The problem of micropollutants in waste treatment facilities

Laurent Mazéas

Environmental and microbial biotechnology course

The problem of micropollutants in waste treatment facilities

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Course Outline

I- Micropollutants problematic

- Definition
- Factors influencing the fate of micropollutants

II- Examples of research work on ISDND and anaerobic digester

- Identification of micropollutants to be taken into account in ISD impact studies
- Diffusion of micropollutants through the sealing barriers of storage facilities
- Biogeochemical cycles of metals in ISD bioreactors
- Biodegradation of organic micropollutants during methanization

How to define micro-pollutants?

The term **"micropollutants"** means organic or mineral substances whose toxic, persistent and bioaccumulative properties may have a negative effect on the environment and/or organisms even at low concentration.

They are present in many products that we consume daily (drugs, cosmetics, phytosanitary products, insecticides, etc.), at home or in industry.

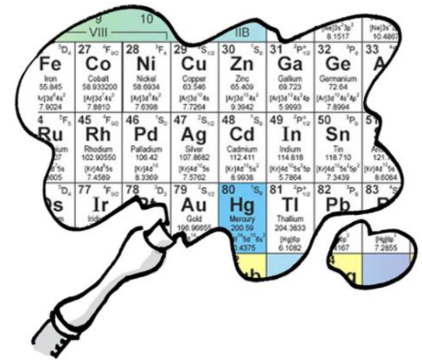
Progress in laboratory analysis is increasingly highlighting their **presence in the aquatic environment** at extremely low concentrations, in the order of one nanogram per litre or microgram per litre (hence the term micropollutants).

Some of these substances are liable to have potentially chronic **direct or indirect effects on ecosystems** (e.g. the feminisation of fish due to endoctrine-effect substances in the aquatic environment), and even on human health.

What are the micro-pollutants families?

- **Metals and metalloids, radioactive elements**

  Lead, cadmium, mercury, arsenic, antimony, radon, uranium



- **Organic micropollutants**

Pesticides

Hydrocarbons

Plastics

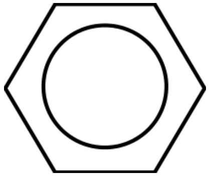
Detergents

Cosmetics

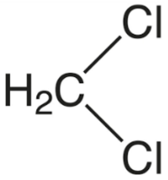
Pharmaceutical products

Exemples of micro-pollutants

Volatile Organic Compounds (VOCs)

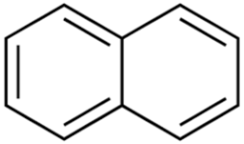


Benzene

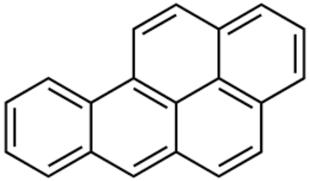


Dichloromethane

Polycyclic Aromatic Hydrocarbons (PAHs)



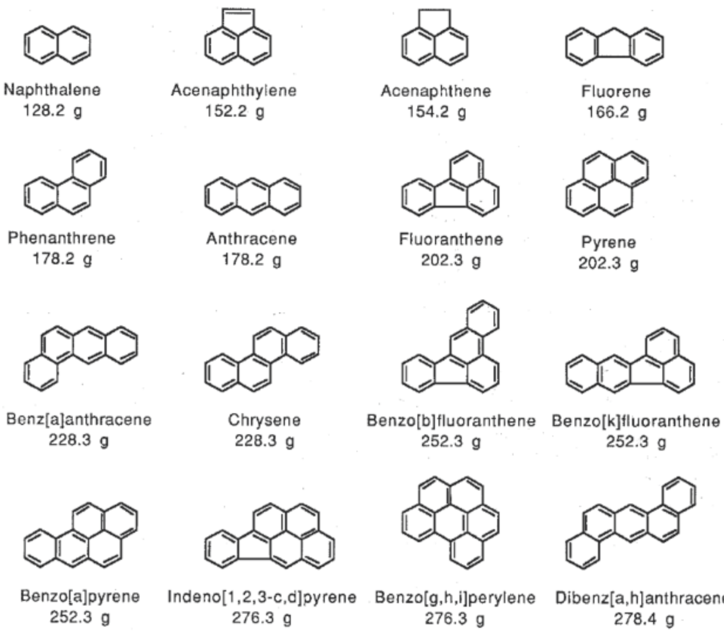
Naphtalene



Benzo(a)pyrene

Polycyclic Aromatic Hydrocarbons (PAHs)

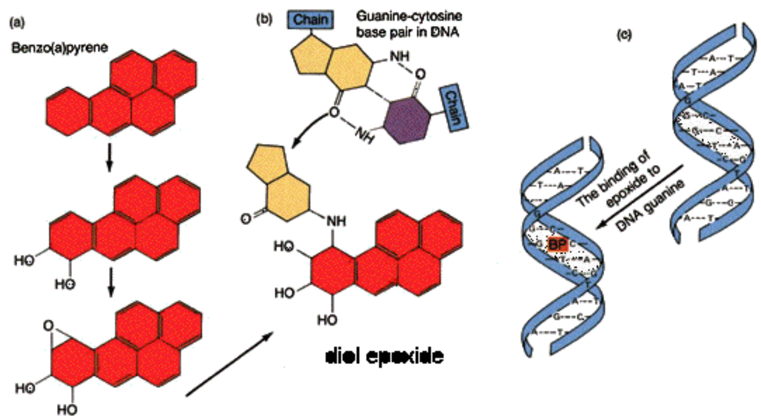
Polycyclic aromatic hydrocarbons are organic compounds containing only carbon and hydrogen—that are composed of multiple aromatic rings



PAHs are uncharged, non-polar molecules found in **coal and in oil** deposits. They are also produced by the **incomplete combustion of organic matter** (for example, in engines and incinerators or when biomass burns in forest fires).

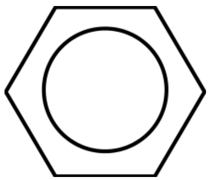
Some **carcinogenic PAHs** are genotoxic and induce mutations that initiate cancer; others are not genotoxic and instead affect cancer promotion or progression

An adduct formed between a DNA strand and an epoxide derived from a benzo[*a*]pyrene molecule (center); such adducts may interfere with normal DNA replication.

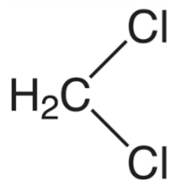


Exemples of micro-pollutants

Volatile Organic Compounds (VOCs)



Benzene



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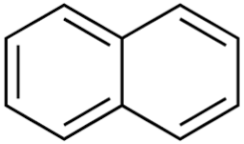
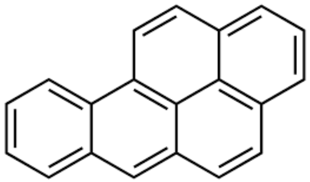
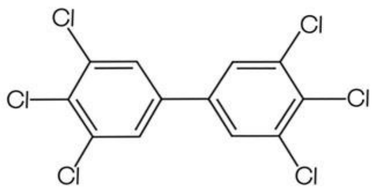


Naphtalene



Benzo(a)pyrene

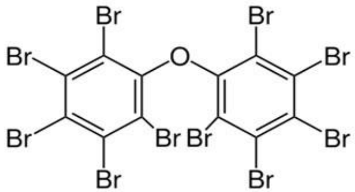
PolyChlorinated Biphenyls (PCBs)



PCB

(3,3',4,4',5,5'-hexachlorobiphenyl)

PolyBrominated Diphenyl Ethers

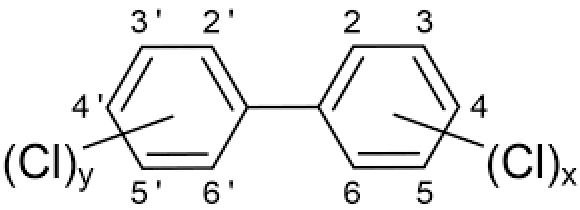


PBDE

(decabromodiphenyl ether)

PolyChlorinated Biphenyls PCBs

A mixture of compounds containing the bisphenyl structure with different numbers (one to ten) and arrangements of chlorine atom attached



PCBs were widely used as dielectric and coolant fluid, in transformers, capacitors

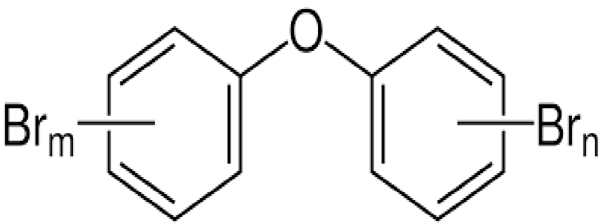
PCBs are persistents in environnent (non biodegradable hydrophobic…)

PCBs are carcinogenic

Dredging of PCBs contaminated sediments

PolyBrominated Diphenyl Ethers (PBDE)

Polybrominated diphenyl ethers or PBDEs, are organobromine compounds that are used as flame retardant.



The family of PBDEs consists of 209 possible substances, which are called congeners.

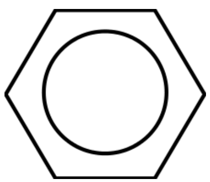
PBDEs have been used in a wide array of products, including:
- building materials,
- electronics,
- furnishings,
- motor vehicles,
- airplanes,
- plastics,
- polyurethane foams,
- and textiles.

PBDEs share the environmental long life and bioaccumulation properties with PCBs

PBDEs can cause cancer in people

Exemples of micro-pollutants

Volatile Organic Compounds (VOCs)



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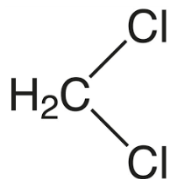
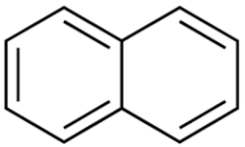


Dichloromethane

Polycyclic Aromatic Hydrocarbons (PAHs)



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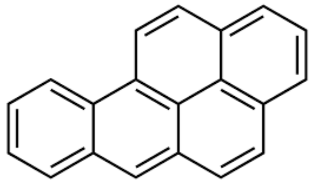

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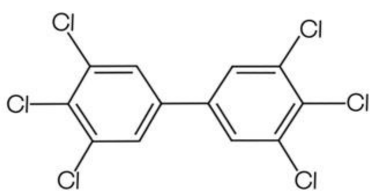

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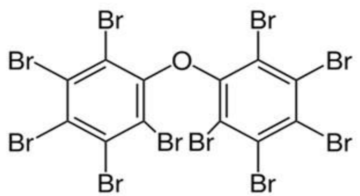
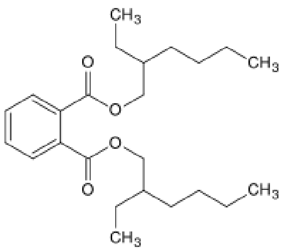


PBDE
(decabromodiphenyl ether)

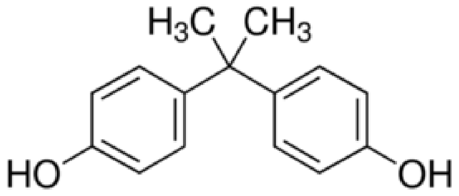
Plastic additives

Plasticizers



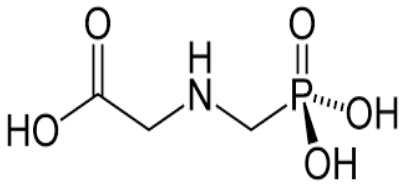
Phtalate

Anti oxydant



Bisphenol A

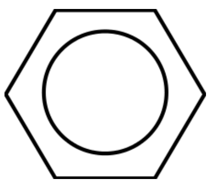
Pesticides



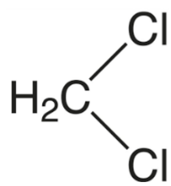
Glyphosate

Exemples of micro-pollutants

Volatile Organic Compounds (VOCs)



Benzene



Dichloromethane

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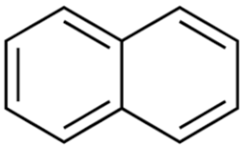
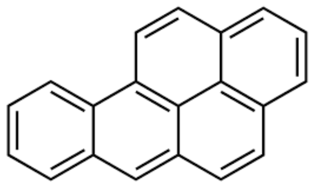


Naphtalene



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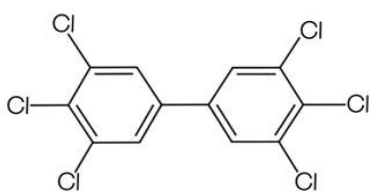

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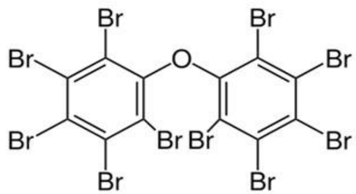

PBDE
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Plastic additives

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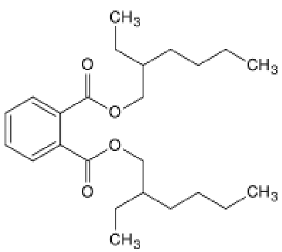
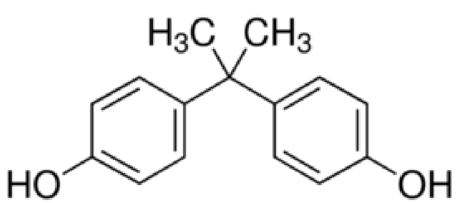


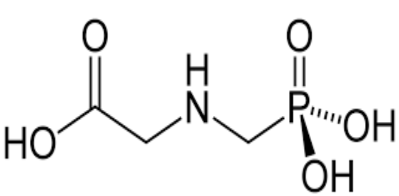
Phtalate

Anti oxydant



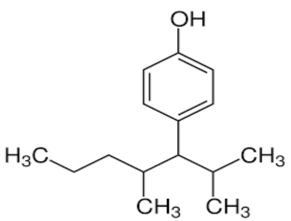
Bisphenol A

Pesticides



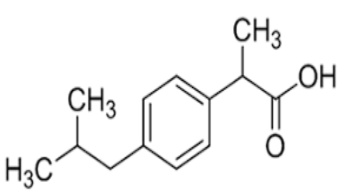
Glyphosate

Surfactants

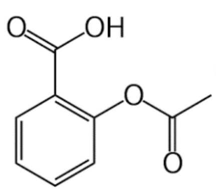


Nonylphenol

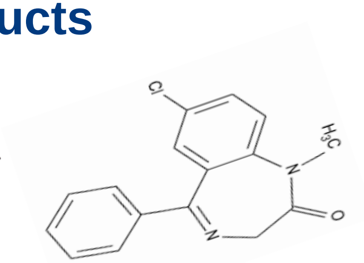
Pharmaceutical products



Ibuprofen



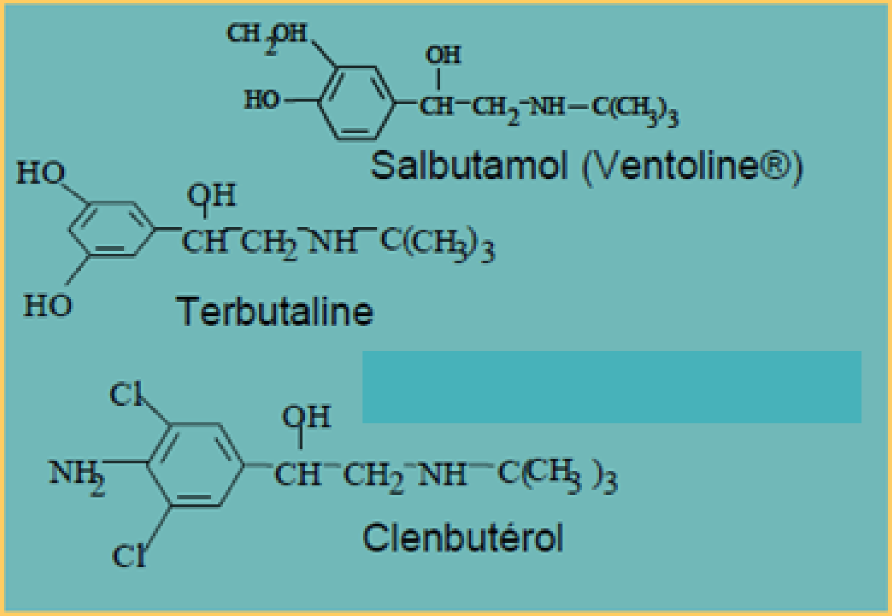
Aspirin

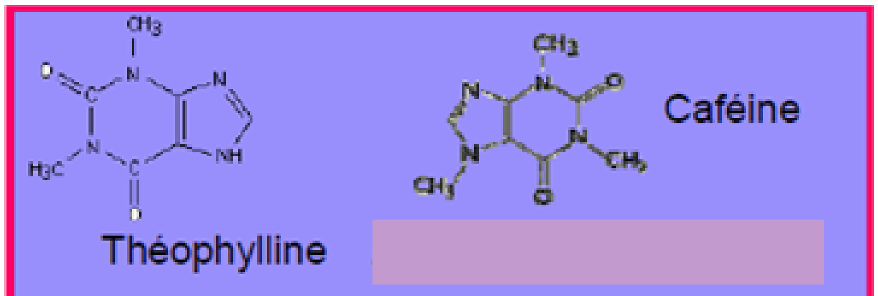


Diazepam

Pharmaceutical products

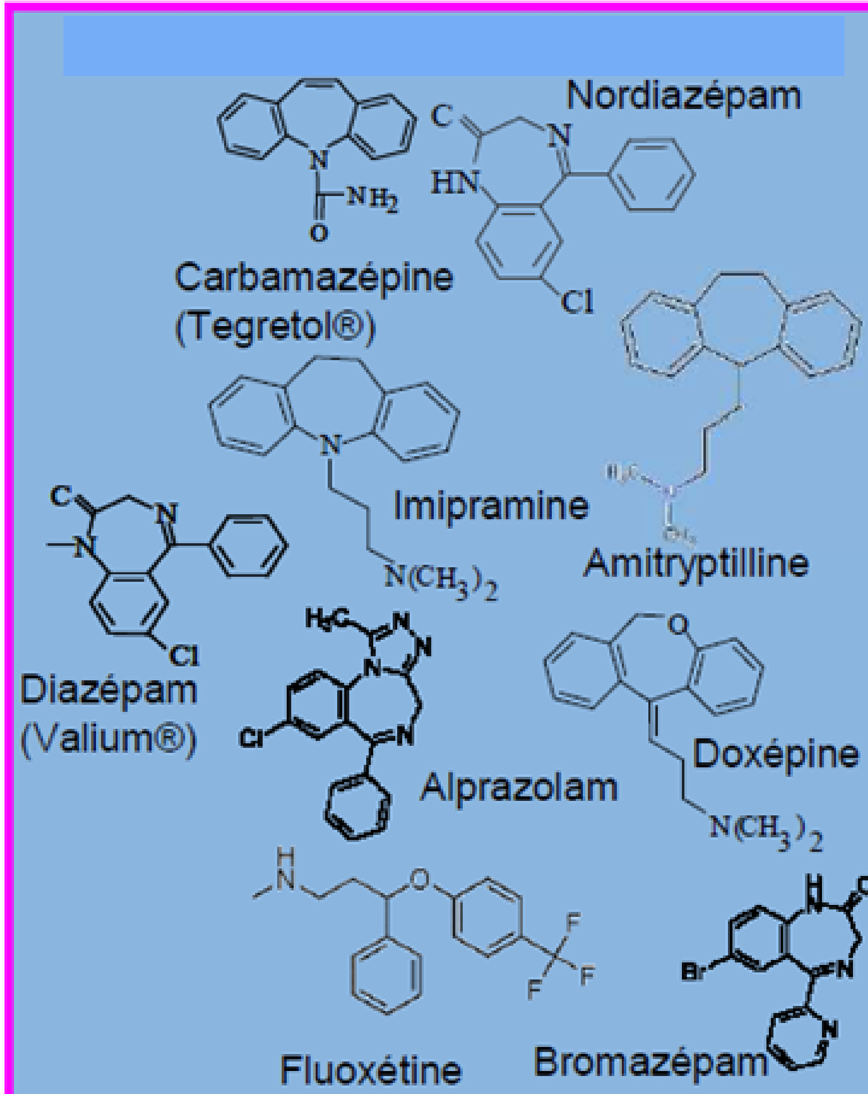
Bronchodilators





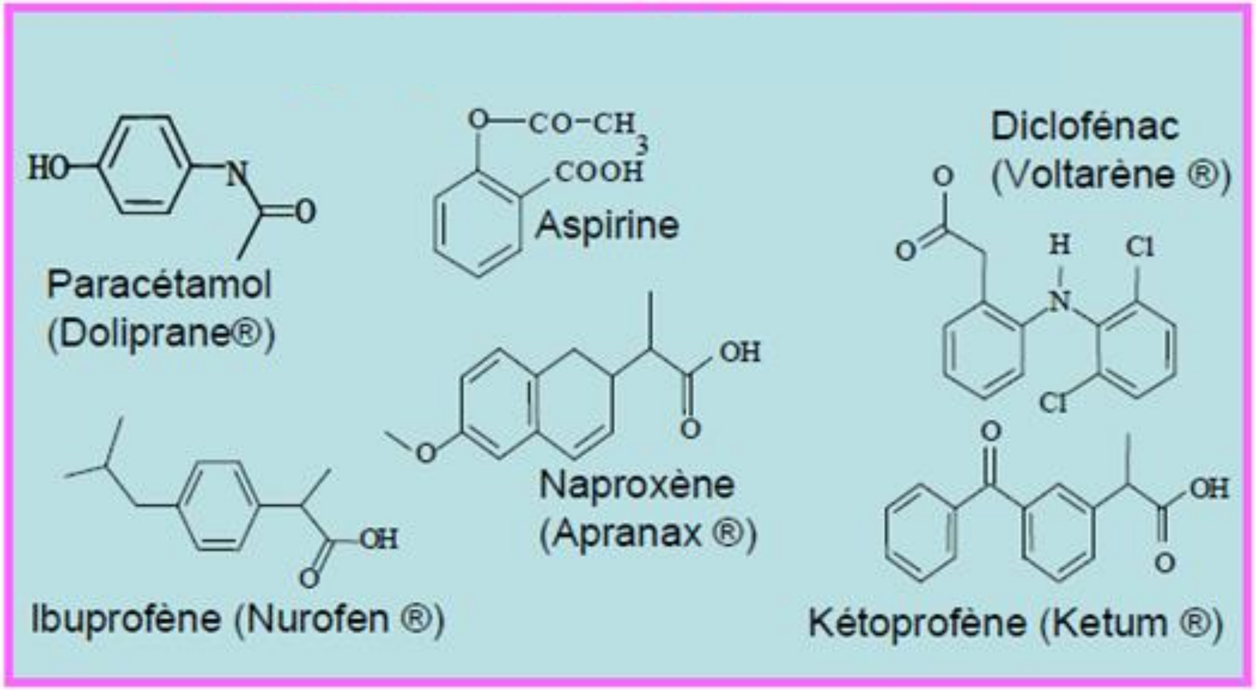
Stimulating agents

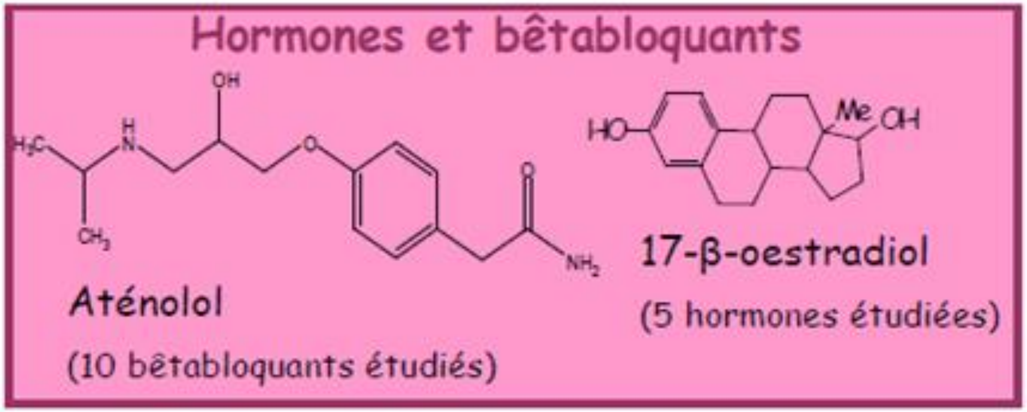
Anxiolytics/antidepressants



Pharmaceutical products

Analgesic/ anti inflammatory





Hormones / beta blockers

Fate of micro-pollutants

The fate of a micro-pollutant will depend on certain properties :

- Volatility/solubility : Henry's Law Constants
- Polarity: Octanol/water partition coefficient (Log KOW)
- Biodegradability : Half life time

VOLATILITY/SOLUBILITY : HENRY'S LAW

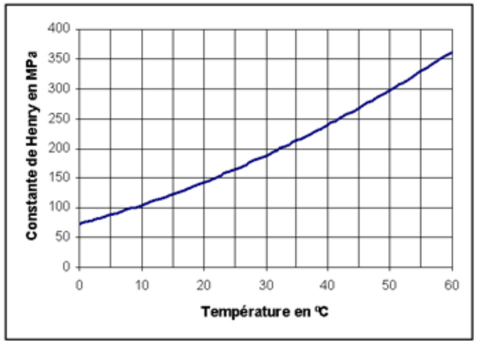
This law establishes a relation between the partial pressure Pi of a pure gaseous body and its molar fraction X^L in a solvent :

$P_i = X^L . K_i$ *K_i is the Henry's law constant*

This law allows to determine the solubility of a volatile substance in a liquid solvent with which this gas is in contact.

The more Ki is great the more the substance is volatile

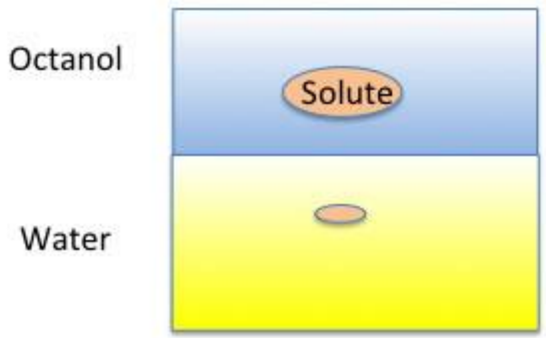
The Henry's law constant depends on the temperature:



Important property to know the mode of exposure to pollutants

Polarity: Octanol/water partition coefficient

Log Kow, is a measure of the differential solubility of chemical compounds in two solvents (octanol / water partition coefficient).



Log Kow = $\text{Log}(C_{oct}/C_{eau})$.

This value makes it possible to apprehend the hydrophilic or hydrophobic nature of a molecule

Indeed, if the Log Kow is positive and very high, it expresses the fact that the molecule considered is much more soluble in octanol than in water, which reflects its lipophilic or hydrophobic character, and vice versa.

Relationship between polarity and bioaccumulation

Log P = Log Kow = Log (Coct/Ceau)

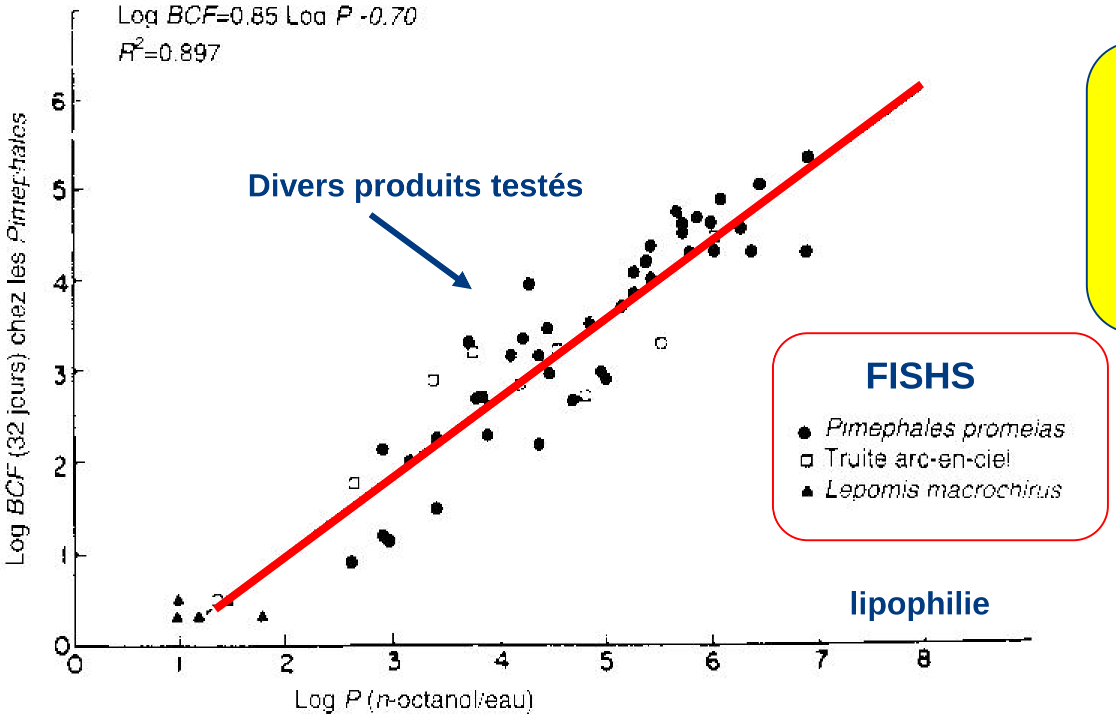
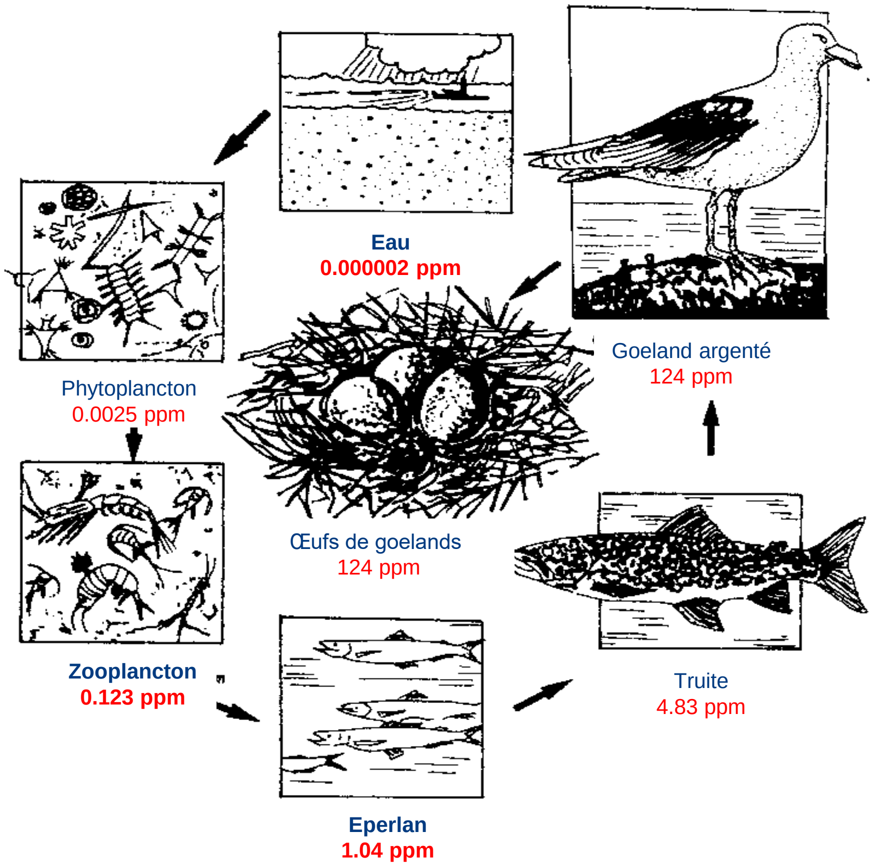


Figure 6-2 — *Corrélation entre le facteur de concentration biologique de trois espèces de poissons d'eau douce et le coefficient de partage n-octanol-eau*. La corrélation a été calculée pour divers produits de lipophilie croissante. ● = *Pimephales promelas* (Fathead minnow), □ = *Salmo gairdneri* (Truite arc-en-ciel). ▲ *Lepomis macrochirus* (Bluegill) (d'après VEITH *et al.*, *Journ. Fish. Res. Board Canad.*, **36**, 1979, p. 1040). **(in Ramade F.)**

Log BCF = a log Kow + b

BCF = bioconcentration factor
= Corganism / Cwater

Bioamplification of PCBs



(Modifié d'après G. Tyler Miller, Jr., *Living in the Environment*, Wadsworth Publishing Company, Belmont, Etats-Unis, 1994.)

Fig. 5. — Exemple de bioamplification des PCBs montrant l'augmentation de leur concentration au fur et à mesure qu'ils s'intègrent dans les maillons supérieurs d'une chaîne alimentaire aquatique.

(in Chassard-Bouchaud)

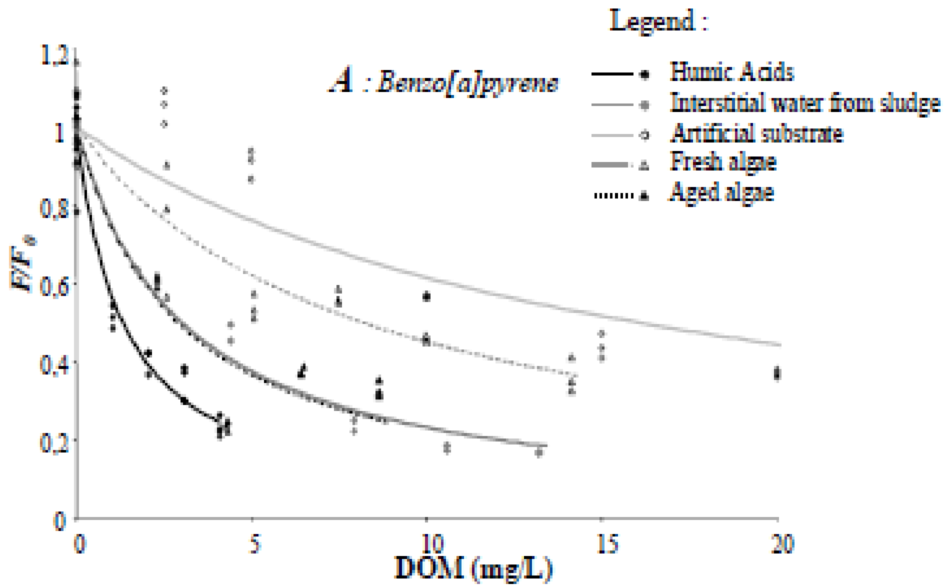


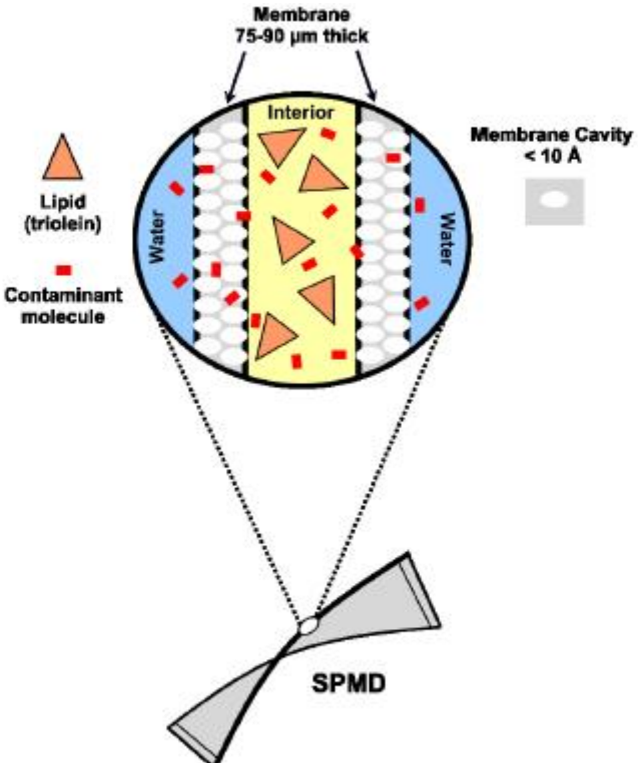
Figure 42. Bioaccumulation du Benzo(a)pyrène en présence de matière organique dissoute de différentes origines, normalisée à la bioaccumulation de Benzo(a)pyrène en eau minérale. D'après Gourlay et al., 2003.

Notion of Bioavailability

EVALUATION OF BIODAVAILABILITY

Apolar organic pollutants

Semipermeable Membrane Device, SPMD



Polar organic polluants

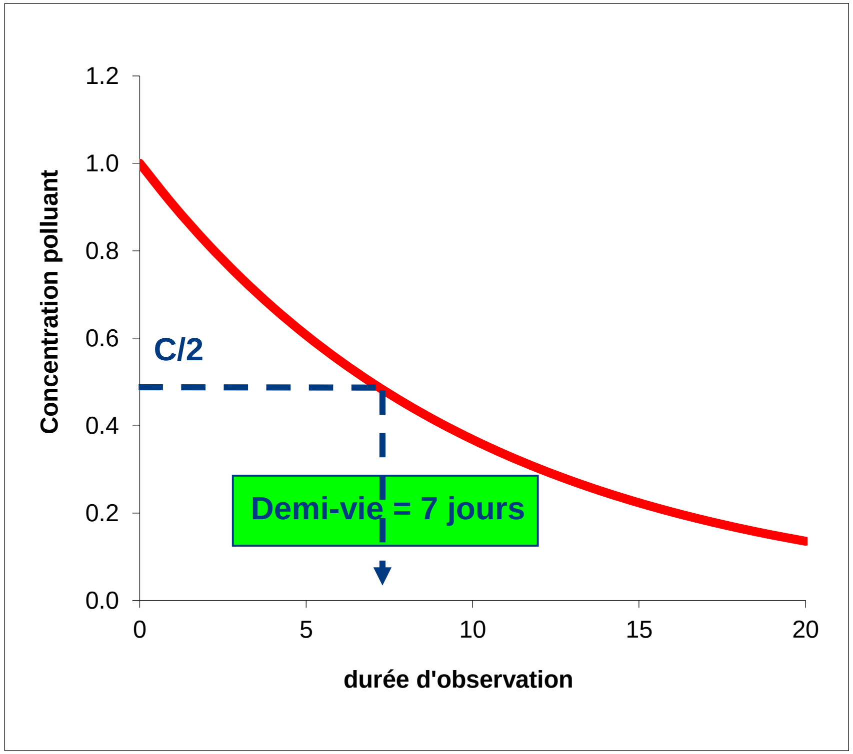
Polar Organic Chemical Integrative Sampler

Metals

Diffusive Gradient in Thin film, DGT

Biodegradability: Half life time

Time required for half of a quantity or concentration of a pollutant to disappear from the biotope or a contaminated organism



Pollutant	Half life time
DDT	15 years
Lindane	2 years
Parathion	130 days
Malathion	11 days

Evaluation of pollutants persistence

Formation of degradation products

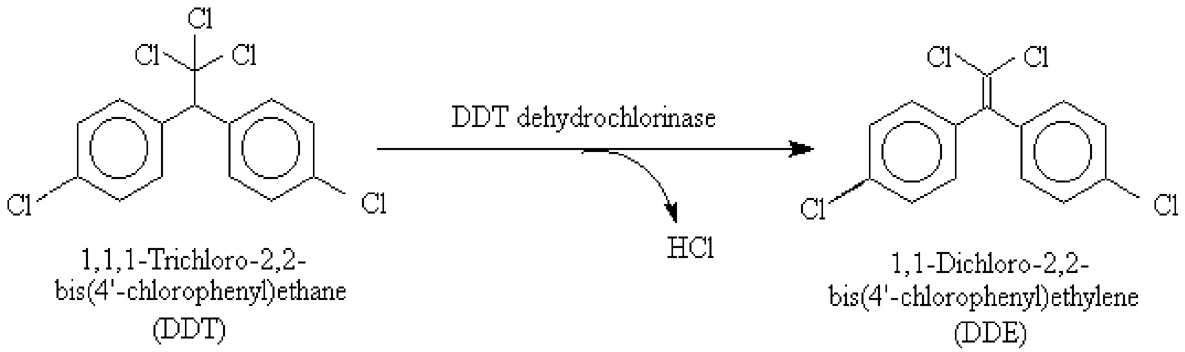
Degradation

Physicochemical action (photooxidation, thermooxidation ...) leading to the more or less complete disappearance of a molecule.

Biodegradation

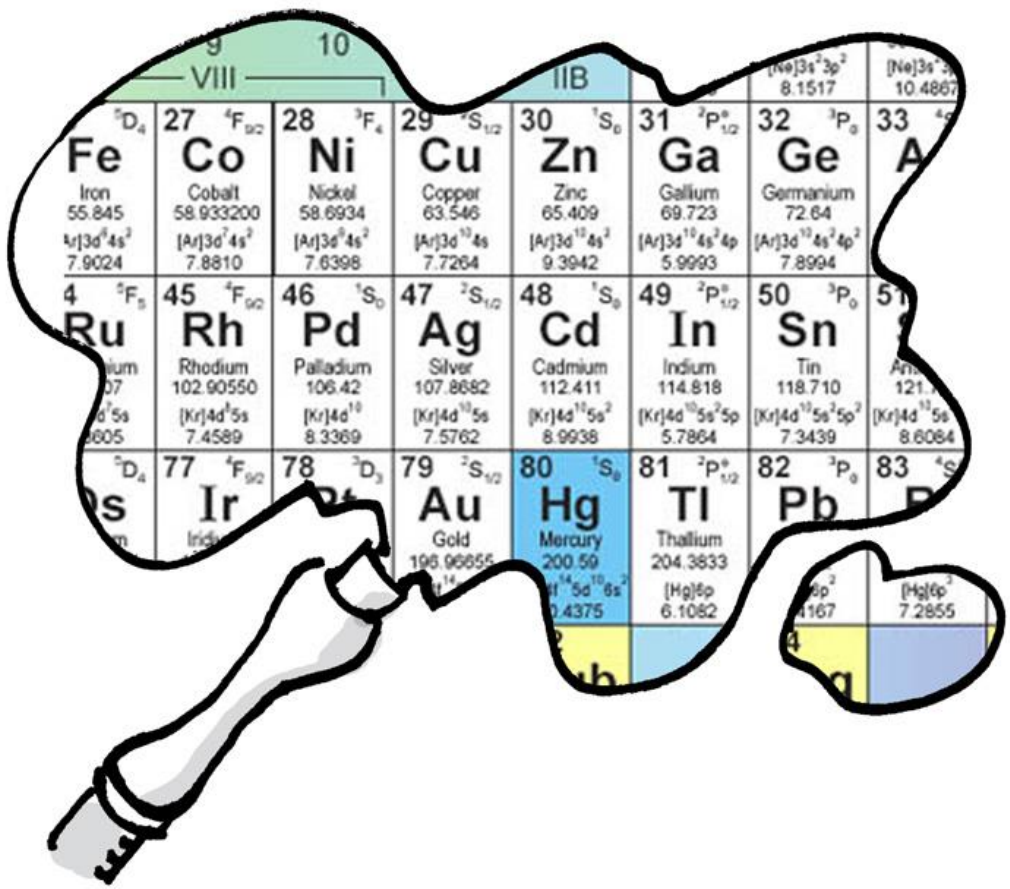
Biological degradation carried out by bacteria, fungi and obtaining metabolites of lower molecular weight.

Primary biodegradation = partial attack of molecules; may result in more persitant, more bioavailable, and sometimes more toxic metabolites than the initial molecule

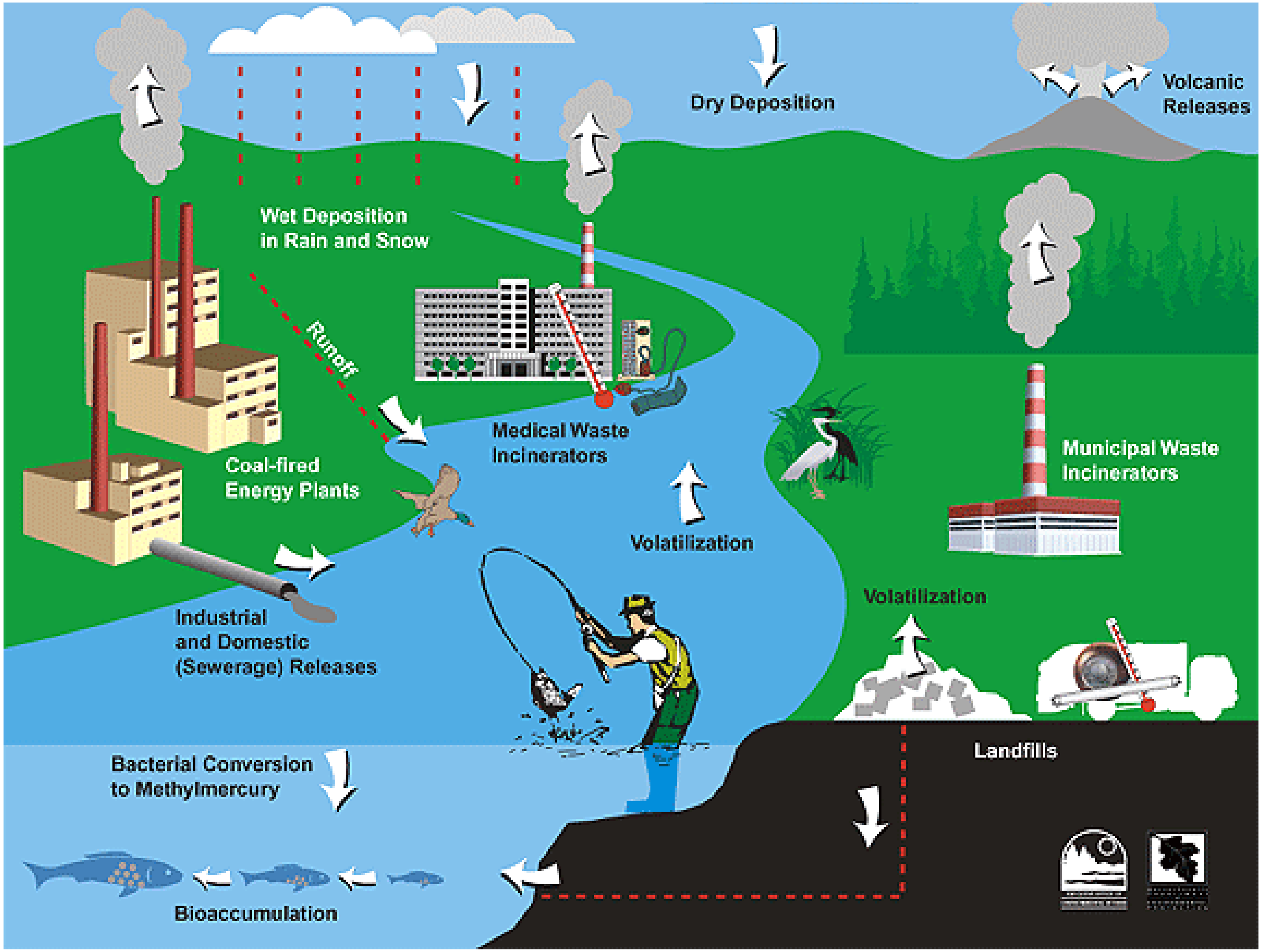


Ultimate biodegradation: complete degradation of the molecule; leads to CO_2, CH_4, water, mineral elements.

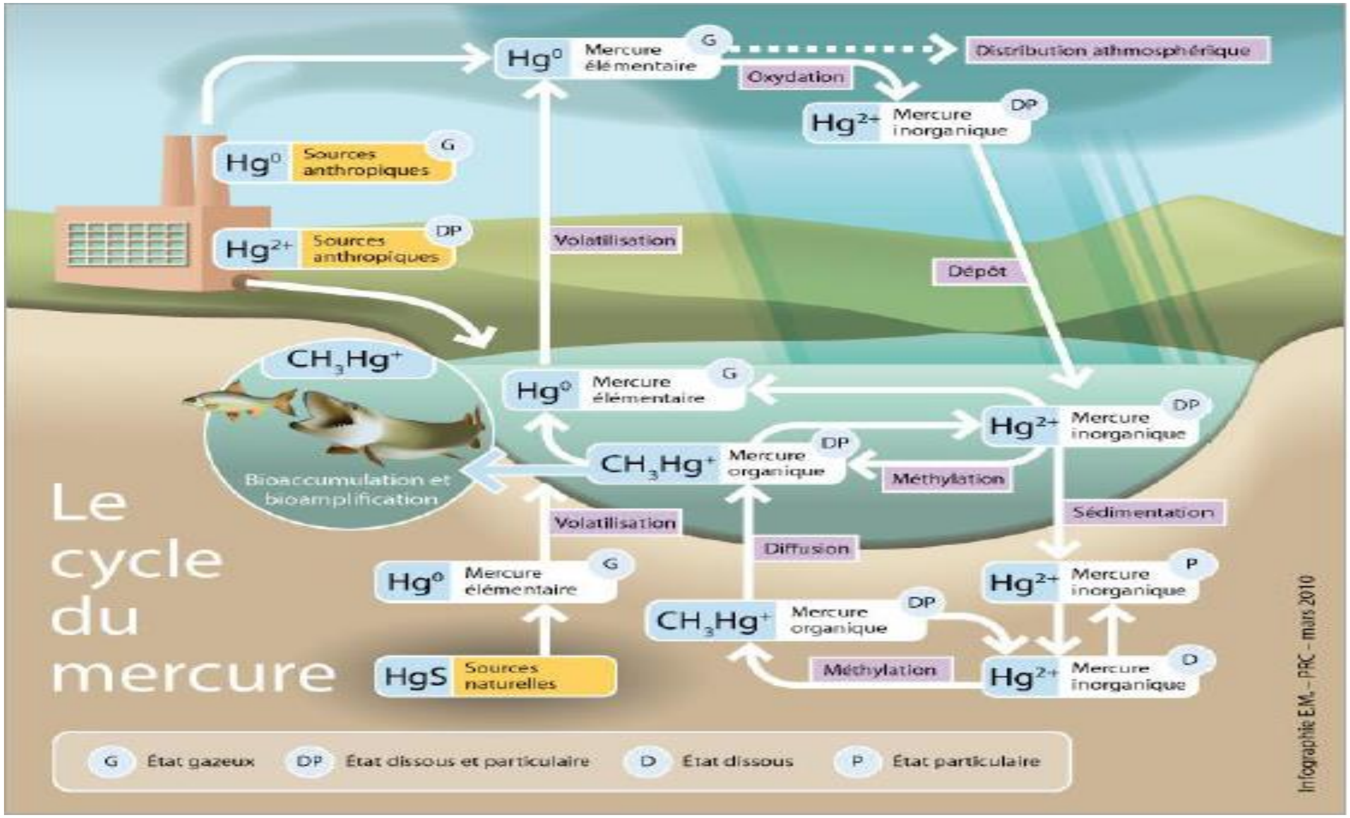
Metallic micropollutants



Source of mercury contamination



Biogeochemical cycle of mercury



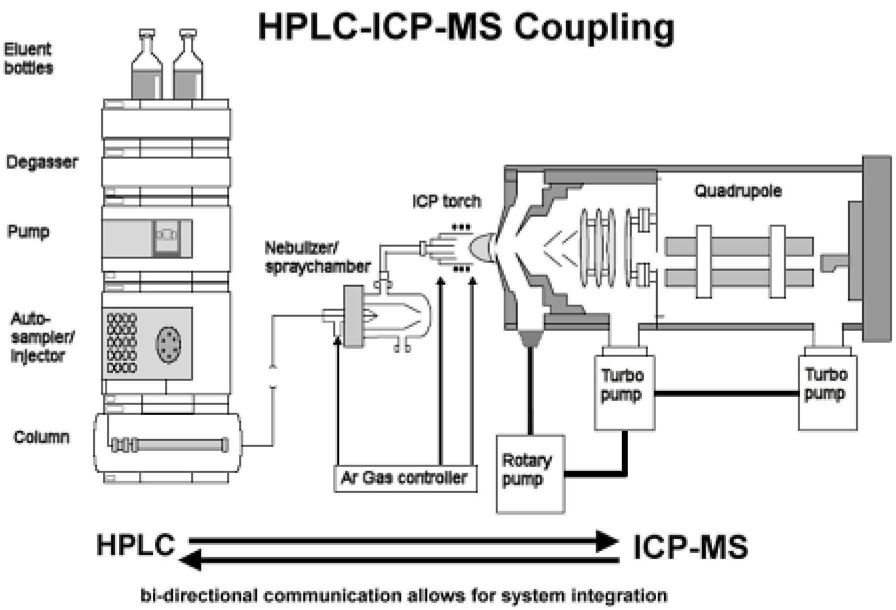
Speciation consists, beyond the measurement of the total concentration of an element in a sample, to separate, identify and measure individually all the chemical forms of this element

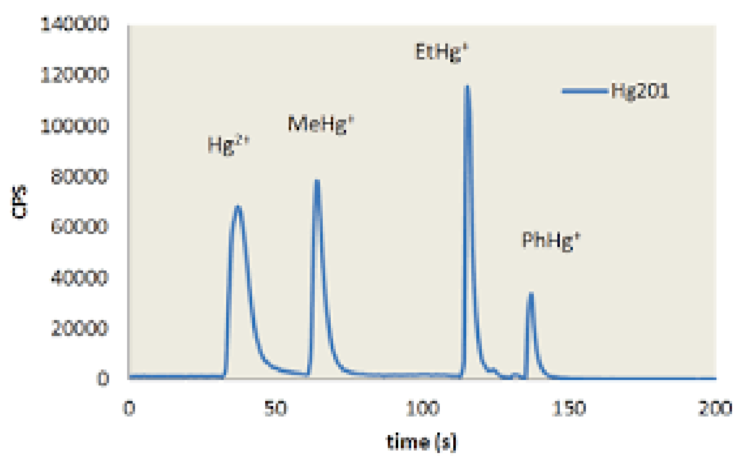
Microorganism can amplify pollution : Minamata case

Why use ICP-MS for metal speciation analysis ?

- It can measure almost the whole periodic table in just about everything

- Analysis of:
  - Elemental concentrations
  - High precision isotope ratio determinations
  - **Species information** when coupled to separation devices





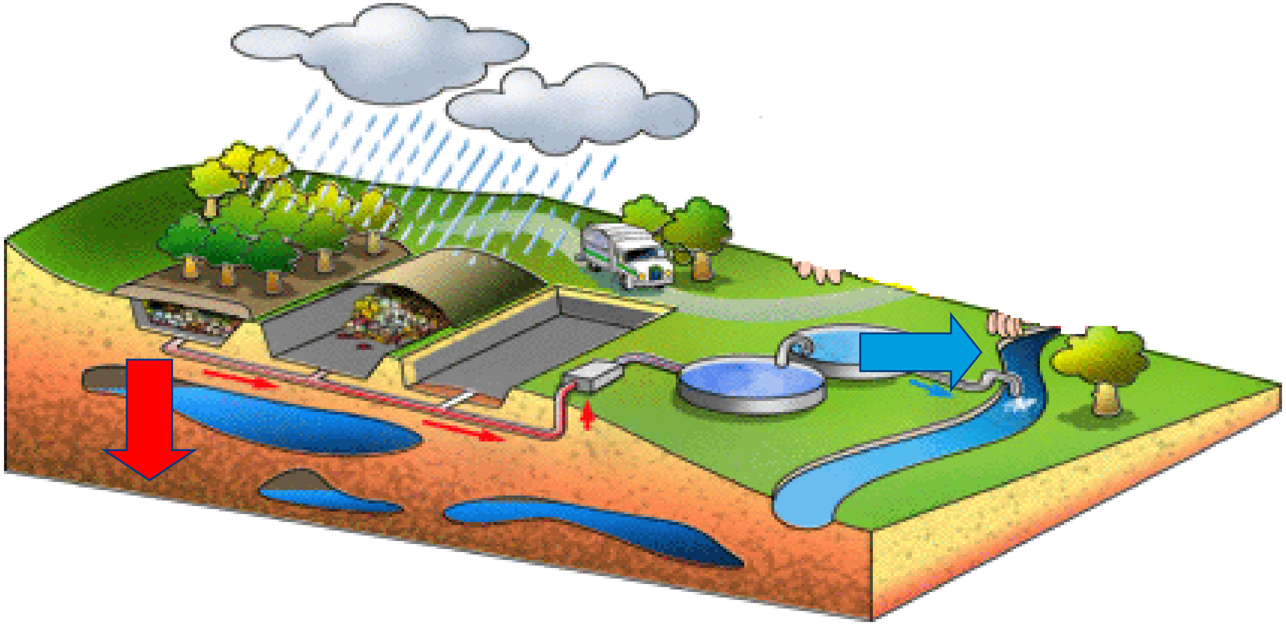
Course Outline

I- Micropollutants problematic

- Definition
- Factors influencing the fate of micropollutants

II- Examples of research work on ISDND and anaerobic digester

- Identification of micropollutants to be taken into account in ISD impact studies
- Diffusion of micropollutants through the sealing barriers of storage facilities
- Biogeochemical cycles of metals in ISD bioreactors
- Biodegradation of organic micropollutants during methanization



❶

Transfers of micropollutants through the sealing barriers

⬇

Contamination of subsoils and groundwater

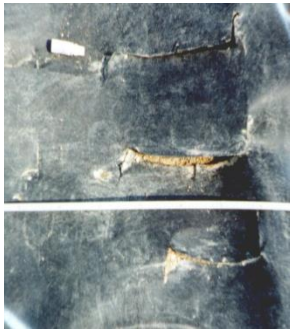
❷

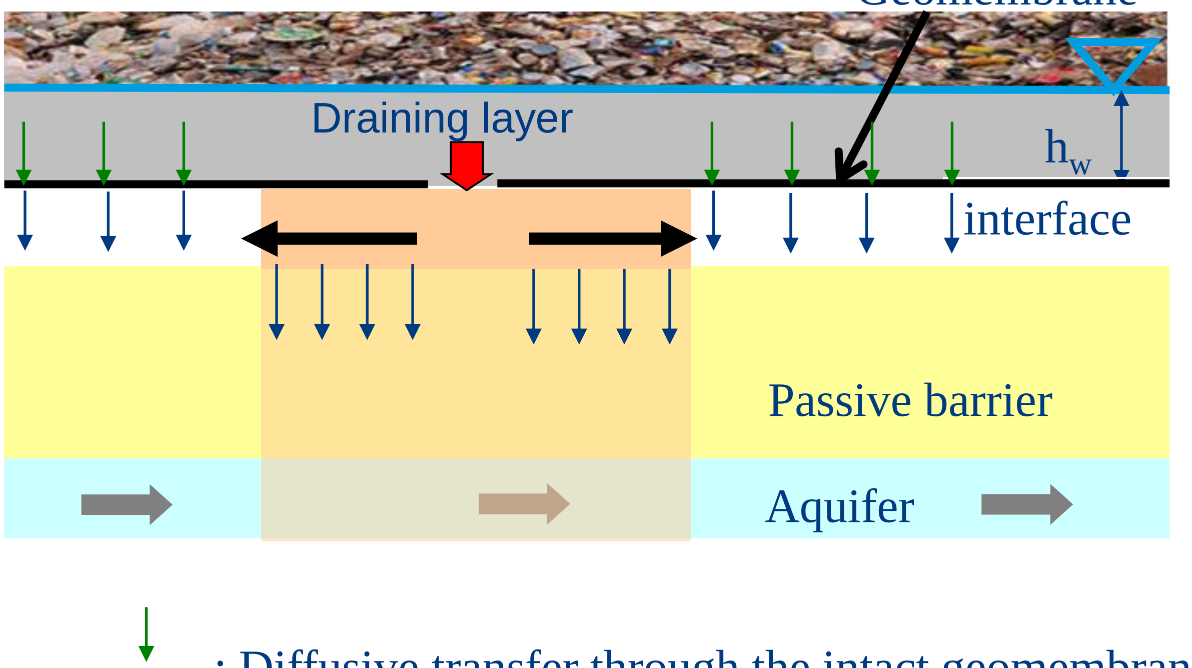
Recalcitrant micropollutants to leachate treatments

⬇

Contamination of surface water

Two basic modes of transfer in the sealing barriers :
- **advective transfers (defects in the geomembrane)**
- **diffusive transfers**





Micro-pollutants found in leachates

Database under access grouping:

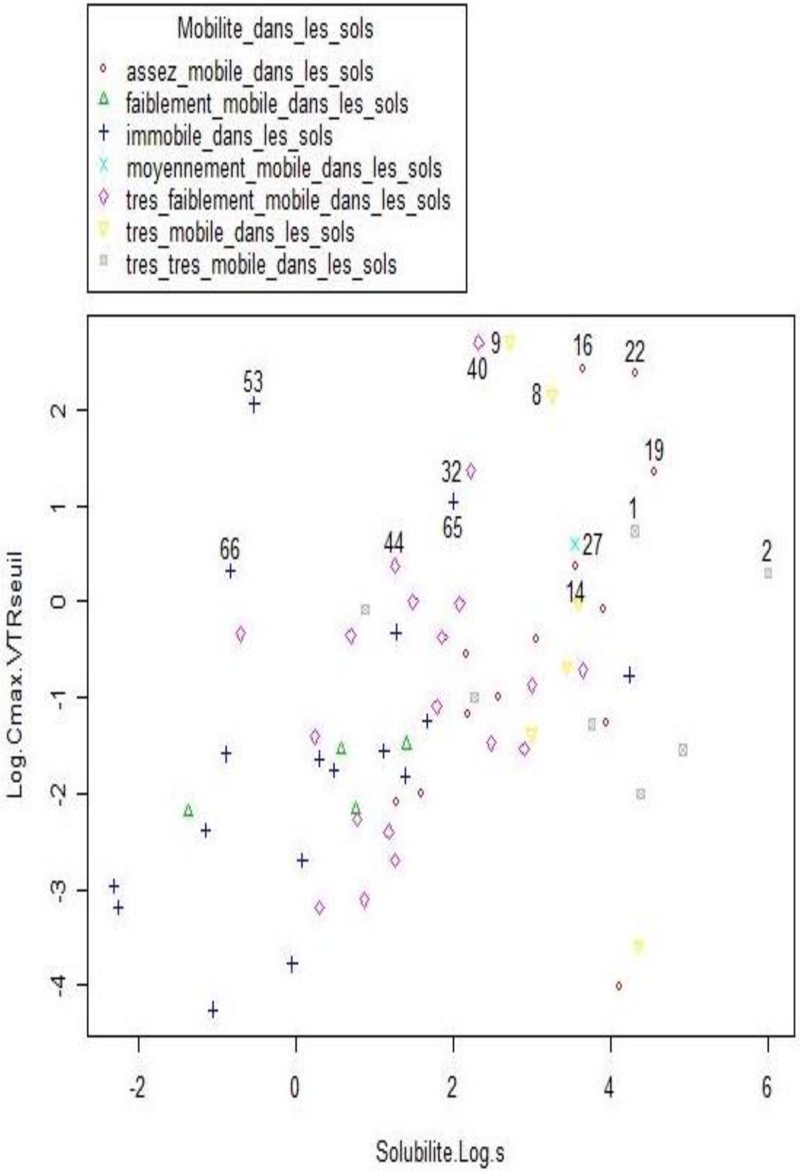
- 33 publications and study reports
- 100 different ISD
- 311 leachate samples
- 402 organic compounds

-The physical-chemical properties (solubility, Koc ...)

-The toxicological properties of pollutants (TRV, CMR classification ...)

→ **no public data in France**

Selection of compounds for impact analysis



1: Dichloromethane
2: 1,4_Dioxane
8: Benzene
9: Toluene
14: Z- 1,2_Dichloroethylene
16: E-1,2_Dichloroethylene
19: Aniline
22: p_Cresol
27: 1,1,2_Trichloroethane
32: Ethylbenzene
40: Bisphenol_A
44: 1,2,4_Trichlorobenzene
53: Bis2_ethylhexylphthalate
65: Aldrin
66: dieldrin

Composition of leachates in France: analysis campaign

The choice of leachate collection sites: 8 sites

Compounds analyzed:

- **Volatile Organic Compounds (VOCs)**
- **Polycyclic Aromatic Hydrocarbons (PAHs)**
- **PolyChlorinated Biphenyls (PCBs)**
- **PolyBrominated Diphenyl Ethers (PBDEs)**
- **Phenols and bisphenol A**
- **Phtalates**
- **Pesticides**
- **Pharmaceutical products**
- **Organometallic compounds**

The organic compounds were analyzed both in the dissolved and particulate phases

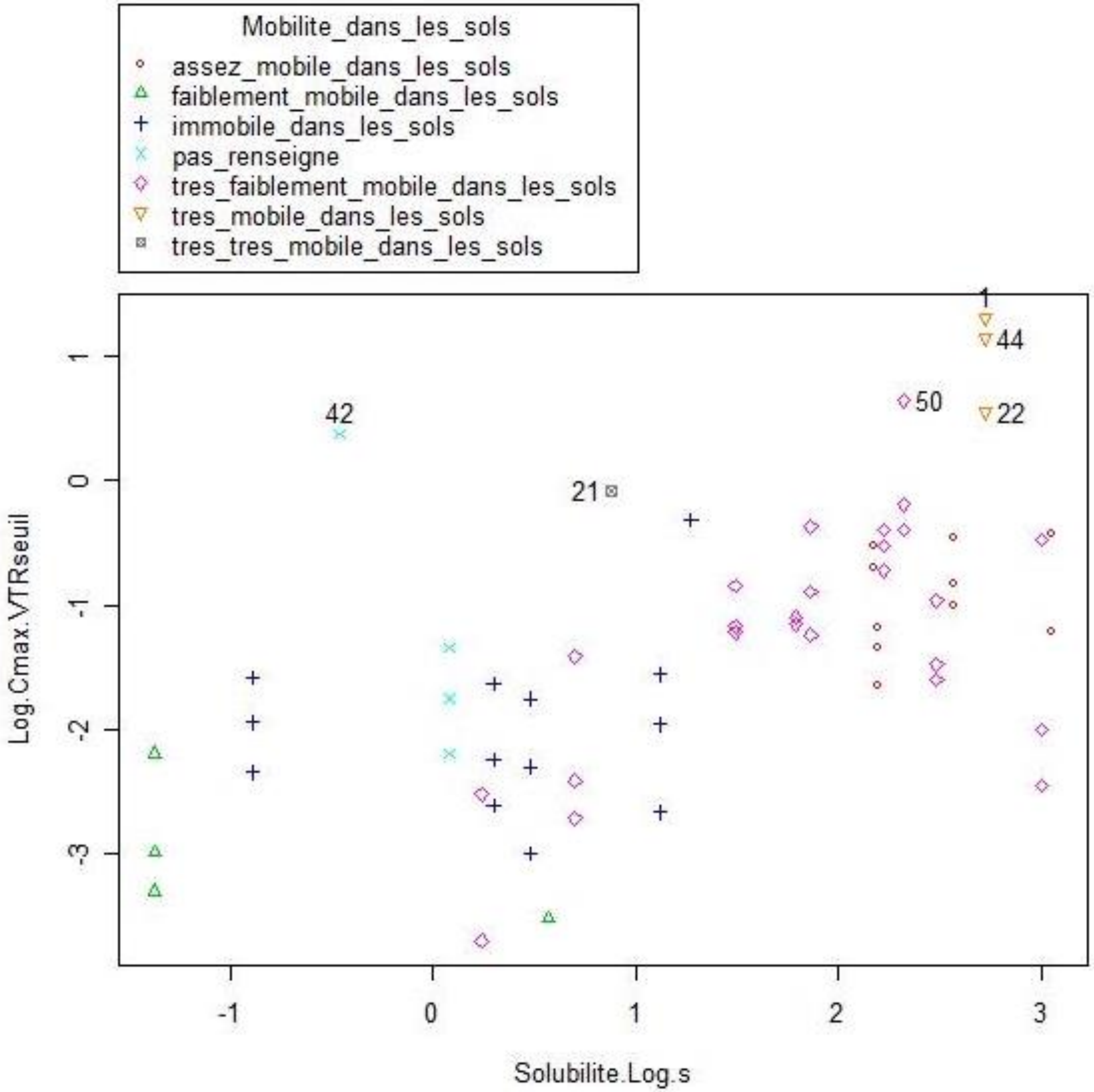
Analysis campaign : main results

- Presence in large quantity of bisphenol A (antioxidant) and phthalates (plasticizer) which are plastic additives with reprotoxic properties
- Presence also of some VOC (mono-aromatic, chlorinated solvent ...) with carcinogenic properties
- Presence of PAHs, PCBs and PBDEs mainly on the particulate phase because these compounds are not very soluble
- Pharmaceuticals and hormones have not been found

CMR compounds found in leachates

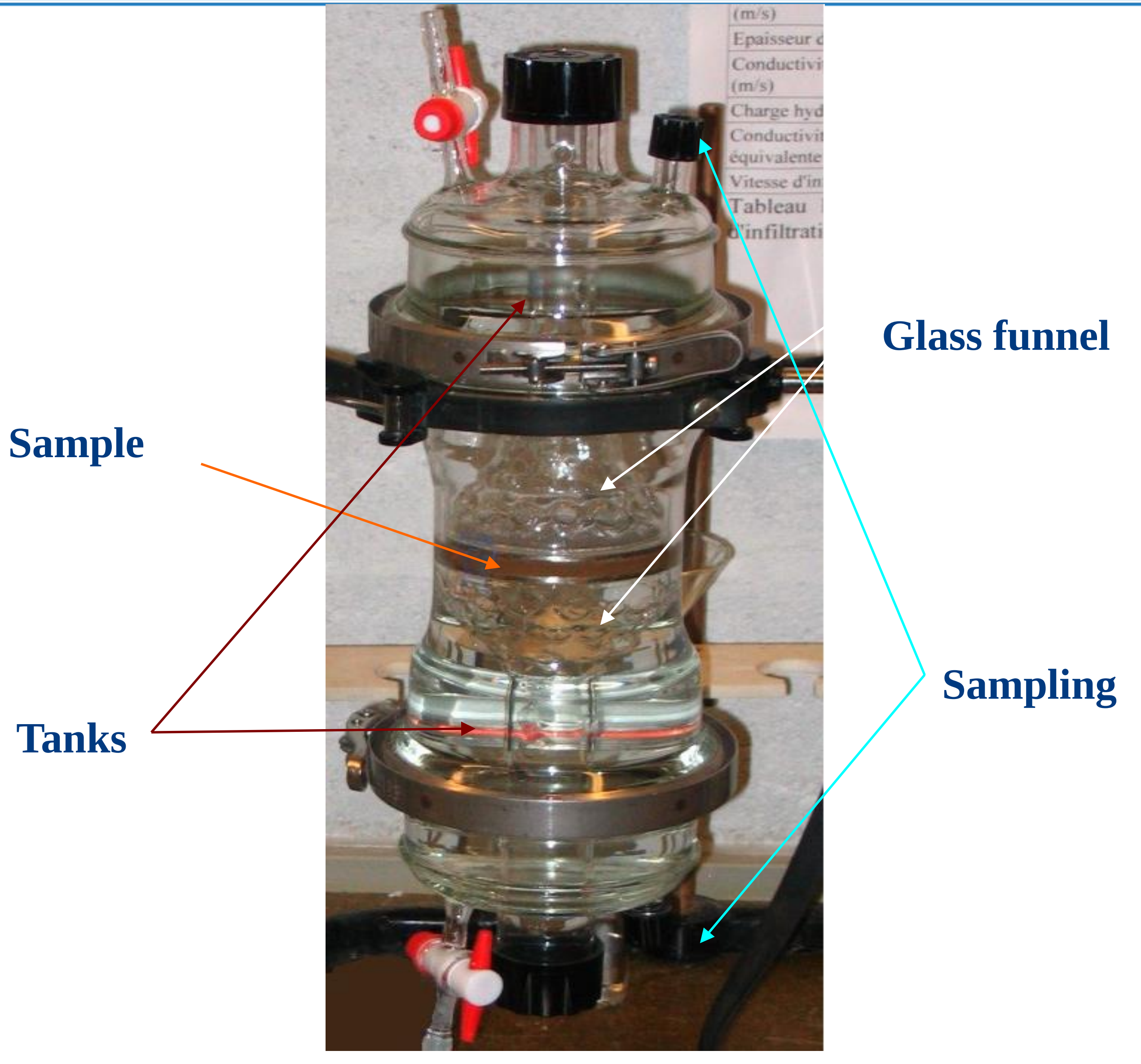
Compounds	CMR Classification	Tracking frequency (%)
Dibutyl phthalate	REPRO 2 / REPRO 3	100
Bisphenol A	REPRO 3	100
Toluène	REPRO 3	100
Benzène	CARC1/MUTA2	100
Dichlorométhane	CARC 3	100
p-dichlorobenzène	CARC3	75
Benz[a]anthracène	CARC 2	62,5
Butyl benzyl phtalate	REPRO 2 / REPRO 3	37,5
Trichloroethylène	CARC 2/ MUTA 3	37,5
Tetrachloroéthylène	CARC 3	37,5
Benzo[e]pyrène	CARC 2	25
Benzo[a]pyrène	CARC 2/ MUTA 2/ REPRO 2	25
Heptachlor epoxide	CARC3	12,5
Heptachlor	CARC 3	12,5

Selection of compounds for impact analysis



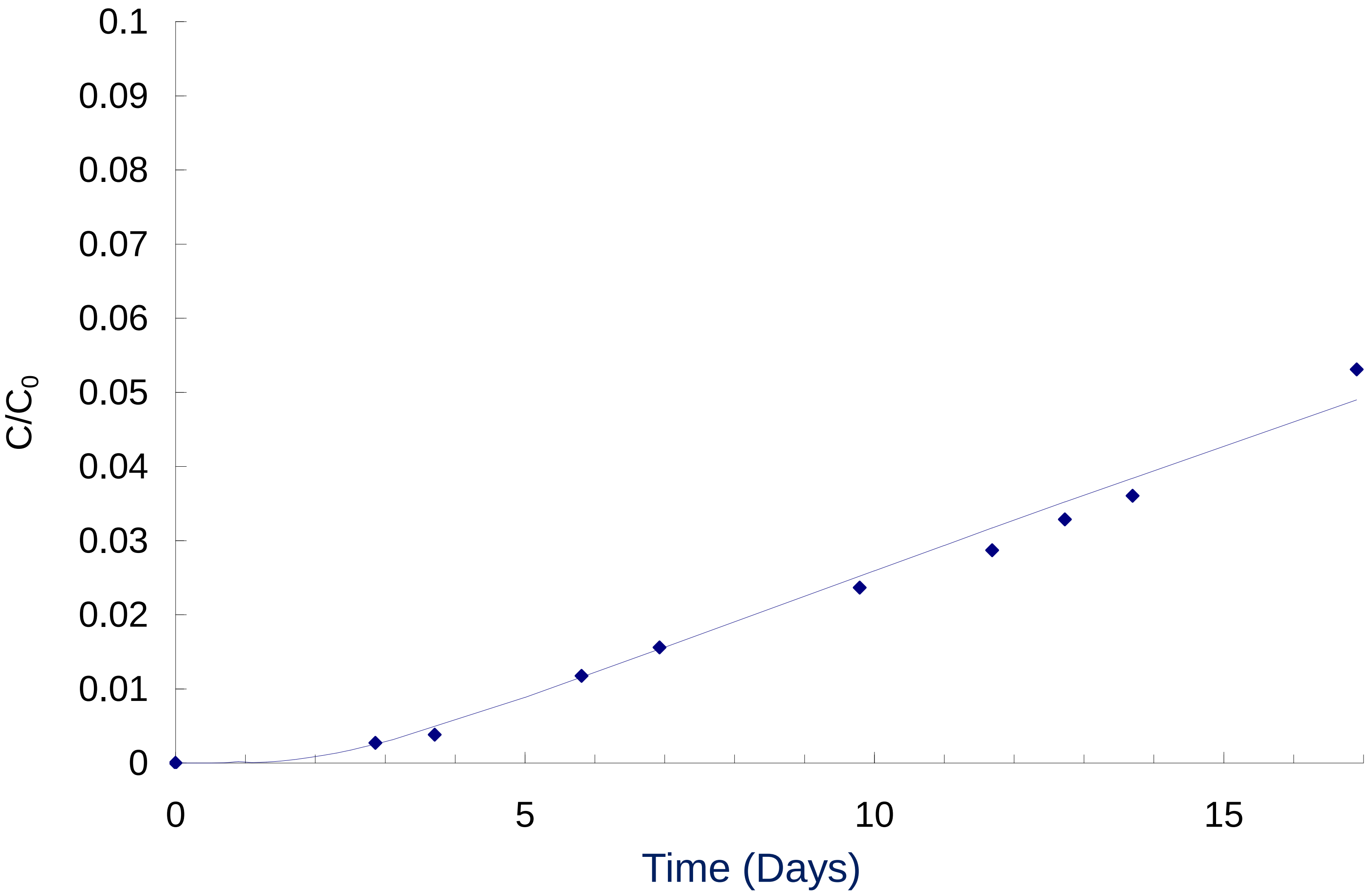
1: Toluène (DIB)
44: Toluène (OM + DIB)
22: Toluène (OM)
50: Bisphenol_A (OM + DIB)
42: Heptachlor_epoxide (OM)

Determination of diffusion coefficients

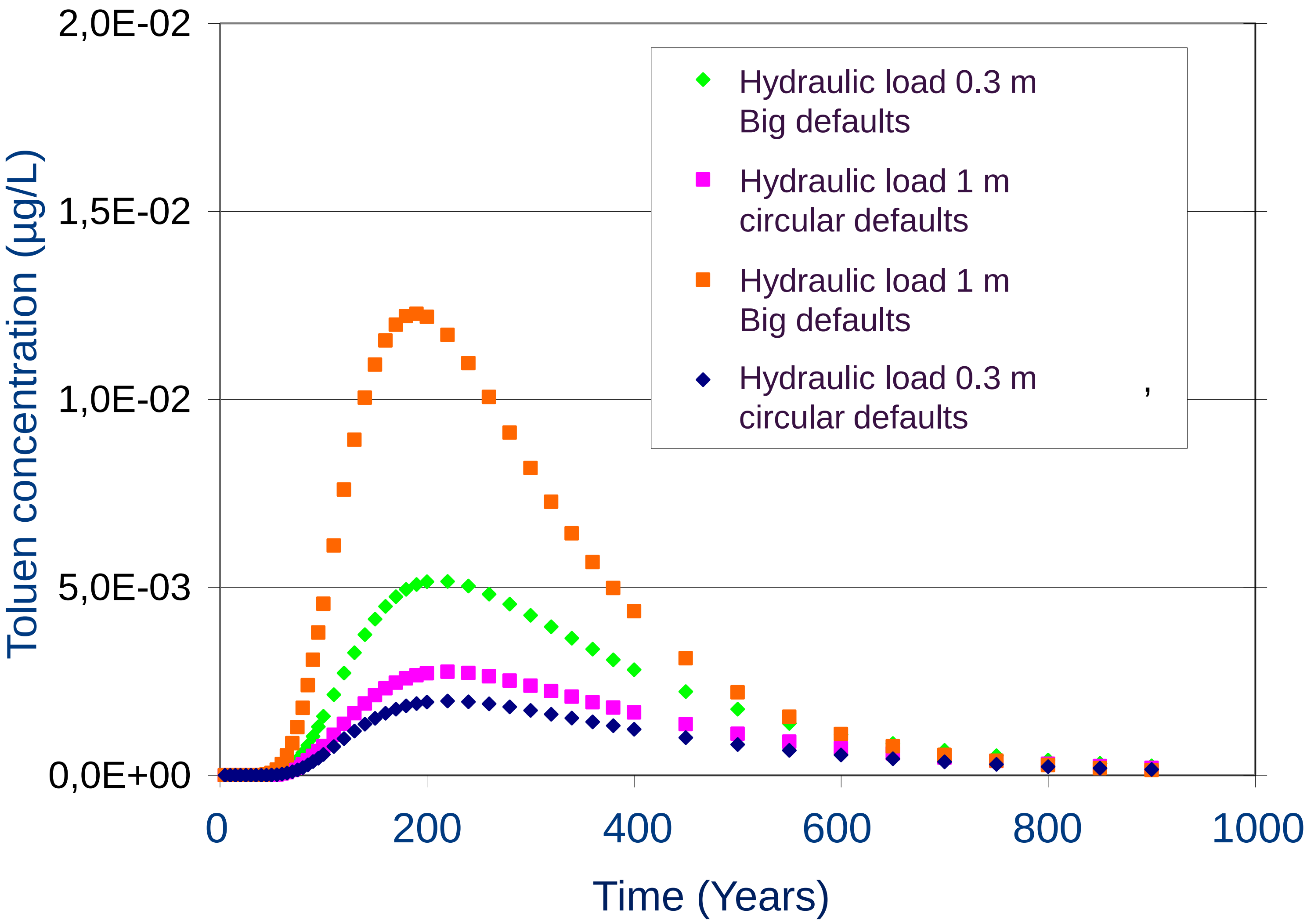


Determination of diffusion coefficients

Toluen



Calculation of the concentration in the aquifer



Assessment of the toxicity of non-hazardous waste storage facility leachates and identification of the chemical agents responsible

université de BORDEAUX LPTC

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR LCABIE

INERIS maîtriser le risque pour un développement durable

Nature of analyzed leachates

Raw leachate

Aerated leachate

Treated leachate

Samples	**Site**	**Characteristics**
Site1-LB	Site 1	Lixiviat brut provenant de plusieurs casiers d'âges différents.
Site1-LA	Site 1	Lixiviat prélevé dans le bassin d'aération recevant le lixiviat site1-LB.
Site1-LT	Site 1	Perméat prélevé en sortie de traitement (évapo-concentration suivie d'une osmose inverse) du site1.
Site2-LB	Site 2	Lixiviat brut prélevé au niveau de la station de relevage du site 2.
Site2-LA	Site 2	Lixiviat prélevé dans le bassin d'aération recevant le lixiviat site2-LB.
Site2-LT	Site 2	Effluent de sortie de traitement (réacteur membranaire suivi d'une filtration sur charbon actif) du site 2.

Evaluation of the toxicity of the organic fraction

Toxicity test

Targeted mechanisms	Methods	Detected molecules	References
Génotoxicity	SOS Chromotest	Genotoxics et pro genotoxics: HAP, nitrosamin , pesticides…	Quillardet et Hofnung, 1985
Dioxin receptor (AhR)	EROD activity	Dioxins et dioxin-likes, HAPs, PCBs	Laville et al., 2004
Estrogen receptor (ER)	Luciferase activity	Steroïds naturals et synthetics, Alkylphenols, Bisphenol A…	Pillon et al., 2005

Toxicity tests results

	Activity		
	Genotoxicity	Dioxin-like	Estrogenicity
Site 1 - Raw	+	++	+++
Site 1 - Aerated	-	+	+
Site 1 - Treated	-	-	-
Site 2 - Raw	-	++	++
Site 2 - Aerated	-	+	++
Site 2 - Treated	-	-	-

Principle of the effect directed analysis approach

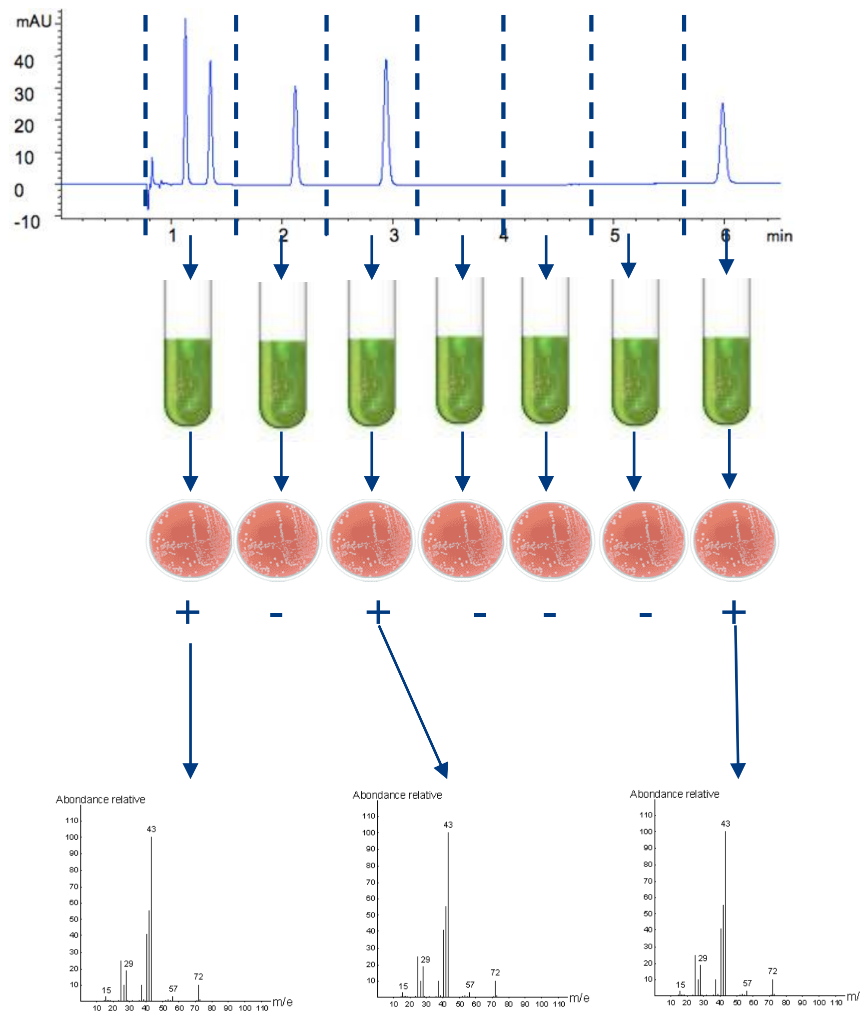
Fractionation of the leachate organic fraction by HPLC

↓

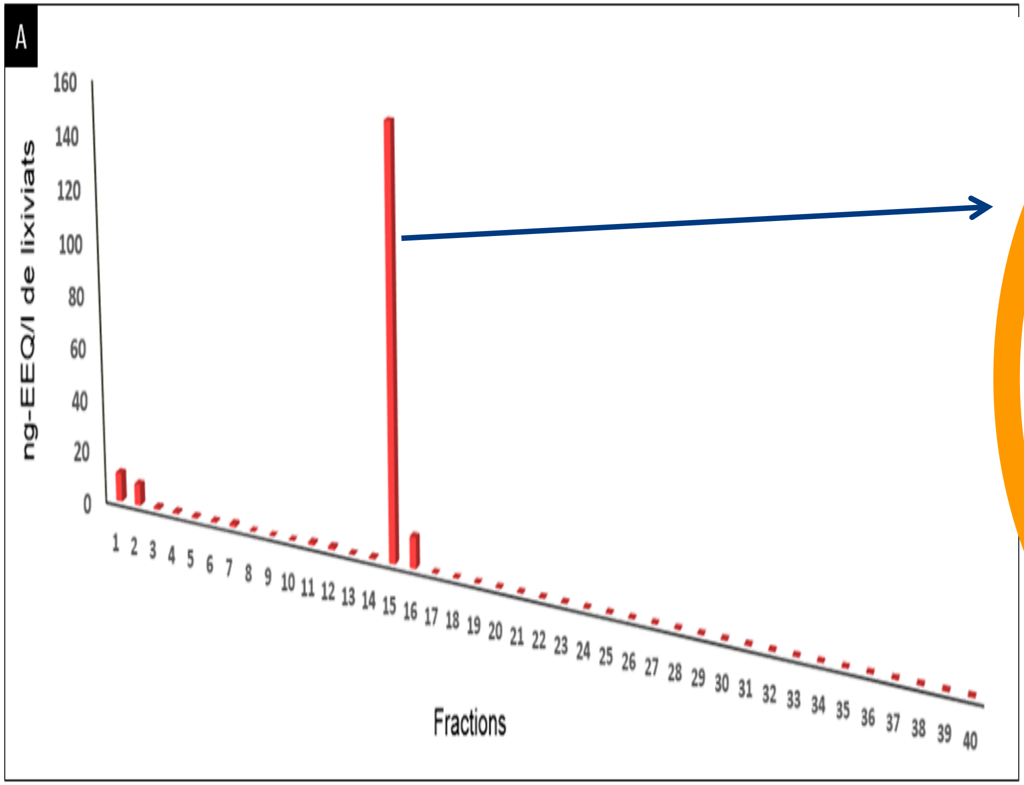
Identification of toxics fractions by toxicity tests (*Genotoxicity, Estrogenicity*)

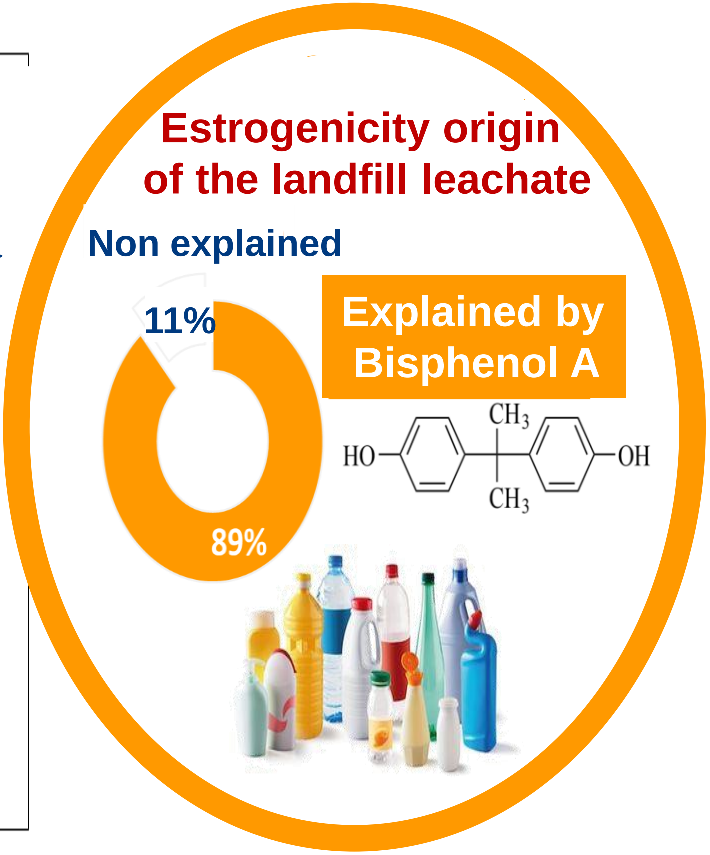
↓

Identification of molecules present in the fractions presenting toxicity by chemical analysis

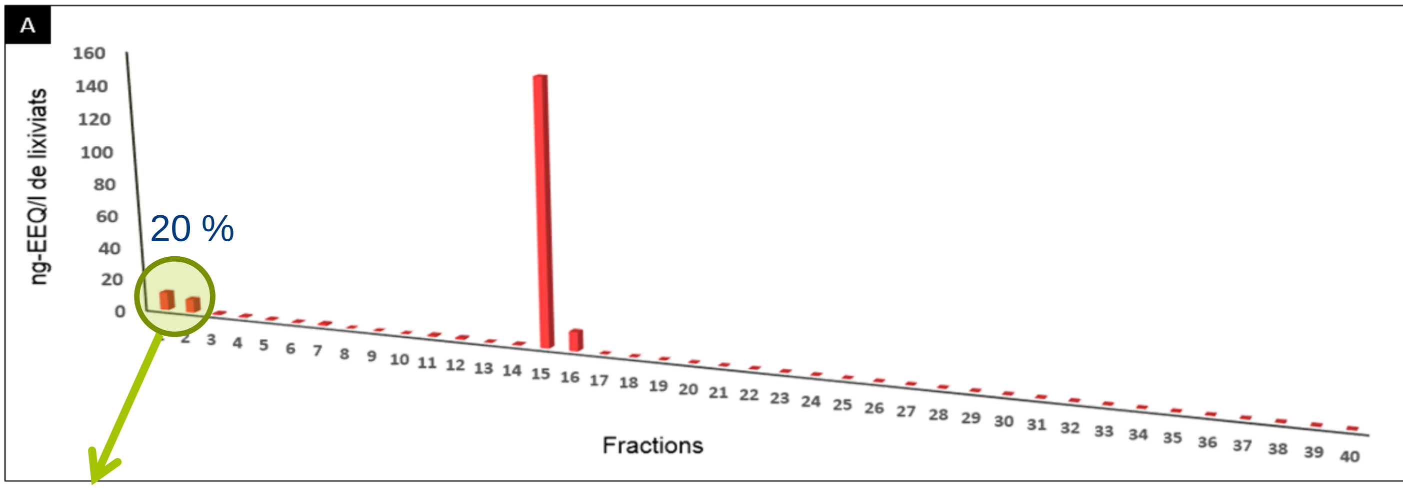


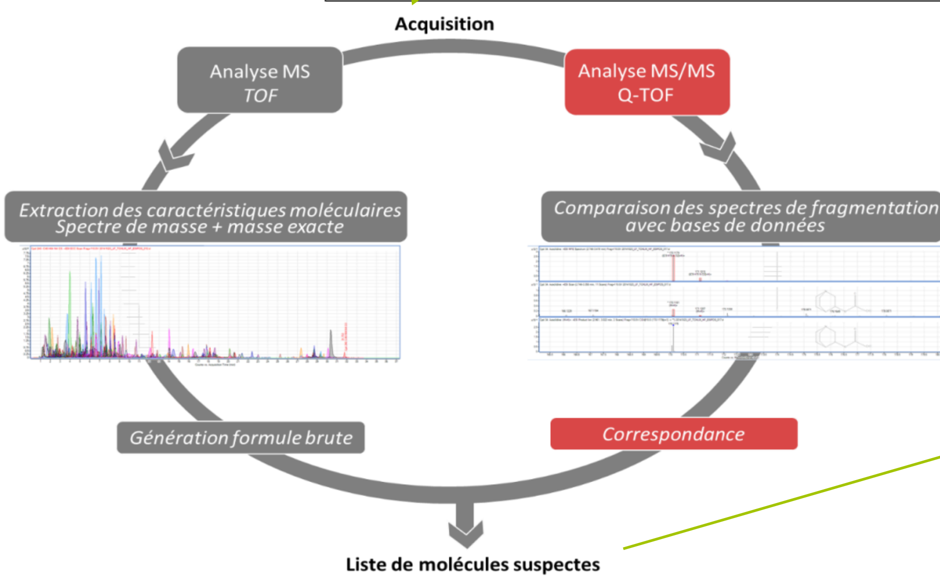
EDA approach to ISDND leachates

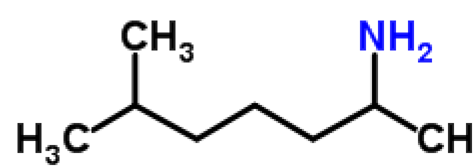




Identification of the responsible compounds







Octodrine

Concentrations of metals in leachates

Concentrations in mg/l

Danemark	Germany	England	Drinking water
0.006	0.005	< 0.04	0.005
0.67	0.6	< 0.47	5.0
0.07	0.065	< 0.17	1.3
0.08	0.28	< 0.05	0.1

Levels of metals in leachates are low.

→ Metal trapping in waste as a precipitate (sulphide, carbonate…) or complexes with organic matter

However, in the long term, there may be significant release of metals when returning to aerobic conditions.

Sulfooxidation: a long-term risk?

sulfo-oxydation

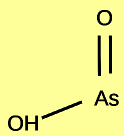
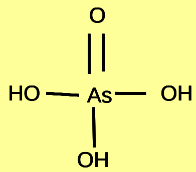
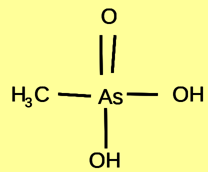
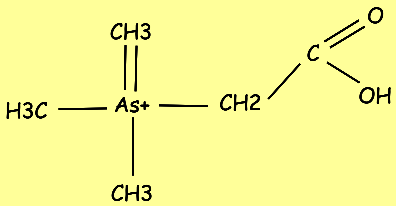
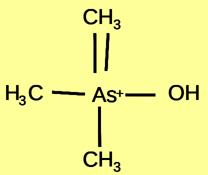
Consumption of sulphides in the presence of oxygen or nitrates (DMA) :

$$MS + O_2 + 2\ OH^- \rightarrow M^{2+} + H_2SO_4$$

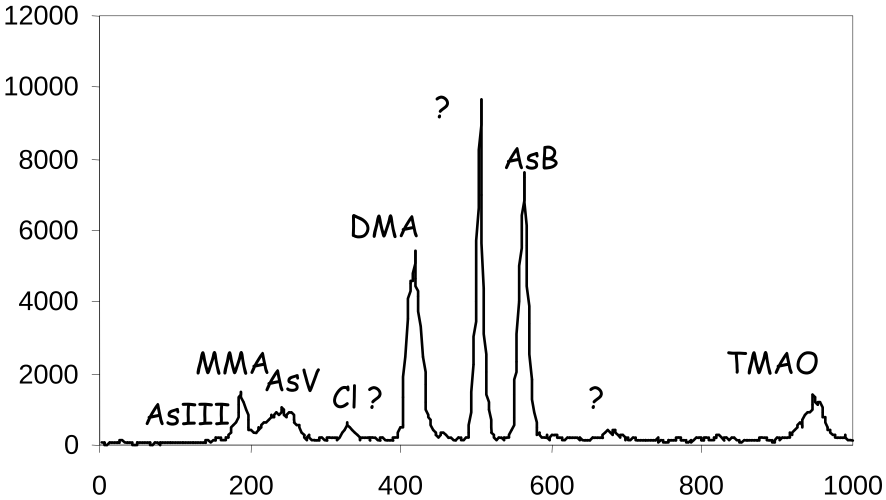
Consequences :

- Significant drop in pH
- Resolubilization of sulphides, hydroxides and carbonates

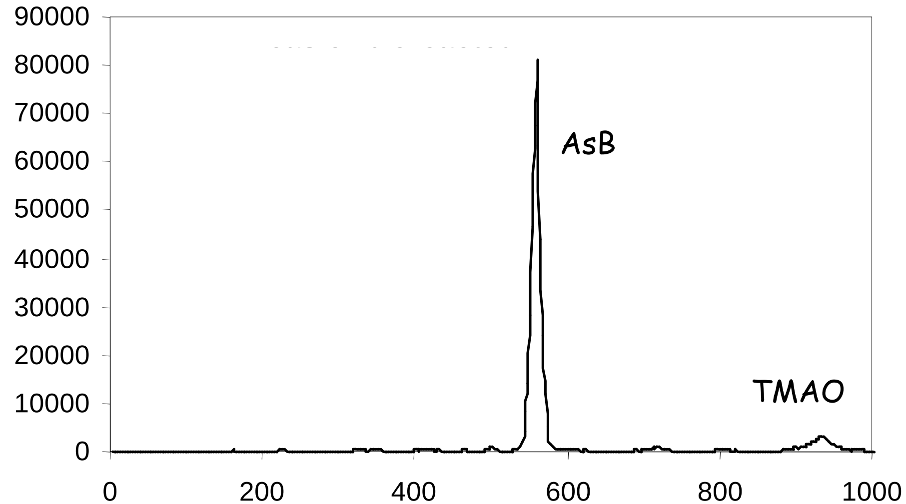
Arsenic speciation

	AsIII	AsV	MMA	AsB	TMAO
					
LD 50	8	22	916	4260	5500
TOXICITY					

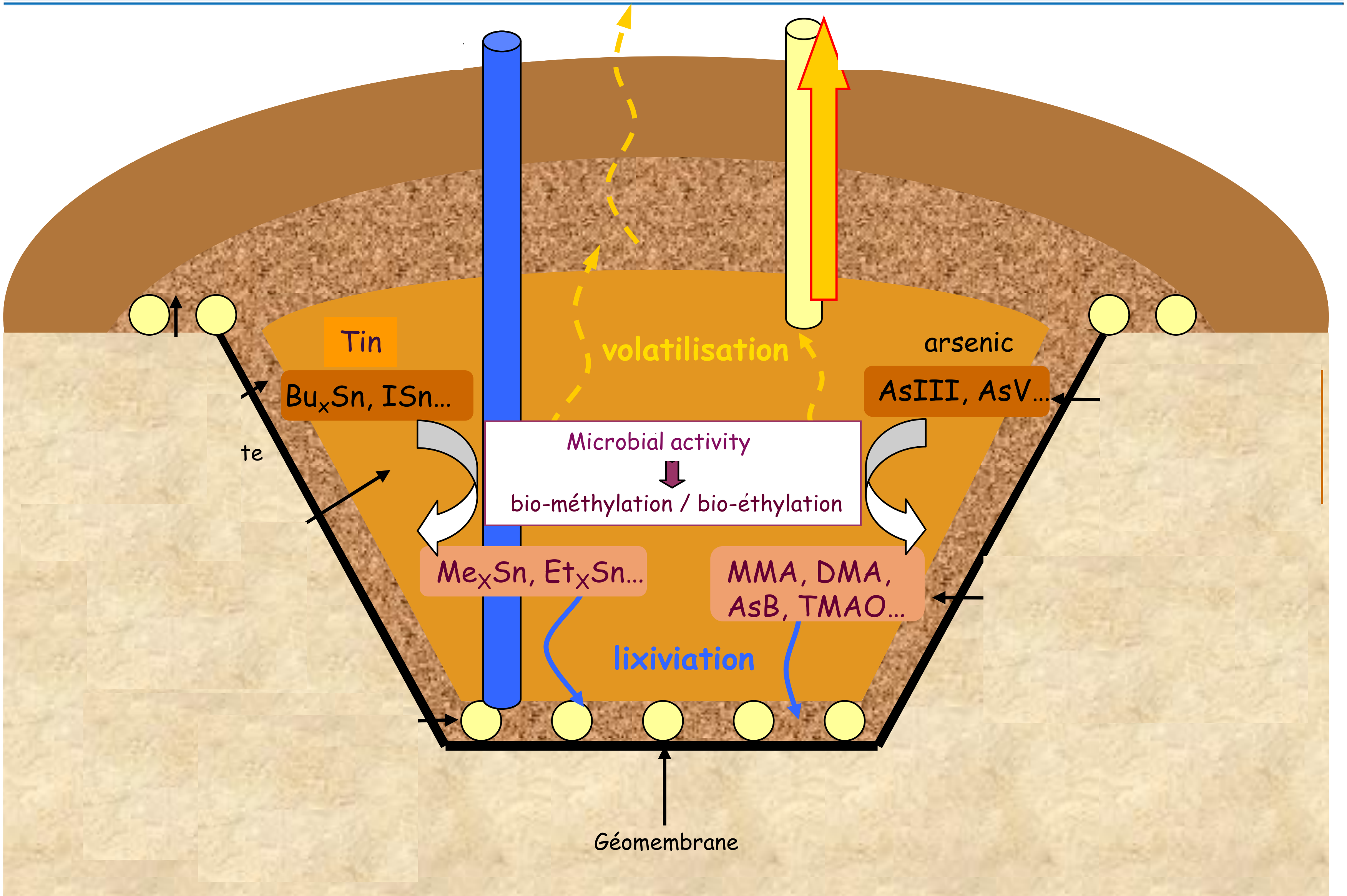
Normal landfill

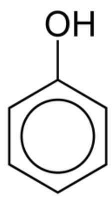


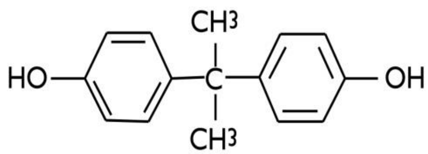
Bioreactor landfill

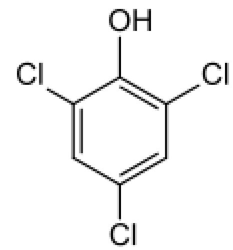


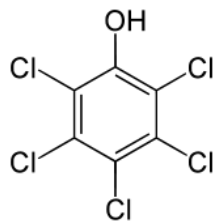
Metals biogeochemical cycles in MSW landfill

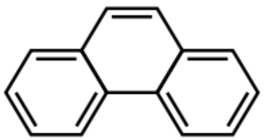




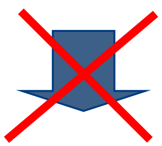








Demonstration of the disappearance of the pollutant



Lowering toxicity

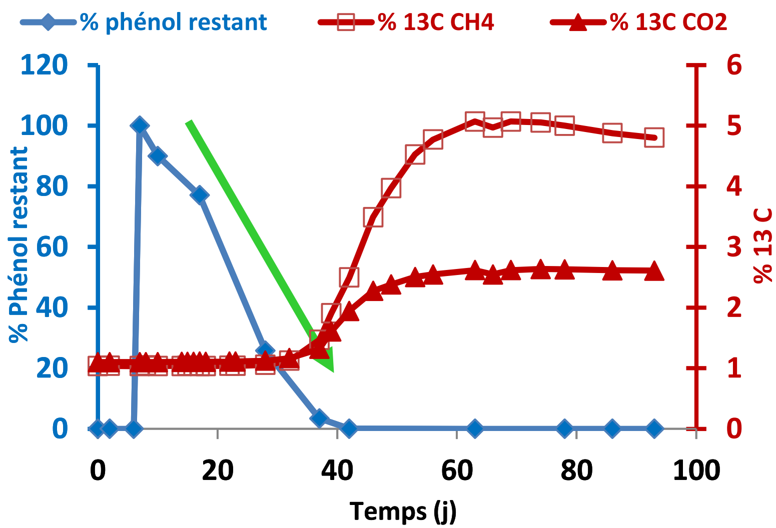
Because the pollutant can :

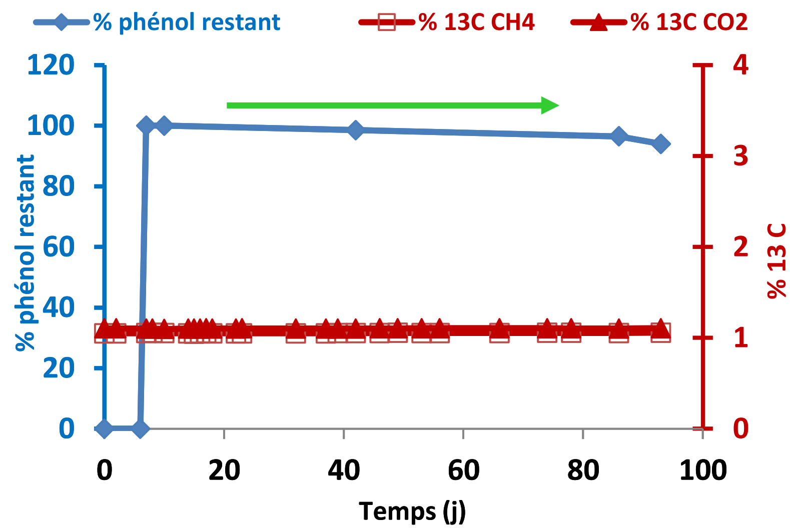
1- Simply be adsorbed on the waste

2- Transformed into a metabolite which may be more toxic than the initial pollutant

PHENOL ECODYNAMICS MONITORING

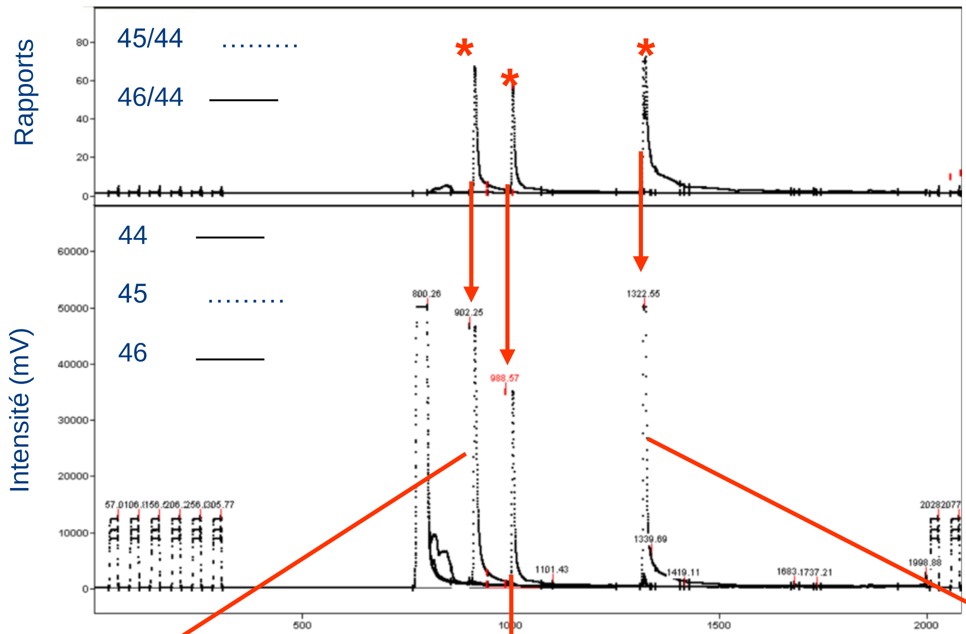
Biotic Incubation — **Abiotic Incubation**



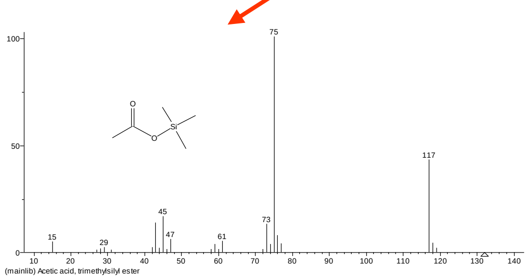


- Demonstration of the biodegradation of phenol
- Degradation of phenol to CH_4 and CO_2

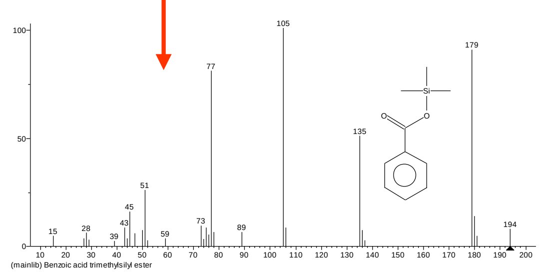
IDENTIFICATION OF DEGRADATION PRODUCTS AT 35°C



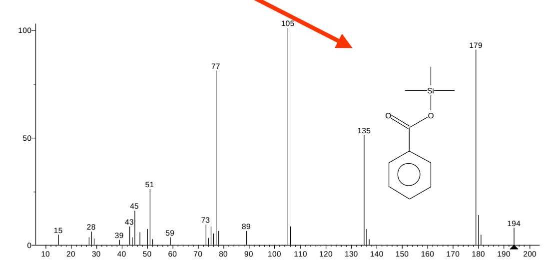
Gas chromatography-isotope ratio mass spectrometry (GC-IRMS)



ACETIC ACID



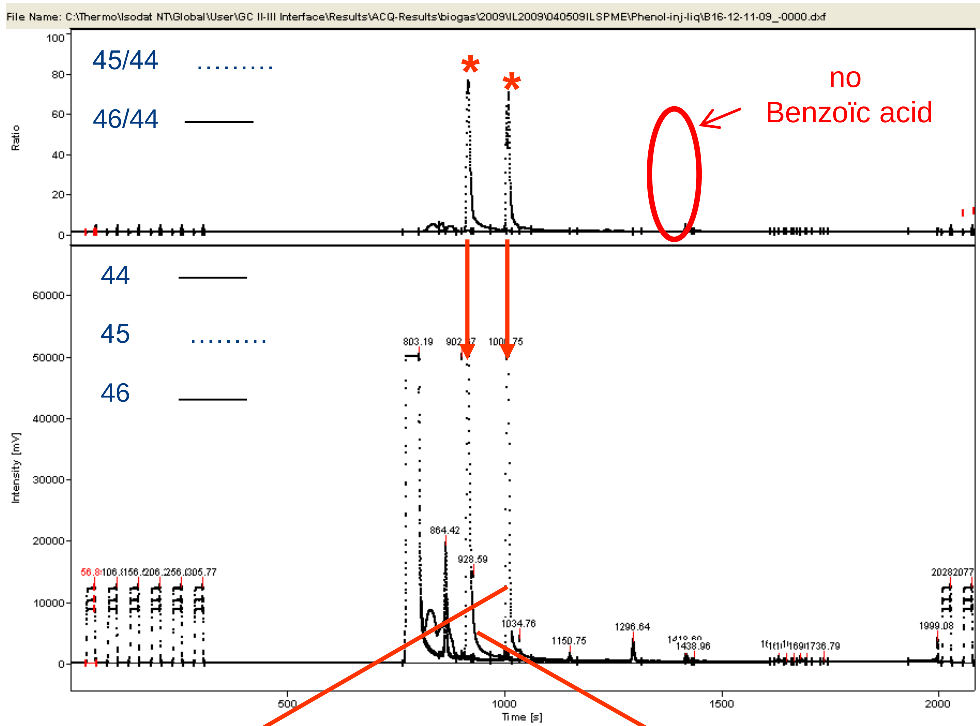
PHENOL



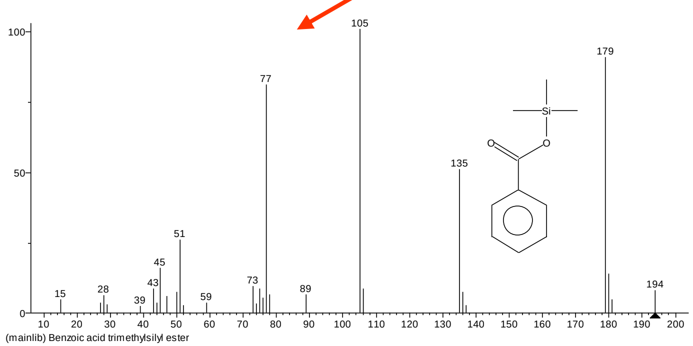
BENZOÏC ACID

- Identify degradation pathways
- Highlight the accumulation of some metabolites

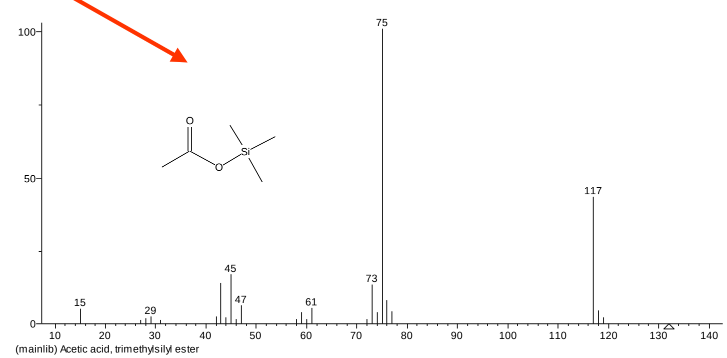
IDENTIFICATION OF DEGRADATION PRODUCTS AT 55°C



GC-IRMS



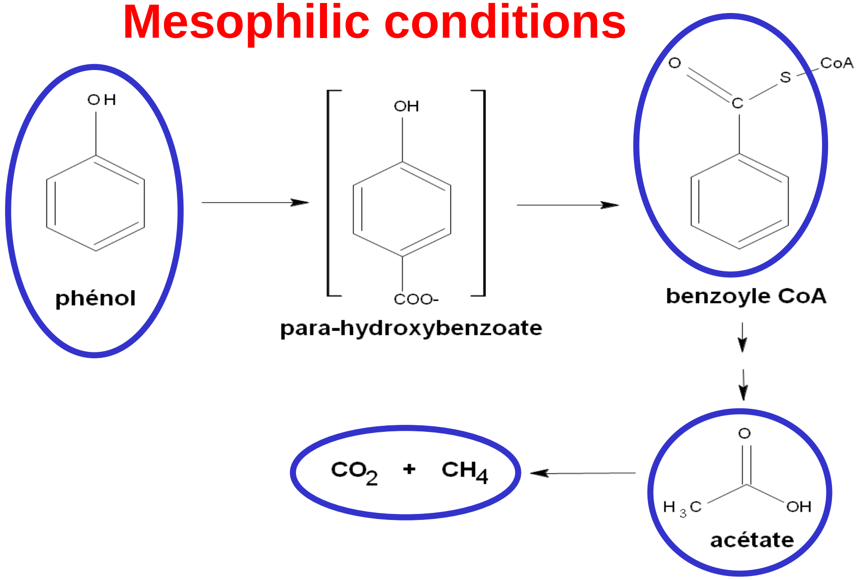
PHENOL



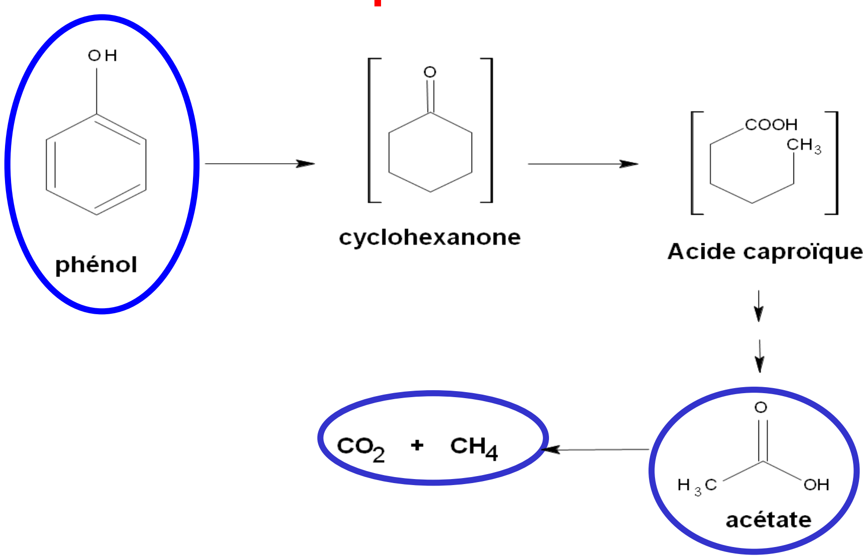
ACETIC ACID

Metabolic pathways of anaerobic degradation of phenol

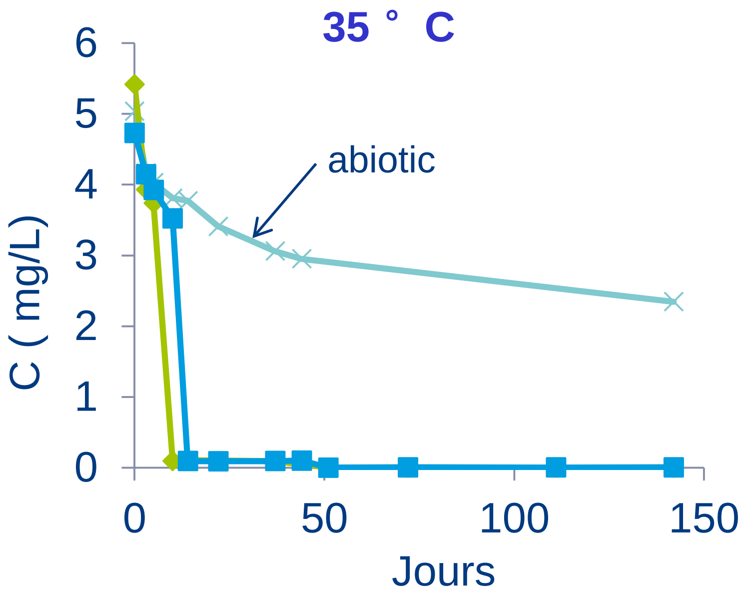
Mesophilic conditions

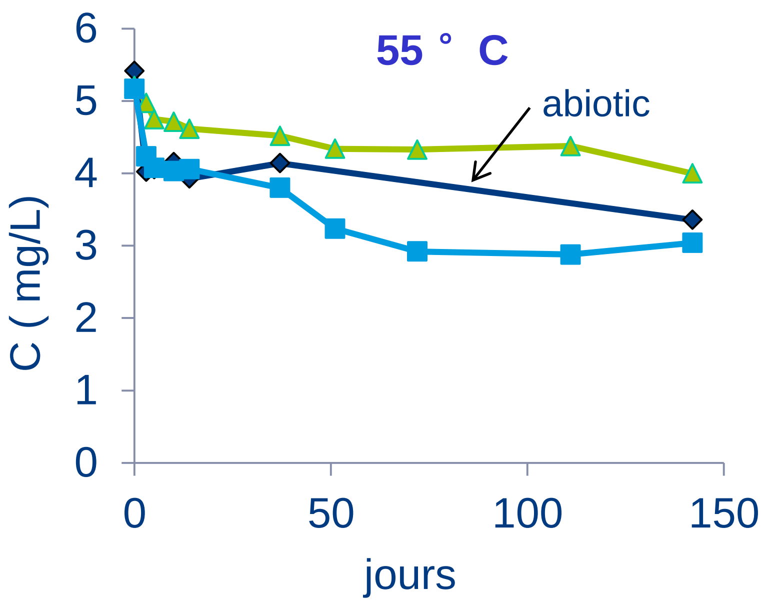


Thermophilic conditions



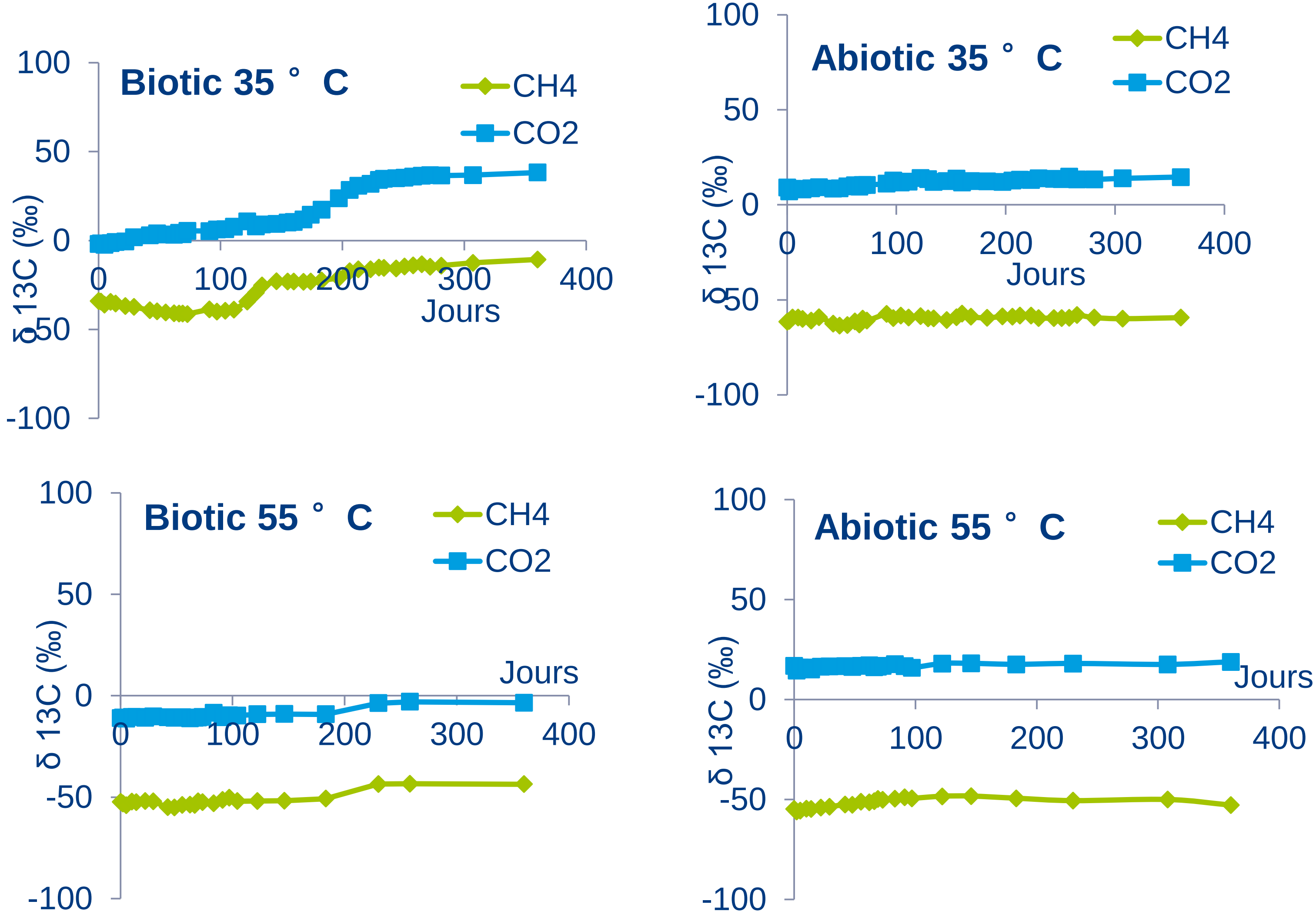
Fate of $^{13}C_6$-2,4,6-trichlorophenol





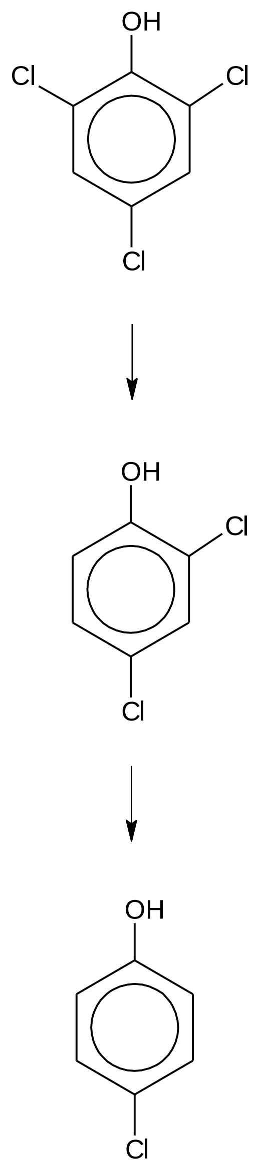
- **Disappearance of 2,4,6-TCP in mesophilic biotic incubations, during anaerobic digestion**
- **Persistance du 2,4,6-TCP at 55 ° C.**

Fate of $^{13}C_6$-2,4,6-trichlorophenol



Natural isotopic composition at 35 and 55 ° C

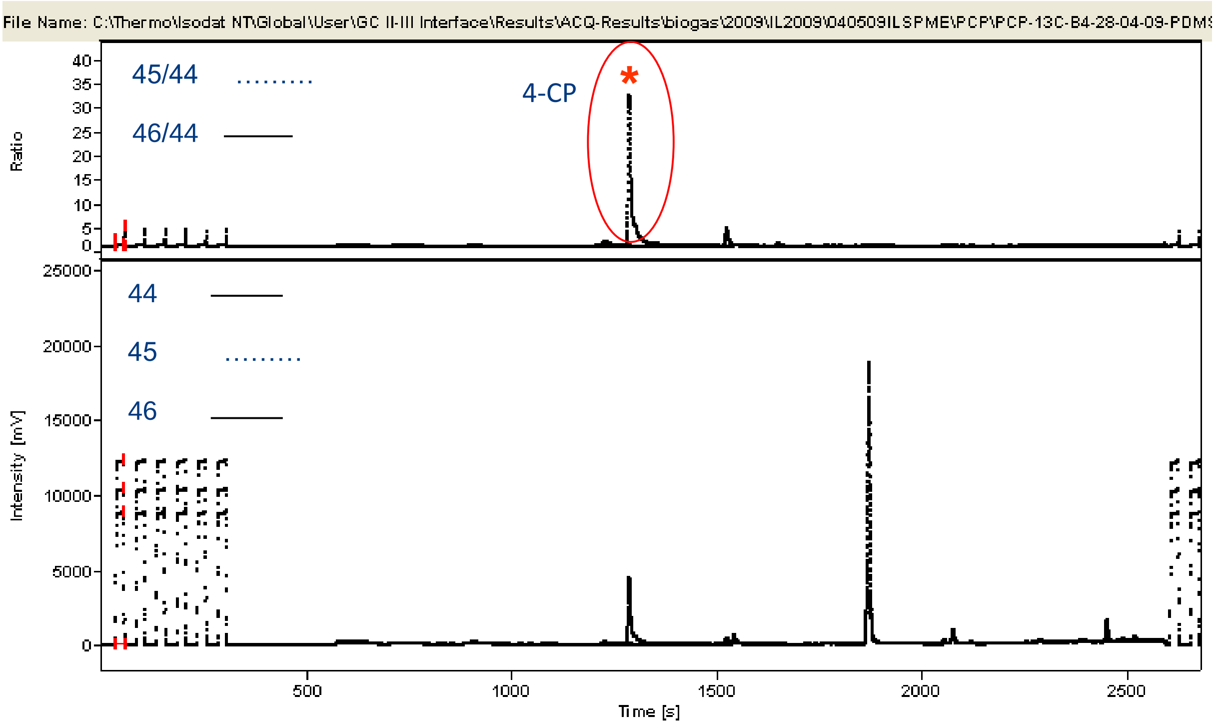
Identification of 13C6-2,4,6-TCP metabolites in incubations at 35 ° C



Presence of 2,4-DCP at 35 ° C

Persistance of 4-CP à 35 ° C

Persistance of $^{13}C_6$-4-CP at 35 ° C

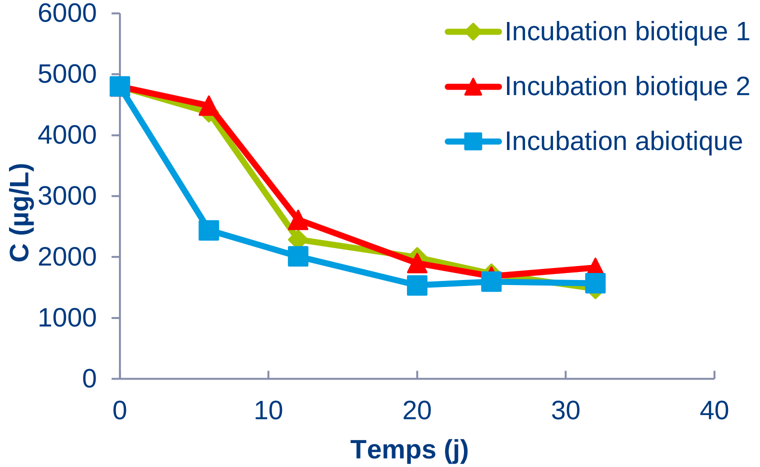


➡ **Persistance du 4-CP à 35° C et absence du phénol comme produit de dégradation du 4-CP**

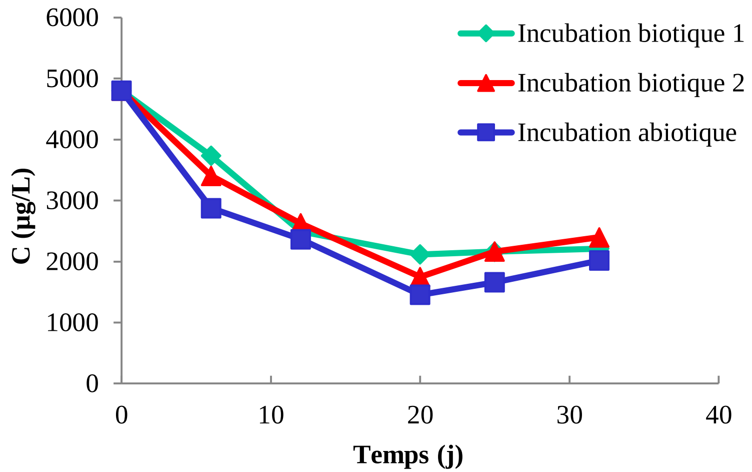
Fate of bisphénol-A

Molecular monitoring (GC-MS)

35°C



55°C



No mineralisation of Bisphenol A but adsorption on waste