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# Kinetics of formation, analysis and ecotoxicity of chlorination by-products generated when using of seawater for industrial processes

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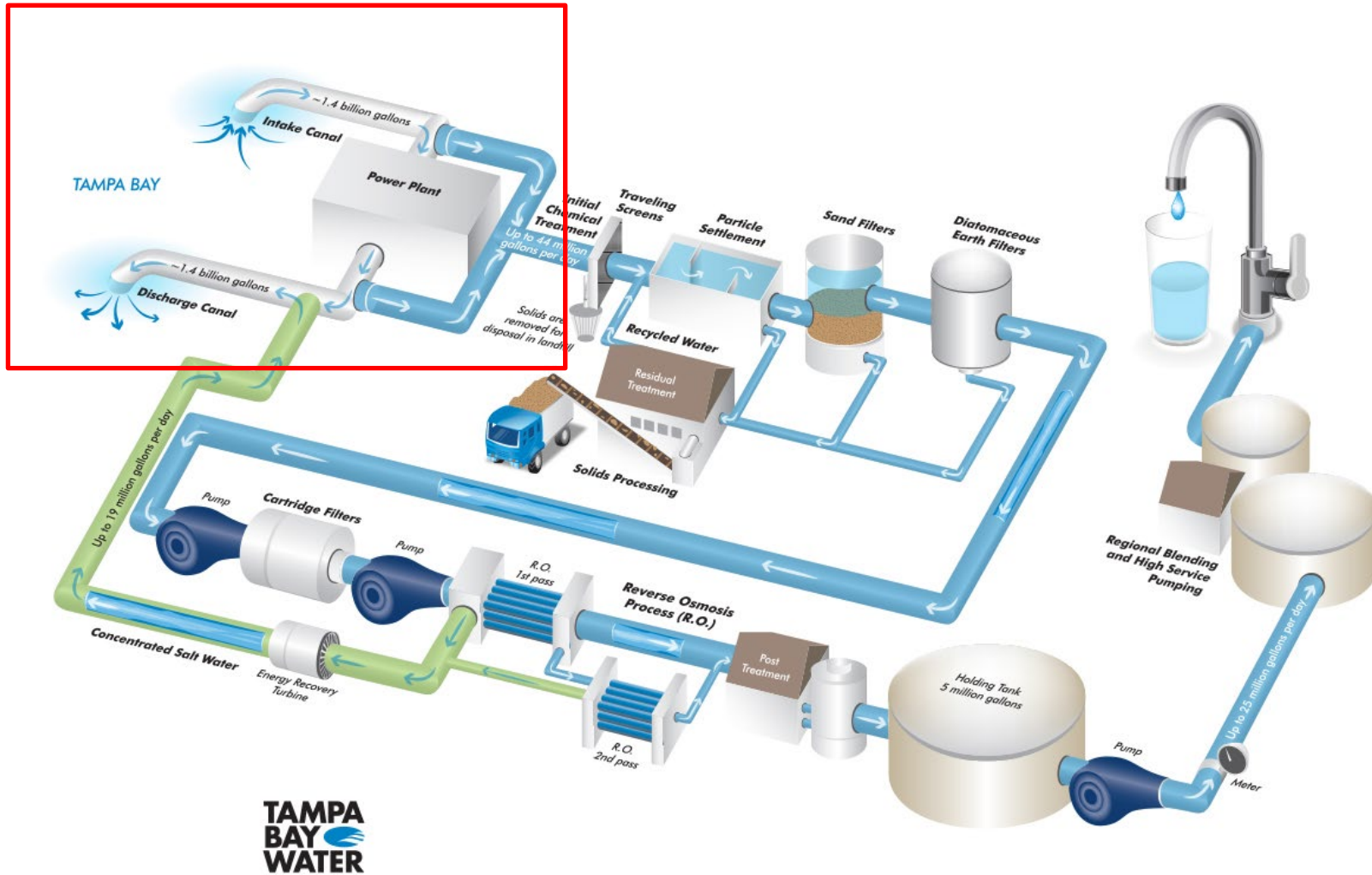
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# Kinetics of formation, analysis and ecotoxicity of chlorination by-products generated when using of seawater for industrial processes

Seawater is used as a source of drinking water or ...



**TAMPA BAY WATER**  
Tampa Bay Seawater Desalination Plant  
Process Diagram

Or as a medium for cooling (petrochemical, steel, thermal and nuclear power plants) or warming purposes (LNG terminals) in costal industries



St Lucie (FL, US) nuclear power plant



Petrochemical site (Fos-sur-mer, France)



Thermal power plant (Fos-sur-mer, France)

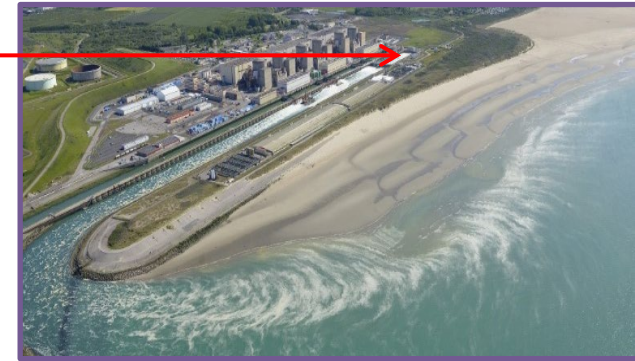
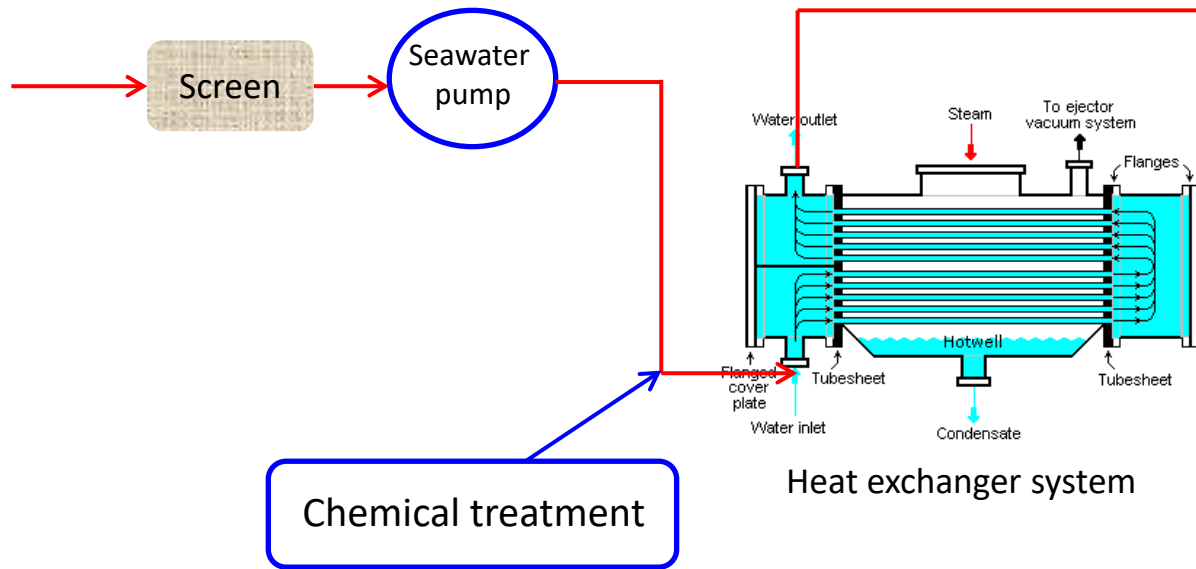


Methane terminal (Fos-sur-mer, France)

To prevent biofouling (micro- and macrofouling), seawater is treated with biocide compounds:

- 1,3-propylene diamine (e.g., Hatacide, Hatasperse, Drewspere, ...)
- (alkyl amino)-3 aminopropane (e.g., MEXEL-432®)
- chlorination : BAT according IPPC EU directive





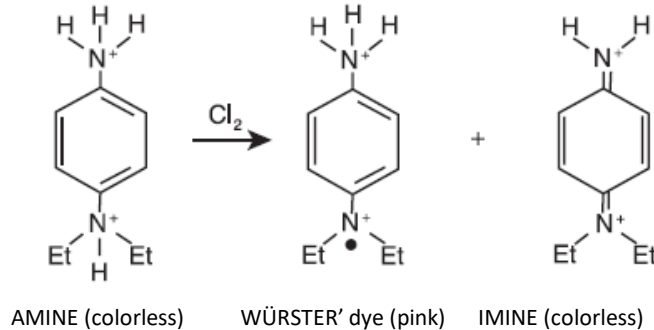
## Chlorination

- mode : continuous at low doses or intermittent at high doses
- use : dissolved gaseous chlorine, sodium hypochlorite or **electrochlorination**
- dose : 0.5 to 1.5 mg/L (low dose) to 10 mg/L (high dose)
- discharge rates : 7,000 m<sup>3</sup>/h to 30,000 m<sup>3</sup>/h (6 to 9 months/year)

## Total Residual Oxidant

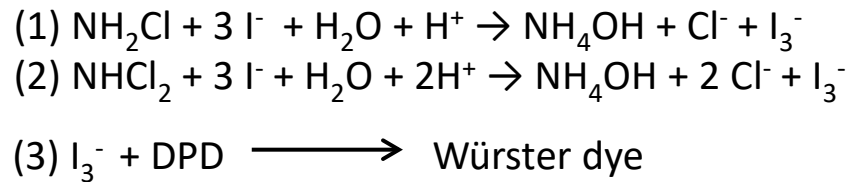
- Based on a colorimetric reaction of chlorine (or bromine) and its inorganic derivatives with DPD (*N,N*-diethyl-*p*-phenylenediamine)

Without  $I^-$   
 →  
 DPD-1



Free available chlorine  
(or bromine)

With  $I^-$   
 →  
 DPD-1 + DPD-2



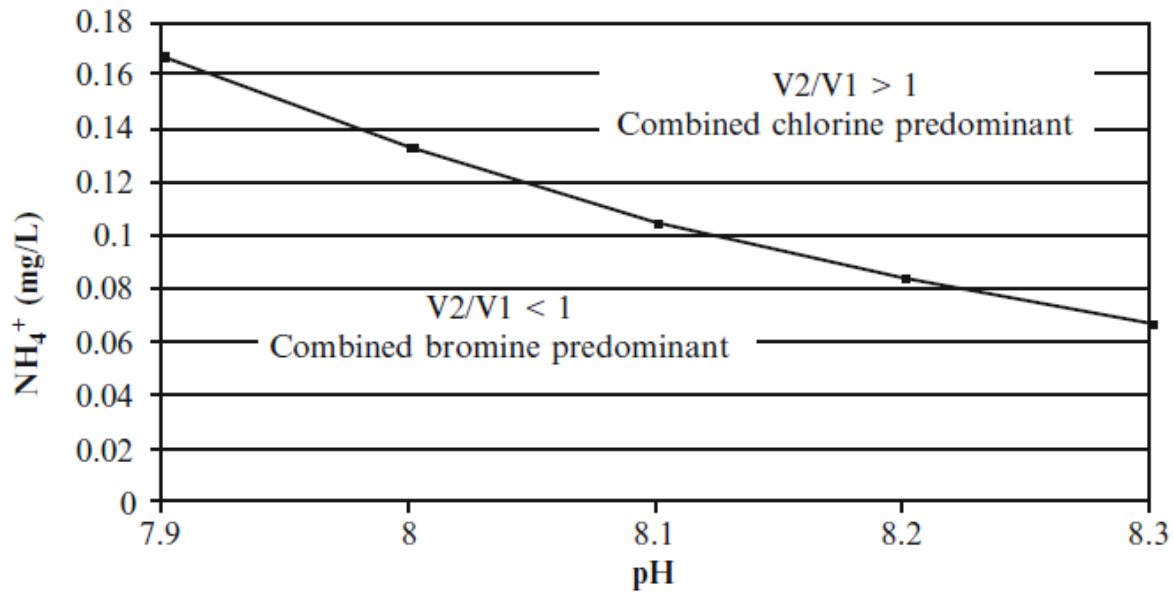
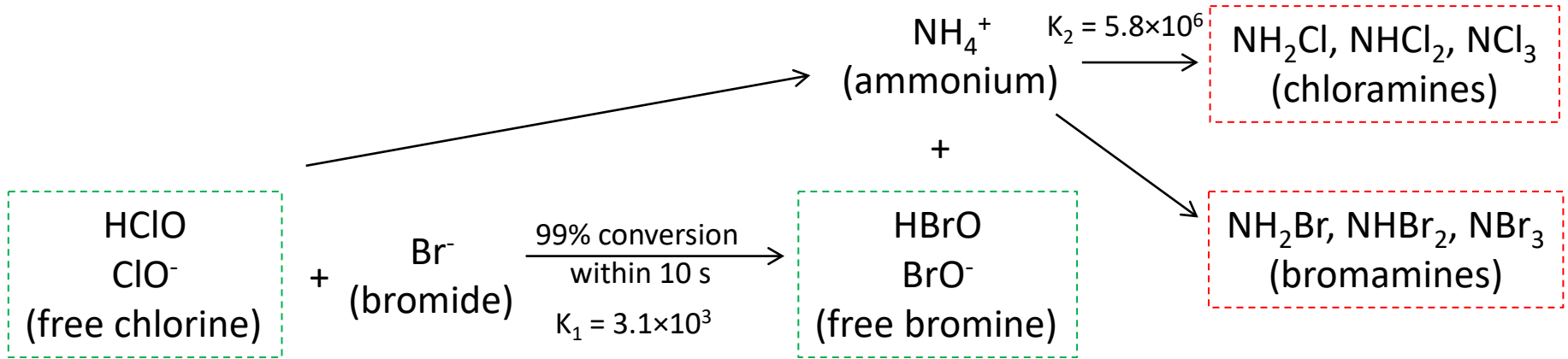
Combined chlorine  
(or bromine)

TRO parameter measures only free chlorine and inorganic forms chlorinated compounds =  $\text{Cl}_2$ ,  $\text{HClO}/\text{ClO}^-$ ,  $\text{NHCl}_2$ ,  $\text{NH}_2\text{Cl}$ ,  $\text{NCl}_3$  and  $\text{CNCl}$



Example of A TRO Analyzer (Hach 1735)<sup>™</sup>

In seawater (and brackish waters), chlorine reacts rapidly with  $\text{Br}^-$  ( $\sim 65 \text{ mg/L}$ ) as follows:





CNBr

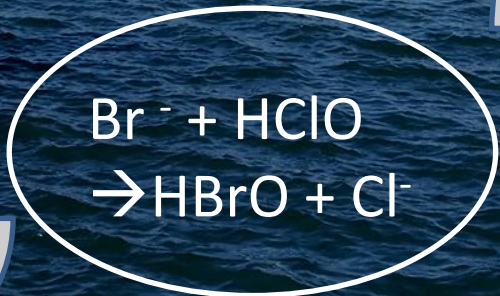
NBr<sub>3</sub>

CHBr<sub>3</sub>, CHClBr<sub>2</sub>, CHCl<sub>2</sub>Br



+ Matière Organique naturelle

THMs, HAAs, HAN, HK, ... bromés



CNBr

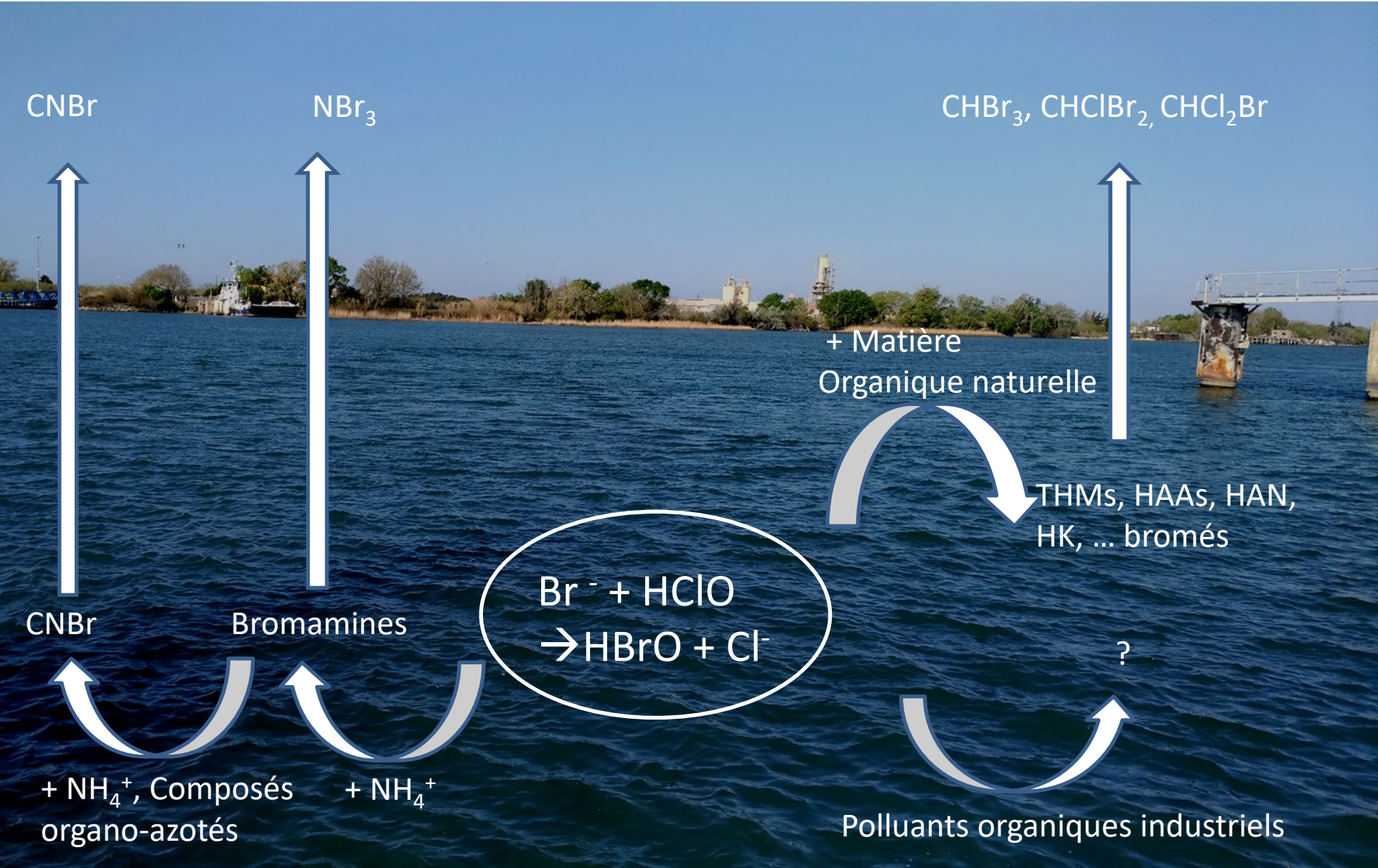
Bromamines

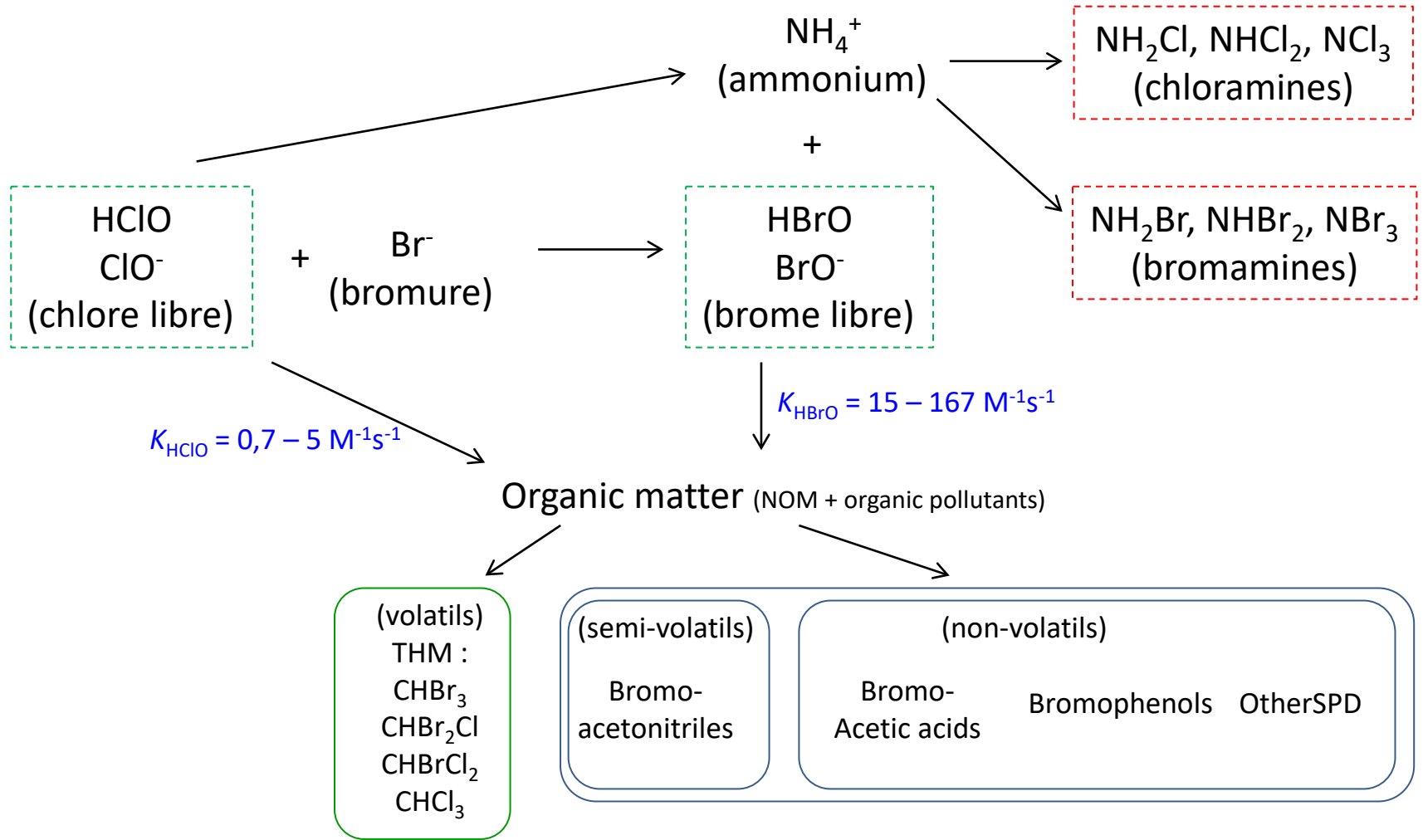
?

+ NH<sub>4</sub><sup>+</sup>, Composés organo-azotés

+ NH<sub>4</sub><sup>+</sup>

Polluants organiques industriels





  Free Oxidants (free chlorine or bromine)

  Combined oxidants (combined chlorine or bromine)

} Measured as *Total Residual Oxidant (TRO)*

  Purgeable organic halogens (POX)

  Extractable organic halogens (EOX)

} POX + EOX = TOX (Total Organic Halogens)

The total organohalogen content in seawater can only be determined by the EOX protocole

↪ Extraction of organohalogen compounds by MTBE (in presence of  $\text{Na}_2\text{SO}_4$ )

↪ Combustion/pyrolysis at 900 °C

↪ Micro- coulometric analysis of HX

Sampling points	TRO (mg/L $\text{Br}_2$ )	EOX (mg/L Br)
Petrochemical plant	0.99	21.6
Methane terminal	0.09	46.6
Methane terminal	<LD	9.27
Thermal power plant	0.23	21.64

Field campaign, Gulf of Fos, France, 2017/10/09

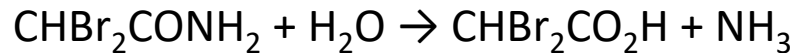


## Chlorination by-products identified at the outlets of coastal industrial plants

↪ Trihalomethanes (THM):  $\text{CHBr}_3$  (95-98%)  $\gg$   $\text{CHBr}_2\text{Cl}$   $>$   $\text{CHBrCl}_2$

THM	$K_1$ (cm/h)	Mean water depth (m)			
		5	10	20	50
$\text{CHBr}_3$ (bromoform)	4.1	3.52	7.04	14.09	35.22
$\text{CHBr}_2\text{Cl}$ (DBCM)	6.8	2.12	4.25	8.49	21.24
$\text{CHBrCl}_2$ (BDCM)	8.9	1.62	3.25	6.49	16.23
$\text{CHCl}_3$ (chloroform)	11.4	1.27	2.53	5.07	12.67

↪ Haloacetonitriles (HAN) : Dibromoacetonitrile



↪ Haloacetic acids: Dibromoacetic acid

Obviously, many other compounds should be formed according reactivity of  $\text{HBrO}/\text{BrO}^-$  with organic compounds



# Water sampling

- At each sampling point, two samples were collected (at the surface and 7-meter depth) using 6-L Niskin bottle
  - 1-L bottle for TOC, TN, Br<sup>-</sup> analysis
  - 1-L bottle for analysis of halogenated byproducts: EOX, THMs, HAAs, HPs, HANs, HALs
  - Temperature, pH, and salinity were determined on-site during water sampling using a CTD-type multi-parameter probe (MS5)
  - Free and total chlorine were determined on-site with DPD spectrometry



# Air sampling

- Air Sampling:
  - On-line: (Proton Transfer Reaction-Time of Flight-Mass Spectrometer, PTR-ToF-MS)



- Off-line : Canisters



# Water and air analysis in the lab

1. Liquid-liquid extraction/preconcentration with MTBE (10:1 v/v)
2. Analysis :
  - THMs, HANs, HAAs and HKs by GC-ECD
  - EOX by combustion/micro-coulometer system
  - Air samples from canister by PTR-ToF-MS\*



\*proton-transfer-reaction time-of-flight mass spectrometry



# Sampling

- Sediments: Ekman sediment sampler

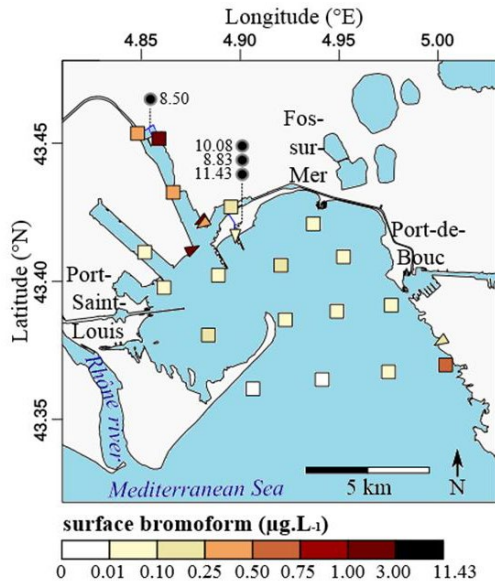


- Biota: Conger eel

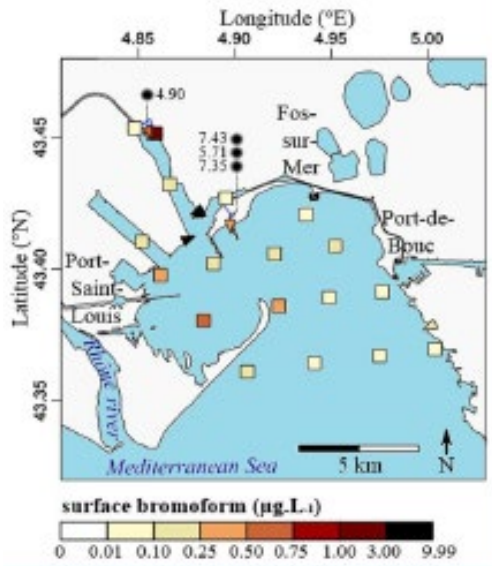


- Samples extracted using accelerated-solvent extraction (ASE 300)

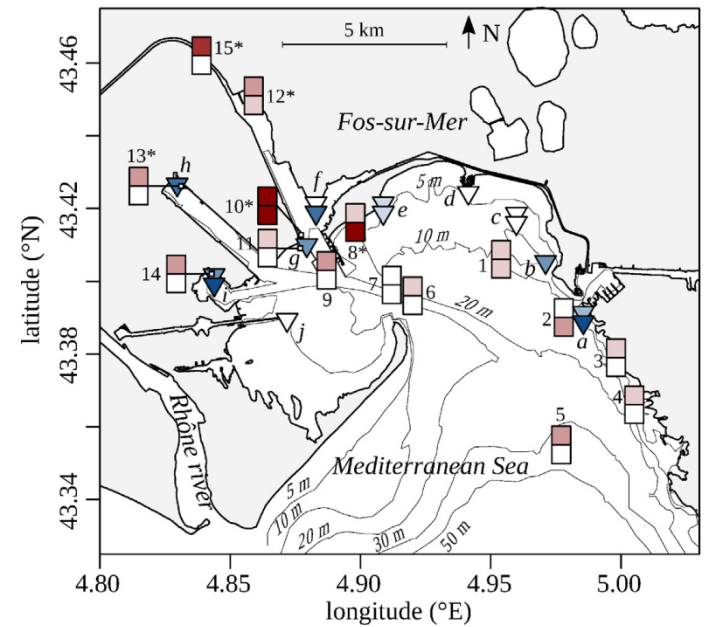
April 2017



October 2017



February 2014



From Boudjellaba *et al.*, STOTEN, 2016



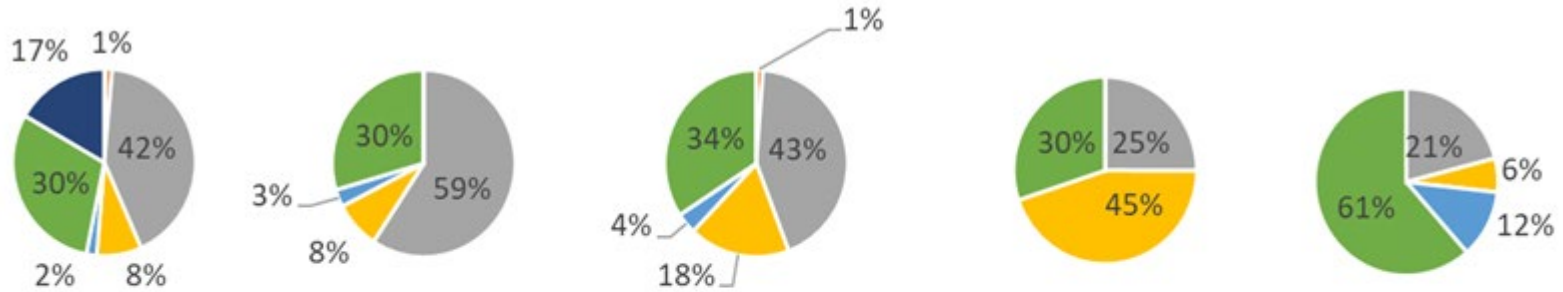
Presence of  $\text{CHBr}_3$  clearly correlated to chlorination of seawater



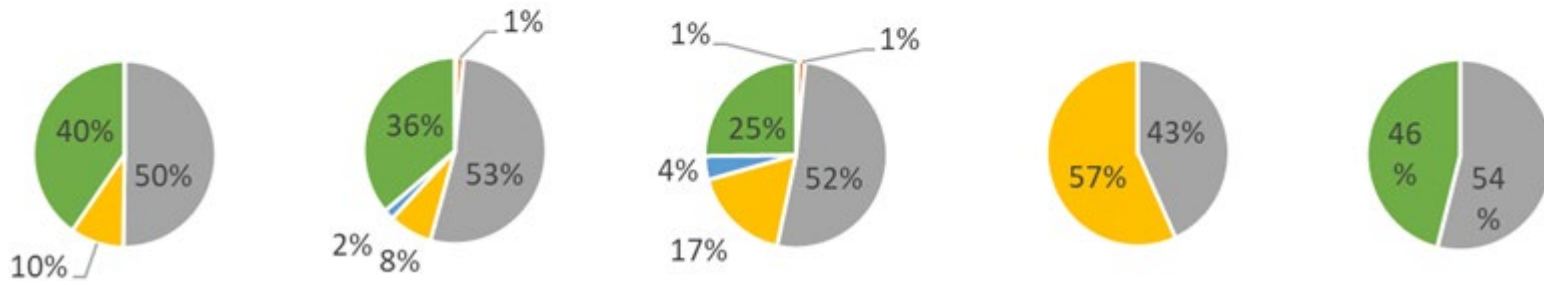
Dissemination within the gulf depending on wind conditions

# Results-Water Analysis (HAA, HAN, Hac)

## Surface outlet discharges

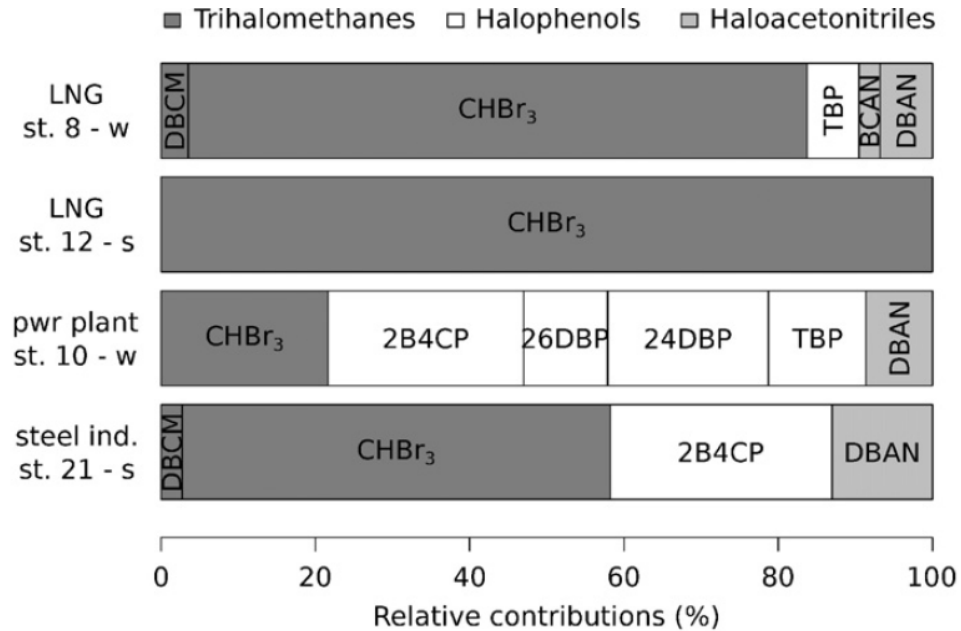


## Depth outlet discharges



- Bromochloroacetonitrile (BCAN)
- Bromoform
- Dibromoacetonitrile (DBAN)
- Bromal hydrate (BH)
- Dibromoacetic acid (DBAA)
- Tribromoacetic acid (TBAA)

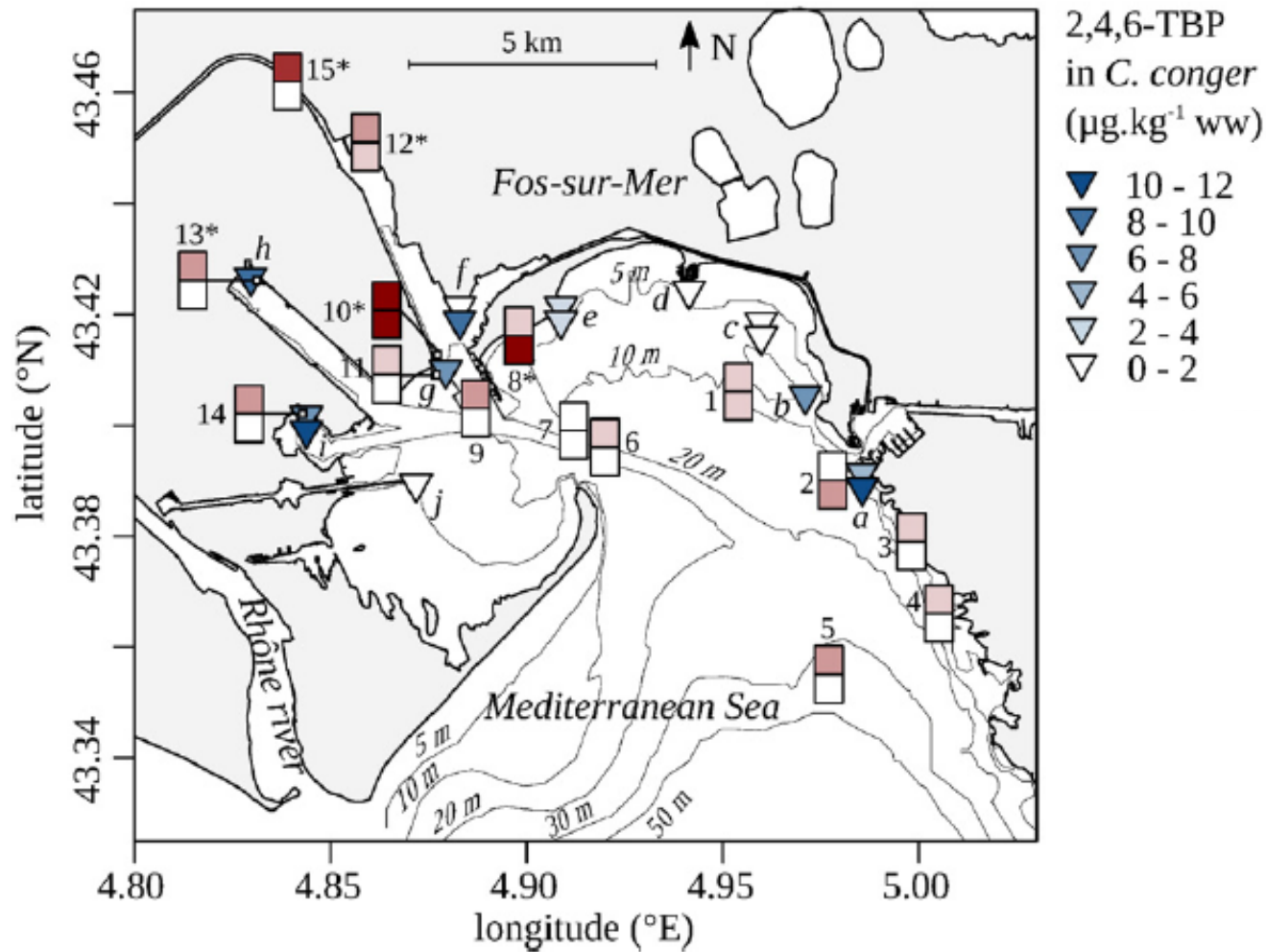
# Results-Water Analysis (halophenols)



↪ Halophenols only detected at the vicinity of industrial outlets

↪ 2,4,6-tribromophenol only found in winter

# Results: Eel conger muscles (halophenols)



# Eco-toxicity

PEC/PNEC values and the corresponding literature toxicity and PNEC data for CBPs identified in the Gulf of Fos.

CBP	Toxicity data				AF	PNEC µg L <sup>-1</sup>	PEC* µg L <sup>-1</sup>	PEC/ PNEC
	Test organism	End point	Conc. mg L <sup>-1</sup>	ref				
Bromoform	<i>C. variegatus</i> (fish)	NOEC, 96 h mortality saltwater	2.9	a	50	58	18.5	0.3
DBAA	<i>P. promelas</i> (fish)	LC <sub>50</sub> , 4 days	69	a	10,000	6.9	3.0	0.4
CDBAA <sup>‡</sup>	<i>C. pyrenoidosa</i> (green algae)	NOEC, 14 day growth freshwater	0.3	a	500	0.6	2.4	4
TBAA <sup>‡</sup>	<i>C. pyrenoidosa</i> (green algae)	NOEC, 14 day growth freshwater	0.3	a	500	0.6	1.2	2
DBAN	<i>P. promelas</i> (fish)	EC <sub>50</sub>	550	a	10,000	55	1.6	0.03
Chloroform	<i>C. dubia</i> (crustacea)	NOEC, 10 day mortality	3.4	a	100	34	1.8	0.05
DBCM	<i>D. magna</i> (crustacea)	NOEC, 21 days	0.06	a	500	0.13	0.8	6.2
TBP	Bacciliariophyceae (diatoms)	NOEC, photosynthesis	0.5	a	1000	0.5	1.5	3
24DBP <sup>‡</sup>	<i>O. mykiss</i> (fish)	NOEC, 21 day growth saltwater	0.21	b	500	0.42	2.4	5.7
26DBP	<i>T. marina</i> (algae CCMP898)	EC <sub>50</sub>	5	c	10,000	0.5	2.0	4.0
2B4CP	<i>T. marina</i> (algae CCMP898)	EC <sub>50</sub>	4.2	c	10,000	0.42	4.0	9.6

References: a (Delacroix et al., 2013), b (Johnson et al., 2012), c (Liu and Zhang, 2014).

\* PEC has been assimilated as the maximum concentration detected in this study.

<sup>‡</sup> For brominated compounds lacking toxicity data, the PNEC values were considered as of their closest resembling chlorinated compound.

Poor reliability of PNEC values towards CBP (high correction factors)

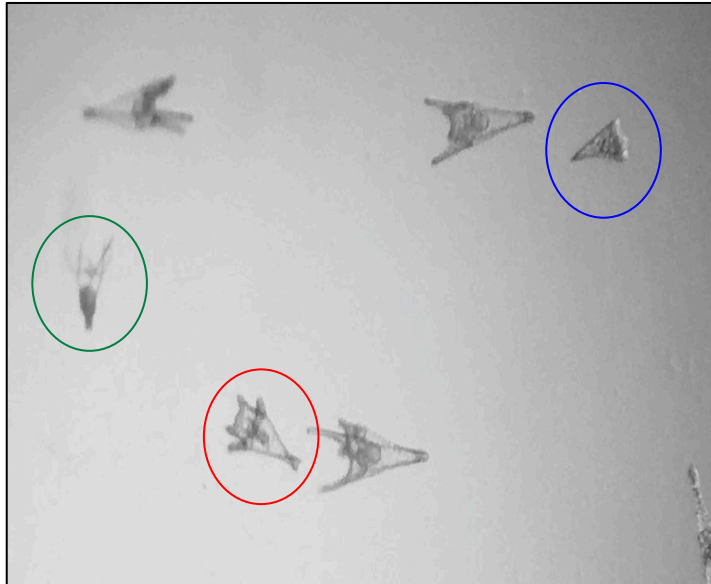


Need to conduct specific ecotoxicological tests with native species

# Eco-toxicity: Dose-response methodology

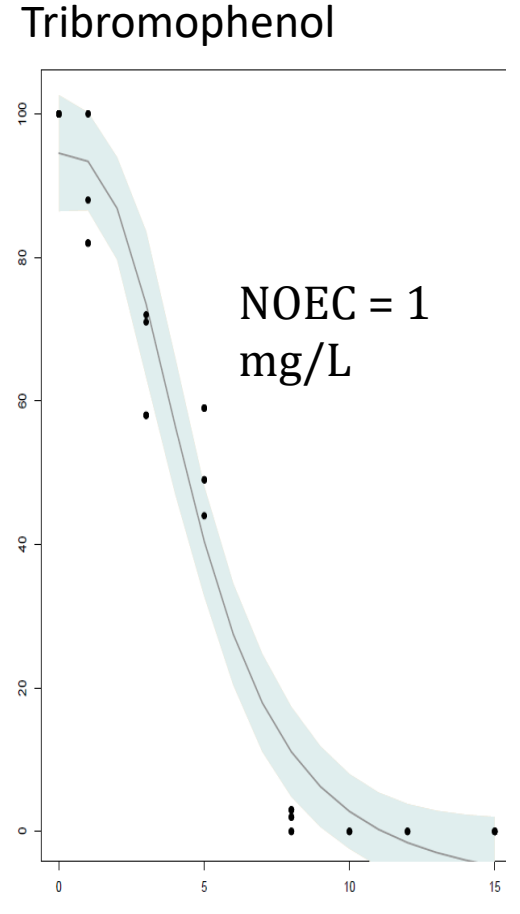
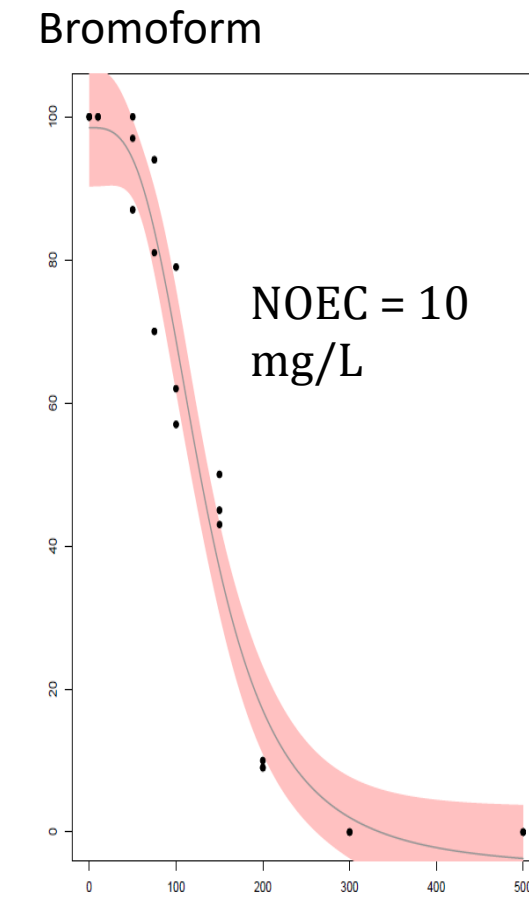
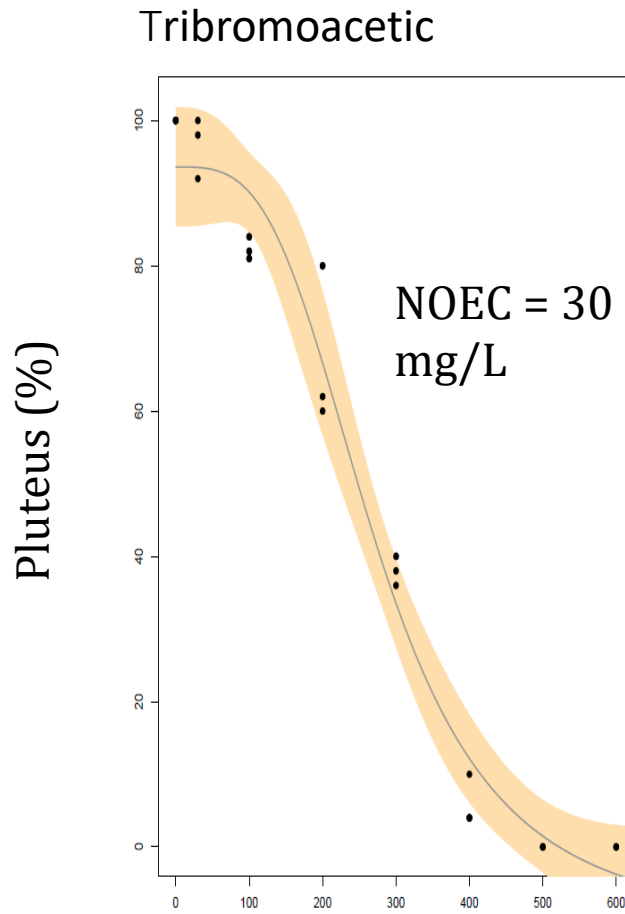
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- Evaluation of toxicity of bromoform, tribromoacetic acid and tribromophenol
- Test based on: mortality, abnormal development rate, stunted growth
- 48 hours of exposure of urchins from NPS



Picture of 48 hours urchin larvae after exposure to anthropogenic compounds

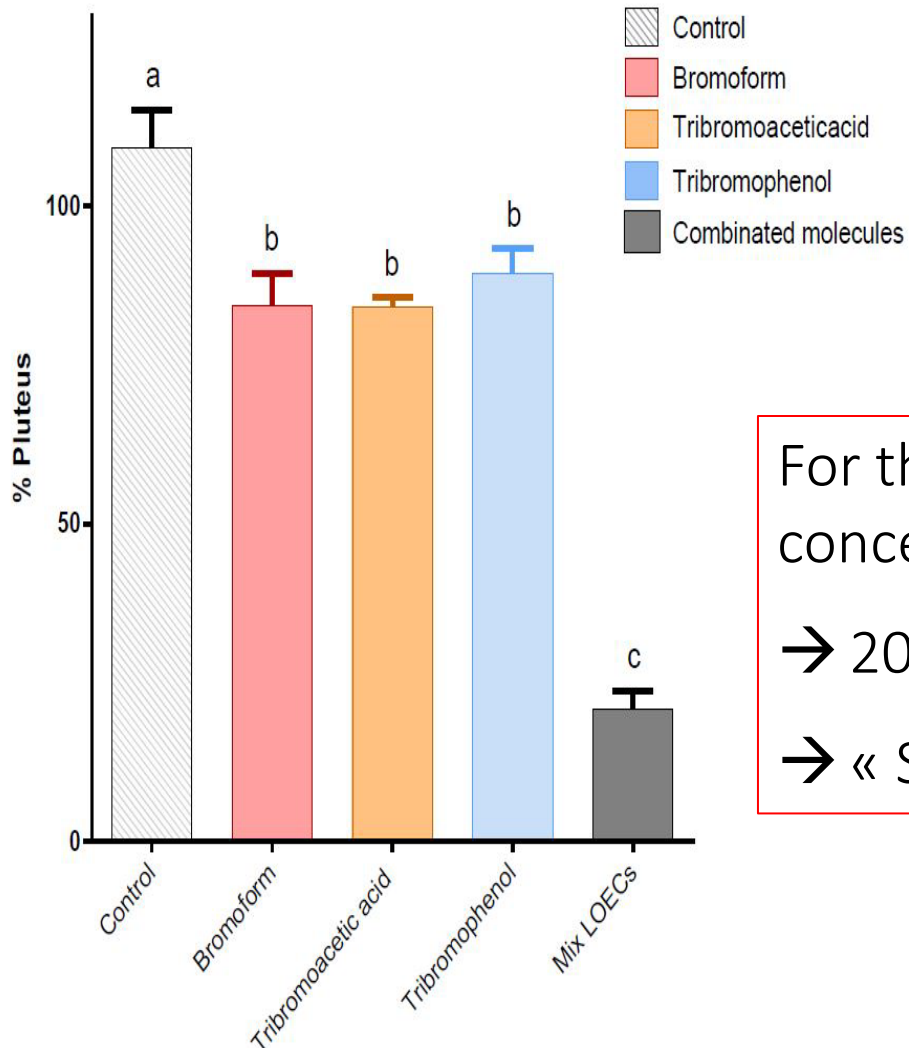
# Eco-toxicity: Dose-response curves



Concentration (mg/L)



# Eco-toxicity: cocktail effects



For the lowest observed effect concentration (LOEC)

→ 20% of pluteus

→ « Synergetic » effect of pollutants

# Conclusions and perspectives

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- $\text{CHBr}_3$  the most found CBP in coastal industrial plants
- Dibromoacetonitrile, dibromoacetic acid, bromal hydrate intermediates of bromoform
- Bromophenols : accumulate in the food web, in sediments (potential health impact?)
- Only 15% of CBP identified in marine environments (according EOX measurement)
- Nature and level of CBP affected by many biotic and abiotic parameters
- Long-term impact of presence of cocktail CBP on the environment?
  - Mithridatization or irreversible impacts (genomic studies)?
- And on human health?

# Acknowledgements

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**Thank you for your attention!**