

Centre d'Alembert – Université Paris-Sud
Centre Interdisciplinaire d'Étude de l'Évolution des Idées,
des Sciences et des Techniques (CIEEIST)



Chimie des eaux naturelles
et impact des activités humaines

Philippe BEHRA

Professeur des universités



www.chimieagroindustrielle.fr/



Orsay, 2 février 2017



Université Fédérale
Toulouse Midi-Pyrénées

Laboratoire de Chimie Agro-Industrielle

UMR 1010 INRA/INPT-ENSIACET

Director: Dr. Gérard VILAREM - Pr. Carlos VACA GARCIA

Chemodynamics and treatment of micropollutants

*Prof. Philippe BEHRA
Pierre-Yves PONTALIER, MCF*

Caroline SABLAYROLLES , MCF

Claire VIALLE , MCF

Research and technology transfer

Research



UMR 1010



CRT 96/7

Technology
transfer



Laboratoire de Chimie Agro-Industrielle



**TOTAL VALORISATION
OF VEGETAL BIOMASS**



AGRORAFFINERY

Non food domain

3 research teams

Knowledges and scientific skills

Fractionnement des
agroressources et
procédés de transformation
agro-industrielle

FAPTA

32
personnes

Réactivité chimique des
agromolécules-Lipochimie

RCAML

24
personnes

Génie analytique et devenir
environnemental des
agroconstituants

GADEA

25
personnes

Toulouse

Tarbes



+ 1 Team for Transfer



10
personnes

Totally: 91 people

Plan

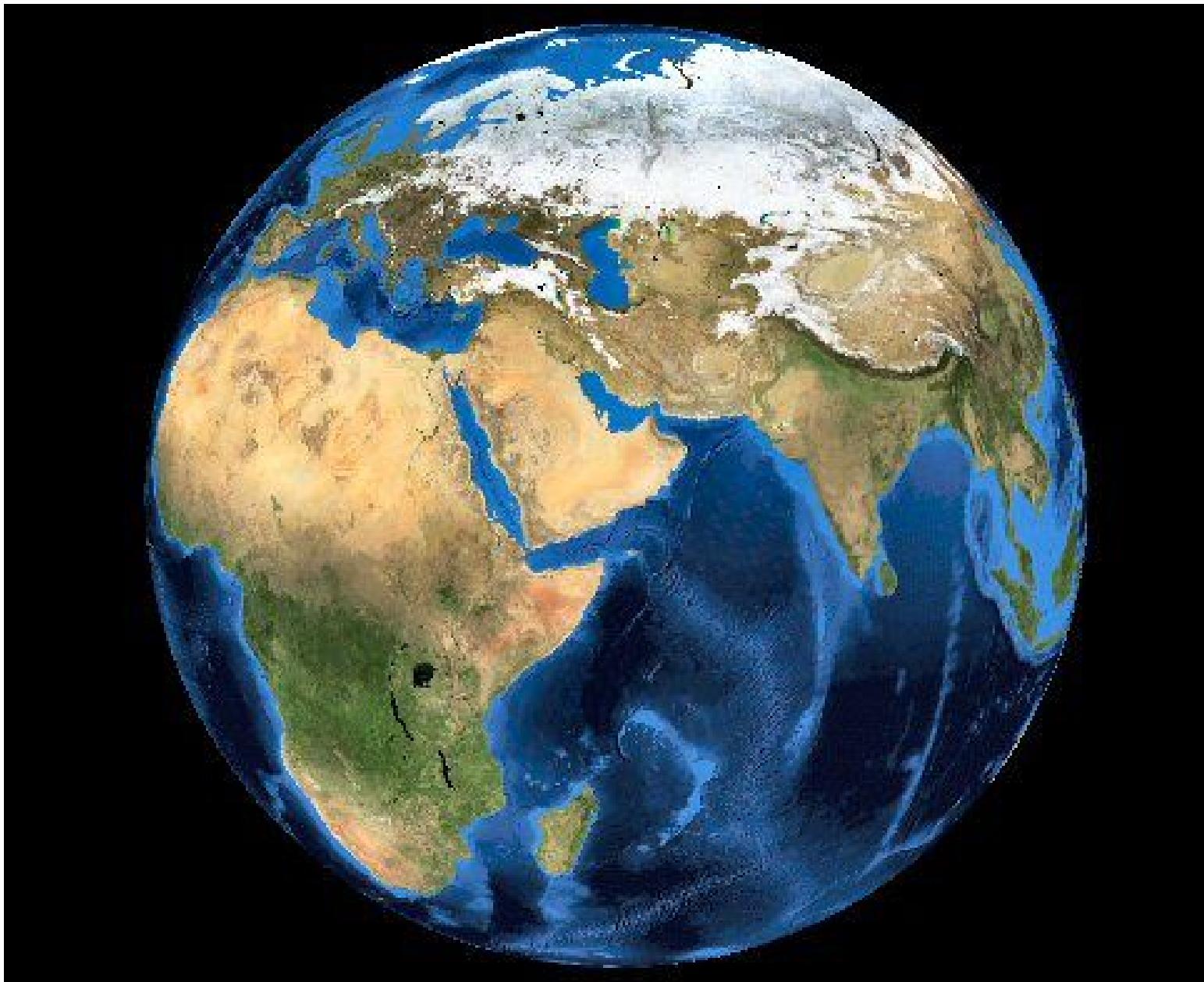
Cycle de l'eau

Qualité de l'eau

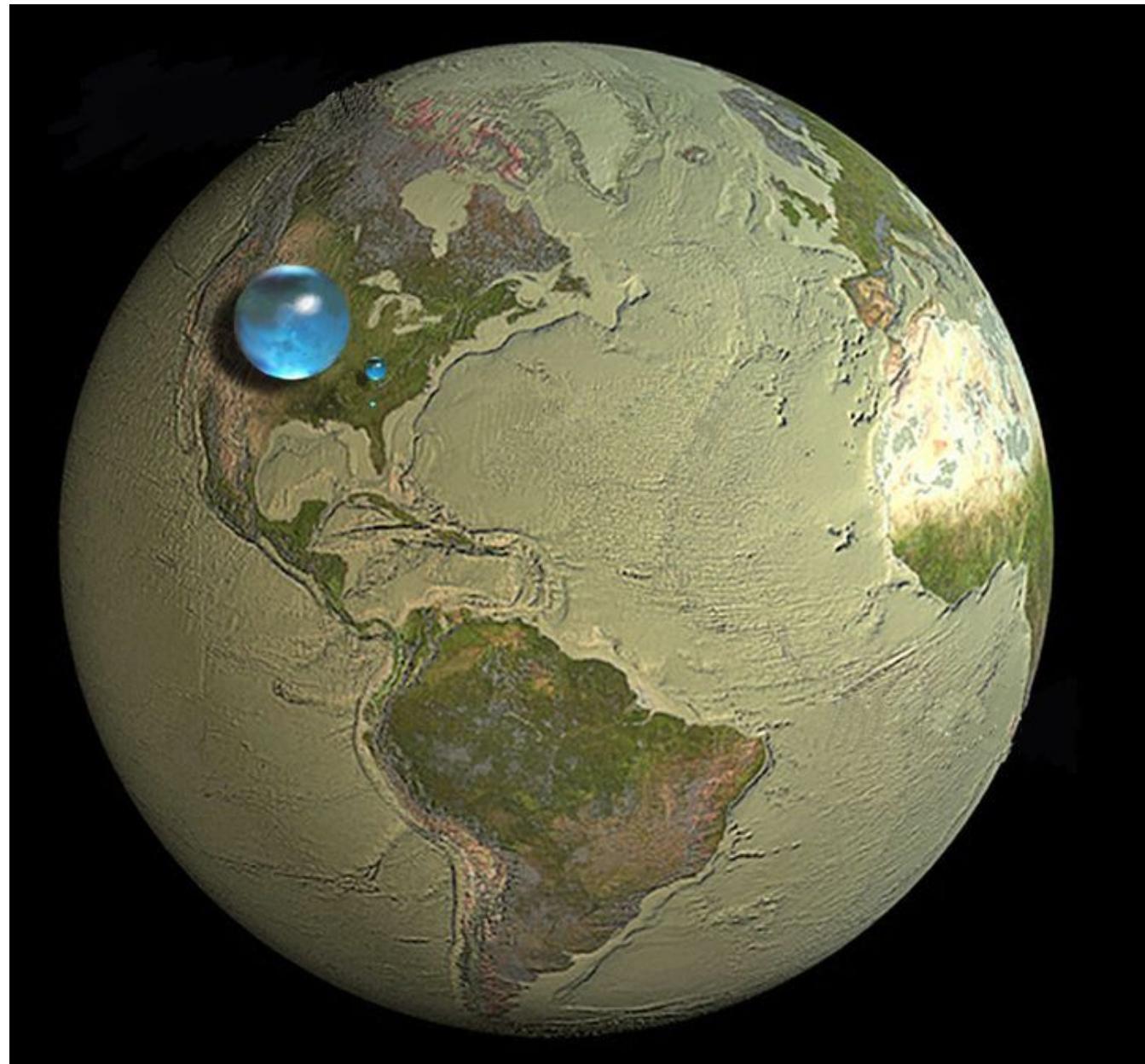
Composition des eaux naturelles

Impact des activités humaines

Cycle de l'eau



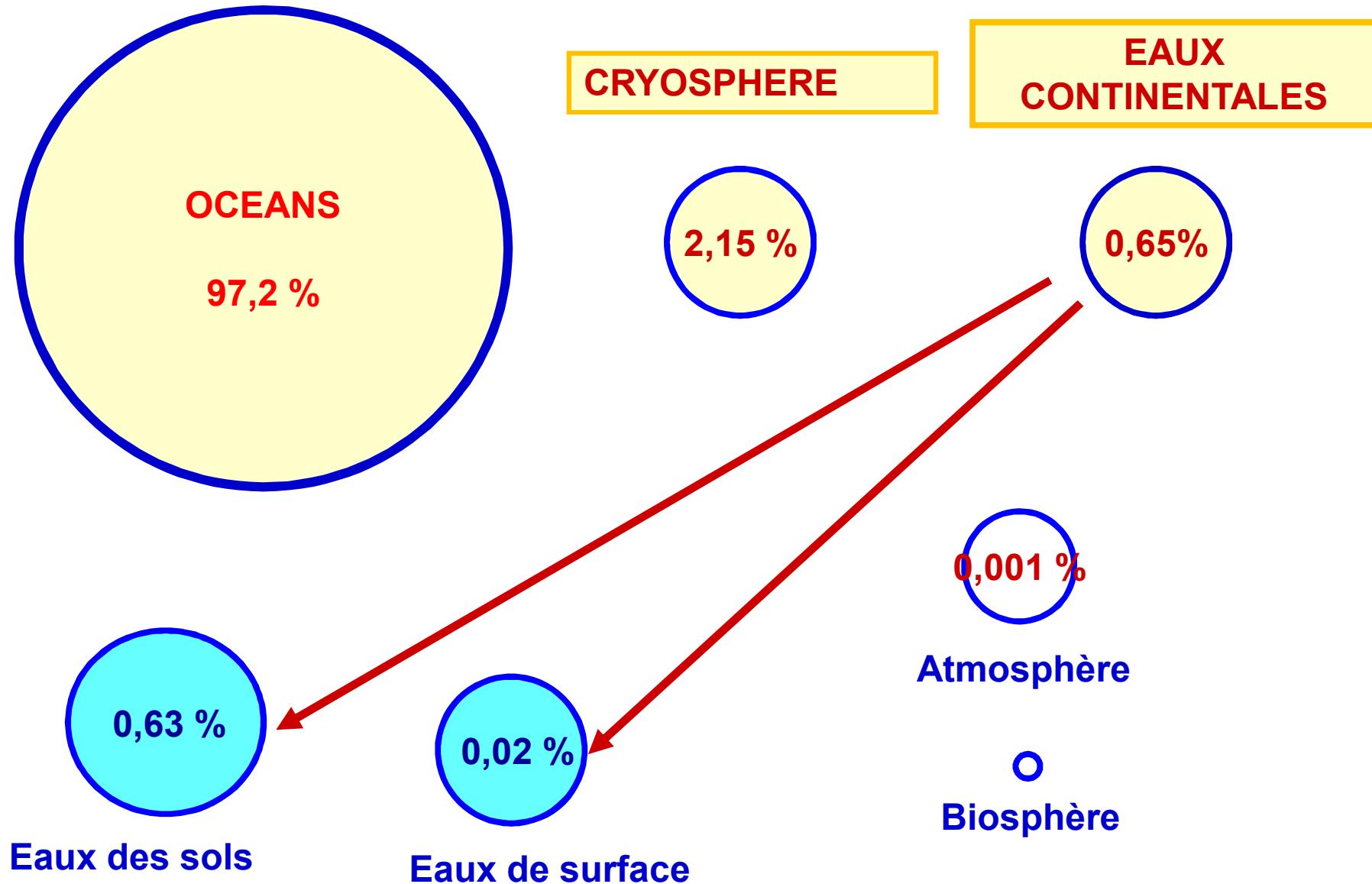
(Philippe Maisongrande, Legos)



$1,4 \cdot 10^9 \text{ km}^3 \text{ d'eau}$

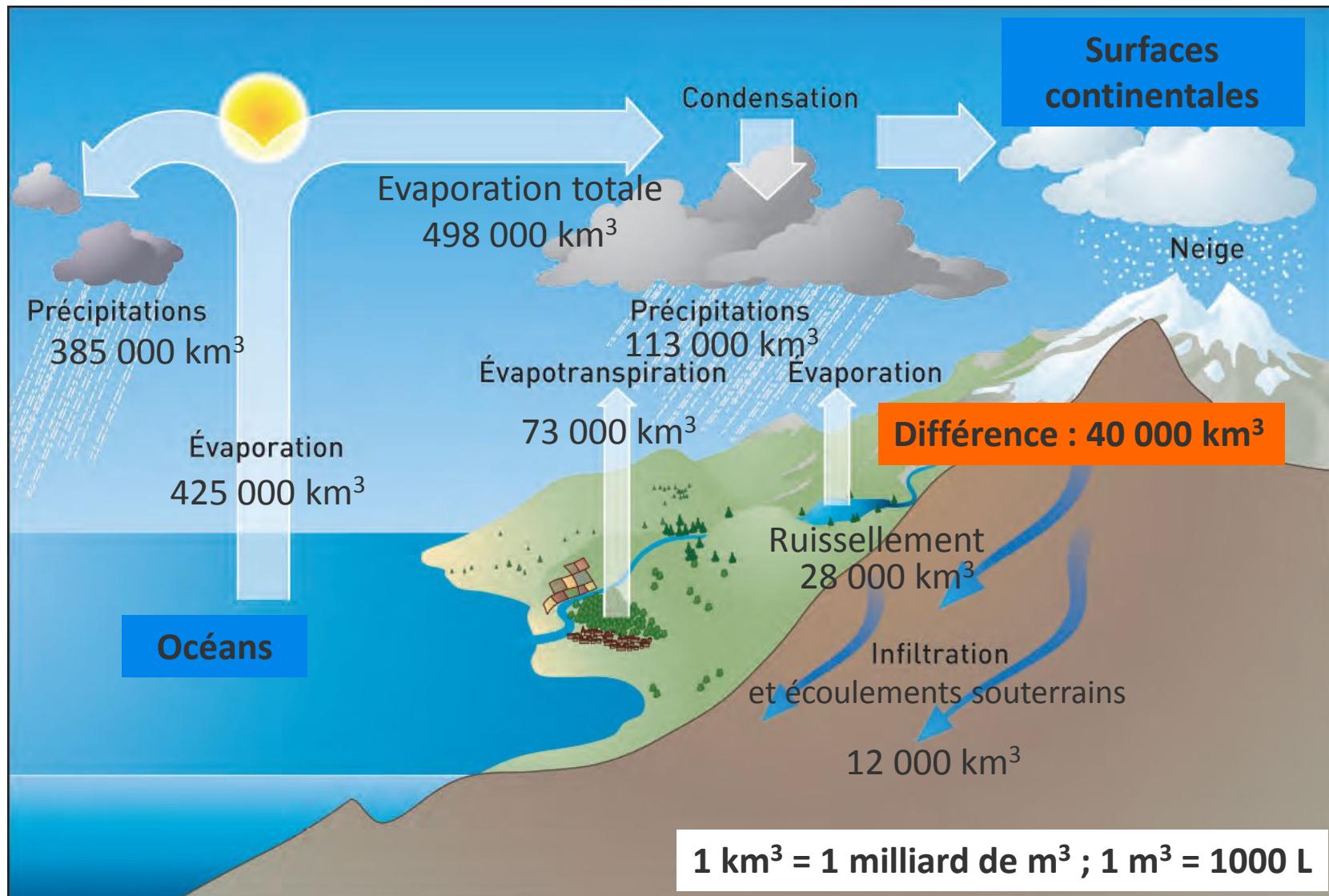
(Philippe Maisongrande, Legos)

Répartition de l'eau sur terre



(Philippe Maisongrande, Legos)

Bilans des flux hydriques annuels sur l'ensemble de la planète exprimés en km³ d'eau



(d'après Ghislain de Marsily, 1995 et 2009)

Demande en Eau

km ³ /a	1900	1950	1990	2000	% (2000)
Agriculture	525	1 130	2 680	3 250	63 %
Industrie	37	178	973	1 290	25 %
Domestique	16	58	470	660	12 %

Crues : 27 500 km³/a

Eaux souterraines : 10 500 km³/a

Glaces : 2 500 km³/a

Total : 5 200 km³/a

Récupérable : ~13 500 km³/a

(de Marsily, 2009)

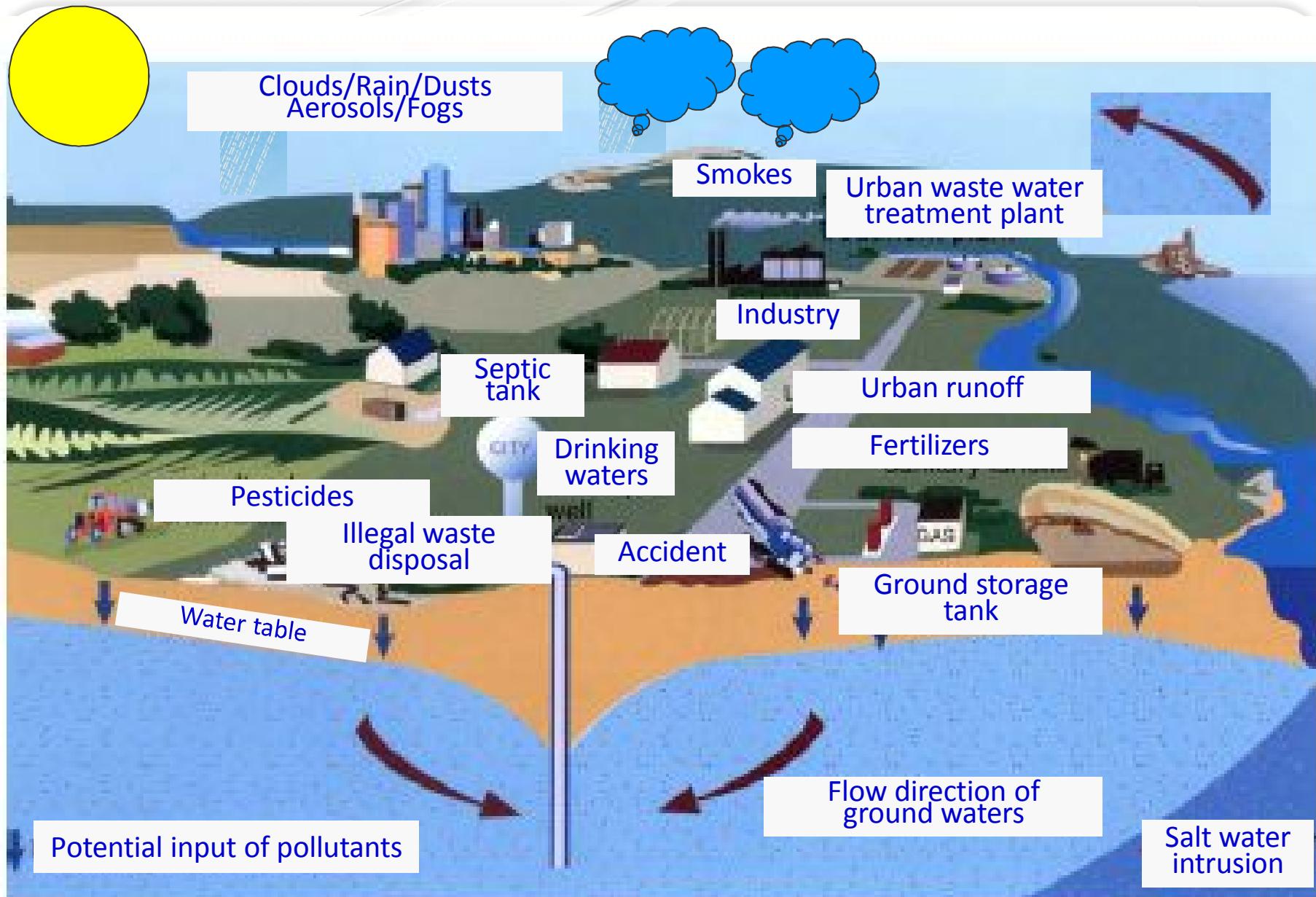
Eau et production agricole

Produits végétaux		Produits transformés et animaux	
Blé, céréales C3	1 000	Huiles	5 000
Maïs, céréales C4	700	Volailles	4 100
Pommes de terre	100	Bœuf	13 000
Maraîchage	200-400	Œufs	2 700
Agrumes	400	Lait	800

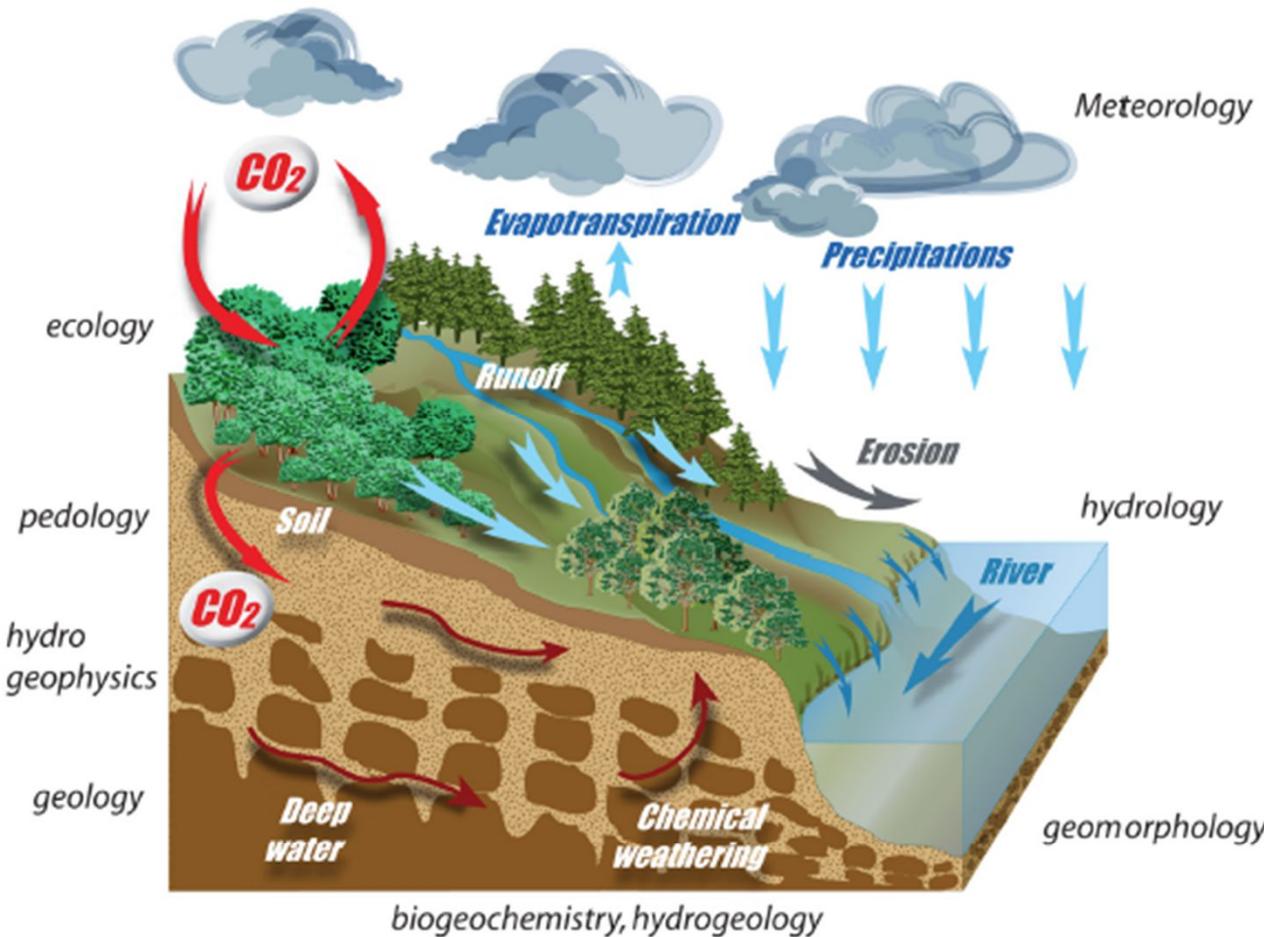
**Volumes d'eau requis en m³/t pour produire les bases alimentaires
Partie consommée brute (non en matière sèche) des différents produits**

(Behra, 2013)

Chimie des eaux naturelles et impact des activités humaines



A SO CRITICAL ZONE?



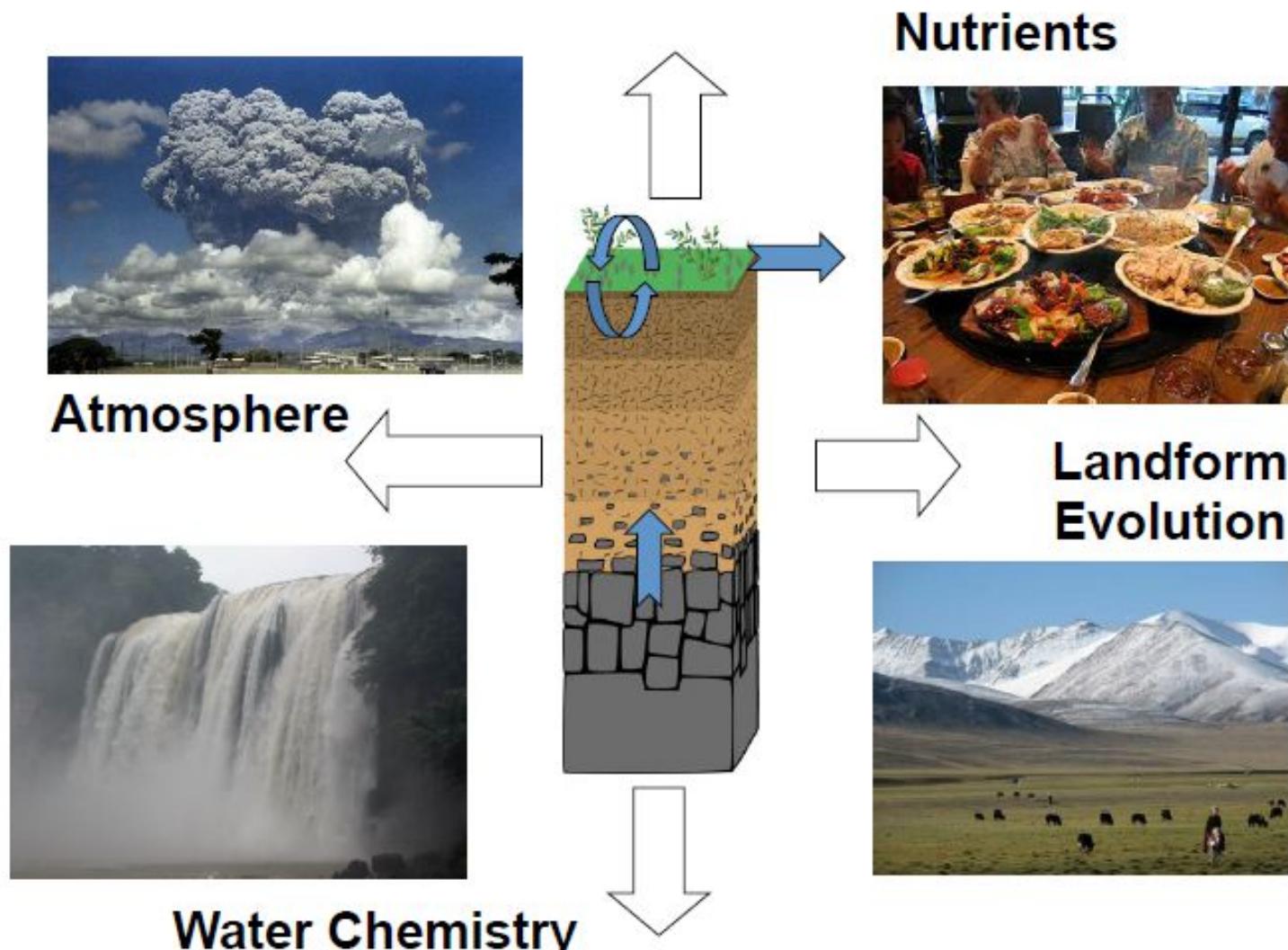
The Critical Zone is defined by the US NRC in 2001 : between the sky and the rocks : a complex bio-physico-chemical reactor with variable characteristic timescales.

We lack an integrated understanding of this zone critical for....

(from Arnaud and Gaillardet, 2016)

A SO CRITICAL ZONE?

FOR THE PLANET



(from Gaillardet, 2016)

Qualité de l'eau

Composition des eaux naturelles

QUALITY OF WATER

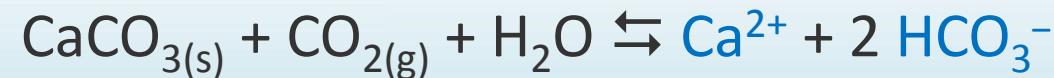
Three basic properties of water

- => **solvent**: dissolution and presence of inorganic compounds in water at equilibrium with minerals
- => **reactant**: chemical reaction with other chemical compounds (e.g. photosynthesis...)
- => **vector**: transport of chemical compounds present in water
[soils – surface and ground waters – living organisms...]

QUALITY OF WATER

Weathering processes: acid-base reactions

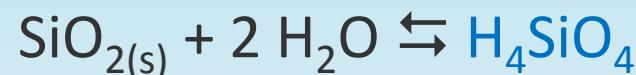
Calcareous



Gypsum



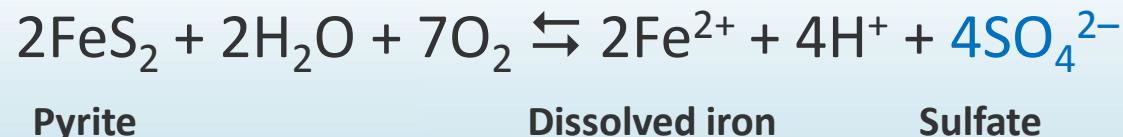
Silica and feldspar



QUALITY OF WATER

Weathering processes: redox reactions

Pyrite



Neutralization by calcite mineral



Production of biomass: redox reactions

Photosynthesis-respiration



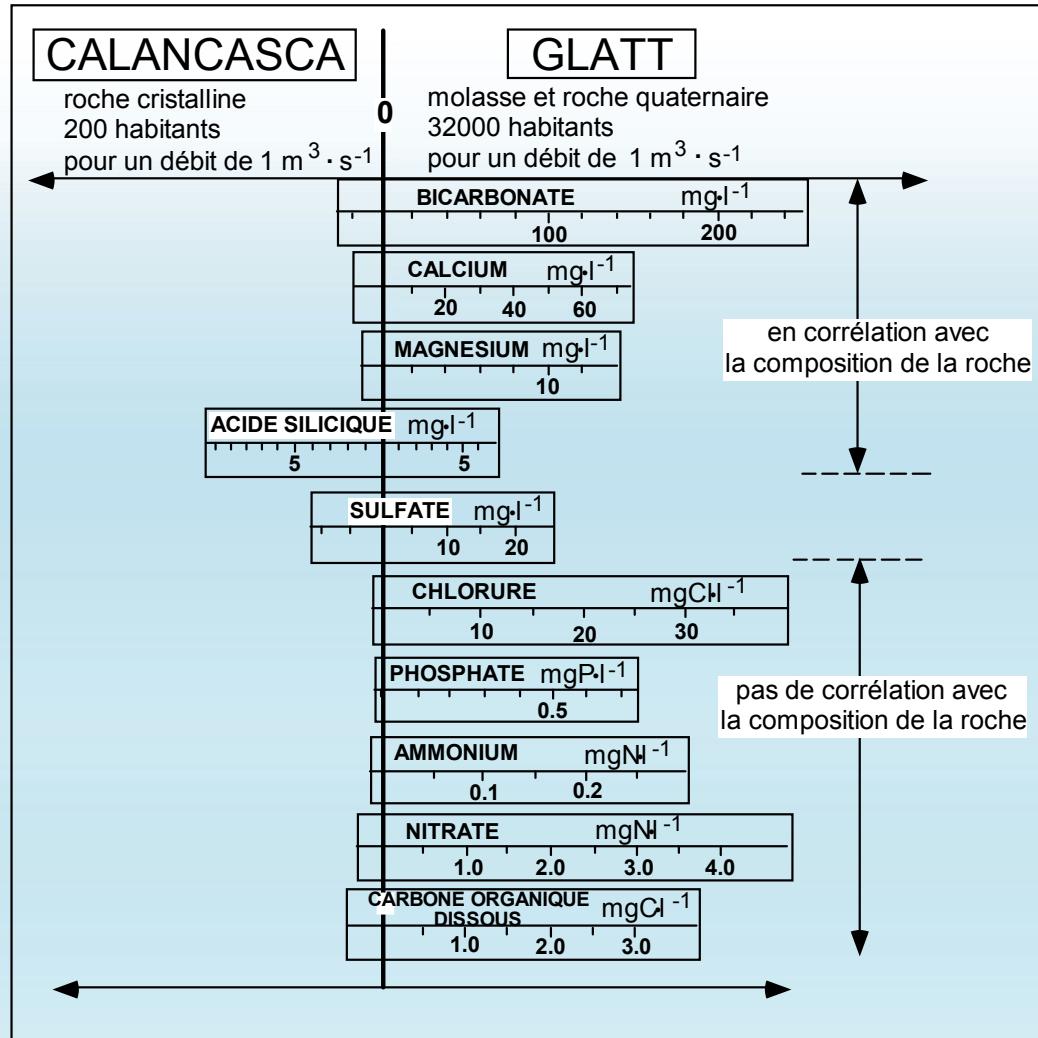
Chemical composition of natural waters

Parameters	“Average” river water ^{a)}	Loire ^{b)}	Seine ^{c)}	Bourget lake ^{d)}	Sea water ^{e)}
pH	6.5 – 8.5	7.0 – 8.3	7.8 – 8.1	7.3	8.1
Ca ²⁺ mM	0.4	0.85	2.4	1.4	10
Mg ²⁺ mM	0.16	0.19	0.21	0.25	55
Na ⁺ mM	0.3	0.5	0.4	0.3	500
HCO ₃ ⁻ mM	1.0	1.6	3.9	(2.8)	2.1
Cl ⁻ mM	0.2	0.3	0.5	0.2	565
SO ₄ ²⁻ mM	0.1	0.15	0.3	0.26	29
H ₄ SiO ₄ mM	0.2		0.06	0.03	0.04 – 0.16

a) from Stumm and Morgan (1996), composition corresponding to the average of river discharge to oceans; b) from Grosbois *et al.* (2000); c) from Roy *et al.* (1999); d) from Irstea, Lyon, and Jacquet *et al.* (2009); e) from Millero (2006)

(Sigg, Behra, Stumm, 2014)

Quality of water: Natural inputs vs. human activities

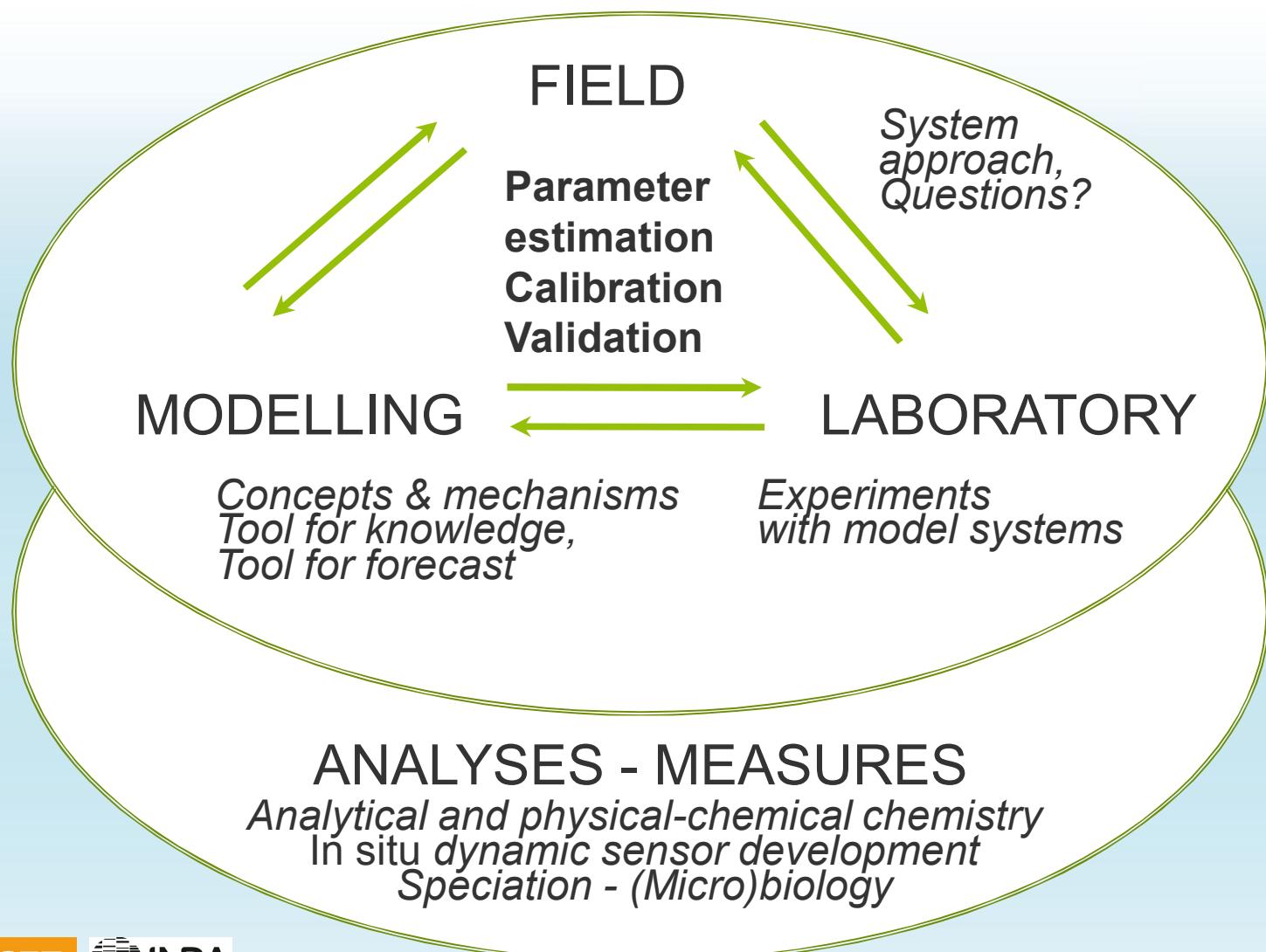


(Sigg *et al.*, 2014)

Comparison between chemical composition of the Calancasca river
(south Switzerland, crystalline substratum) and the Glatt river (Swiss plateau, calcareous)

Chemodynamics of compounds

Methods for studying chemical behavior in heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



Qualité de l'eau

Impact des activités humaines

Hg problematic in the Amazon basin

- Indigenous communities in Bolivia:

A high [total Hg] in hair

from 12 to 35 µg/g
(90 % MeHg⁺)

**WHO limit in hair:
10 µg/g MeHg⁺**

(Laffont *et al.*, 2009, ES&T, 43, 8985-8990)



© L. Maurice/IRD

Aims in Bolivia

Tracing the sources of Hg in a natural environment

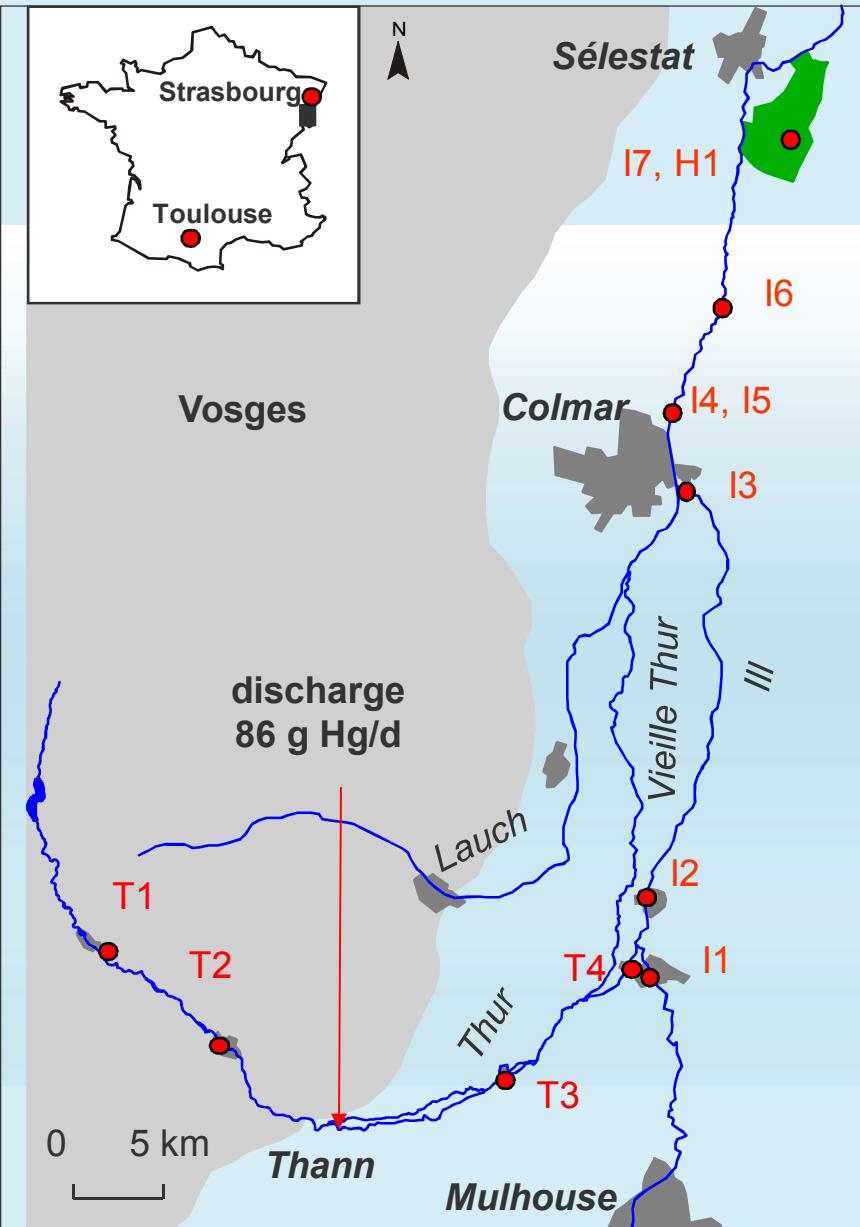
Using significant differences in isotopic fractionation of:

Origin of the sources:

- Hg used by gold-miners
 - Hg in cultivated or slash and burned soils
(eroded in rainy season)
 - Hg from rock weathering
 - Atmospheric Hg
- }
- anthropogenic
- }
- natural

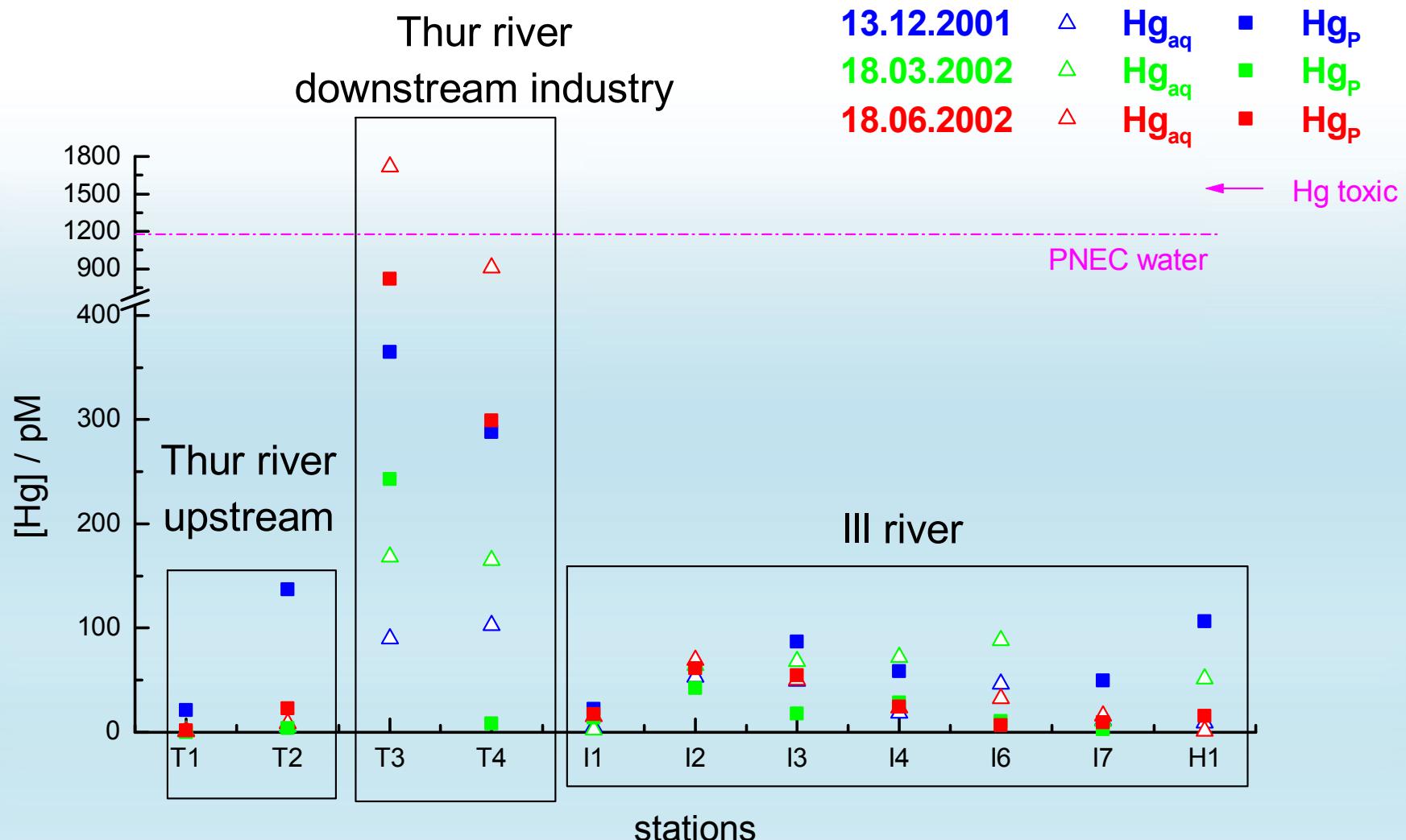
In : bed-rock, soils, sediments, fishes and human hair

See works by Laure Laffont, Jeroen Sonke, David Amouroux, Laurence Maurice & PhB



Sampling sites (12 locations, 100 km)

Hg in surface waters of the Thur and III rivers (Alsace, France)

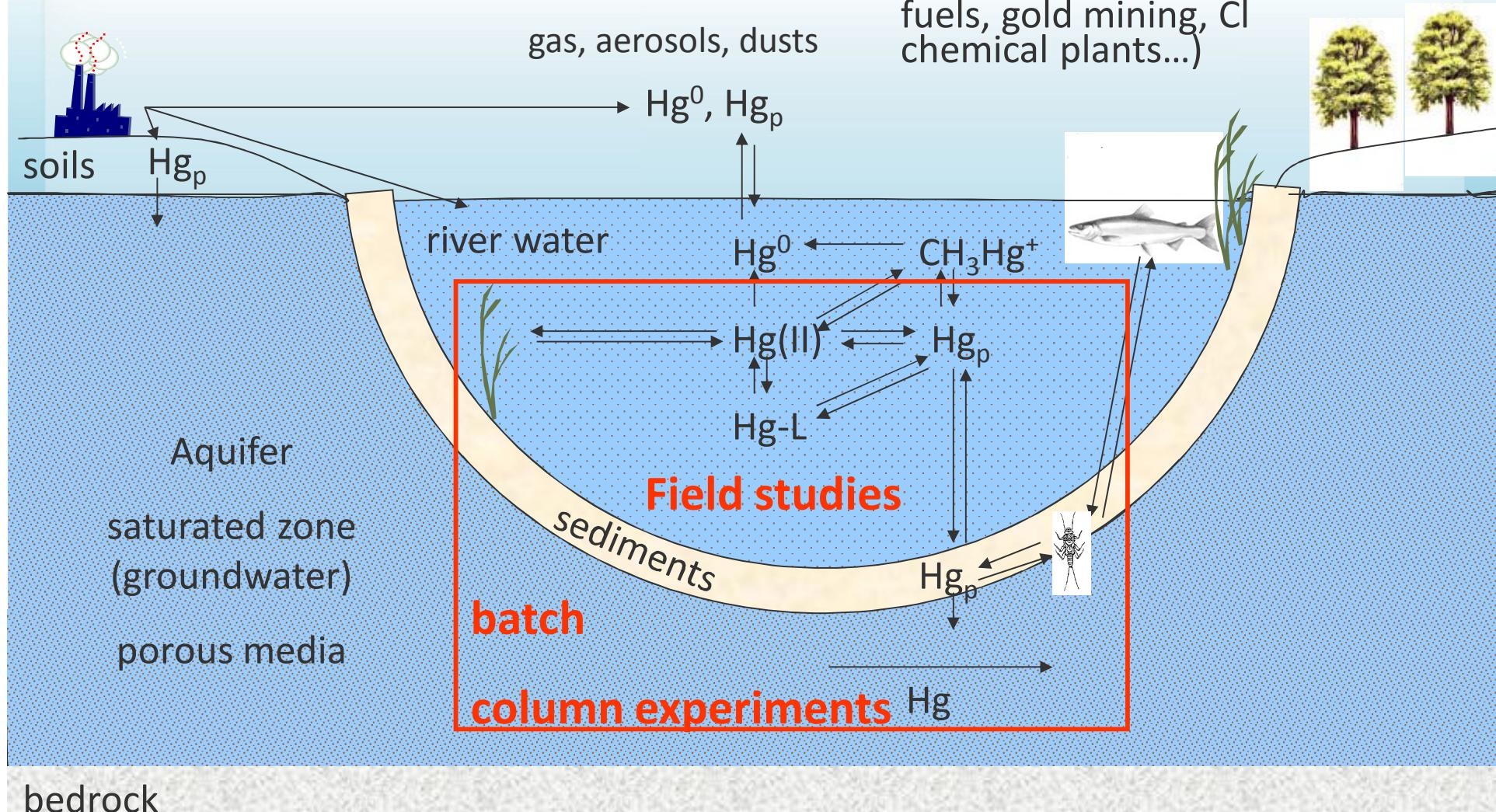


Hg transported either in the dissolved (0.8 pM - 1.7 nM)
or particulate phases (0.1 - 819 pM)

(from V. Wernert, F. Frimmel, Ph. Behra)

Understanding the mechanisms controlling the biogeochemical cycle of trace contaminant, e.g. mercury

Identification and quantification
of industrial sources (86 g/d)



Speciation: complexation and sorption processes

Solid phases

Particulate organic particles:

living organisms,

phytoplanktons and biological debris,

macromolecules,

humic substances

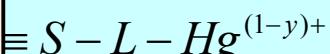
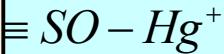
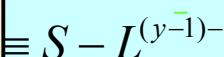
Inorganic particles:

CaCO_3

Fe, Mn, Al, Ti, Si
(hydr)oxides

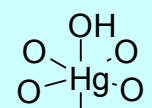
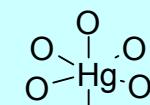
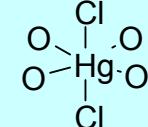
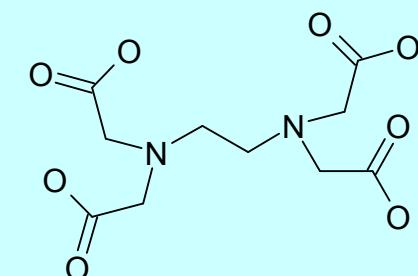
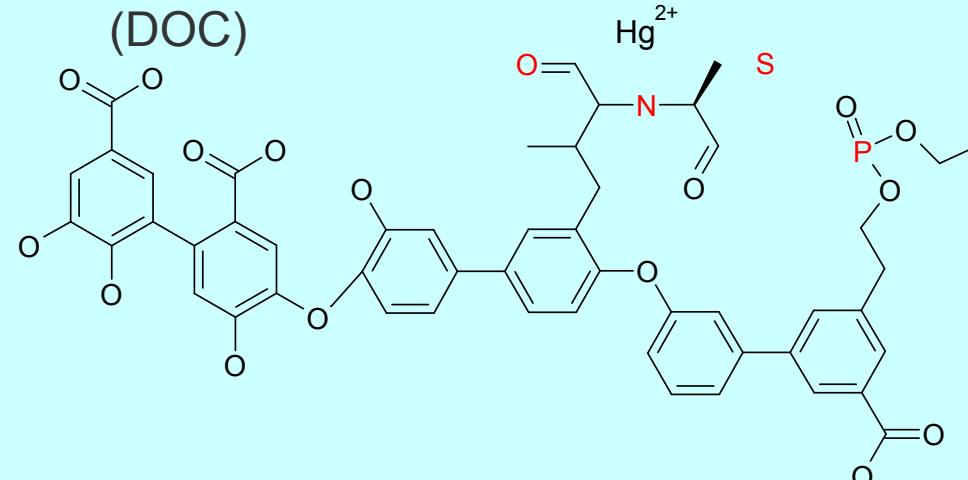
Alumino-silicates
(clays)

FeS_2



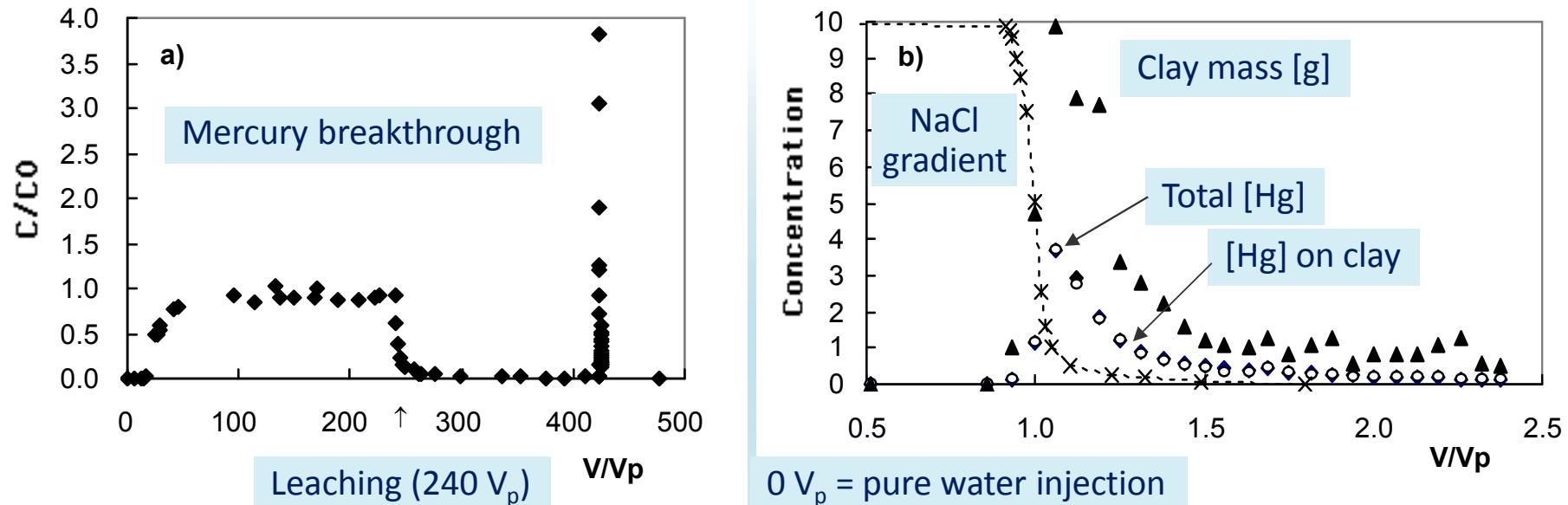
DDL

dissolved organic carbon



Aqueous phase

What about colloid transport or their potential scavenging role in contaminant transport?



Role of clay mobility after their peptisation in Hg(II) transport through natural quartz sand

- a) Injection of $0.5 \mu\text{M}$ Hg(II) with NaCl ($I = 10 \text{ mM}$) to steady-state condition ($C/C_0 \approx 1$)
Then injection of NaCl ($I = 10 \text{ mM}$) alone
When $[\text{Hg}] \approx 0$, injection of pure water leading to clay peptisation
- b) Each sample divided in 3: total [Hg], [Hg] after centrifugation (expressed as C/C_0) and clay mass. NaCl gradient given

(after Behra, Geoderma, 1986)

What about colloid transport or their potential scavenging role in contaminant transport?

letters to nature

Re and Al_2O_3 were heated with laser beams from both sides. Acting like planar heat sources, the two 'hot plates' eliminate the axial temperature gradient in the sample between the plates. Temperature variation is less than 3% within roughly 30 μm diameter at 2,500 K. Before the melting experiments, the sample was scanned with a laser beam and heated to about 2,000 K to reduce the pressure gradient and to produce a high-pressure solid-phase assemblage. For stable and smooth temperature control, temperatures were increased by adjusting an aperture placed near the beam exit, stepwise, instead of by adjusting power. Each step corresponds to a 50–100 K increase. A 30- μm spot was homogeneously heated by opening the aperture (increasing the step). At the onset of melting, temperature remains constant or drops slightly with the step increment, and then drastically increases (>400 K) within one step. To ensure the reliability of the melting criteria used in this study, we conducted melting experiments at pressures (16–27 GPa) overlapped by the multi-anvil apparatus and the diamond-anvil cell, using the same starting material, and obtained consistent melting temperatures (Fig. 3). We also used the same melting criteria to determine the melting temperature of MgSiO_3 –perovskite previously studied by other investigators, and our results agree with these recent determinations^{13,14} (Fig. 3). The temperature runaway phenomena near the onset of melting observed in simple and complex samples were probably a result of the latent heat of melting, followed by melt migrating away from the heated spot because of the large thermal pressure and, finally, the Re foils would have been heated without sample in between. No chemical reaction between Re and sample was observed in the multi-anvil experiments on a scale of 1 μm . The

Migration of plutonium in ground water at the Nevada Test Site

A. B. Kersting*, D. W. Efurd†, D. L. Finnegan†, D. J. Rokopt, D. K. Smith* & J. L. Thompson†

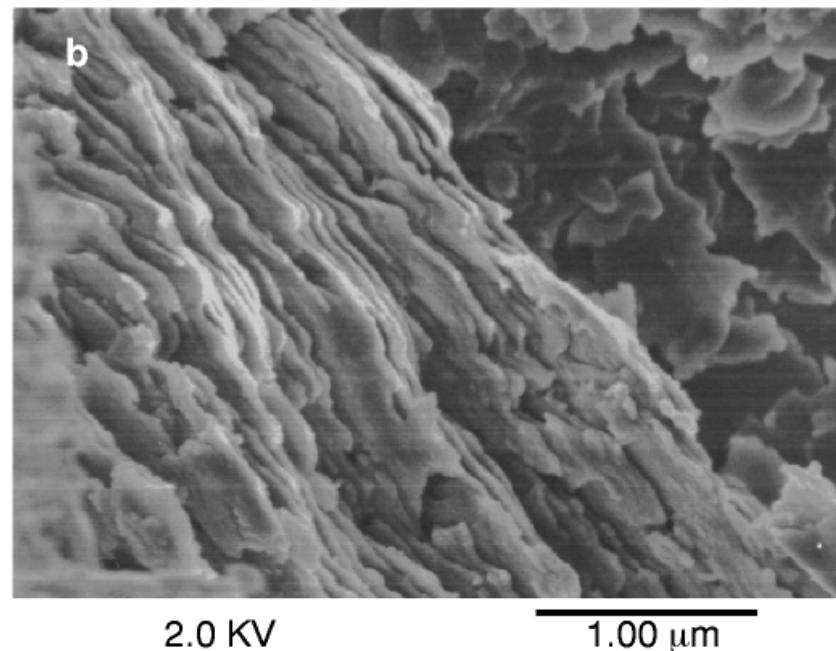
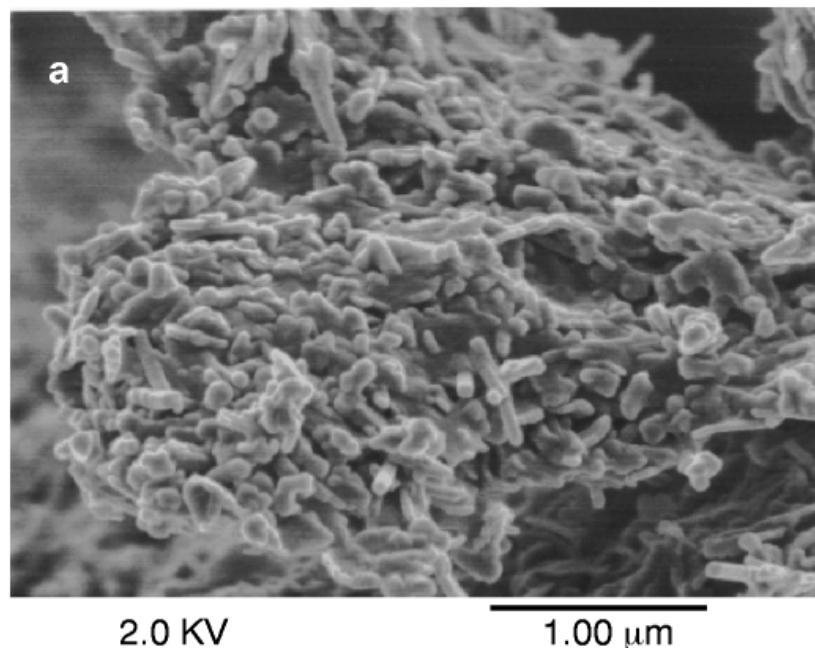
* Isotope Sciences Division, PO Box 808, L-231, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

† Chemical Science and Technology Division, MS J514, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Mobile colloids—suspended particles in the submicrometre size range—are known to occur naturally in ground water^{1,2} and have the potential to enhance transport of non-soluble contaminants through sorption³. The possible implications of this transport mechanism are of particular concern in the context of radio-nuclide transport. Significant quantities of the element plutonium have been introduced into the environment as a result of nuclear weapons testing and production, and nuclear power-plant accidents. Moreover, many countries anticipate storing nuclear waste underground. It has been argued that plutonium intro-

Nature 397, 56–59 (7 January 1999)

What about colloid transport or their potential scavenging role in contaminant transport?



a, The tabular, lath-shaped morphology of the zeolite, mordenite;

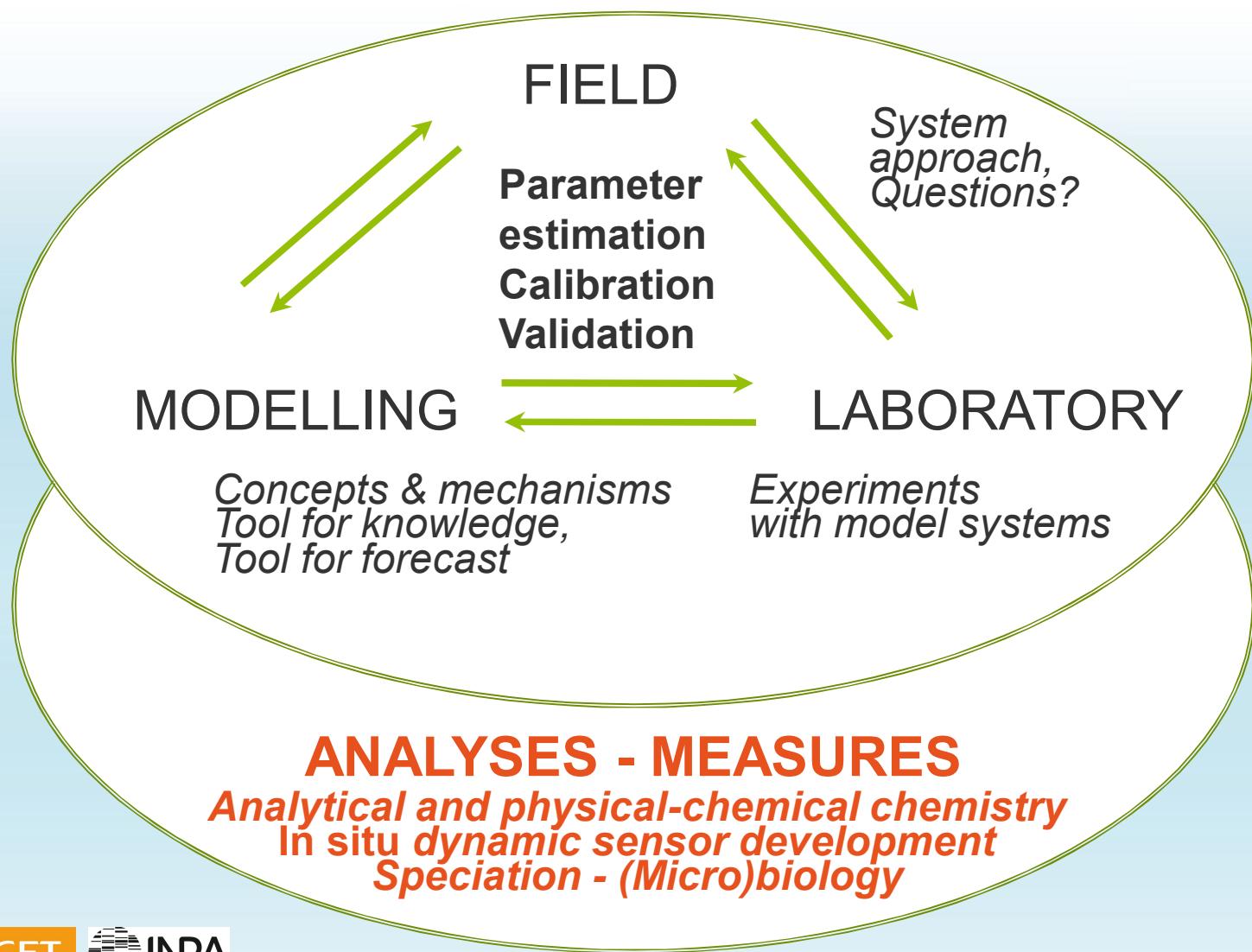
b, the platy appearance of the clay, illite.

The two distinct morphologies were observed in all three size fractions ($> 1 \mu\text{m}$, $1\,000\text{--}50 \text{ nm}$, and $50\text{--approx. } 7 \text{ nm}$)

(from Kersting *et al.*, Nature 397, 1999)

Chemodynamics of compounds

Methods for studying chemical behavior in heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



NEW INNOVATING CHEMICAL SENSORS/MIACTIS-MAISOE-CRITEX-IEDD

EQUIPEX PROJECT: CRITEX

**PARC NATIONAL D'ÉQUIPEMENTS INNOVANTS POUR L'ÉTUDE SPATIALE ET TEMPORELLE
DE LA ZONE CRITIQUE DES BASSINS VERSANTS**

COORDINATOR: JÉRÔME GAILLARDET (INSTITUT DE PHYSIQUE DU GLOBE DE PARIS)

TASK 4.3: INNOVATING CHEMICAL SENSORS

TASK LEADERS: PHILIPPE BEHRA & FRANÇOIS PRÉVOT (IPGP, UNIV. PARIS DIDEROT)

OBJECTIVES: DEVELOP OF NEW SYSTEMS FOR *IN SITU* PHYSICO-CHIMICAL MONITORING

EQUIPMENT FOR A PLATFORM:

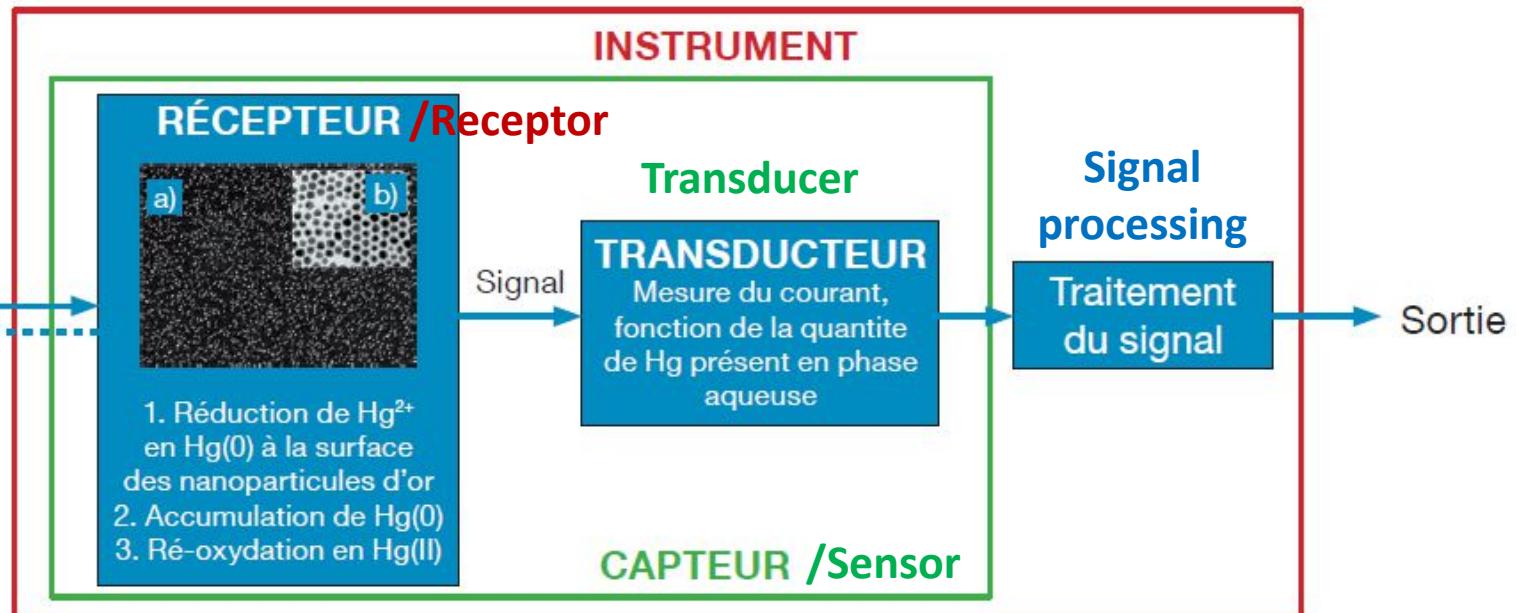
**RAMAN MICROSPECTROSCOPE, QUARTZ MICROBALANCE, SURFACE PLASMA RESONANCE,
POTENTIOSTAT**

SENSOR PROJECTS: Hg SPECIATION, CH_{4(aq)}, NUTRIENTS (Si, PO₄³⁻, NO₃⁻), BORON, PESTICIDES



Analyte or target

Analyte ou cible :
 Hg^{2+} en phase aqueuse
 (milieu acide ou chloruré)



Récepteur composé de nanoparticules d'or (AuNP) électrodéposées (image a – diamètre moyen des AuNP : 15 nm) ou synthétisées par voie organométallique (image b – diamètre moyen des AuNP : 7 nm) sur du carbone vitreux pour l'analyse électrochimique du mercure dissous dans l'eau à des concentrations de l'ordre du ng/L. D'après T. HEZARD *et al.*, 2012, K. FAJERWERG *et al.*, 2013. © Photo a) ELSEVIER. © Photo b) LCC (P.-J. DEBOUTTIÈRE). ■

(Fajerwerg, K., Behra, P., Gaillardet, J., 2015. Capteurs de la qualité des eaux, *in Eau à Découvert*, codirigé par A. Euzen, C. Jeandel et R. Mosseri, CNRS Éditions, Paris, 2015, à paraître)

Analyses of polar pesticides and glyphosate in Mekong Delta



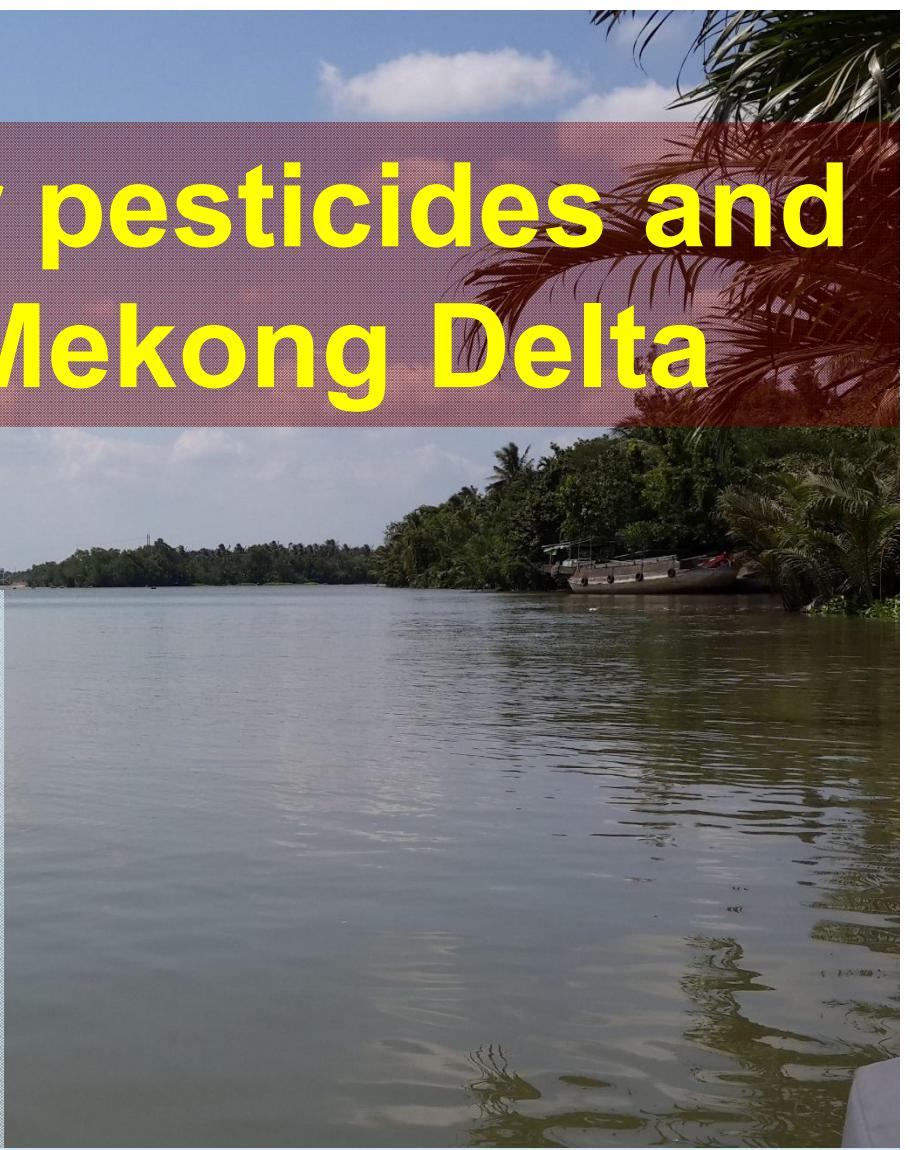
*Tran-Thi Nhu-Trang¹, Do Minh-Huy¹,
Nguyen T. Thu-Thao¹, Chau Quoc-Hung¹,
Tran L. Thanh-Thien¹, Nguyen Thien-Thao²,
Didier Orange³, Philippe Behra⁴*

¹ Department of Analytical Chemistry, University of
Science Ho Chi Minh City (Vietnam)

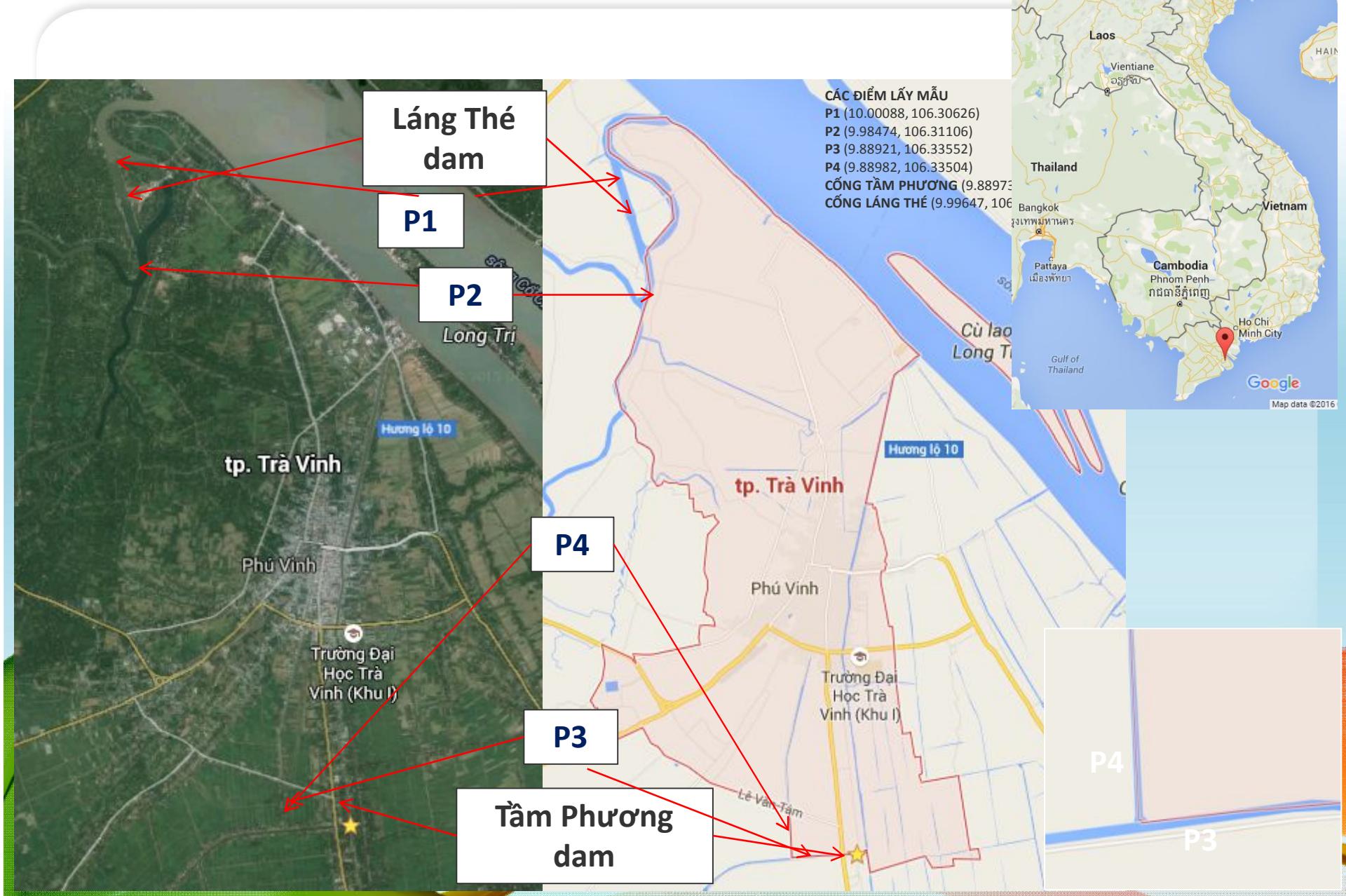
² Tra Vinh University, Tra Vinh Province (Vietnam)

³ Ecologie Fonctionnelle & Biogéochimie des Sols
& des Agro-Ecosystèmes, IRD, CIRAD, INRA,
Montpellier SupAgro, Montpellier, France

⁴ Laboratoire de Chimie Agro-industrielle (LCA),
Université de Toulouse, INPT, Toulouse (France)

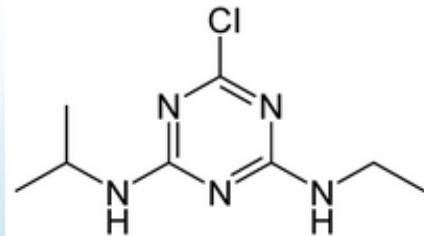


Tra Vinh: a coastal Vietnamese province in Mekong Delta with about 75 % of the land (175 550.38 ha of agricultural land)

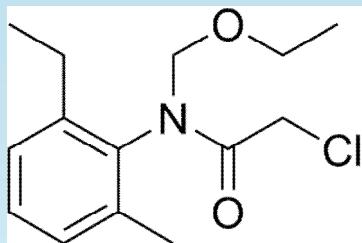


Emerging organic micropollutants

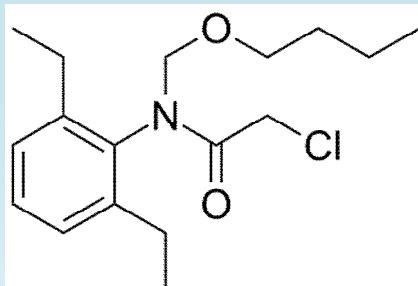
Polar pesticides ($\log K_{ow}$ 1.6 – 4.5)



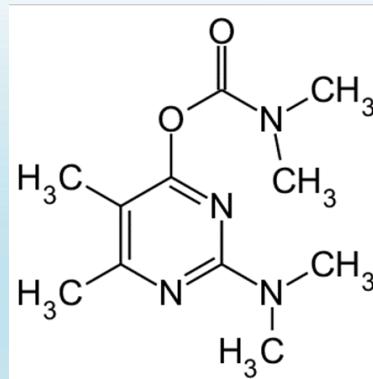
Atrazine



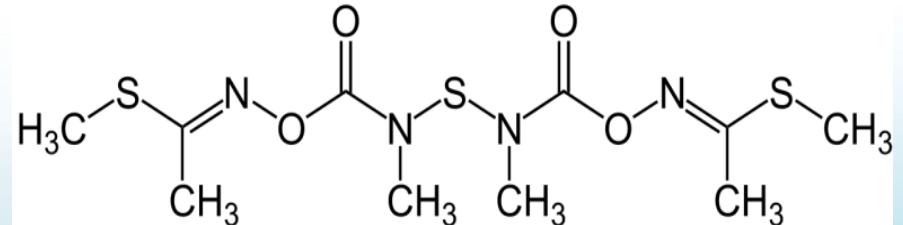
Acetochlor



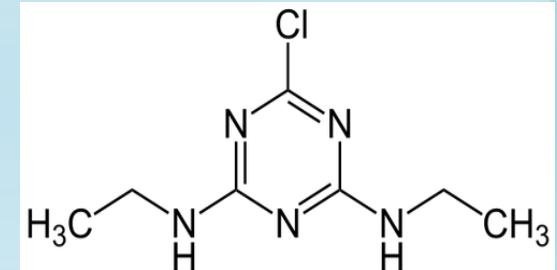
Butachlor



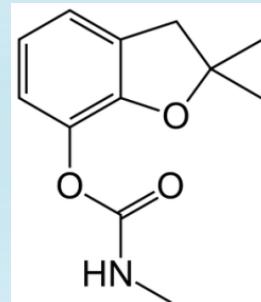
Pirimicarb



Thiodicarb

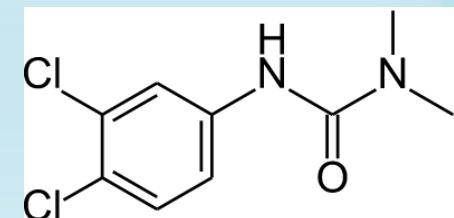


Simazine



Carbonfuran

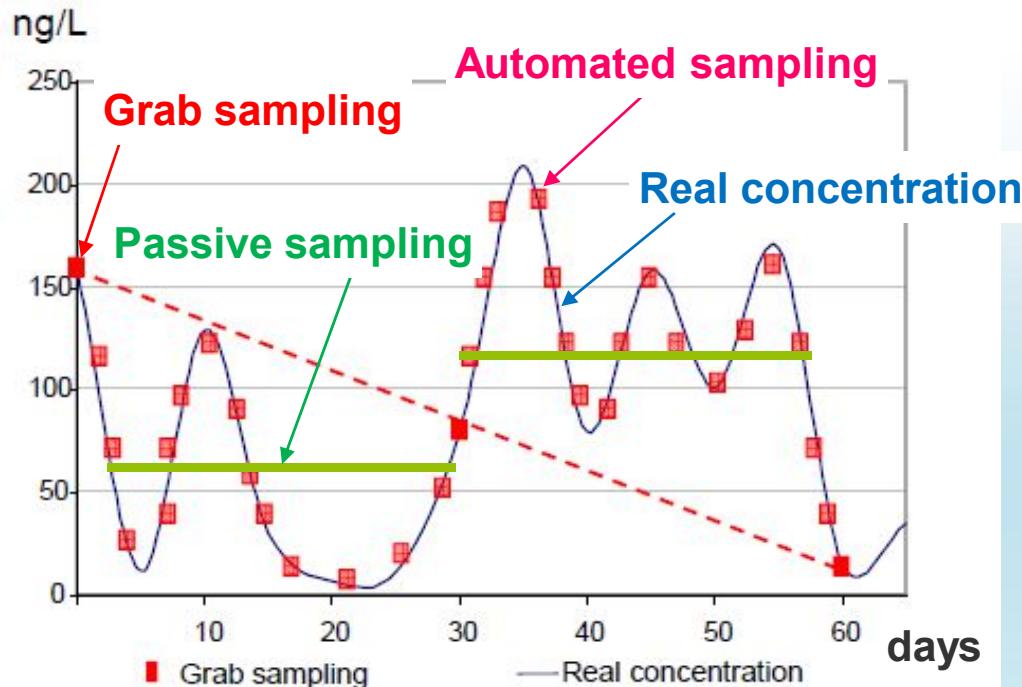
banned
in the EU



banned
in USA

Diuron

ACTIVE (GRAB) AND PASSIVE SAMPLING



► **Grab sampling:**
Lack of reliability because of low sampling frequency

► **Automated sampling with high frequency:**
Better reliability but

- time consuming
- expensive

=>

Incompatible with routine analysis

- **Passive sampling:**
- Acquisition of a time weighted average concentrations since devices continuously exposed
 - Lower quantification limits since analytes being concentrated *in situ*

Sampling in **June and July 2015**, and **March and April 2016** at 4 positions of Tra Vinh rivers:

- P1 at outside (about 0.5 km) and P2 at inside (about 1 km) from Lang The dam;
- P3 at inside (about 1 km) from Tam Phuong dam and P4 at a small canal near the rice fields (1.5 km from Tam Phuong dam).

Sampling sites



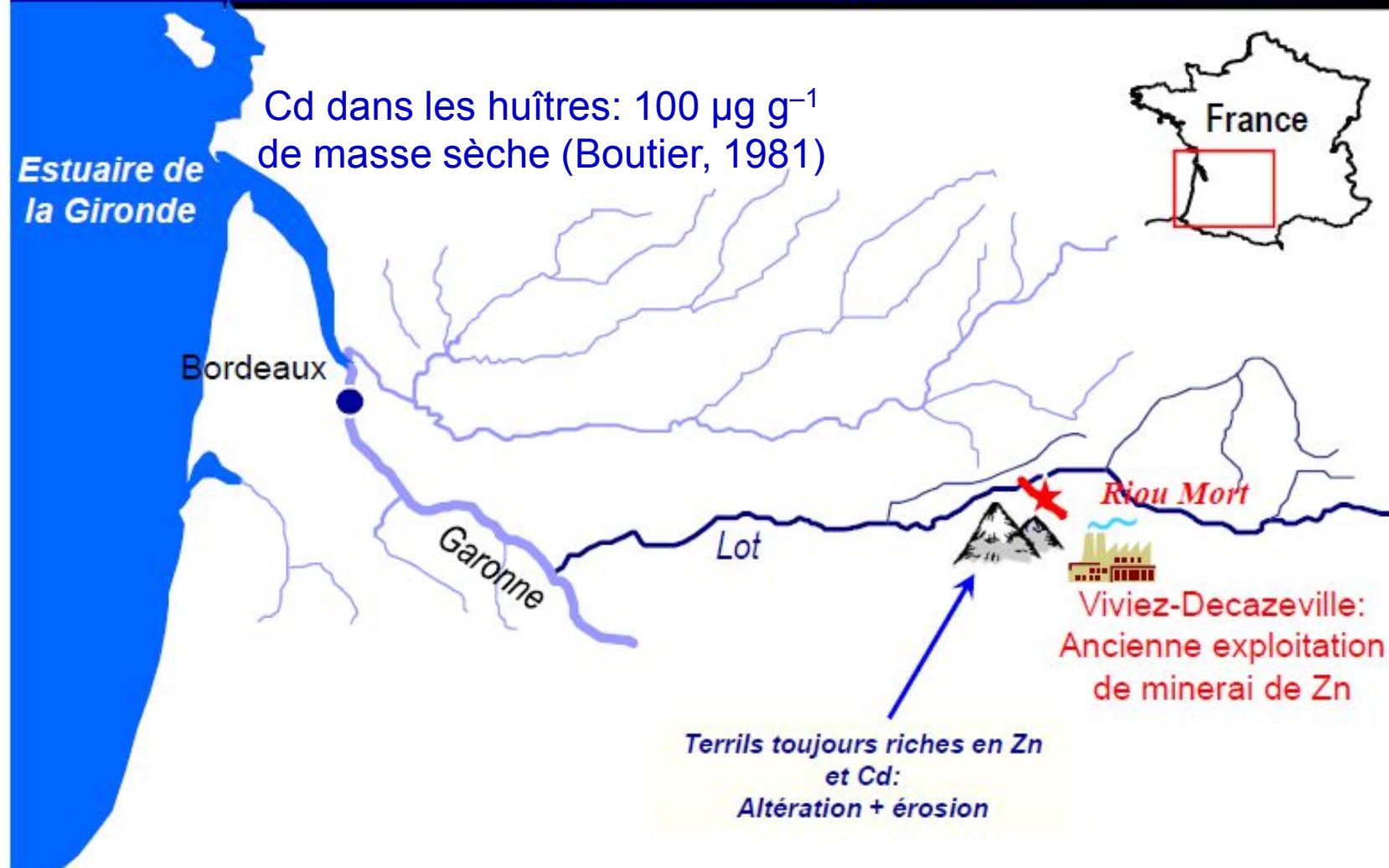
CONCLUSION

- ✓ Preliminary results: as in surface water, POCIS being a useful tool, especially for the screening of substances at low concentration levels that are not detected by laboratory analysis of spot samples
- ✓ Presence of atrazine and 2,4-D in Tra Vinh rivers as to be considered and necessary to pay more attention since surface waters here being not only used for agricultural cultivation but also for aquaculture and particularly for local people activities

Ongoing study

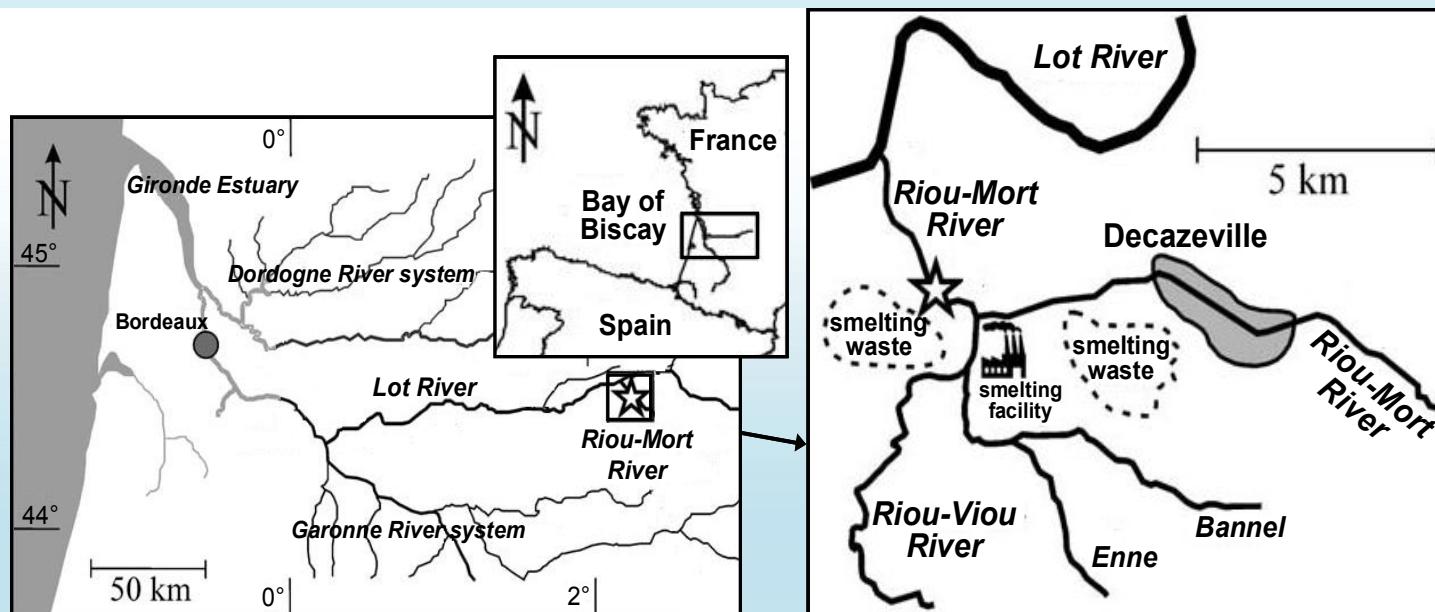
- Sorption of these organic compounds on sediments and colloids
- Transport mechanisms in surface water and to/through groundwater
- Development of new chemical sensors to selectively determine the pollutant targets (**USTH PhD thesis of Huy Do**)
- Impact of ecosystem

Bassin versant du Lot amont (S.-O. France)



Audry et al., 2004

Study of the temporal variation of the concentrations of the dynamic metal fractions in the Riou-Mort stream



The Riou-Mort watershed:

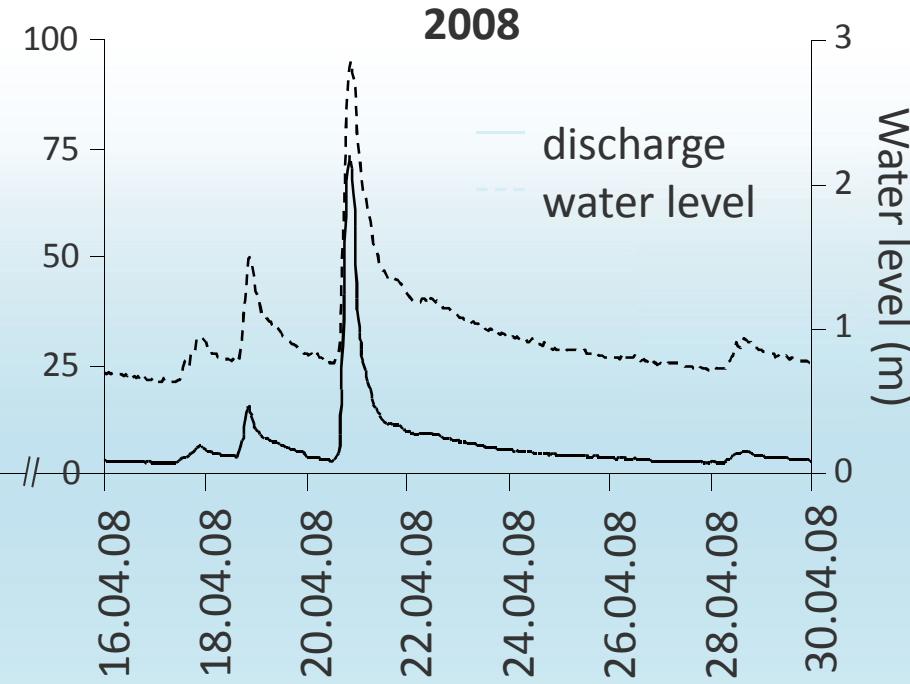
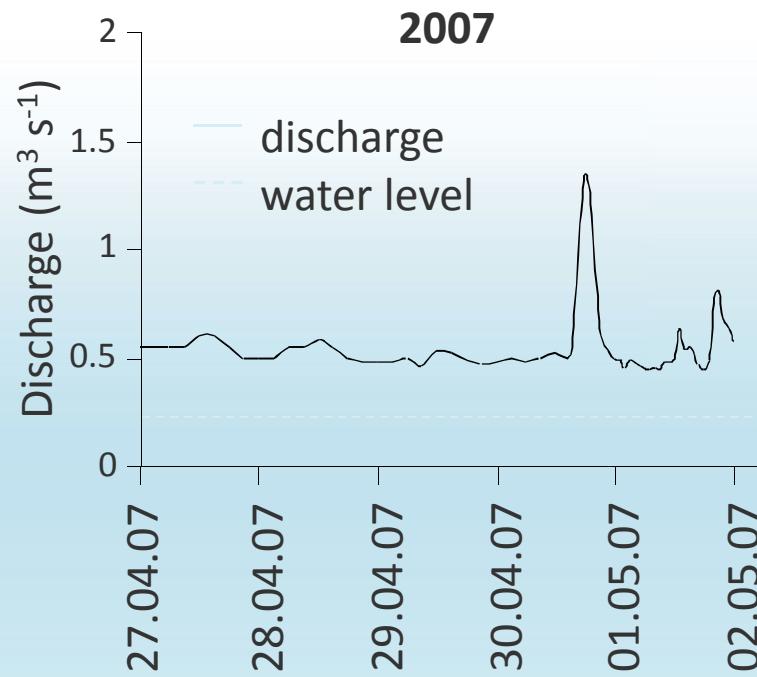
- affected by leaching and mechanical erosion of metallurgical wastes from former mining and ore smelting activities.
- known as the major source of the historical polymetallic pollution of the Lot-Garonne-Gironde fluvial-estuarine system

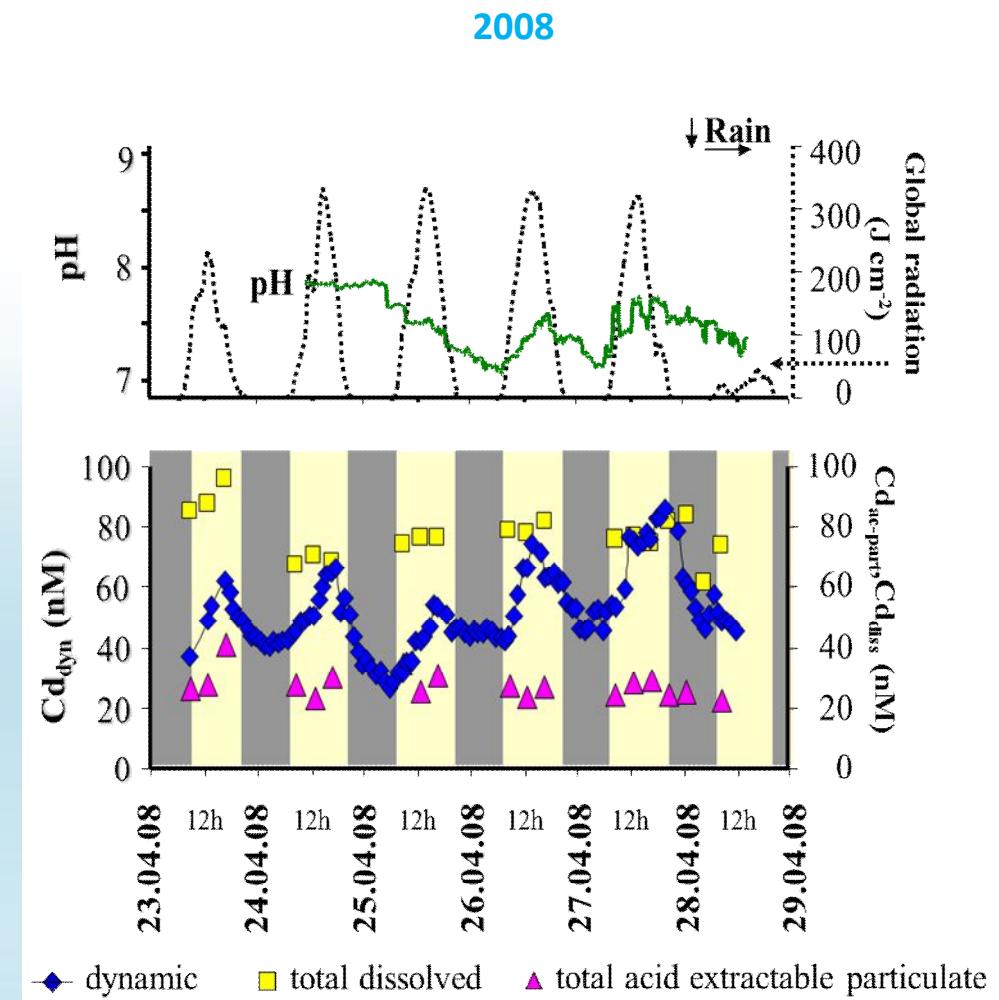
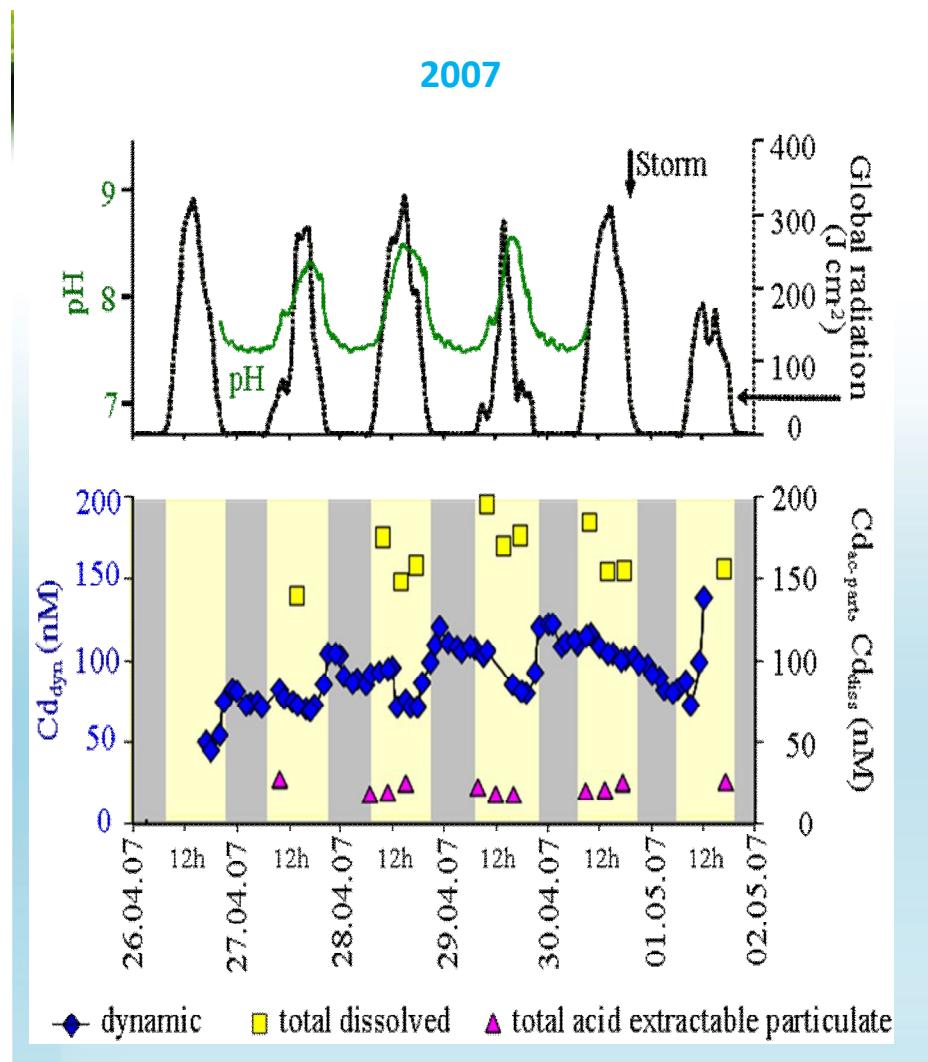


EU project ECODIS: *Dynamic sensing of chemical pollution disasters and predictive modelling of their spread and ecological impact (2005-2008)*

Experimental conditions:

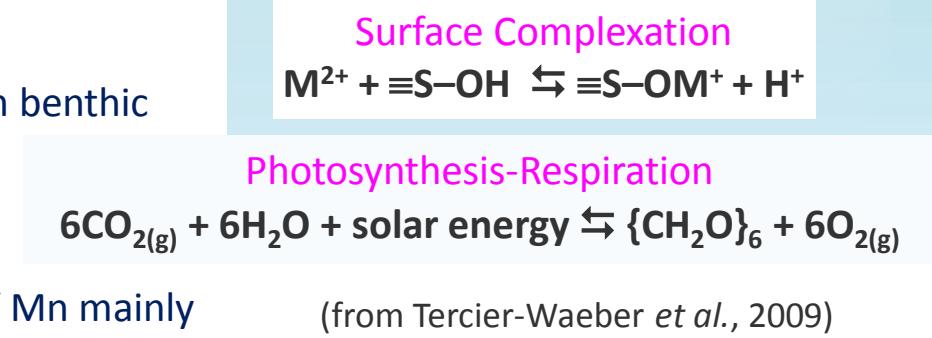
Measurements at the Riou-Mort Joanis site were performed in Spring 2007 and 2008 which were characterized by large difference in hydrological conditions

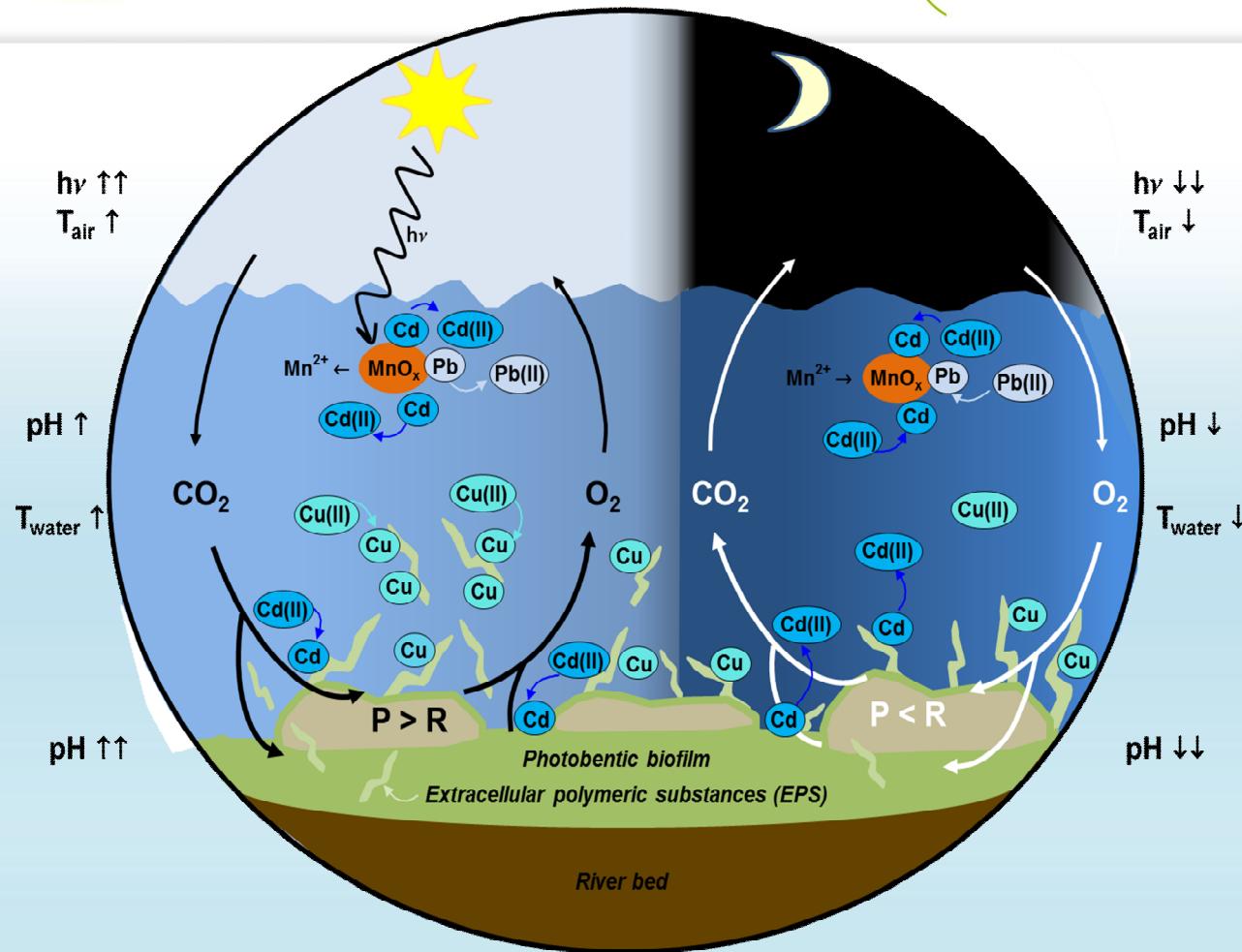




Cd dynamic in Riu-Mort river (Aveyron) :

- Noon-midnight: Control of Cd dynamic by sorption on benthic periphyton due to increasing pH and of photosynthesis/respiration
- Noon-midnight: control of Cd dynamic by dissolution/precipitation processes of (hydr)oxides of Mn mainly





Photosynthesis-respiration



Different processes may control the diurnal cycles of the dynamic Me species

(in Behra, 2013; from Tercier-Waeber *et al.*, 2013)

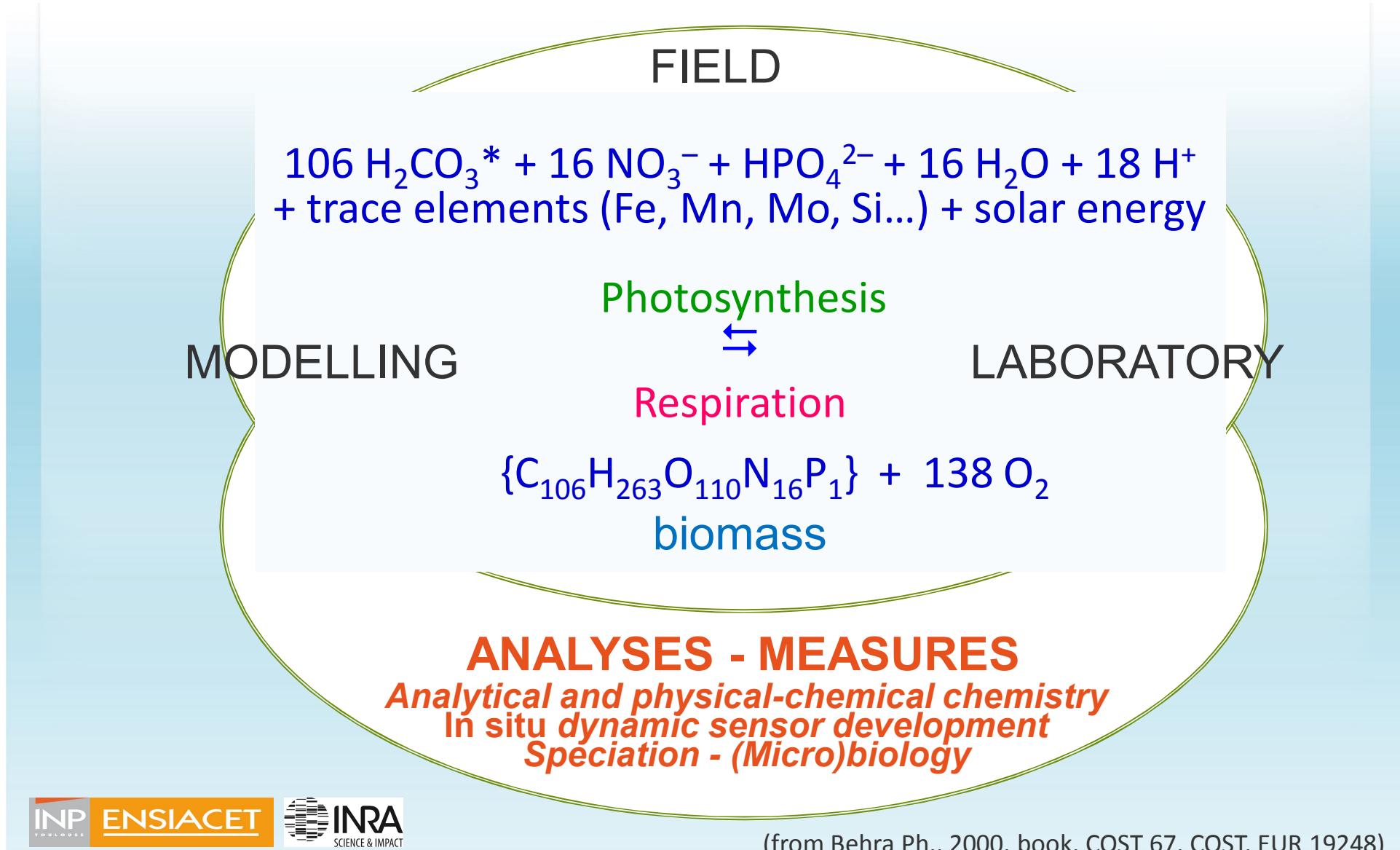
Example of Riou-Mort river

Importance of *in-situ* monitoring systems at the field site:

- For following the different parameters by *in situ* dynamic sensors with continuous measurement and at high frequency (**meaning?**)
- * For a better understanding of biogeochemical cycles of elements, nutrients, contaminants and xenobiotics in natural systems, the impact of human activities on inland waters to sea waters (including ground, soil and surface waters...)

Chemodynamics of compounds

Methods for studying chemical behavior in heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



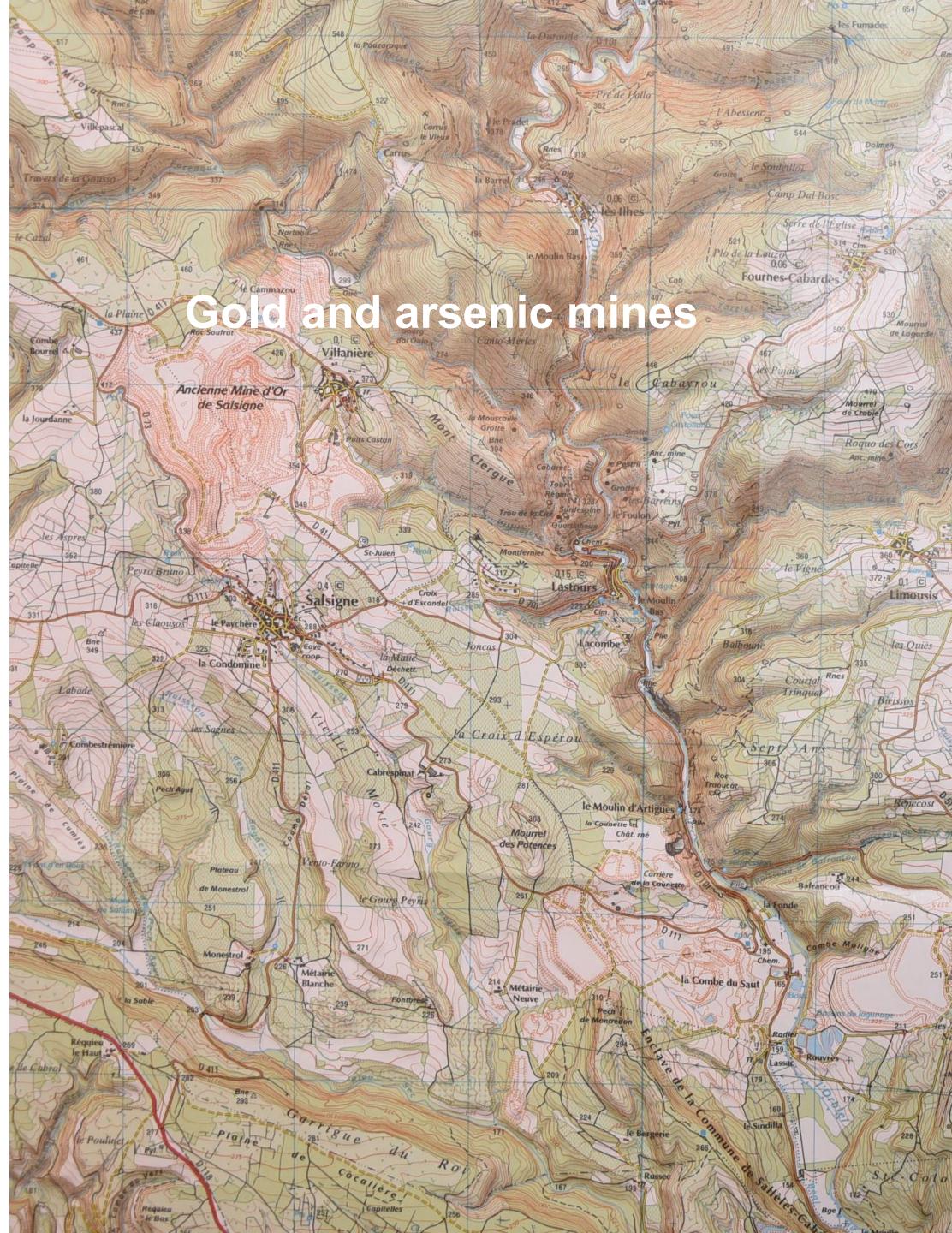
Lake: algal bloom et eutrophication



©Philippe Behra

Field site after remediation: Example of Salsigne (south of France)







Old mine shaft

(Frédéric Ogé)



"Inerted" waste disposal site

(Frédéric Ogé)

DIMANCHE 30 OCTOBRE 2016

Agence de Carcassonne, tél : 04 68 11 90 11 • redaction11@ladepeche.fr

vallée de l'Orbiel

Pollution : des recommandations

► l'essentiel

La situation environnementale des anciens sites miniers dans la vallée de l'Orbiel reste préoccupante. C'est le sens donné à un long communiqué publié cette fin de semaine par le préfet de l'Aude.

Faut-il lire ce texte comme un rappel des précautions à ob-





(Frédéric Ogé)





Gypsum formation



(Philippe Behra)



LA MINE DE SALAU PORTE BIEN SON NOM

Il est à la frontière espagnole, côté ariégeois, dans une zone déserte qui compte peut-être un habitant au kilomètre carré. Charlie a parlé il y a un peu plus d'un an d'un projet «minier» délirant, soutenu en son temps par le Montebourg, quand il rêvait de réindustrialiser la France, marinière en sautoir.

En deux mots, des amis de l'homme tentent de rouvrir la mine de Salau, fermée en 1986, où se cachaient des réserves de

tungstène, mais aussi d'amiante, toutes deux fatalement entortillées. De nombreux anciens mineurs se cognent des maladies respiratoires et des cancers bronchiques (un remarquable documentaire en ligne : mediacoop.fr/rubrique/documentaires/mine-de-rien).

Où en est-on? Mystère. Fin octobre, le secrétaire d'Etat à l'Industrie socialo a accordé à la société Variscan un permis d'exploration, à la recherche de tungstène, et donc d'amiante.

«C'est le flou le plus total», raconte à Charlie un opposant local décidé. La politique de Variscan n'est que pure esbroufe. L'un de ses deux dirigeants, Michel Bonnemaison, a même fait miroiter un jour, avant de se reprendre, la création de 1 000 emplois. »

Variscan a visiblement la cote auprès de Hollande et de ses petits amis d'Ariège, ce qui ne manque pas d'intriguer. Car sa filiale française, créée par une société australienne, a des

apparences vaporeuses. Ce qui n'empêche pas les fins de mois plantureuses. Selon des documents internes à Variscan, le directeur de sa filiale française, qui n'a encore rien produit, recevrait la bagatelle de 15 000 euros par mois. Et son directeur exécutif, 6 500 euros. Payés depuis l'Australie. On

quoi!!! des Australiens!
rouvrir nos mines!
et puis quoi!!!
à eux le tungstène
et à nous le cancer!
est-ce qu'on va
faire les poches
à leurs kangourous
et chier d'dans,
après?

aimerait être sûrs que ces excellents citoyens paient en France des impôts sur le revenu.
F. N.

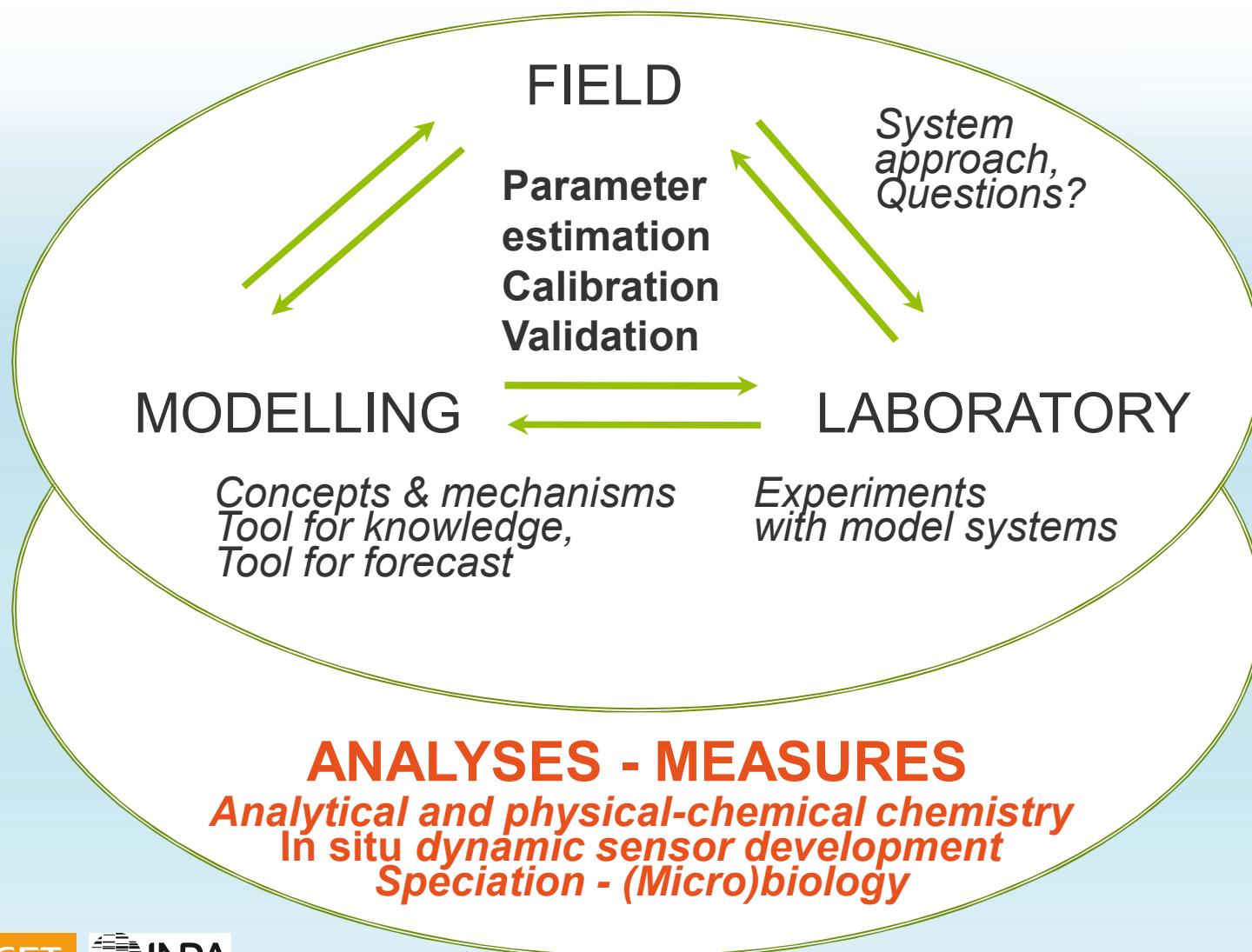
Fabrice Nicolino

Conclusions

Nécessité de **connaître les mécanismes physico-chimiques** pour une meilleure compréhension de l'impact des activités humaines et d'**intégrer ces mécanismes dans les modèles** afin de prévoir le comportement des contaminants à différentes échelles de temps et d'espace

Chemodynamics of compounds

Methods for studying chemical behavior in heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



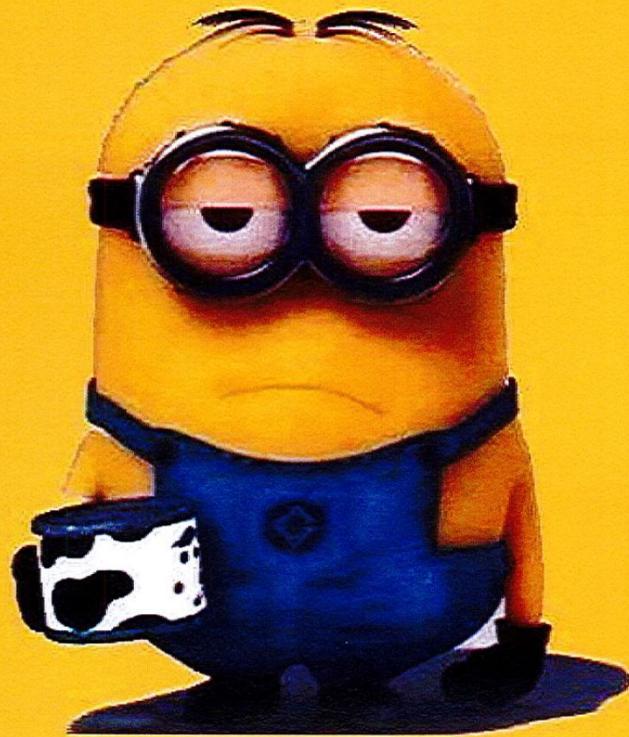
CONCLUSIONS

Objectif : application aux systèmes réels

Nécessité de considérer les variations spatiales et temporelles des échanges aux interfaces ainsi que les hétérogénéités des systèmes complexes (**aucun besoin de purification des phases solides ou du fractionnement de la matière organique naturelle**) en prenant en compte :

- la **spéciation vraie** aussi bien dans la phase aqueuse **en utilisant des capteurs dynamiques *in-situ*** qu'aux interfaces
- l'**hydrodynamique effective** et
- la **réactivité effective** au niveau de ces interfaces

**L'eau est l'élément le plus
essentiel de la vie.**



**Parce que sans eau, tu ne
peux pas faire de caféou de thé !**

Acknowledgment:

- STAE Foundation for funding MAISOE project and granting Pierre-Jean Debouttière, Laure Laffont, Teddy Hezard
- Vincent Collière (LCC) for SEM-FEG pictures, Yves Coppel (LCC) for NMR analyses
- Laure Laffont, Jeroen Sonke, Laurence Maurice Lars-Eric Heimburger, Feida N (GET laboratory) for Font Estramar water samples and AFS analyses, David Amouroux (IPREM, UPPA)
- K. Fajerwerg (LCC), P. Gros, D. Evrard (LGC), B. Dubreuil (LCA)
- J.-J. Ehrhardt (LCPME, Nancy), J. Lützenkirchen, V. Wernert, J. Carayrou, R. Mosé (IMF, Strasbourg), F. Frimmel (Uni. Karlsruhe)
- Yann Sivry (Uni. Paris Diderot), S. Audry (GET), M. Tercier-Waeber (Uni. Genève)
- Tran-Thi Nhu-Trang, Do Minh-Huy, Nguyen T. Thu-Thao, Chau Quoc-Hung, Tran L. Thanh-Thien (VNUHCMc), Nguyen Thien-Thao, Didier Orange
- Frédéric Ogé (Prodig CNRS, Paris), Jérôme Gaillardet (IPG, Paris)
- Laura Sigg & Werner Stumm (ETH Zürich, EAWAG)

Centre d'Alembert – Université Paris-Sud
Centre Interdisciplinaire d'Étude de l'Évolution des Idées,
des Sciences et des Techniques (CIEEIST)

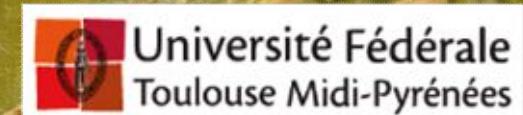


**Chimie des eaux naturelles
et impact des activités humaines**

Merci pour votre attention



www.chimieagroindustrielle.fr/



Orsay, 2 février 2017