Biodegradable, labile, leachable, dissolved, colloidal and calculated fractions of hydrophobic organic contaminants of five sediments

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Introduction : the risk assessment of HOC in dredged sediments

65 million tons/year of sediment dredged in France (Marine, river ...)

8 million tons exceed regulatory thresholds (N1 and N2 for marine and fluvial S1, French regulations on sediment dredging)

Waste Classification

- Hazardous (H1 to H15) ?
- If not : Reuse can be for example:

- **Embankment,**
- **Road construction**
- **Landscape mounds**
- **Concrete objects, …**

The risk assessment for HOC is based on:

- Total content
- Partition coefficients

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Material and methods : 5 sediments

	Unit	Evry	Dunkerque	Lens	Marseille	Nimy Blaton
Origin		Highway storm basin	Marine harbor	Canal	Marine harbor	Canal
Localization		48°36’34.99’’N 2°25’56.15’’E	51°2’33.01’’N 2°21’34.36’’E	50°26’13.77’’N 2°53’0.24’’E	43°19’21.50’’N 5°21’37.05’’E	50°30’9.26’’N 3°41’56.53’’E
Water column	m	2	8	7	10	6
TOC	%	3.20	2.85	13.9	4.93	10.6
∑ 14 PAH[1]	µg kg^{-1}	2550	7710	45700	37100	3360
∑ 7 PCB[2]	µg kg^{-1}	75	541	539	3530	318
TPH (C_{10}-C_{40})	mg kg^{-1}	4590	3170	9580	5340	6310
Texture		Sandy-silty	Silty-sandy	Clayey silt	Silty-sandy	Clayey silt

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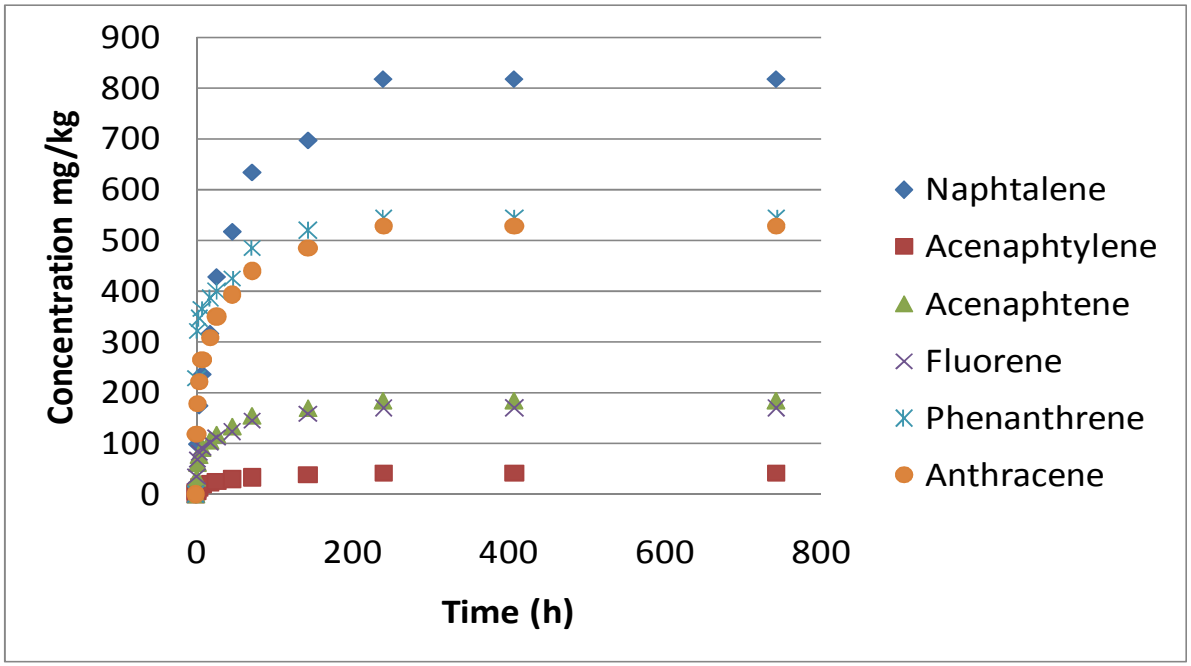
Material and methods : Tenax extraction

13 successive extractions → fractions with fast, slow and very slow desorption rate

considered in the literature as biodegradable (fast desorbing), labile (slow desorbing) and recalcitrant (very slow desorbing) fractions



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Material and methods : Passive sampler

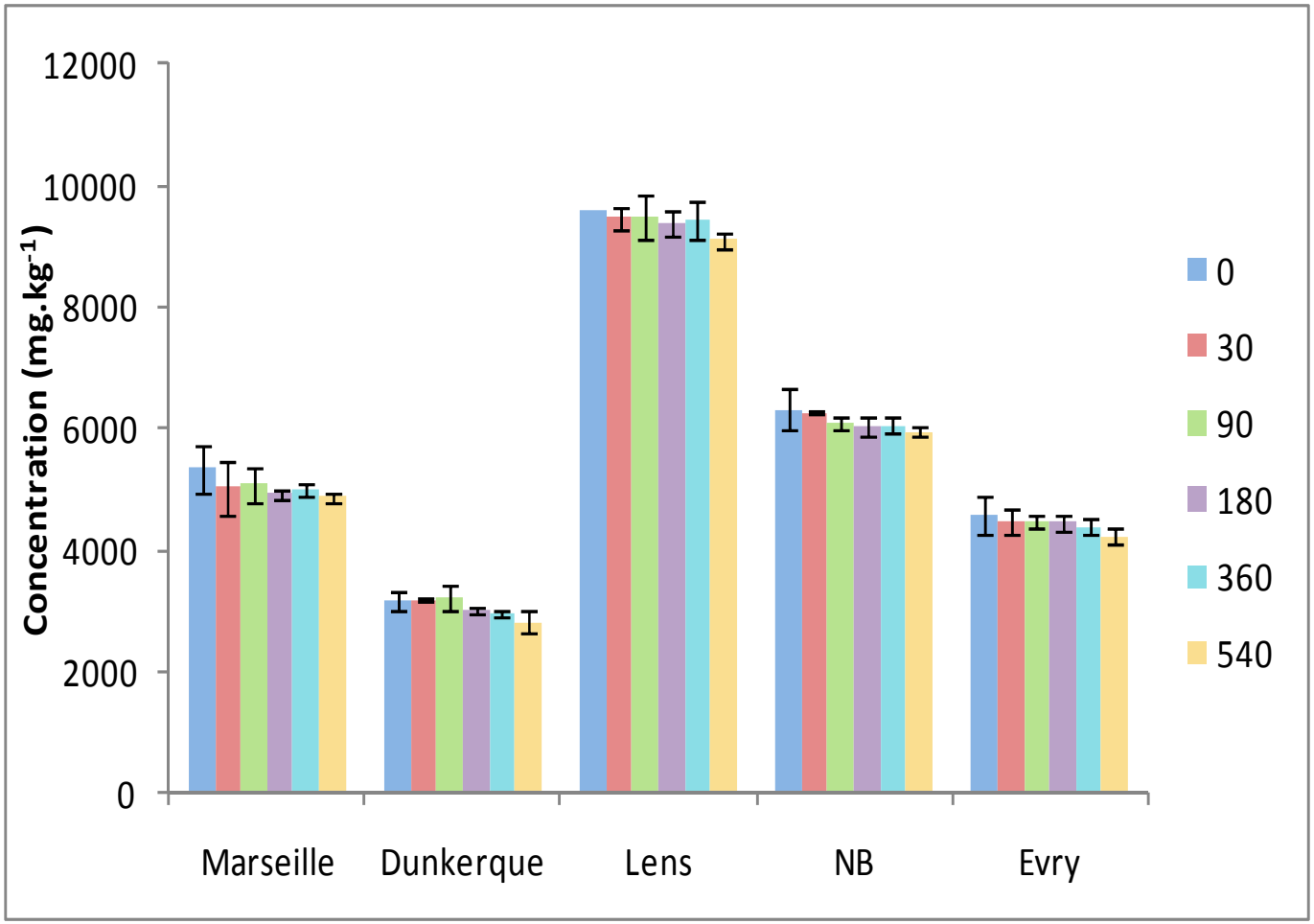
LDPE strips 46 days equilibrium

Quality control, Deuterated Reference compounds

→ Soluble concentration of HOC (10^{-12} g/l)

Results : Effect of maturation on TPH content for 540 days... (oxic conditions)

Average reduction of 9 % in 18 months



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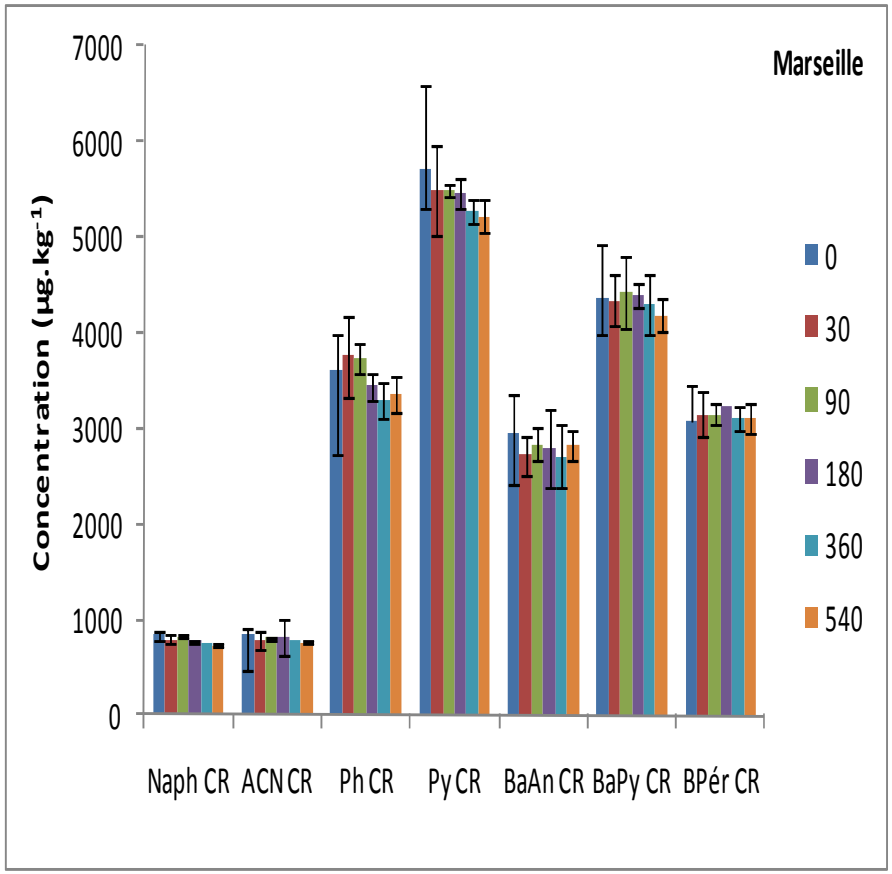
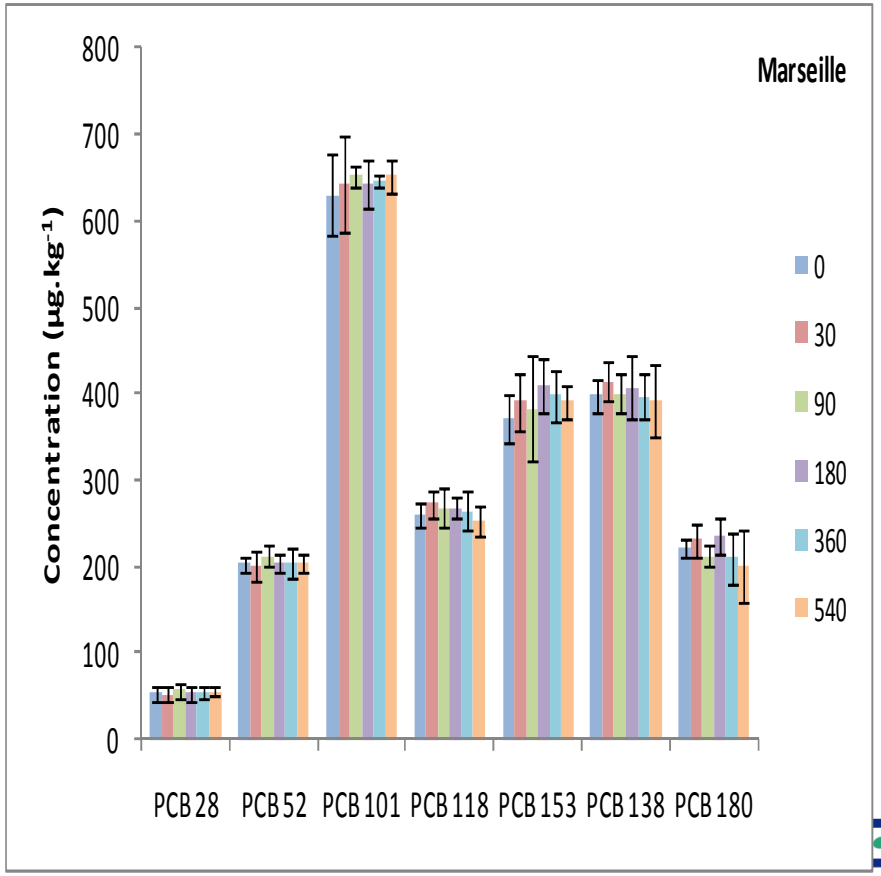
Results : Effect of maturation on HOC content for 540 days... (oxic conditions)

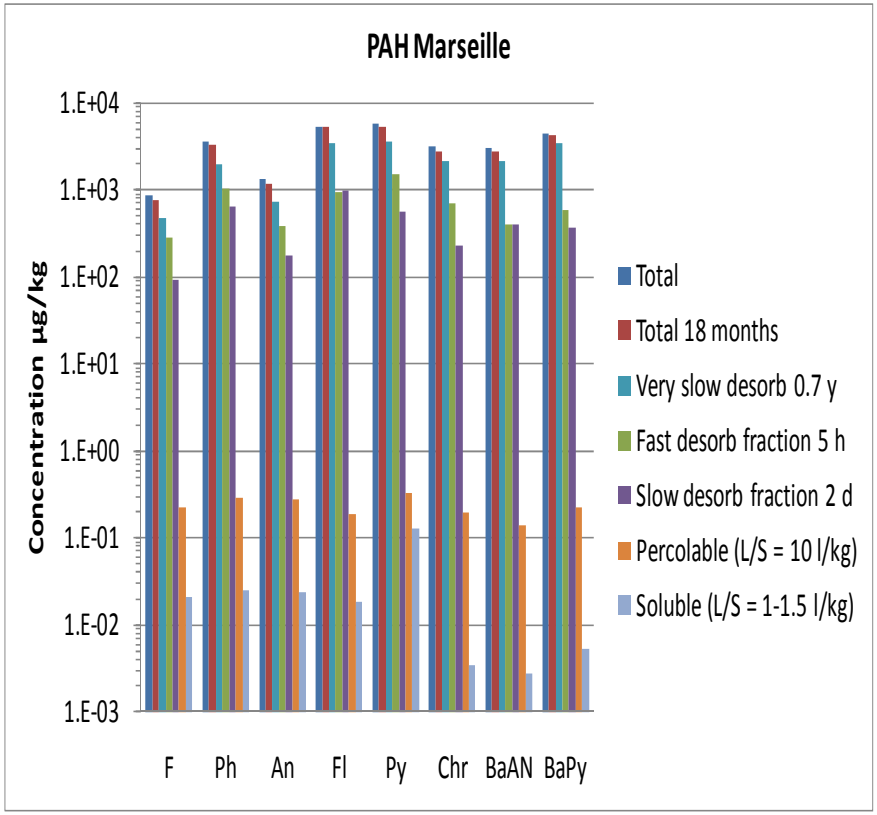
Average reduction of 13 % in 18 months for the lightest PAHs, and no reduction for the other PAHs and PCBs

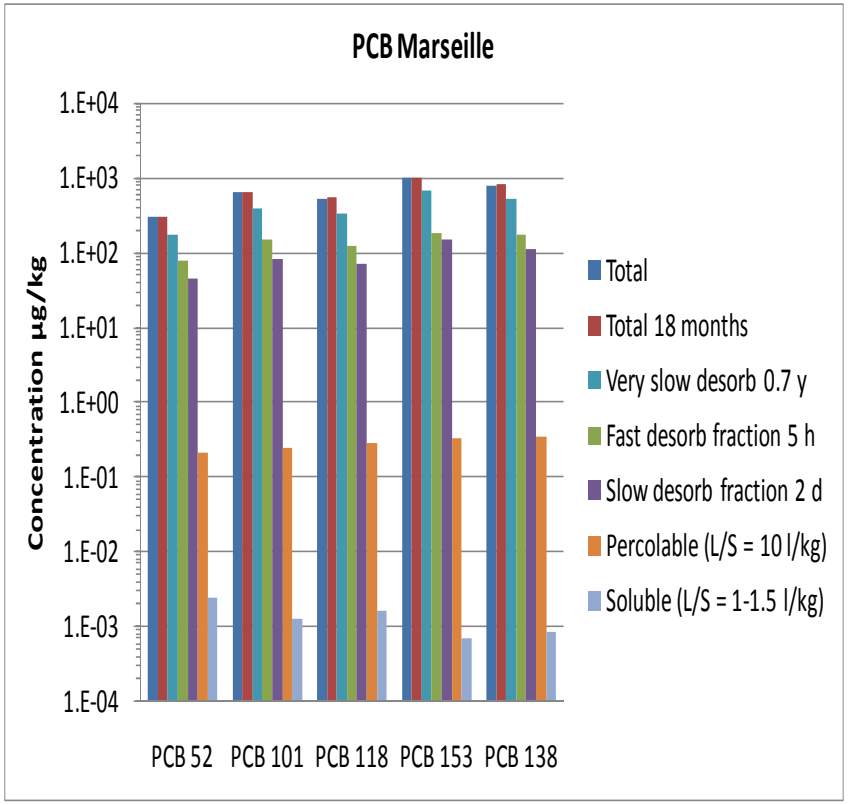




Results : Speciation of HOC in the solid phase (1/3)

Tenax fractions with the time to desorb 90 % of each fraction





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Results : Speciation of HOC in the solid phase (2/3)

Fast desorbing fraction for PAHs and PCBs (minimum and maximum relatively to the total content)

PAHs	Min	Max	PCBs	Min	Max
Naph	0.25 (NB)	0.41 (Evry)	PCB 28	0.27 (Dunk)	0.46 (Evry)
ACNY	0.19 (Lens)	0.34 (Evry)	PCB 52	0.26 (Mars)	0.41 (Evry)
ACN	0.21 (NB)	0.39 (Evry)	PCB 101	0.22 (NB)	0.37 (Evry)
F	0.14 (NB)	0.32 (Evry)	PCB 118	0.23 (NB)	0.31 (Evry)
Ph	0.12 (NB)	0.35 (Evry)	PCB 153	0.18 (NB)	0.27 (Evry)
An	0.18 (NB)	0.28 (Evry)	PCB 138	0.20 (NB)	0.31 (Evry)
Fl	0.10 (NB)	0.27 (Evry)	PCB 180	0.15 (NB)	0.25 (Evry)
Py	0.14 (NB)	0.33 (Evry)			
Chr	0.13 (NB)	0.22 (Evry)			
BaAN	0.06 (NB)	0.19 (Evry)			
BaPy	0.07 (NB)	0.16 (Lens)			
Ipy	0.08 (NB)	0.15 (Evry)			
DBA	0.08 (Mars)	0.22 (Evry)			
Bper	0.03 (Mars)	0.12 (Evry)			

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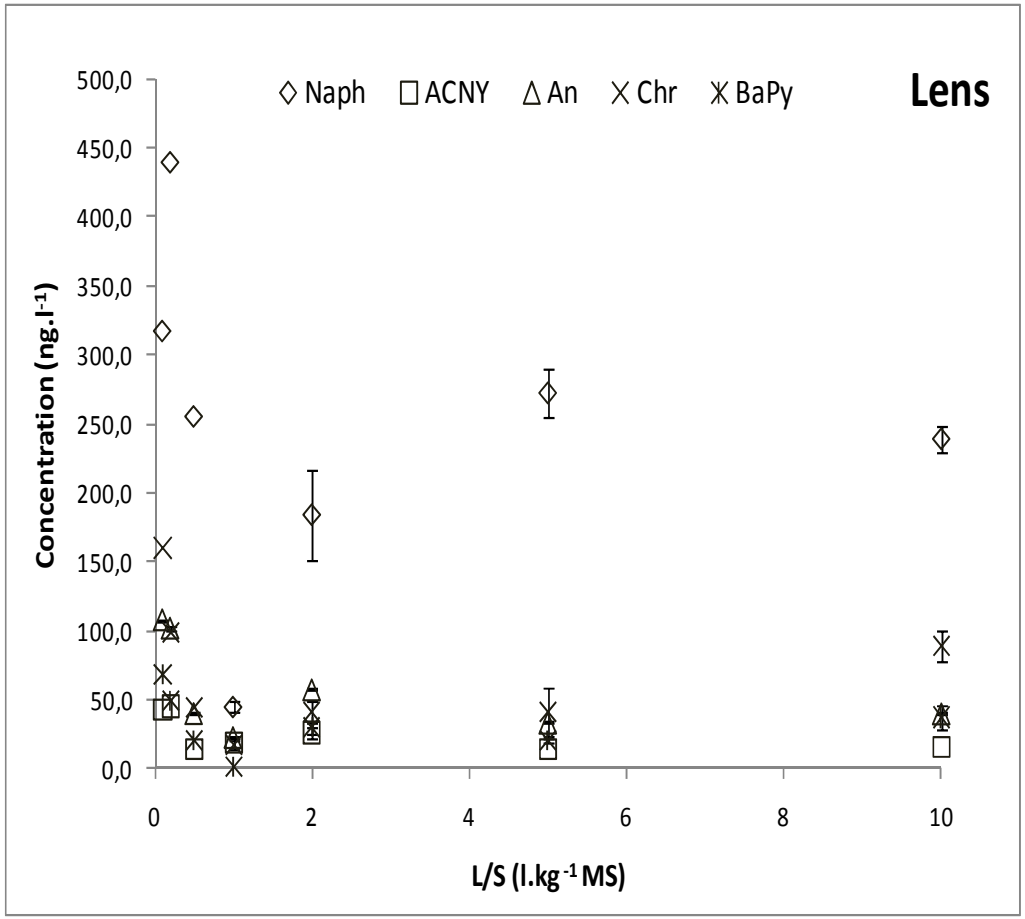
Results : Speciation of HOC in the solid phase (3/3)

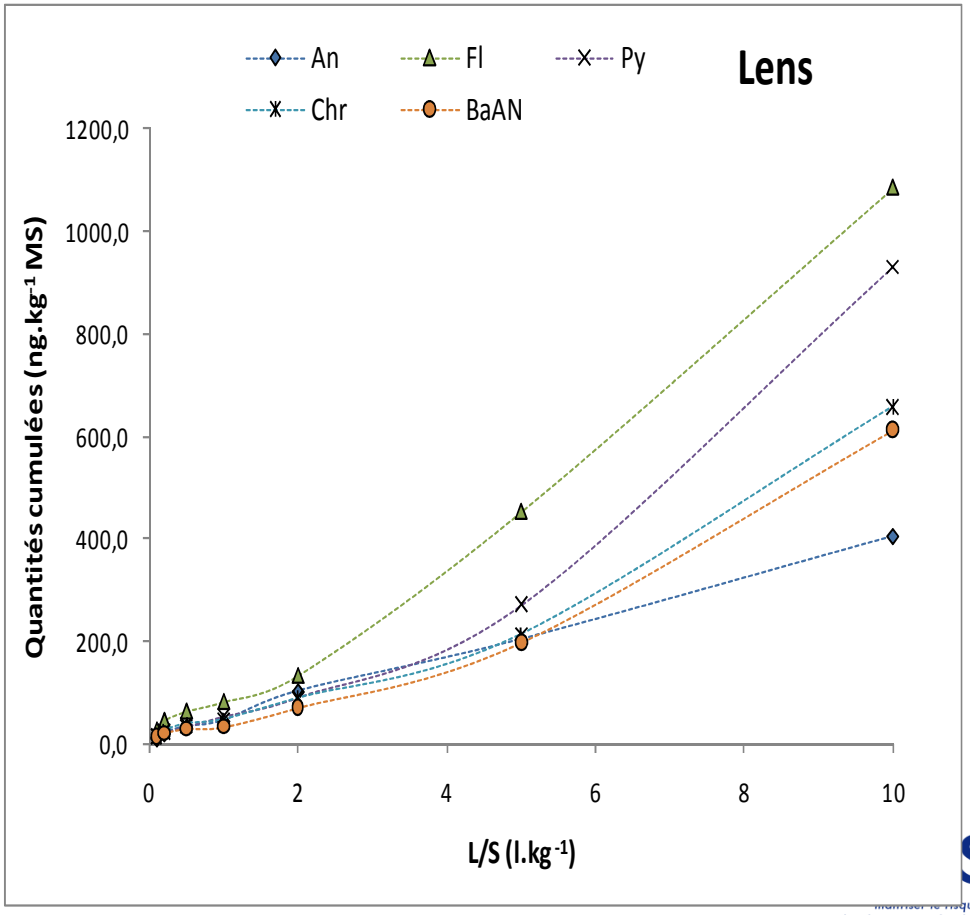
This is moderately consistent with the observations of the aging test in 18 months for PAHs and does not match to the PCB…

→ Can be used as a maximum biodegradable or desorbable fraction

Results : Percolation of HOC (1/4)

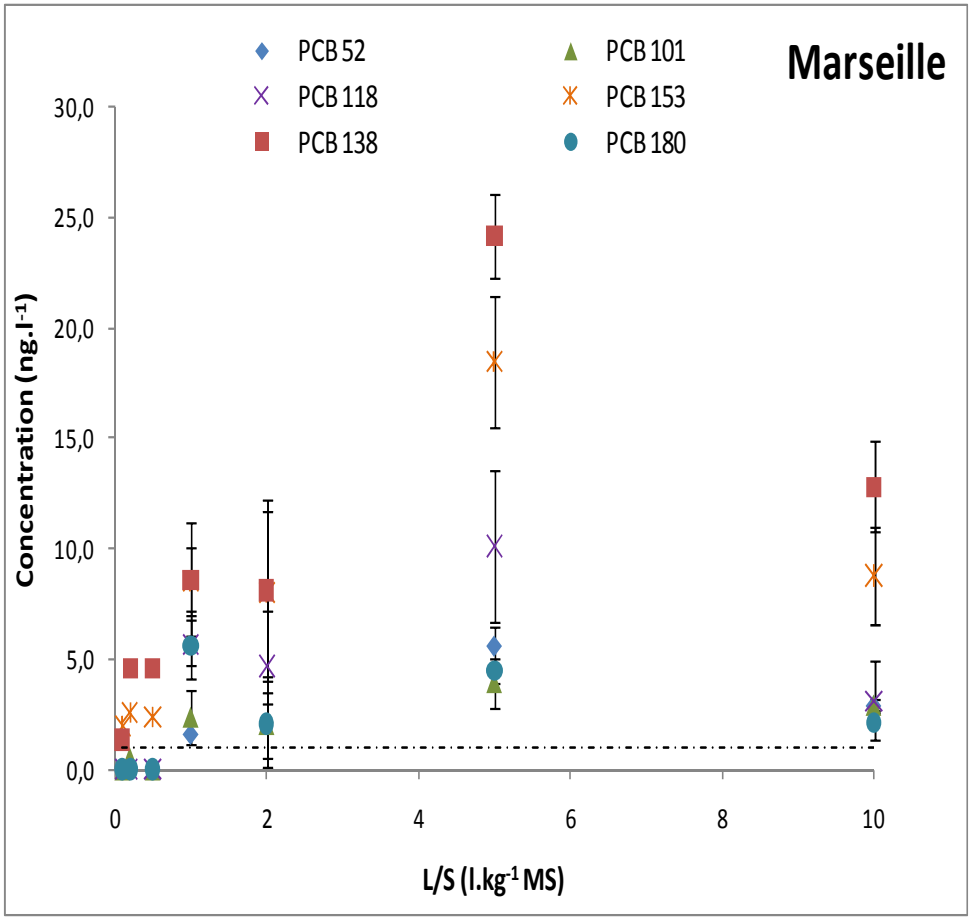
Concentrations and cumulated concentrations of some PAH during percolation test of the sediment of Lens

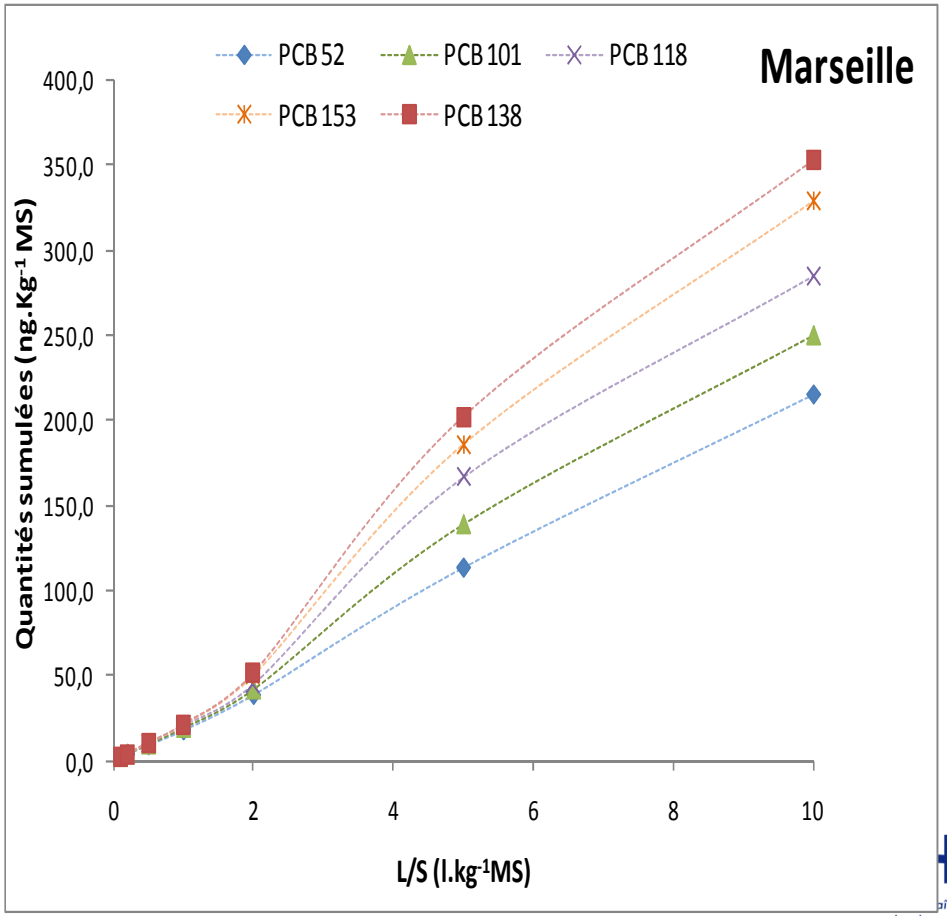




Results : Percolation of HOC (2/4)

Concentrations and cumulated concentrations of some PCB during percolation test of the sediment of Marseille



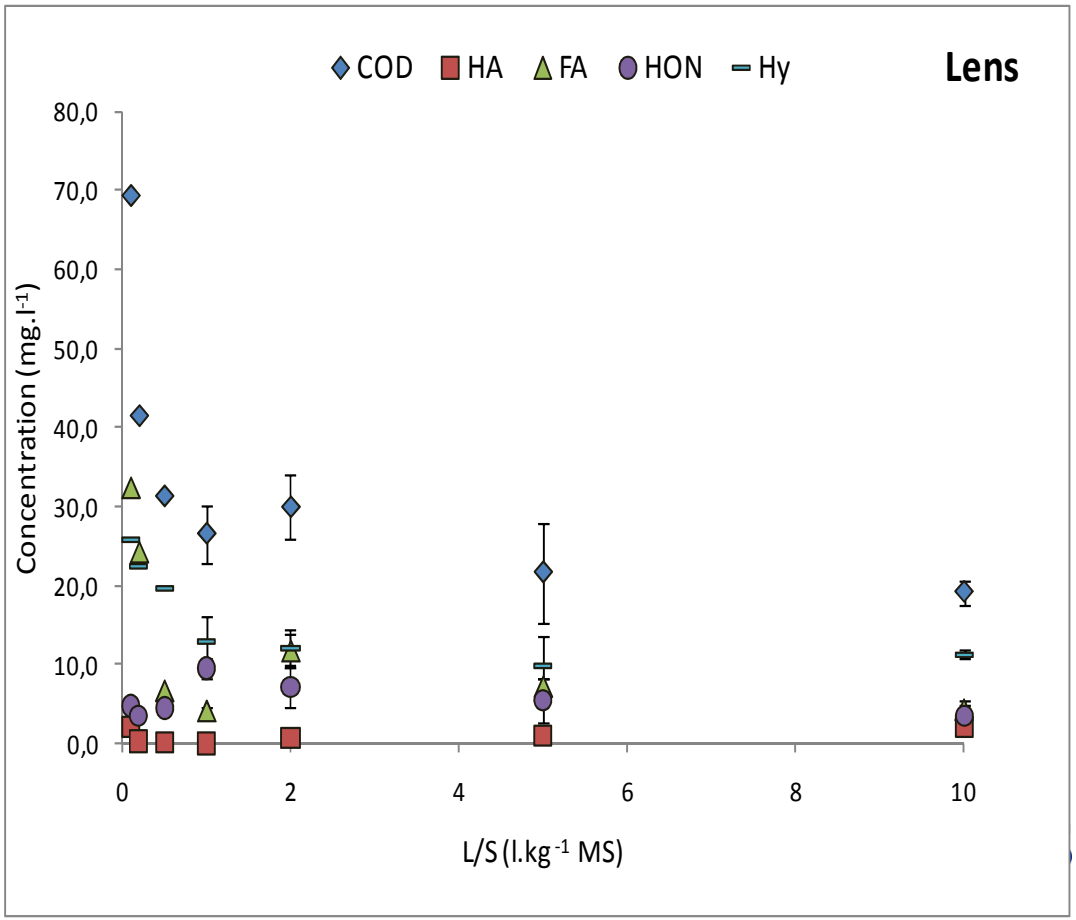


Results : Percolation of HOC (3/4)

Concentrations of colloidal dissolved organic carbon (DOC), and its functional fractions :

- fulvic acids FA,
- humic acids HA,
- hydrophilic organic carbon Hy,
- and hydrophobic neutral organic carbon HON

(ISO/CD 12782-4 and -5)



Results : Percolation of HOC (4/4)

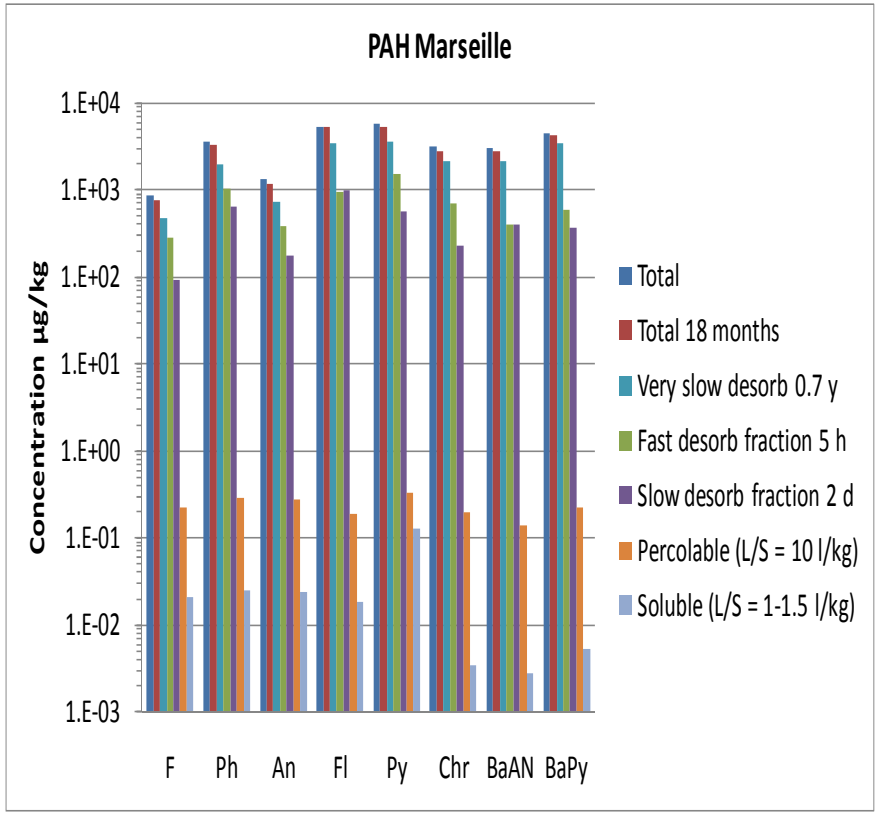
The cumulative amount of percolated contaminant represents between 0.04% (PAHs, 2 – 7 µg/kg) and 0.52 % (PCBs, 0.1 µg/kg for Marseille only) of the total contaminant concentrations.

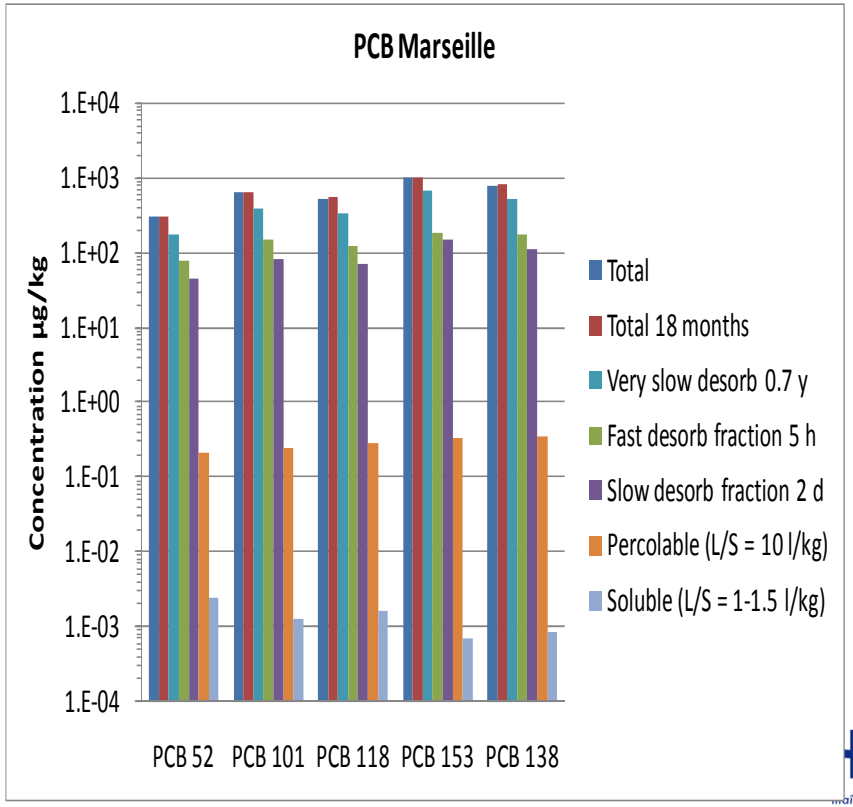
The emission is controlled by the presence of colloidal dissolved organic carbon (DOC) :

- the lightest PAHs (3.37 < log Kow < 5.22) and PCBs are correlated with **hydrophobic neutral organic carbon HON**
- the heaviest PAHs with log Kow > 5.22 are correlated to the **humic acids HA**

Results : Dissolved concentrations (1/5)

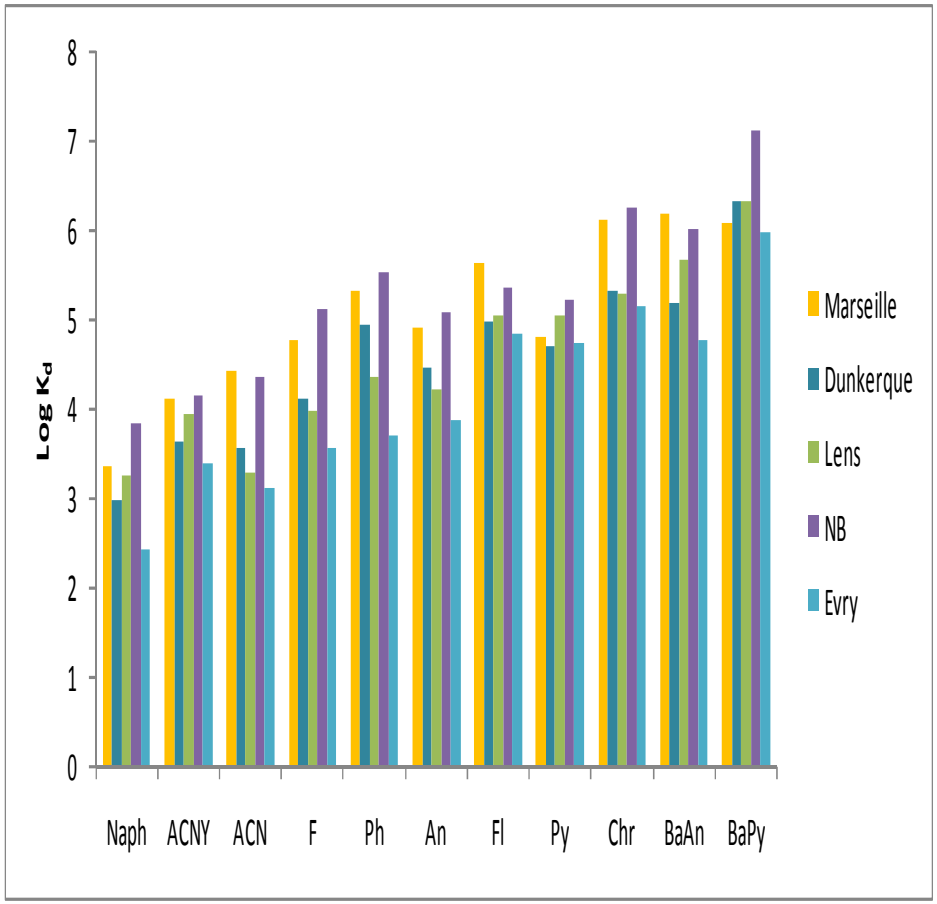
Dissolved concentrations were measured by passive samplers (adsorption on strips of LDPE at 13 different times during 46 days in the laboratory) with levels of up to below 10^{-11} g/l for PAHs and 10^{-12} g/l for PCBs.

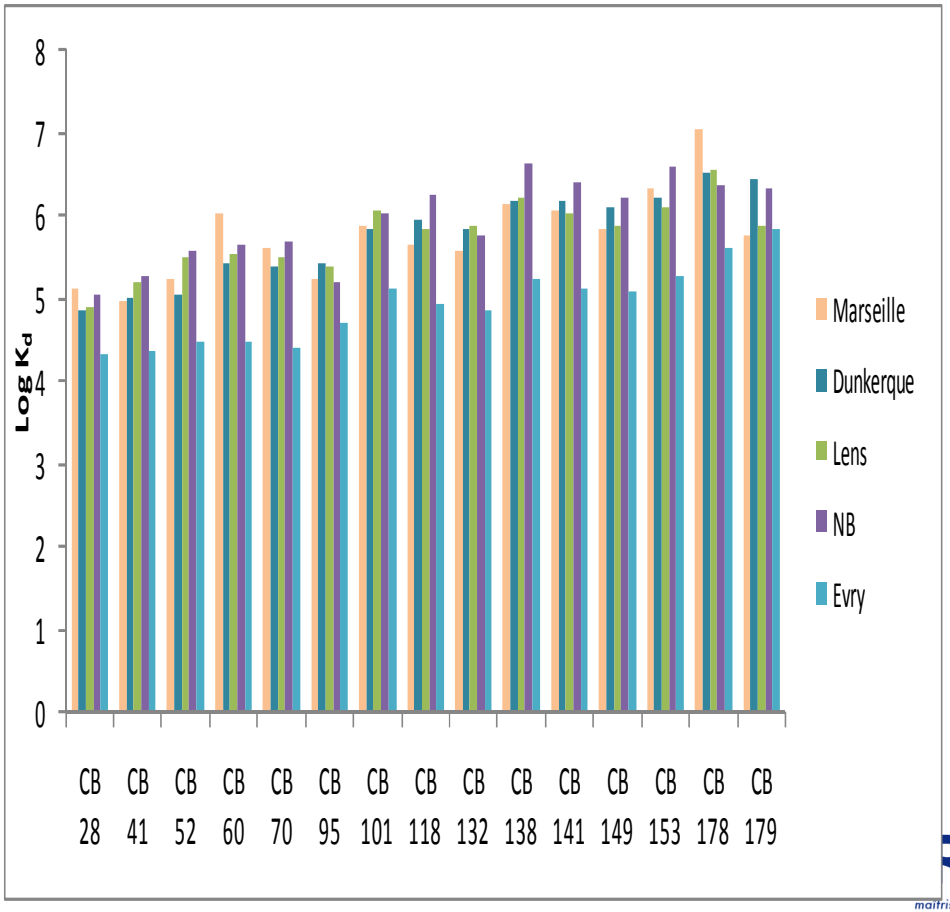




Results : Dissolved concentrations (2/5)

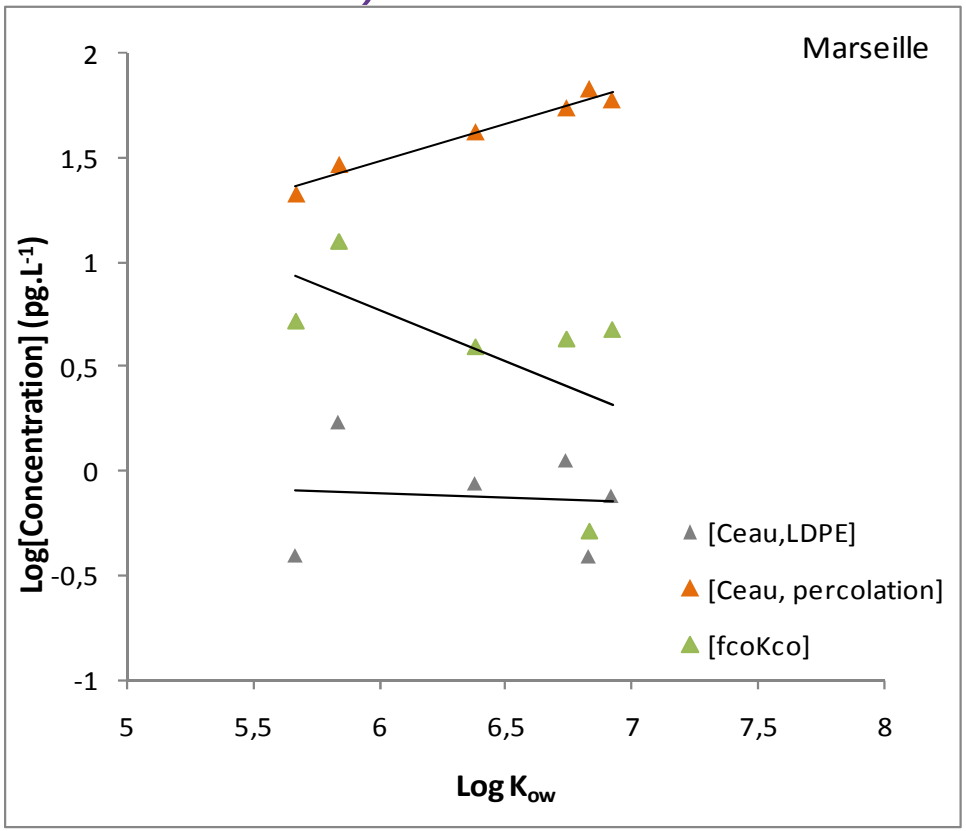
The resulting Kd values can be calculated

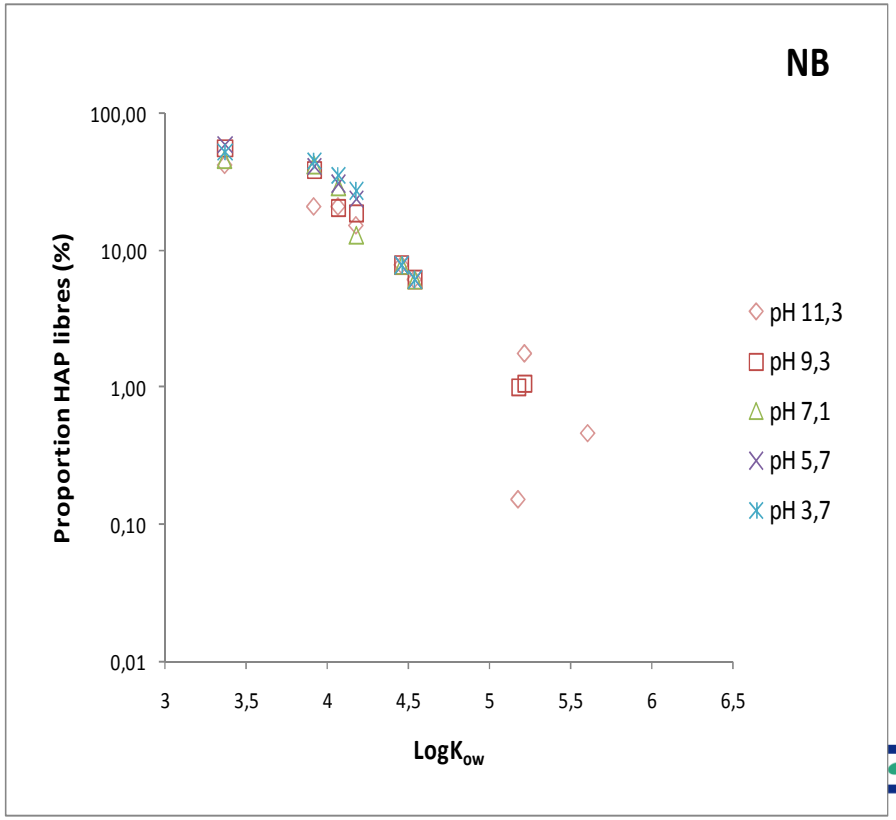




Results : Dissolved concentrations (3/5)

Concentrations of PCBs in pore water (Ceau LDPE), percolation (Ceau, percolation) and by calculation with Kd (fcoKco) for sediment of Marseille does not match… This is due to the colloidal part : f.i. the free dissolved PAHs in leachate at different pH (sediment of Nimy-Blaton) is low…





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Results : Dissolved concentrations (4/5)

The dissolved fraction is 0.0037 % (PAHs) and 0.0005 % (PCBs) of the total concentration. Details can be found in Charrasse et al 2014.

These low levels are largely explained by the presence of a "natural" adsorbent, the soot (quantified as black carbon) (results not shown).

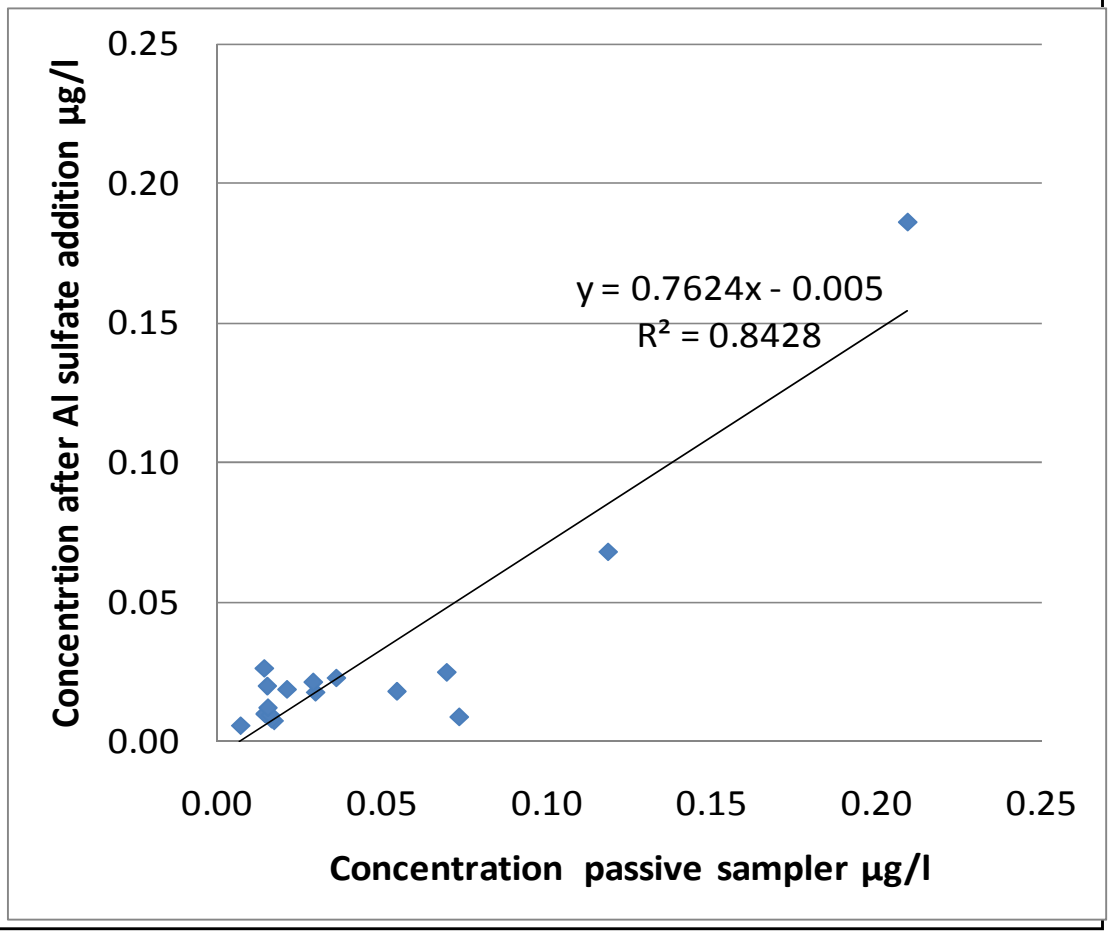
PAHs are associated with each 20% or more (for naphthalene) to 99.9% or more (for the highest molecular mass) to organic colloids

When detected (sediment Marseille and Lens), the PCBs 28 and 52 are associated with 81% or more to the colloidal fraction.

Results : Dissolved concentrations (5/5)

A simple method of determining dissolved after floculation by aluminum sulfate concentrations (Laor and Rebhun, 1997; Hawthorne et al. 2005a and b) provides 75% of the concentrations measured by passive sampler, but with limits of quantification of 2 10^{-8} g/l, significantly higher.

The concentration difference before and after the floculation gives the colloidal content.



Conclusion (1/2)

It is shown that:

- Hydrophobic organic compounds of these old sediments are poorly or not degradable in 18 months under aeration;
- The fraction degraded in 18 months in the laboratory is moderately consistent with so-called "fast" (Tenax extraction) fraction for PAHs and not for PCBs. This fraction is a maximum biodegradable fraction
- The percolable fraction is significant (between 0.04 % and 0.52 % of the total solids phase PAHs and PCBs) and is totally controlled by the colloidal organic carbon, and in particular humic acid HA and hydrophobic neutral organic carbon HON fractions. It is greatly reduced by the ripening (> 50 %);
- The free dissolved fraction (between 0.0037 % and 0.0005 % of the total solids phase PAHs and PCBs) can be measured either by the (time-consuming and long lasting) method of passive samplers, or by a simple method of flocculation of colloids in the eluates with aluminum sulfate for the highest concentrations;

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Conclusion (2/2)

- The approach of emission concentrations by solubility equations underestimates largely the concentrations by not taking into account the vectorization by organic colloids.

The measurement must prevail on modeling to evaluate the emission of HOC from sediments, mainly due to colloidal emission.

As no general transport equations for colloids has emerged, the transfer of contaminants vectorized by colloids in saturated or unsaturated soil should be studied by field work.

Acknowledgments

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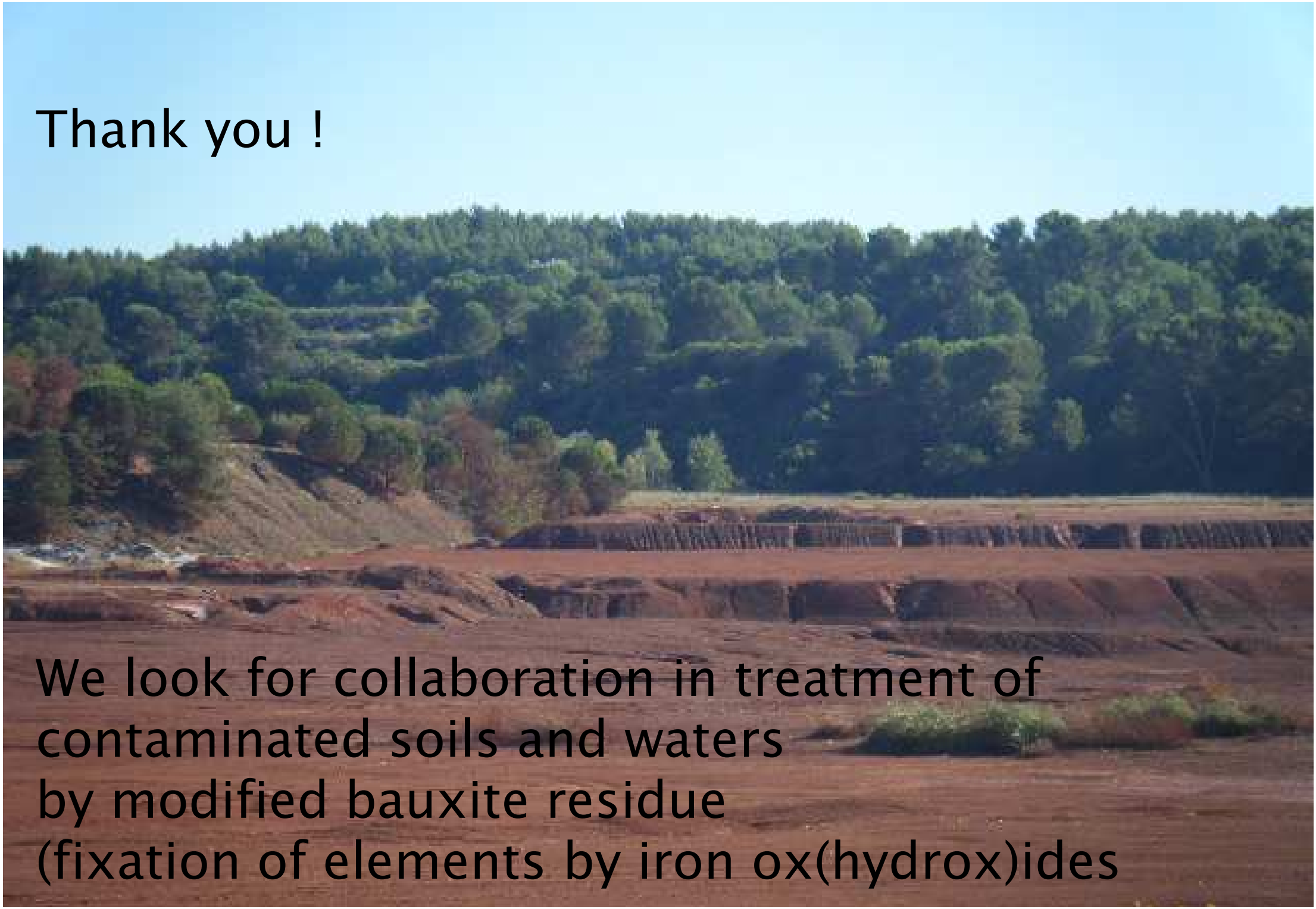

Thank you !

We look for collaboration in treatment of contaminated soils and waters
by modified bauxite residue
(fixation of elements by iron ox(hydrox)ides