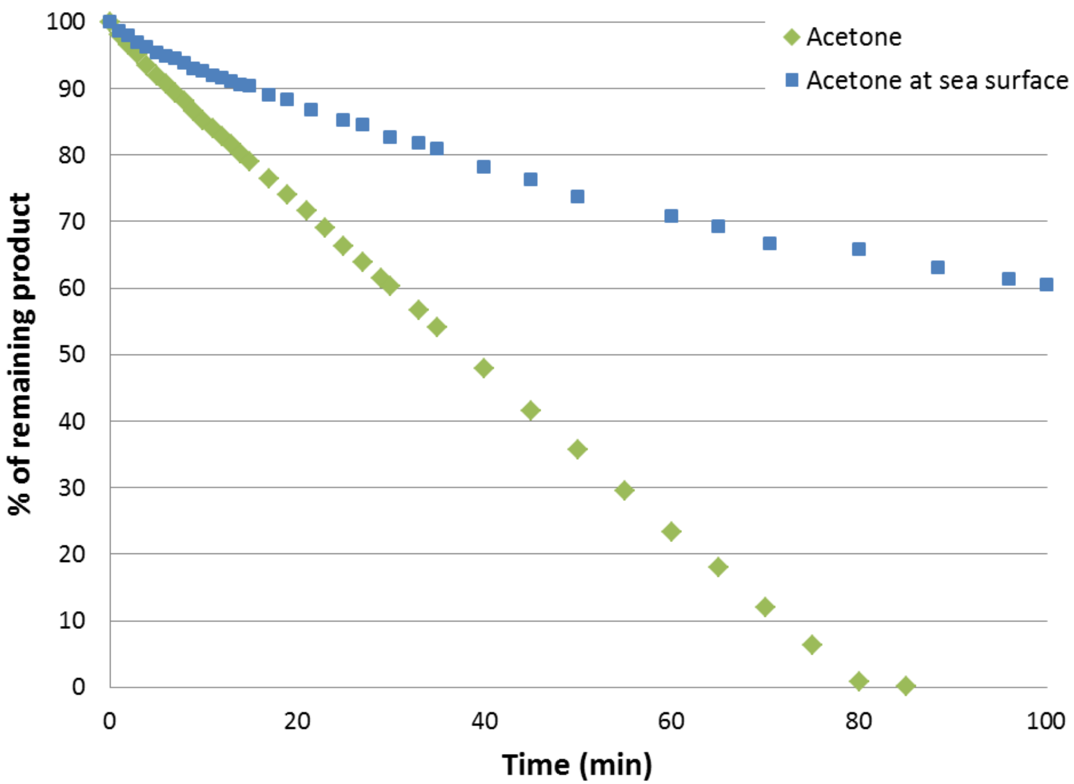


Co-funded by the European Commission, DG-ECHO

Laboratory characterisation – Results

- Evaporation kinetics – HNS at sea surface

Data processing in progress



- Acetone = miscible with water

- Lower evaporation rate when in surface due to the competition between evaporation and dissolution

Co-funded by the European Commission, DG-ECHO

Evaporation rate

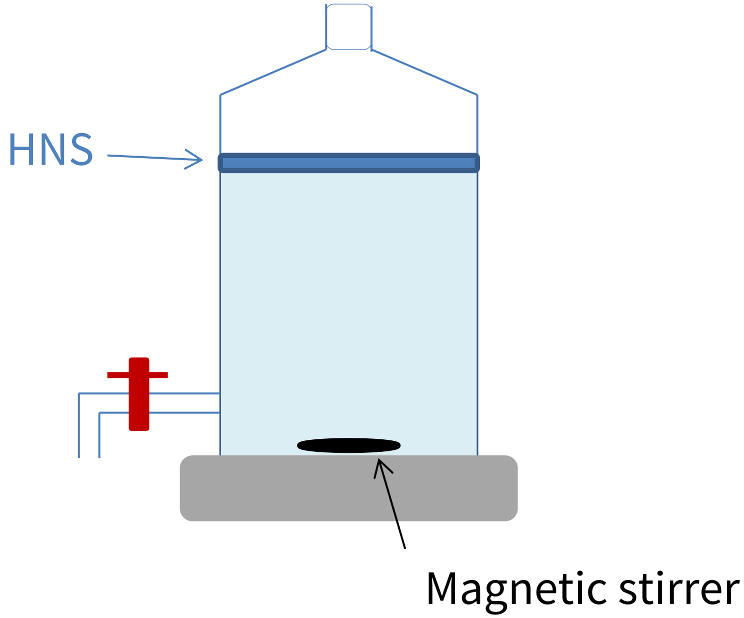
- Surface tension increases as the temperature drops, decrease in the evaporation rate
- Vapor pressure and evaporation are well correlated
- Evaporation rate is lower when the product is at the water interface
- **Need to maintain our efforts on this parameter**

Co-funded by the European Commission, DG-ECHO

Laboratory characterisation – Results

- Dissolution kinetics - Protocol:

For each HNS, at a defined temperature and salinity, 3 replicates



- Volume of HNS defined in order to be above the theoretical solubility limit

- Sampling of 10 mL of water followed by GC-FID or GC-MS analysis

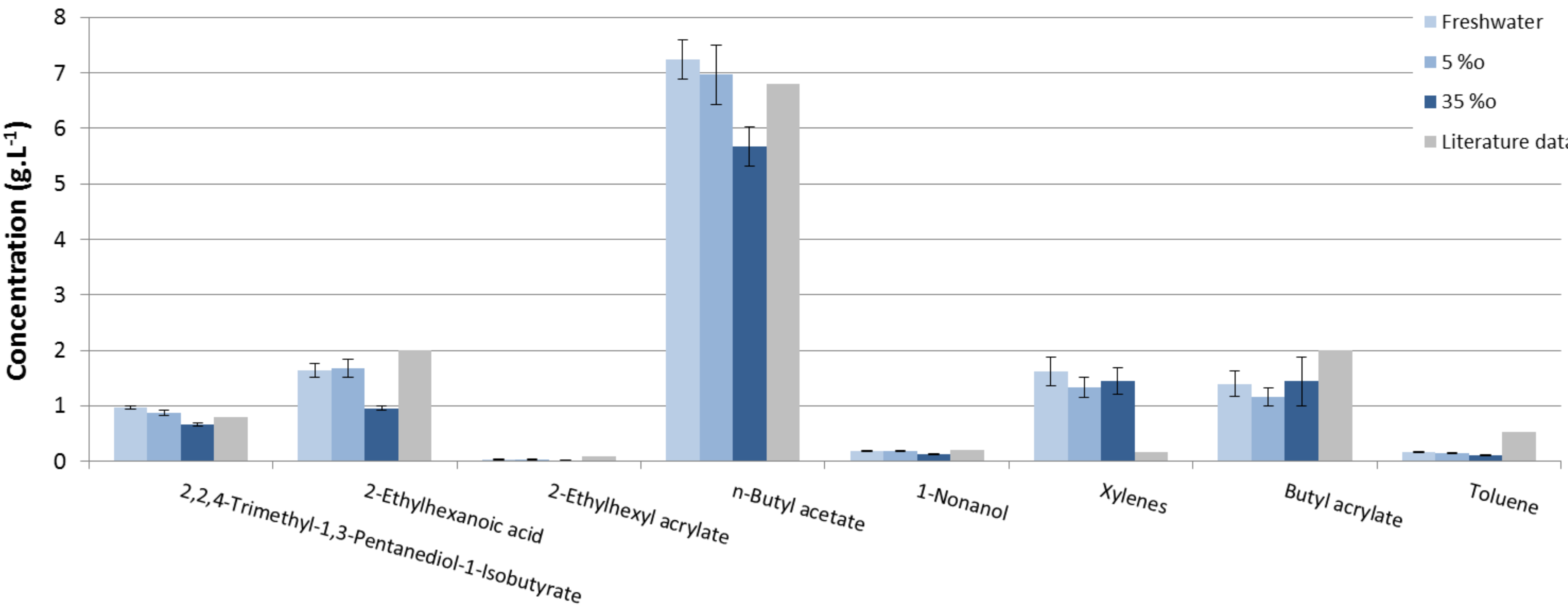
- Experiment continued until a stable concentration is reached

Co-funded by the European Commission, DG-ECHO

Laboratory characterisation – Results

- Dissolution kinetics

Experiments still in progress



Dissolution rate

- For a chemical, wide range of solubility limit in the literature
- For acids and dissolvers, the salinity decreases the limit of solubility
- Effect of the temperature on the solubility limit?
- **Need to maintain our efforts on this parameter**

Conclusions

- Huge amount of tests performed at lab
- Good correlation between our results and the scientific literature (at 20°C and for fresh water)
- Significant effect of the temperature on the surface tension, which is involved in the evaporation rate
- 2 evaporation rates: HNS alone or HNS on water
- For some HNS, the dissolution can be affected by the salinity

Need to perform experiments at a pilot scale to characterise the dissolution rate and the evaporation rate simultaneously

Thank You

Merci

{HNS-MS}

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

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

Co-funded by the European Commission, DG-ECHO