USTH – Université de Toulouse

Master Degree
« WATER, ENVIRONMENT, OCEANOGRAPHY » (WEO)

2018-2019

WEO42

Samplers and Sensors

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Keywords:
Sensors – Analyte – Detection – Integrated systems – Passive and dynamic sensors

Objective:
- Introduction of some notions with respect to the integrated systems including physical, chemical and biological sensors
- Showing the importance of such tools for a better understanding of the water cycle from the point of view of water quantity and quality, and a smarter management of the quality of natural, drinking and waste waters

Main part of the courses:
- Introduction of integrated systems and sensors: from definitions and principles to application of different techniques of detection; interest of such tools (measurements, monitoring, data analysis and interpretation, and observation *vs.* modelling
- Presentation of the different types of sensors (chemical, biological, physicochemical, physical); their performance and limits (size, cost, lifetime..., biofouling...)
- Passive *vs.* dynamic sensors
- More advance with respect to detection systems (optical, electrochemical…) for dynamic *in-situ* sensors
- Integration and networking for data management

Keywords:
Sensors – Analyte – Detection – Integrated systems – Passive samplers and dynamic sensors

Objective:
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- Showing the importance of such tools for a better understanding of the water cycle from the point of view of water quantity and quality, and a smarter management of the quality of natural, drinking and waste waters

Lectures: October 2018 and January 2019

Control: multiple-choice questionnaire (1 h) + report: deadline January 28th, 2019

Lecturers:
Dr. Tran Thi Nhu Trang
(Faculty of Chemical Engineering and Food Technology – Nguyen Tat Thanh University – HCMc – ttntrang@ntt.edu.vn)
Prof. Philippe Behra (Toulouse INP – philippe.behra@ensiacet.fr)

Sensors

Interests/Why?

Necessity of developing new sensors for continuous analyses, able to communicate, and if possible, at low cost:

for a better understanding and knowledge of:

water cycle

water pathways in the critical zone

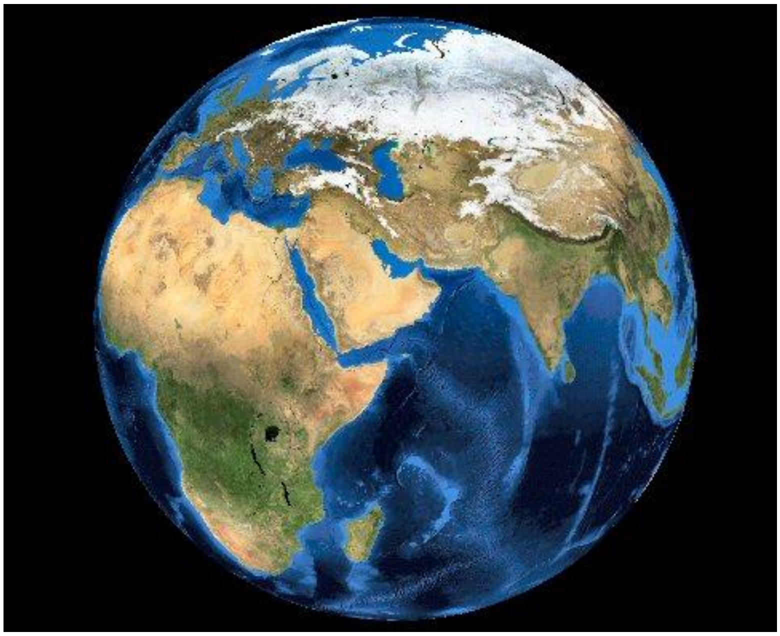
for a more clever management of:

quality of natural and drinking waters

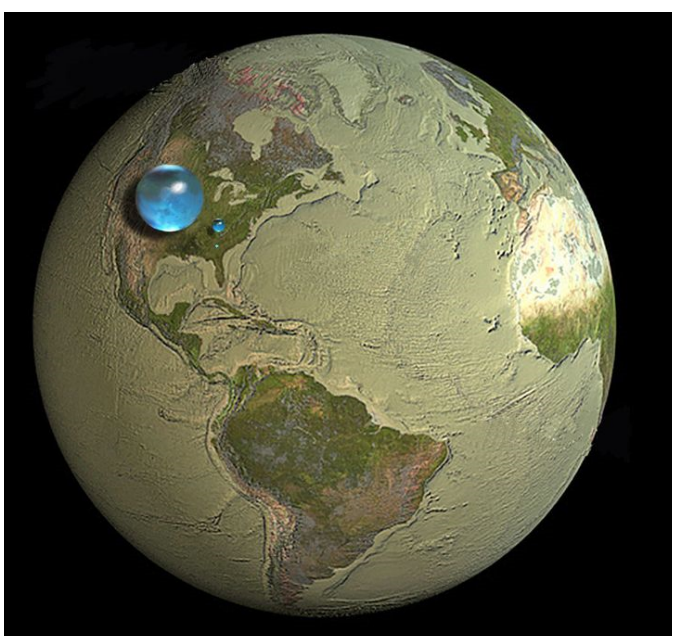
urban waste and effluent water

Necessity of a better monitoring of water quality by *in situ* sensors in the frame of global changes and the pressure on limited water resources

Complementary and essential tools of classical analytical laboratory methods and remote sensing data



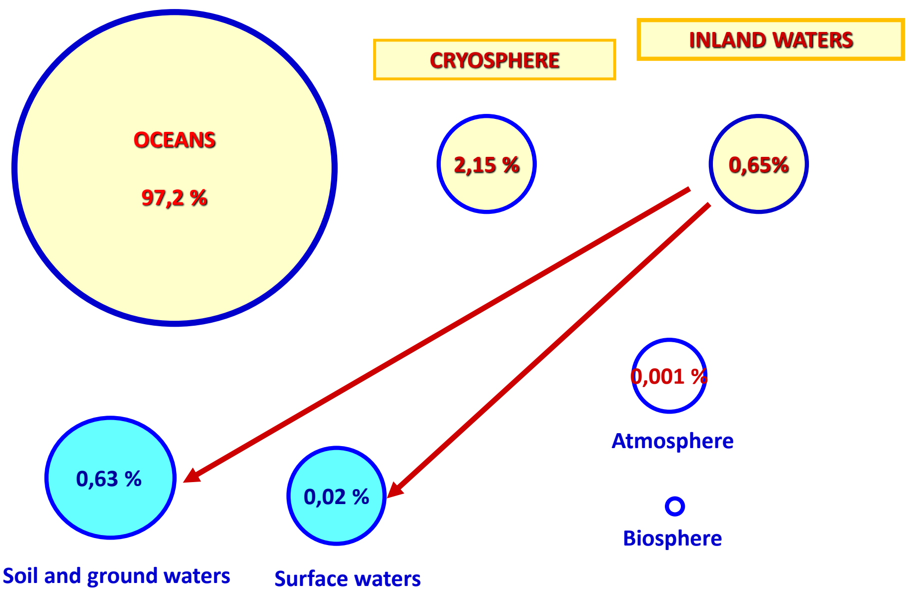
(Philippe Maisongrande, Legos)



$1{,}4.10^9$ km^3 of water

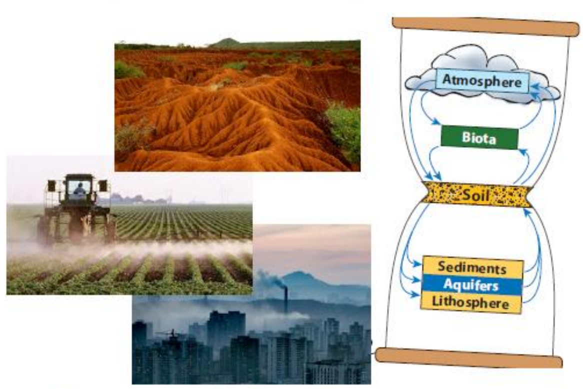
(Philippe Maisongrande, Legos)

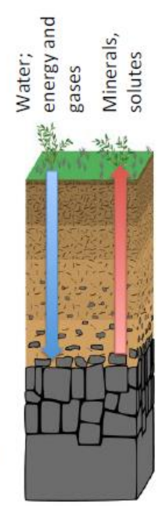
Water repartition on the Earth



(Philippe Maisongrande, Legos)

The Critical zone, our habitat, under threat



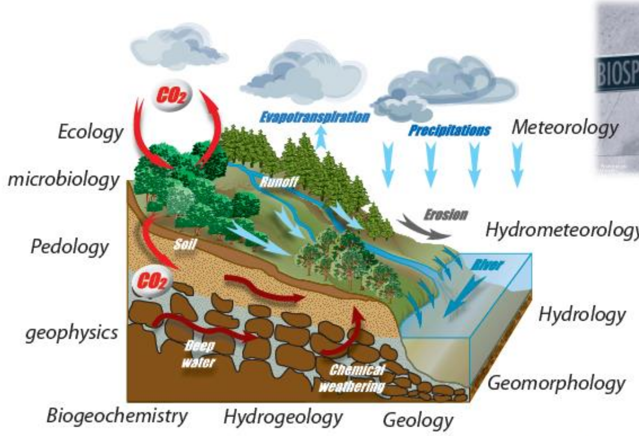


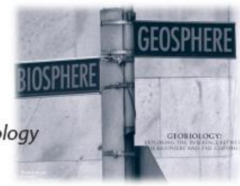
Despite the Critical Zone's importance to terrestrial life, it remains poorly understood:

- **How does the CZ form?**
- **How does it function?**
- **How will it change in the future?**

A SO CRITICAL ZONE?

The critical Zone, a systemic approach, at the cross road of disciplines

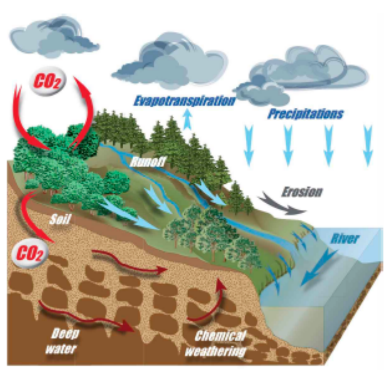




See Tansley and Billings, 2014, New Physiologist

(from Arnaud and Gaillardet, 2016)

A unique overarching question



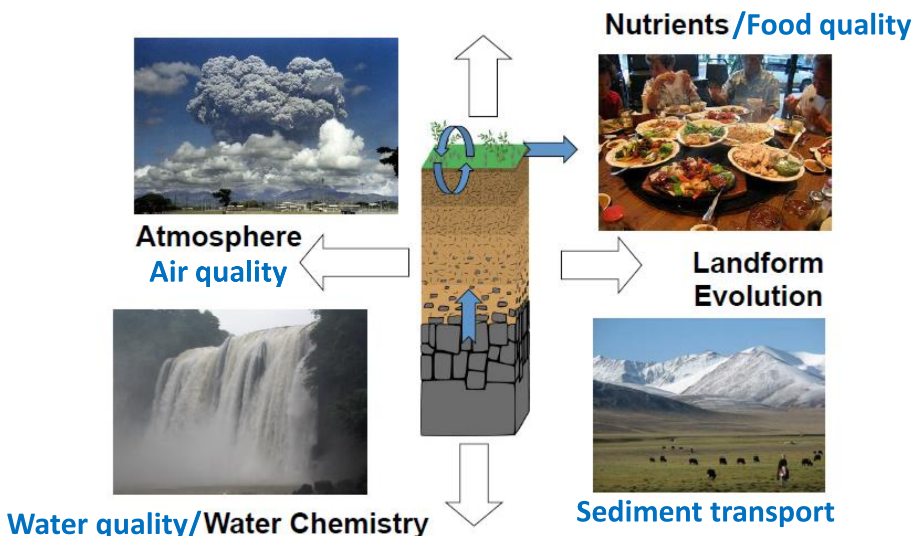
*How can we quantitatively predict (“**earthcast**”) the response of the earth surface to natural and human perturbations of variable amplitude and frequency?*

(Anderson et al., 2003)

Answering this question requires an integrated scientific approach and therefore NETWORKS.

CRITICAL ZONE

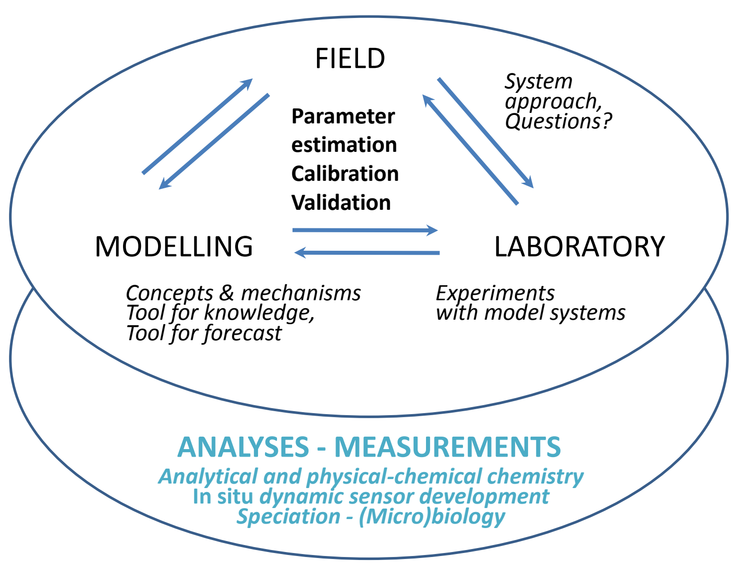
FOR THE PLANET



(from Gaillardet, 2016)

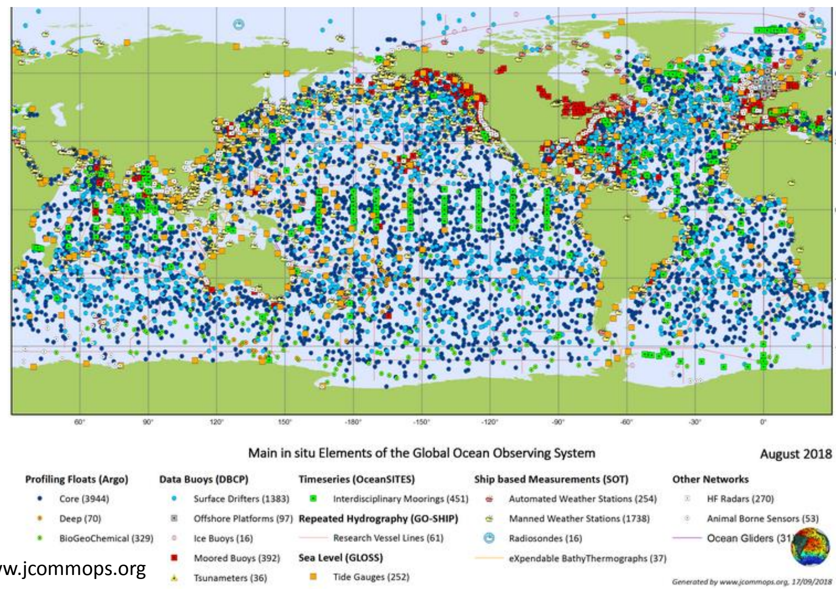
Chemodynamics of compounds

Methods for studying the critical zone as heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



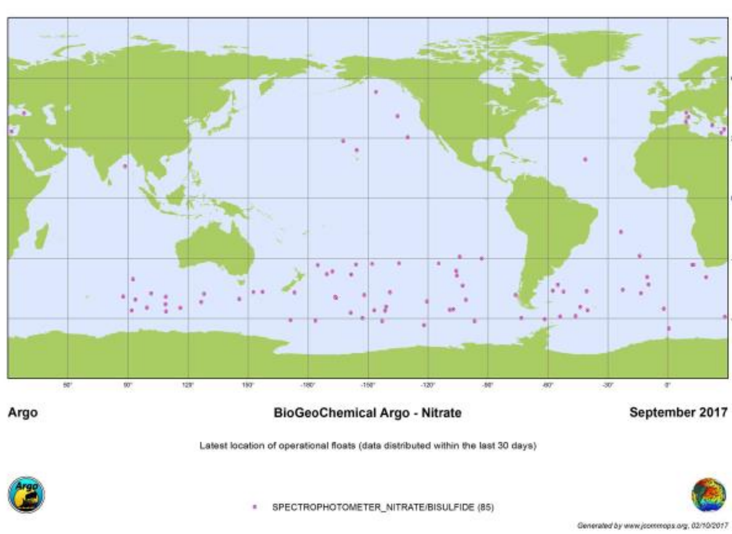
(from Behra Ph., 2000, book, COST 67, COST, EUR 19248)

Why do we need autonomous *in-situ* sensors?



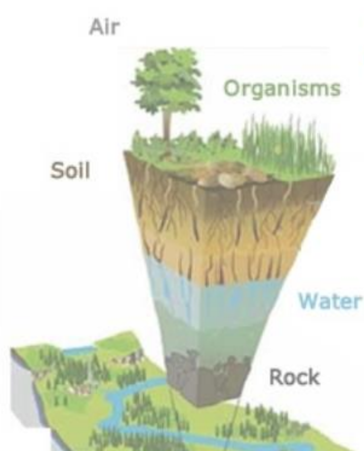
www.jcommops.org

Why do we need autonomous *in-situ* sensors?



US CZO SITES: (2008-2016)

Brantley et al., ESURF, (in open discussion)



RBV
RÉSEAU DES BASSINS VERSANTS

Challenging equipments for the temporal and spatial exploration of the Critical Zone at the catchment scale.

Jérôme Gaillardet, Laurent Longuevergne and Nicolas Arnaud

RÉSEAU DES BASSINS VERSANTS

CRITEX: Breakthrough

1. Develop new sensors. We are LATE despite the environmental urgency.

2. Instruments « state to the practice »: mature instruments used together on the same sites: synergic approach instrument-driven.

RÉSEAU DES BASSINS VERSANTS

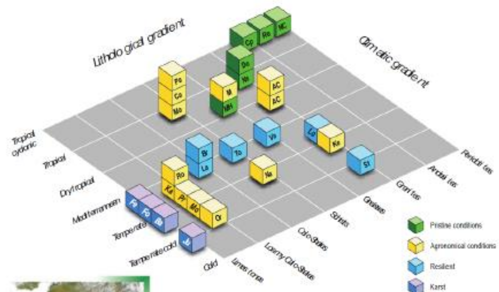
CRITEX: Breakthrough

1. Capturing the high frequency on long time series: mass and energy budgets.

2. Repeated campaigns to capture the « hot moments » et « hot spots » of the Critical zone

RÉSEAU DES BASSINS VERSANTS

Rivers as messengers of the Critical Zone.



More than 20 funded long-term observatories from the different environmental institutions and covering large climatic and anthropogenic gradients.

2011-2017
direction : Jérôme Gaillardet
Guillaume Nord.

Prototypes

RÉSEAU DES BASSINS VERSANTS

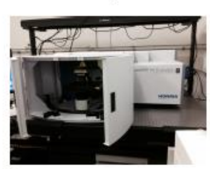
WP2.3. Hymenet, water, salinity and temperature probe (X. Chavanne et J. P. Frangi, IPGP-Université Paris Diderot)

WP1. µwave scintillometry J. M. Cohard, Hélène Barral, LTHE

WP4. The RIVER LAB The chemical river symphony P. Floury, J. Gaillardet, G. Tallec, IPGP-IRSTEA

WP8.3. Passive integrative sensors (B. Chague, P. Négrel, F. Gal, BRGM)

WP4. Hydrosedimentary plateform (high frequency) (M. Tiecelin, G. Nord, M. Estèves, LTHE): RIPLE



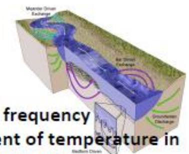
WP4. Development of new µsensors (Raman spectroscope), P. Behra, B. Dubreuil, Ensiacet

Instruments « state of the practice »

WP2.1. hydrogravimetry and hydrogeodesy, the mass of water (J. Hinderer, EOST) (iGrav+Scintrex)

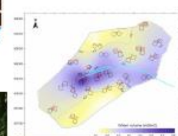
WP5. IDEVA: the drone revolution (C. Delacourt, J. Ammann, P. Allemand & P. Grandjean LGL Lyon).

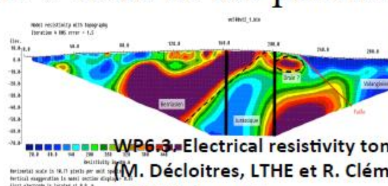
WP1.2. Tower flux and IR scintillometry, (B. Cappelaere, F. Arpin-Pont, J. P. Chazarin, J. Demarty, HSM, L. Prévot, LISAH, J. M. Cohard, LTHE).

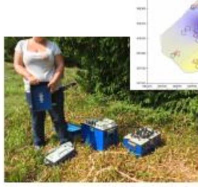


WP3. : high frequency measurement of temperature in the CZ. (J. P. Malet, EOST, O. Bour et T. Le Borgne, Géosciences Rennes).

Instruments « state of the practise »



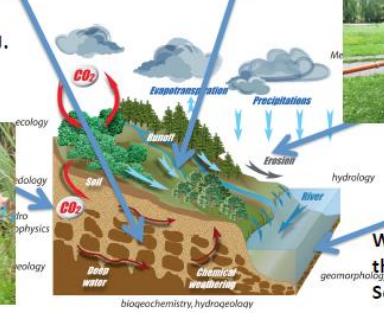




WP6.3. Electrical resistivity tomography (M. Décloitres, LTHE et R. Clément, M. Dorel, IRSTEA): Syscal Pro

WP6.2. RMP (A. Legchenko, LTHE et J. F. Girard, EOST).

WP6.5 CS-AMT P. Saihlac,EOST



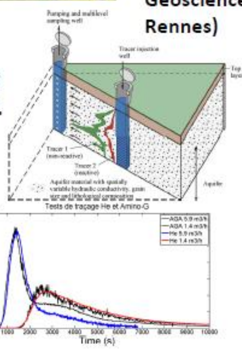
WP6.1. seismic the music of the CZ (L. Bodet, UPMC).

WP8.2. Isotopic tracing of the water molecule(M. Sebilo, UMPC, PICARO

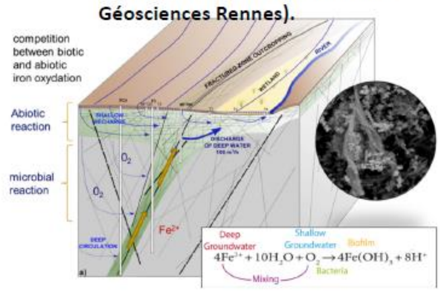
Observation and experimentation in bore holes

WP7.2. Automated winch for periodic hydraulic tomography (N. Lavenant, O. Bour, J. Schuite, L. Longuevergne, Géosciences Rennes)

WP8.1. In-situ high-frequency measurement of dissolved gas. (T. labasque, E. Chatton, L. Aquilina, Géosc. Rennes)
Eliot Chatton



WP7.3. Tracer tests (T. Le Borgne, T. Labasque, O. Brochet, L. Aquilina, Géosciences Rennes).



RÉSEAU DES BASSINS VERSANTS

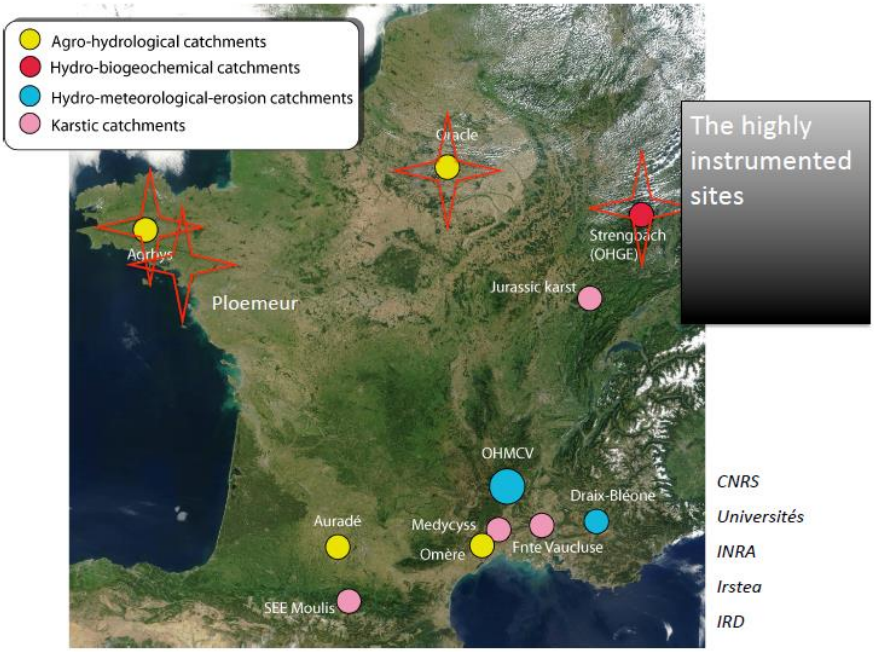
Timescales of instrument utilization

± day
Site characterization

± 15 days
Hot moment monitoring

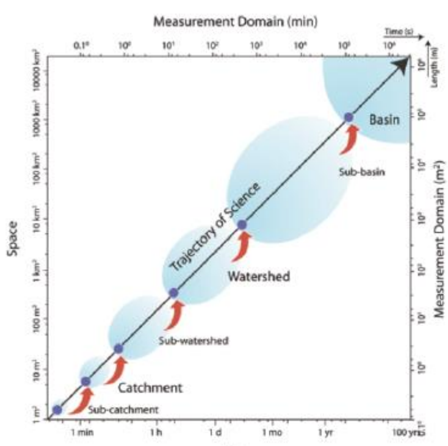
Repeated campaign to adress hydrological variability

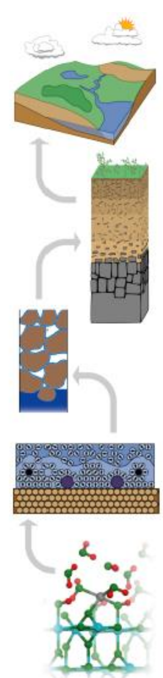
3 years
High frequency over long period of time: mass budgets

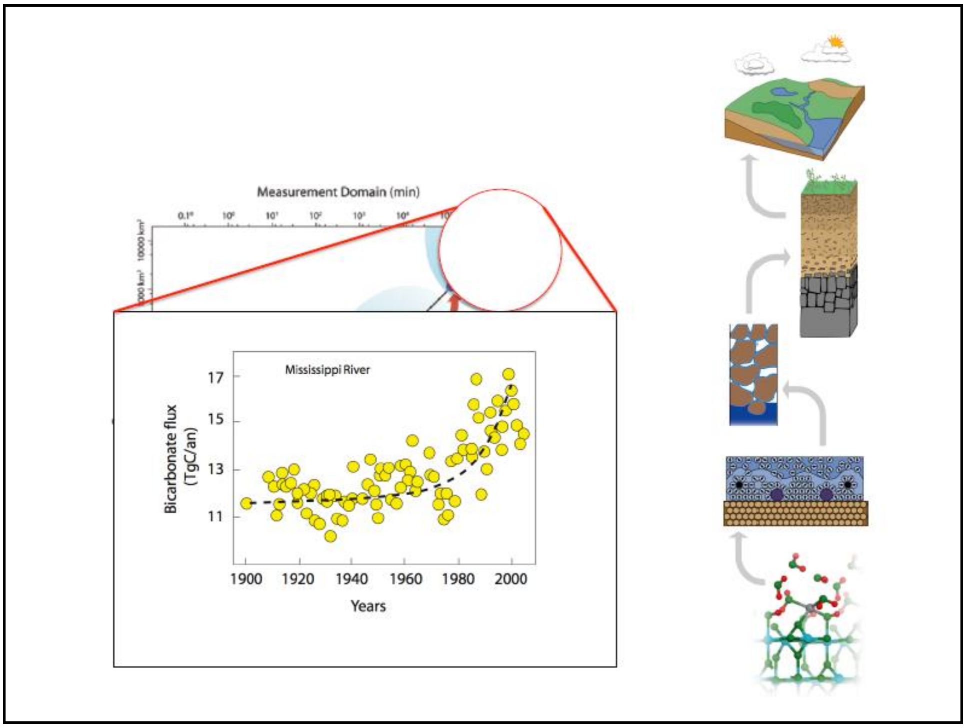


CNRS
Universités
INRA
Irstea
IRD

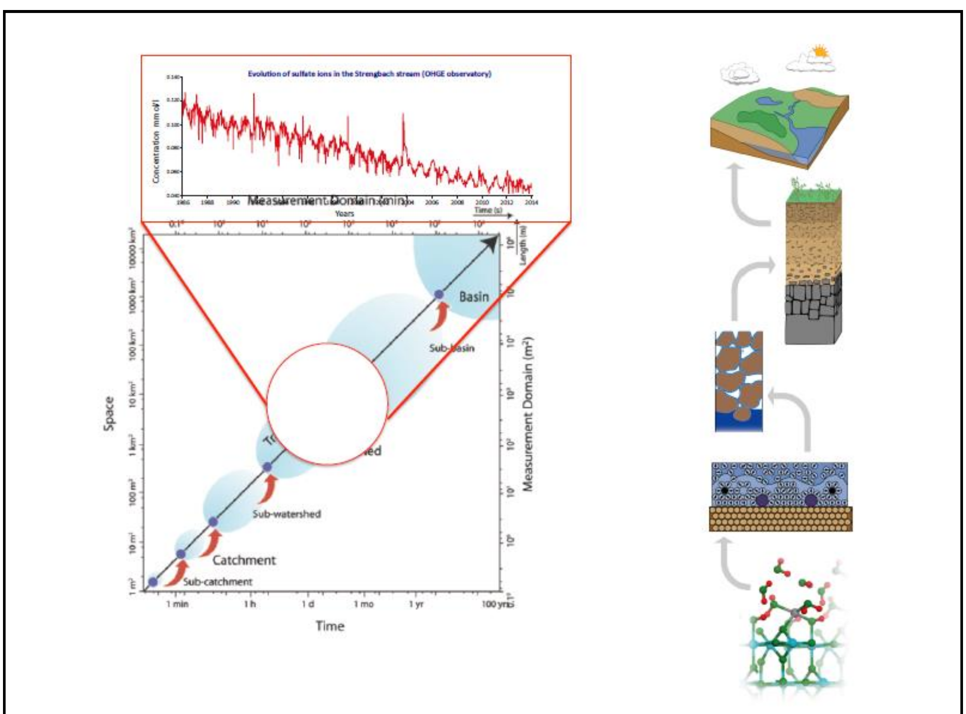
Temporal series



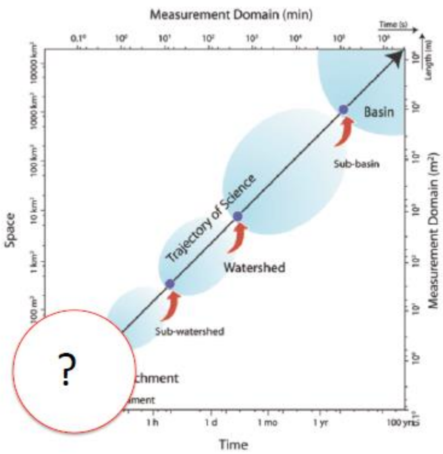


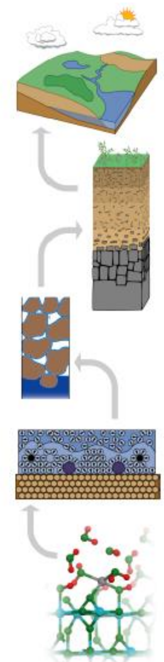


Measurement Domain (min)
Mississippi River
Bicarbonate flux (TgC/an)
Years

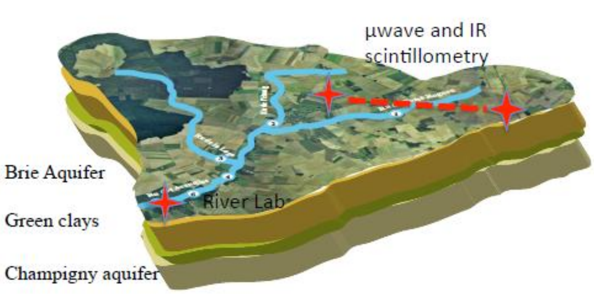


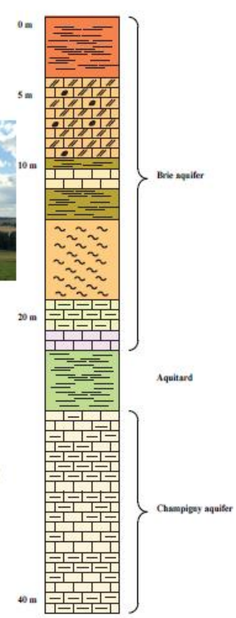
Evolution of sulfate ions in the Strengbach stream (OHGE observatory)
Basin
Sub-watershed
Catchment
Sub-catchment
Space
Time
Measurement Domain (m²)





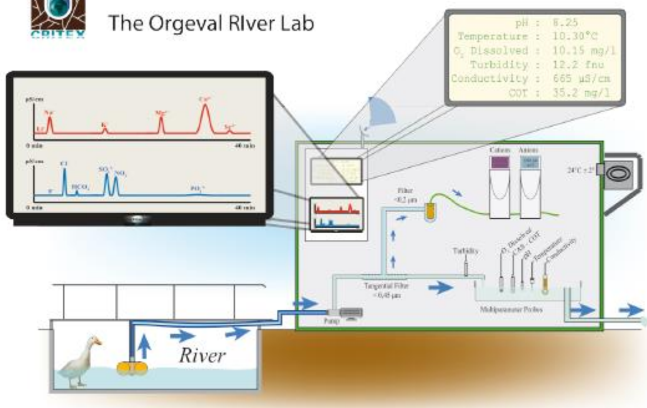
The Orgeval CZO





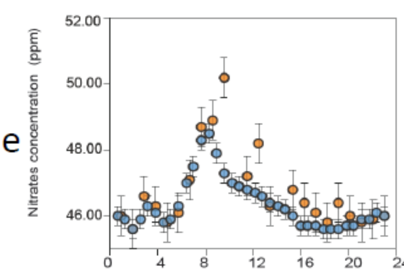
P. Floury (PhD thesis, 2017), J. Gaillardet, G. Tallec (IPGP-Irstea)

The Orgeval RIver Lab



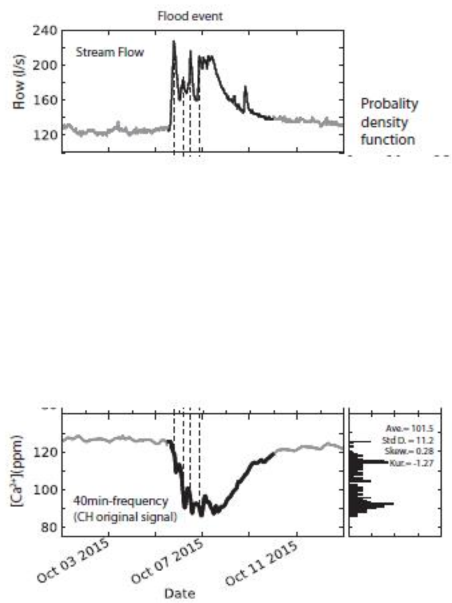
The advantages of the lab in the field

- More stable
- Comparison between the Lab and the River Lab.
- Saves human resources
- Needs little operation



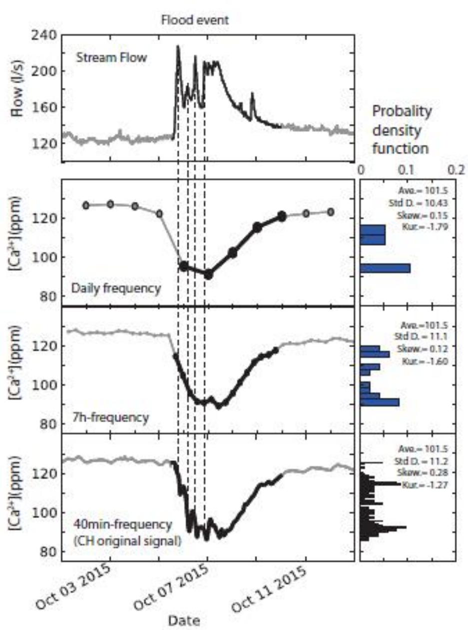
Paul Floury (PhD thesis, 2017)

Listening to the potamochemical symphony



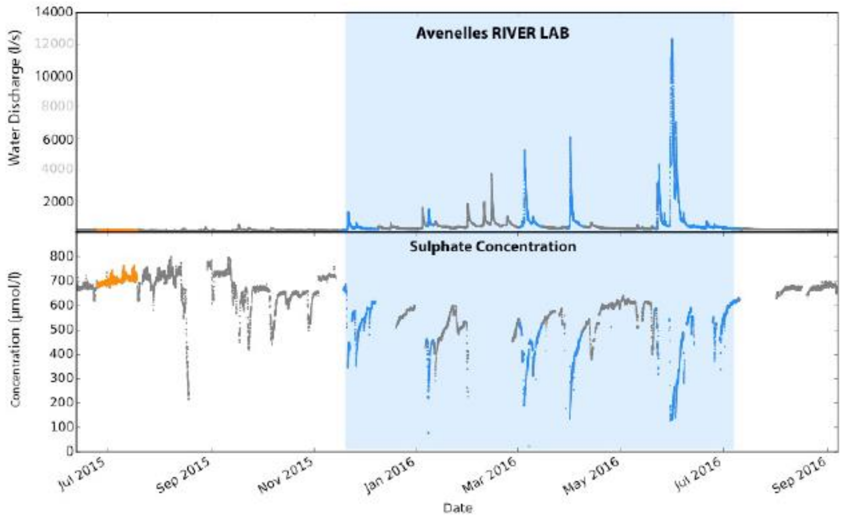
P. Floury (PhD thesis)

Listening to the potamochemical symphony



P. Floury (PhD thesis)

One year of data (15 000 data)



P. Floury (PhD thesis)

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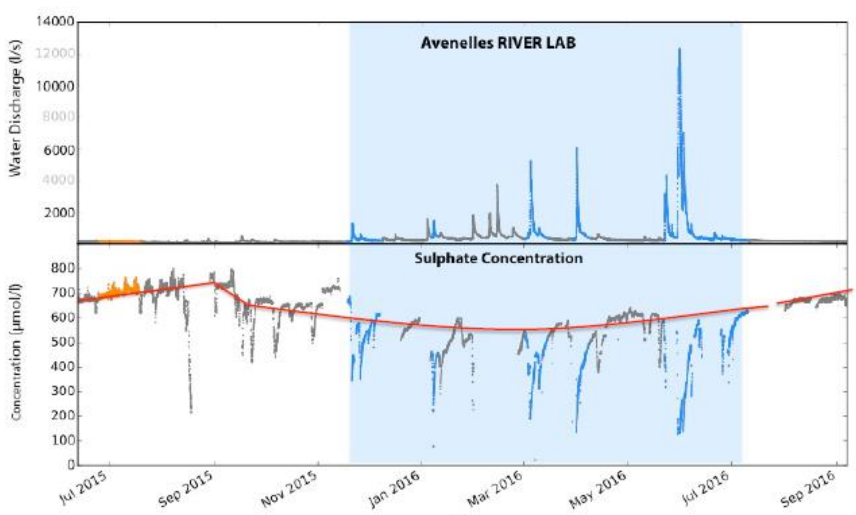

P. Floury (PhD thesis)

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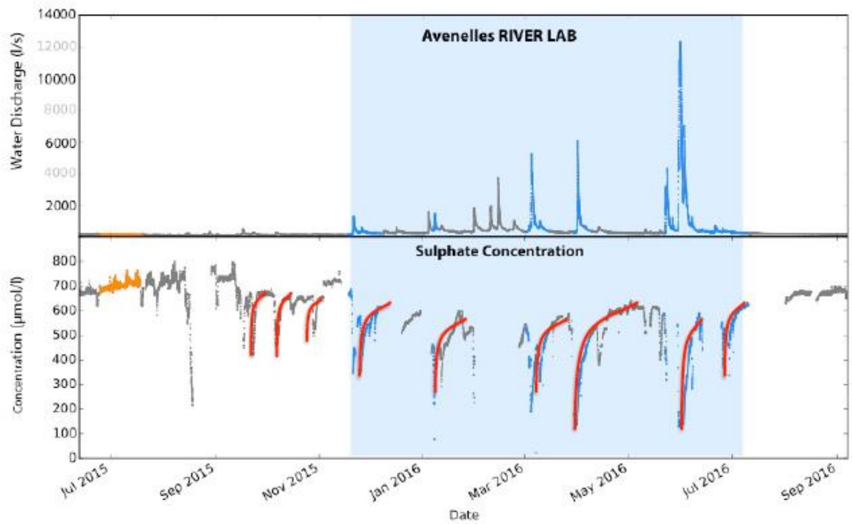
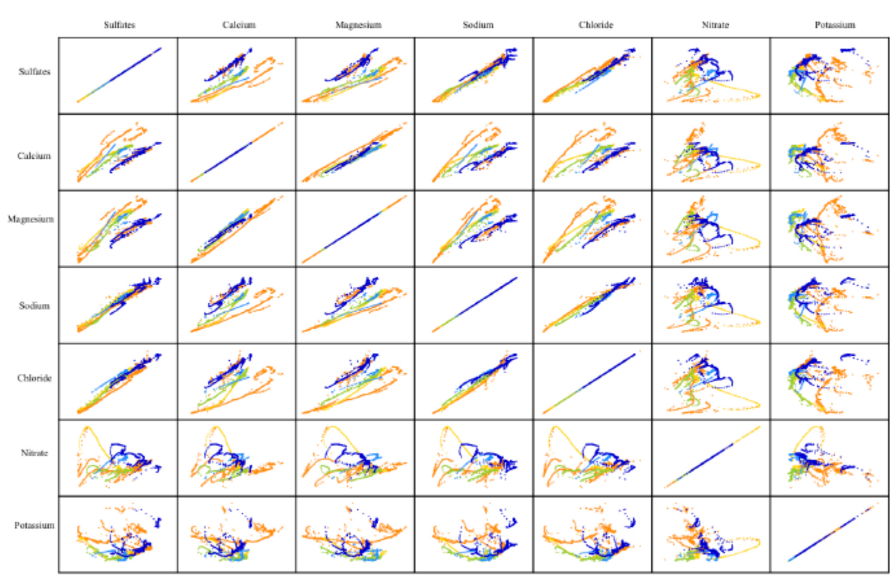


P. Floury (PhD thesis)

The instrumental ensemble of the Orchestra



P. Floury (PhD thesis)

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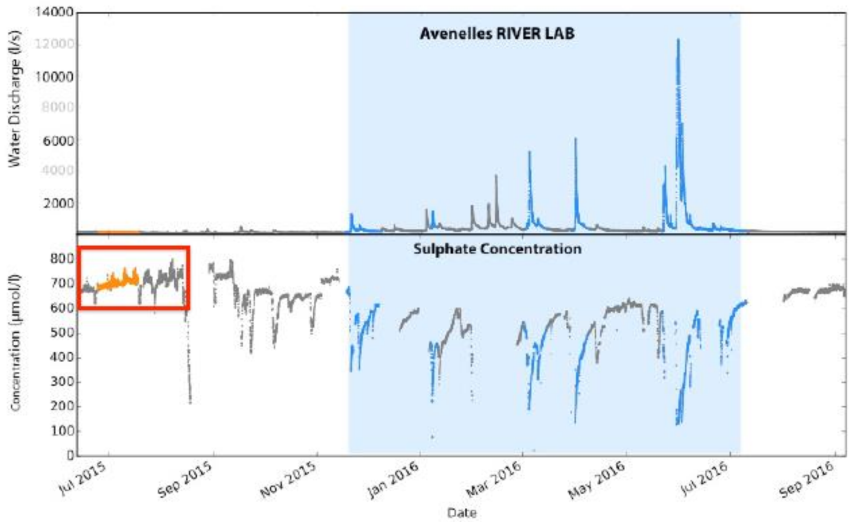
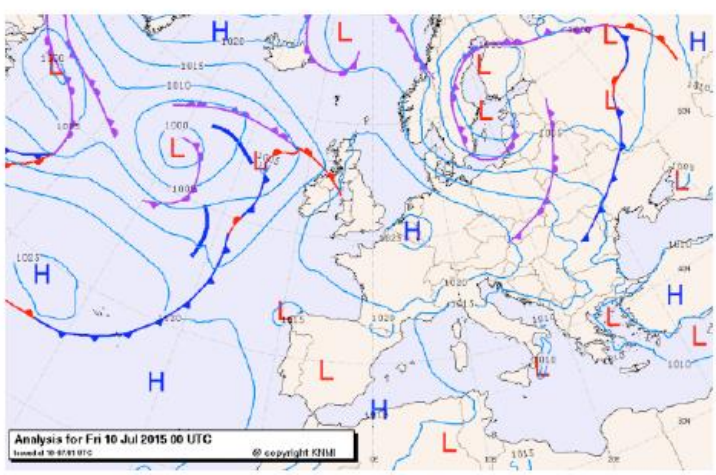
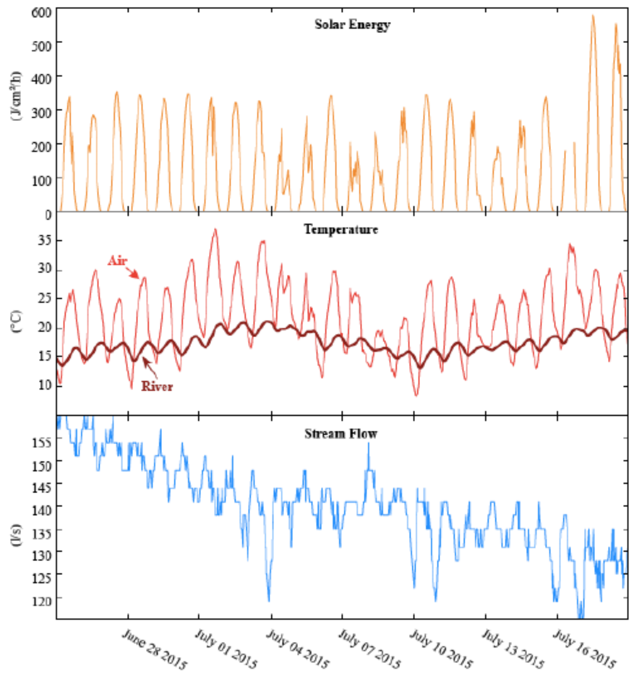


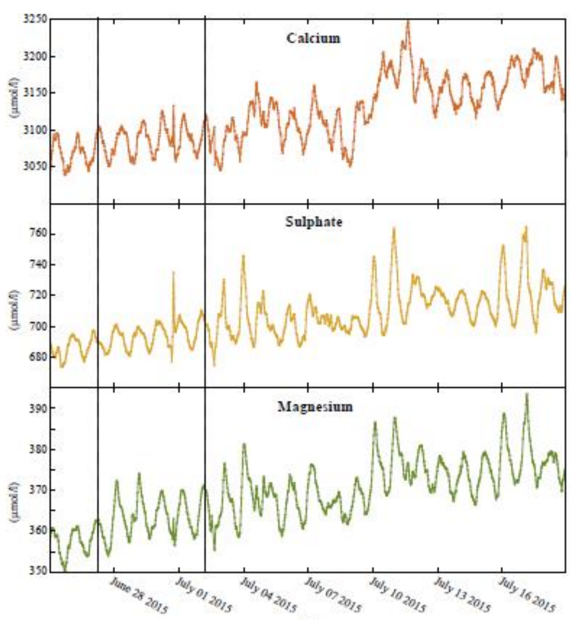
P. Floury (PhD thesis)

July 2015's drought at Orgeval





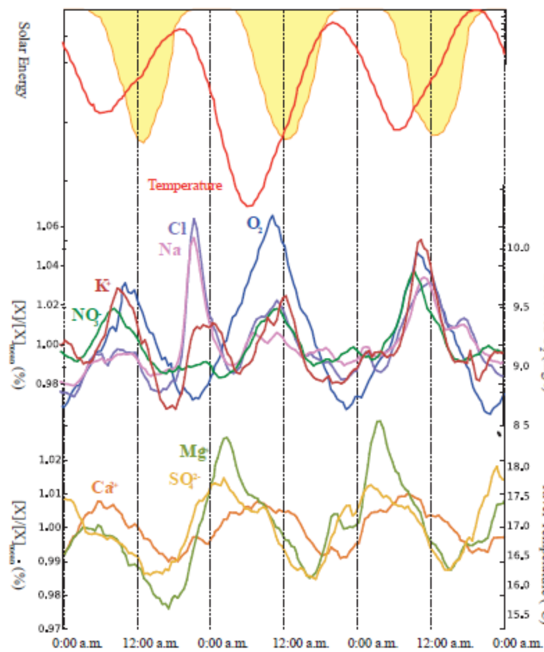
P. Floury (PhD thesis)



Day-Night variations of concentrations:

Max of SO4-Mg just after midnight

P. Floury (PhD thesis)



all elements do not behave similary: not a ET effect

Mg and SO_4 covary: mixing processes with a gypsum-rich aquifer

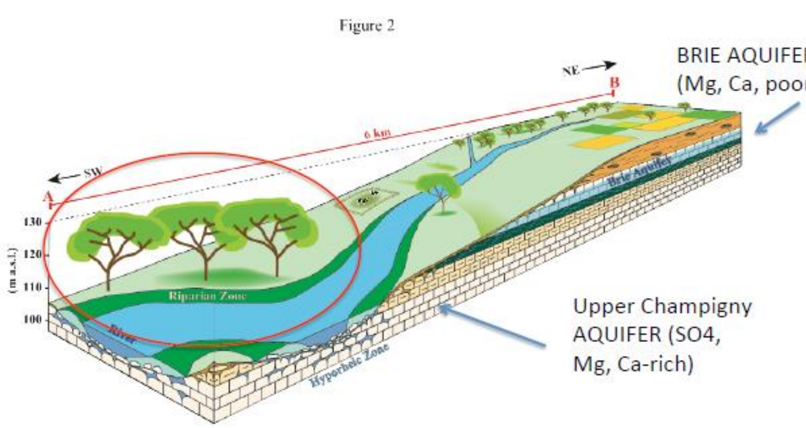
Ca is not in phase with Mg

NO_3 and O_2 (± K) covary: biogeochemical processes

Na and Cl have a more eratic behavior

P. Floury (PhD thesis)

A complex music



BRIE AQUIFER (Mg, Ca, poor)

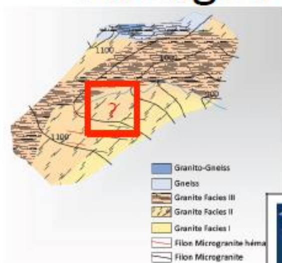
Upper Champigny AQUIFER (SO4, Mg, Ca-rich)

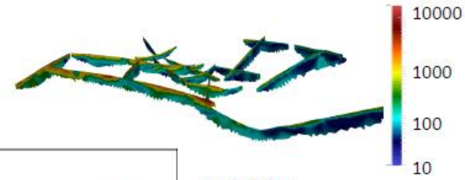
Hypotheric Zone
Riparian Zone where ET can modulate the flux of Champigny aquifer

Mixing between aquifers
Evapotranspiration processes
Complicating mechanisms occuring in the hyporheic zone.

P. Floury (PhD thesis)

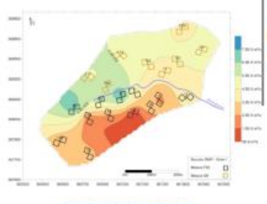
Strengbach – from CZ structure

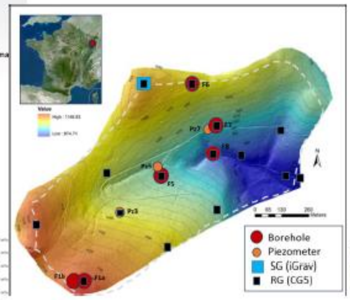




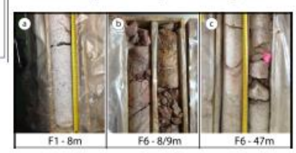
Resistivity
Structure of weathered zone

MRS sounding
Transmissivity



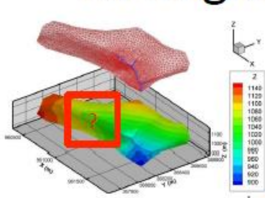


Drilling/borehole tools
Deep water pathways

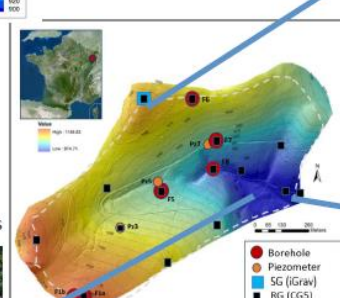


M.C. Pierret *et al.*

Strengbach – to CZ dynamics



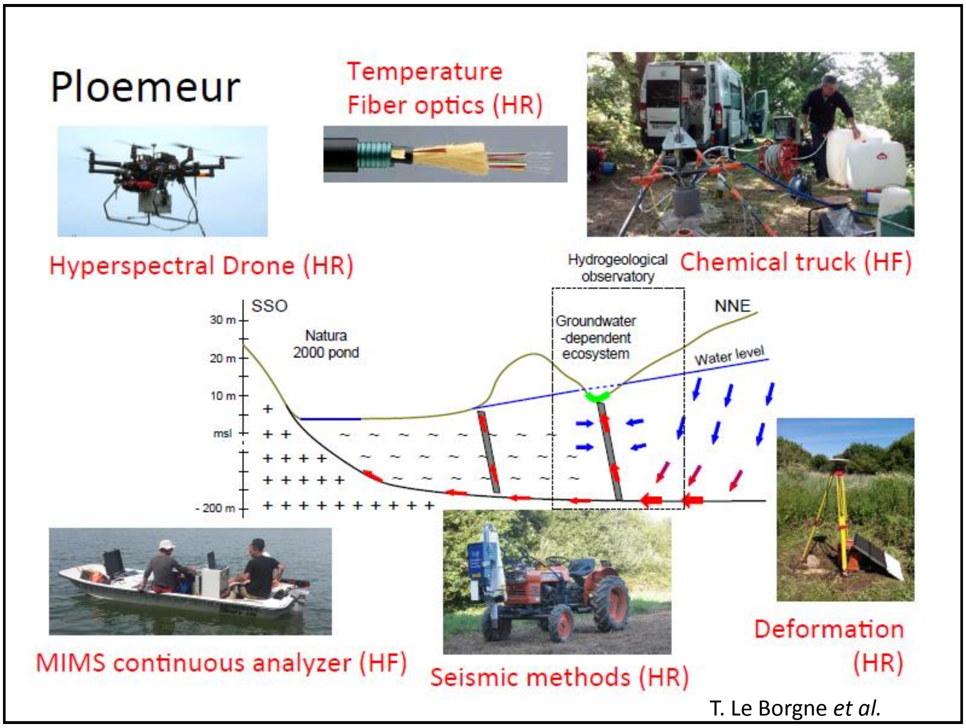
Gravimetry
Distributed storage changes

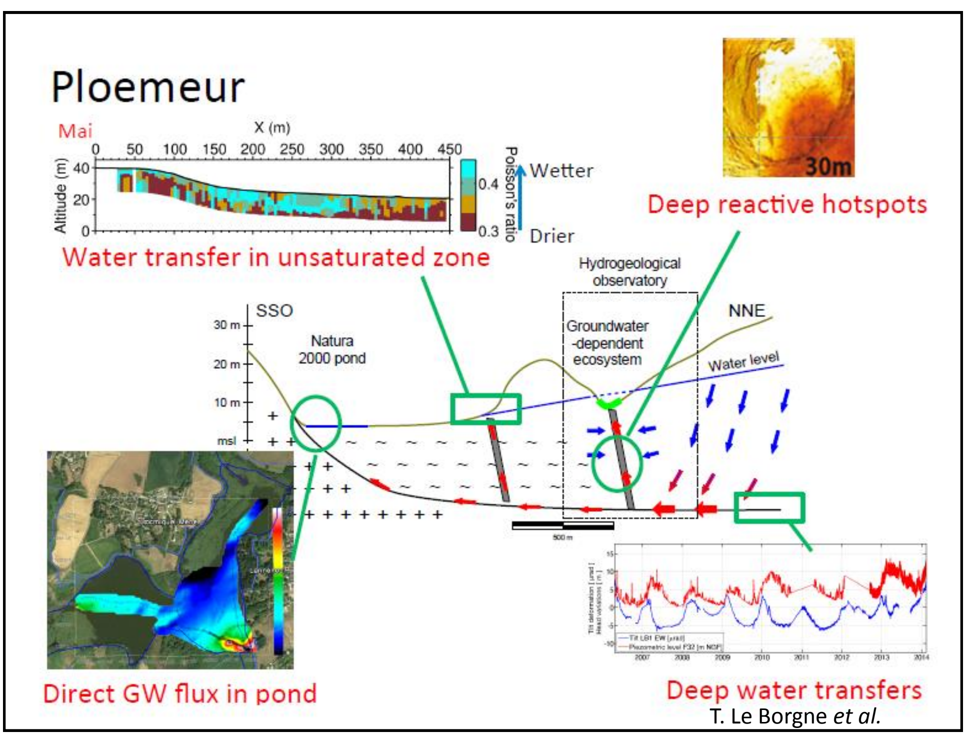


Audio-Magneto-telluric
Distributed storage changes

River lab (HF)
Water pathways

M.C. Pierret *et al.*


Ploemeur
Temperature
Fiber optics (HR)
Hyperspectral Drone (HR)
Hydrogeological observatory
Chemical truck (HF)
SSO
NNE
30 m
20 m
10 m
msl
- 200 m
Natura 2000 pond
Groundwater -dependent ecosystem
Water level
MIMS continuous analyzer (HF)
Seismic methods (HR)
Deformation (HR)
T. Le Borgne et al.


Ploemeur
Mai
X (m)
0 50 100 150 200 250 300 350 400 450
Altitude (m)
40
20
0
0.4
0.3
Poisson's ratio
Wetter
Drier
30m
Deep reactive hotspots
Water transfer in unsaturated zone
Hydrogeological observatory
SSO
NNE
30 m
20 m
10 m
msl
Natura 2000 pond
Groundwater -dependent ecosystem
Water level
Direct GW flux in pond
Deep water transfers
T. Le Borgne et al.

Sensors

Definition

Sensors: measurement device made of a receptor and a transducer

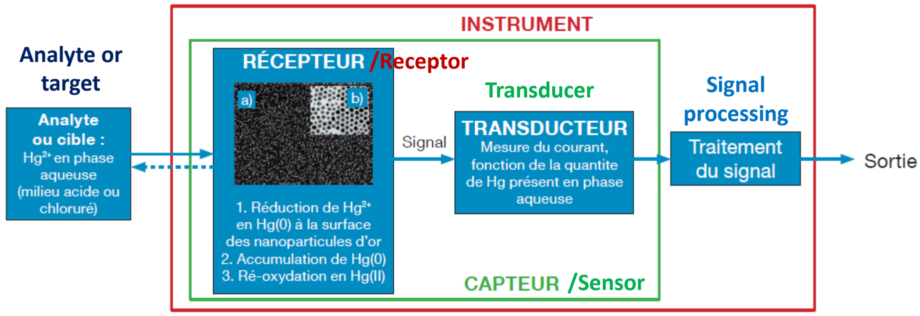
Receptor: may be physical, chemical or biological, used to measure physical, chemical or biological parameters via the specific recognition of a target (analyte) or a target family

Passive sensors *vs.* dynamic sensors

"Passive" sensor/sampler: source of energy delivering a signal being out the system
(examples: DGT [Diffusion Gradients in Thin-Films],
POCIS [Polar Organic Chemical Integrative Samplers]...)

"Active" sensor: sensor delivering the signal itself

"Dynamic" sensor: measured done at high frequencies, from second or less to few minutes, with respect to a passive sensor needing very often a longer period of acquisition time (from several hours to some weeks)



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). ■

Interaction between receptor and target (analyte) shown by a transducer transforming the signal of interaction in a signal being measurable and quantifiable

Integrated system: device for measurement made of the sensor and the data processing system until the numerical value

(Fajerwerg, K., Behra, P., Gaillardet, J., 2015. Capteurs de la qualité des eaux, *in Eau à Découvert*, eds. by A. Euzen, C. Jeandel and R. Mosseri, CNRS Éditions, Paris, 2015; and Ralf D. Prien, 2007)

Chemical, physical or biological sensor

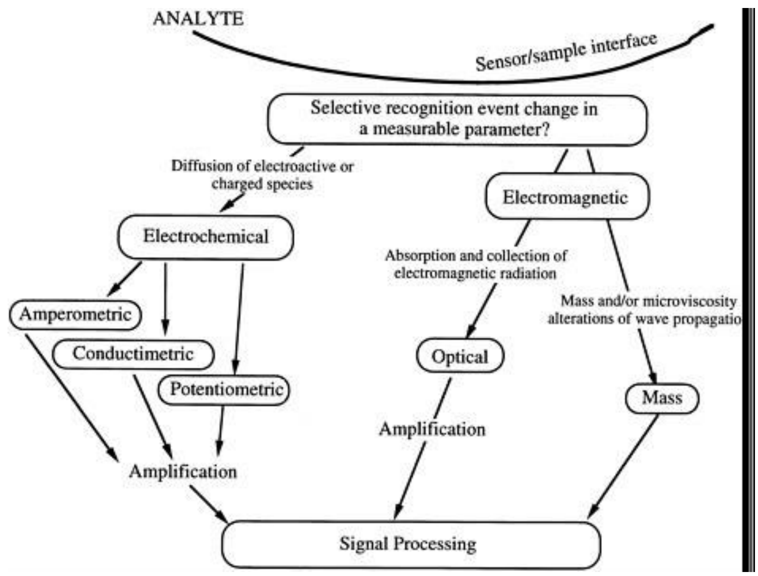
Actual properties:

Biological and chemical sensors being too complex devices, generally optimized for a particular application

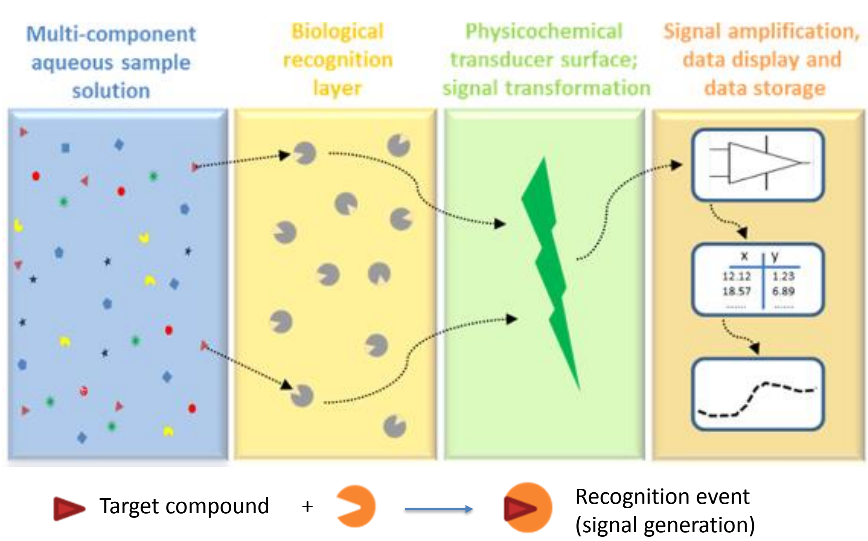
Requested properties:

- Simple
- Robustness
- Sensitive
- Selective
- Limit of detection
- Fast
- Cheap
- Packaging size

Direct-reading, selective, chemical sensors



New biochemical sensor for herbicide *in-situ* analysis



Topic of Huy Minh Do
USTH PhD

Suginta *et al.*, 2013, Chem. Rev. 113, 5458–5479.

Chemical reactivity can involve a very wide range of chemical phenomena, including:

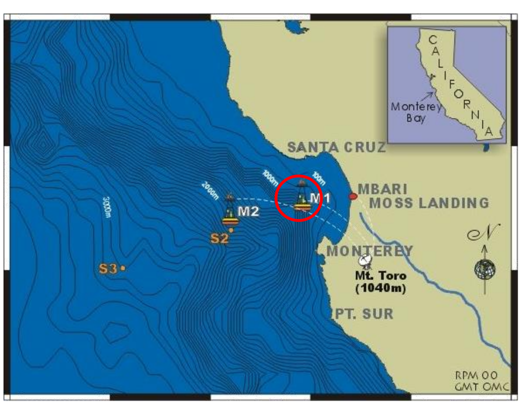
Recognition of size/shape/dipolar properties of molecular analytes by molecular films, phases, or sites:
Being bioreceptor sites, structures allowing molecular recognition or host-guest interactions, or ceramic or other materials with templated cavities
Molecular recognition leading to selective, strong binding or ab/adsorption of analyte to the sensor material

Selective permeation of analyte in a thin-film sensor:
If reversibility of binding or permeation of analyte, re-used (*i.e.*, recycled) of the sensor film in repeated measurements
Stoichiometrically consumption of the sensor material for irreversible binding of analyte to the sensor, or side reactions with interferants, shortening its useful lifetime

Catalytic reaction cycle of the sensing materials:
Resulting in analyte consumption

Temporal resolution: Example of NO_3^- and $O_{2(aq)}$

Nitrate data from ISUS instrument at MBARI mooring M1 in Monterey Bay
(http://www.mbari.org/chemsensor/m1/isus_m1.htm)



picture: MBARI

Temporal resolution: Example of NO_3^- and $O_{2(aq)}$

Why NO_3^- and dissolved $O_{2(aq)}$?

Photosynthesis

$$6\ CO_2 + 6\ H_2O + \text{sun energy} \leftrightarrows \{CH_2O\}_6 + 6\ O_2$$

Respiration

$$106\ H_2CO_3^* + 16\ NO_3^- + HPO_4^{2-} + 16\ H_2O + 18\ H^+$$
$$+ \text{trace elements (Fe, Mn, Mo...)} + \text{sun energy}$$

Photosynthesis

$\leftrightarrows$

Respiration

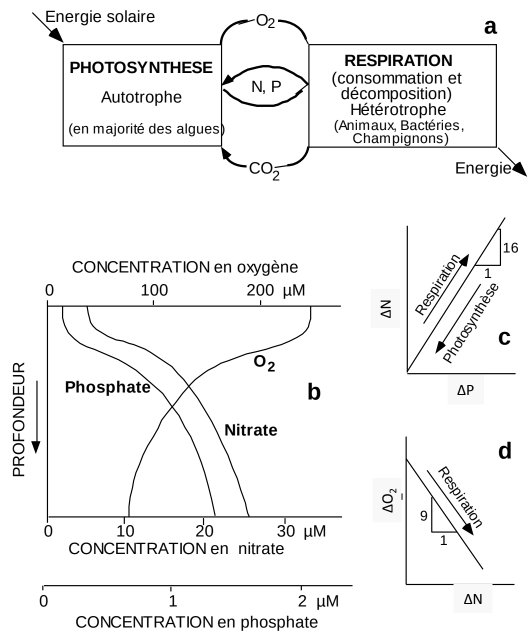
$$\{C_{106}H_{263}O_{110}N_{16}P_1\} + 138\ O_2$$

ou

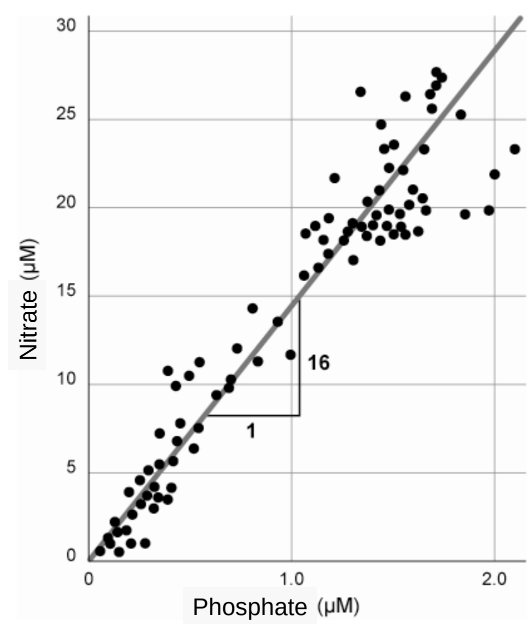
$$\{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_1\} + 138\ O_2$$

Algae protoplasm

Redfield's ratio: $\Delta C : \Delta N : \Delta P \approx 106 : 16 : 1$

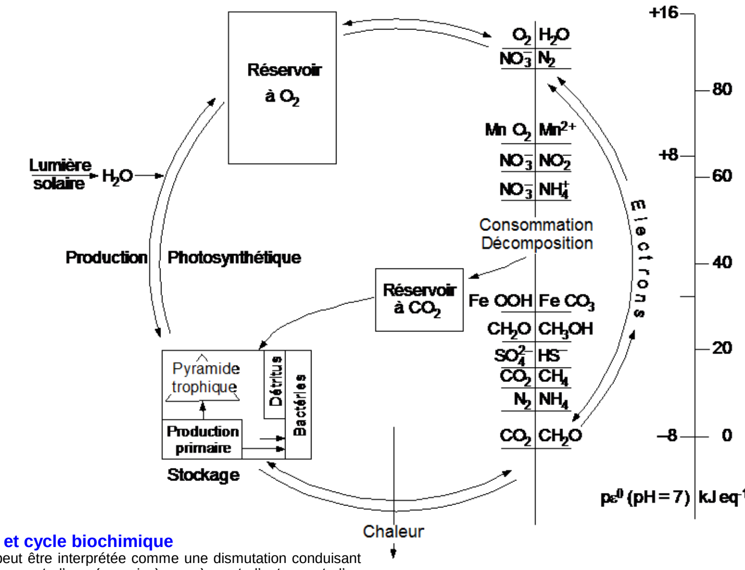


Sigg et al., 2014



Sigg et al., 2014

Correlation nitrate *vs.* phosphate in North Atlantic



Photosynthèse et cycle biochimique

La photosynthèse peut être interprétée comme une dismutation conduisant à la formation d'une part d'un réservoir à oxygène et d'autre part d'un réservoir à réducteurs constitué par la matière organique (la biomasse contenant des liaisons à haute énergie faisant intervenir H et des composés constitués de C, N, S et P). Les organismes non-photosynthétiques ont tendance à rétablir l'équilibre en décomposant catalytiquement les produits instables issus de la photosynthèse et en fournissant de l'énergie. L'échelle de $p\varepsilon^0$ sur le côté droit donne une indication de la séquence des réactions d'oxydoréduction dans les eaux naturelles.

Sigg et al., 2014

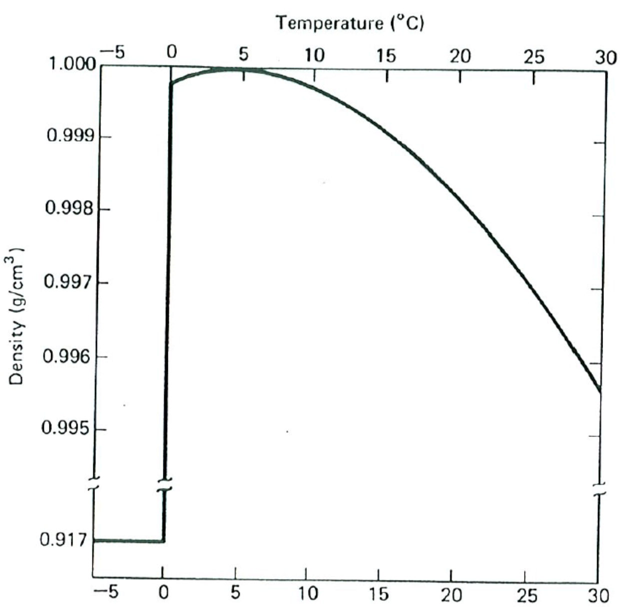


Figure 14-6 Density of pure water at 1 atm as a function of temperature.

Drever, 1988

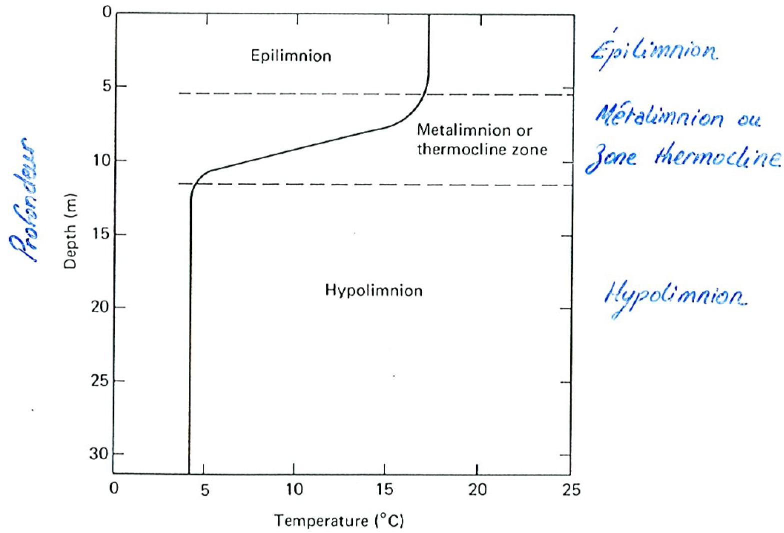


Figure 14-7 Typical summer temperature distribution for a lake in a temperate climate.

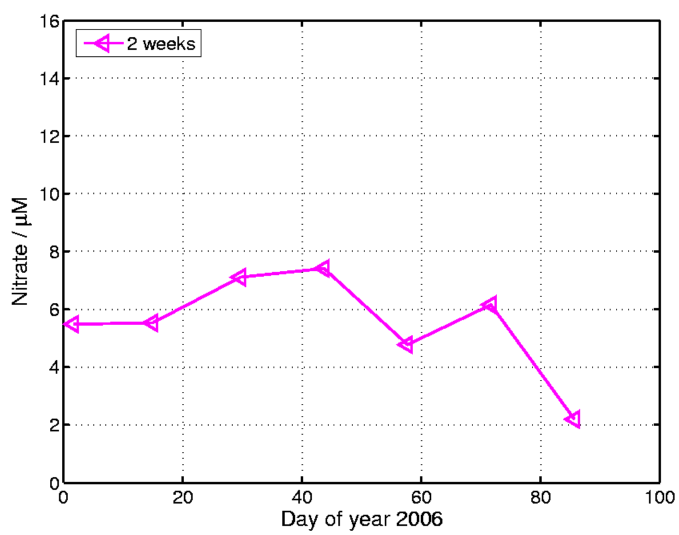
Distribution profile of temperature

Drever, 1988

Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

Environmental Sensors Conference - Biarritz

Temporal resolution: An example



Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

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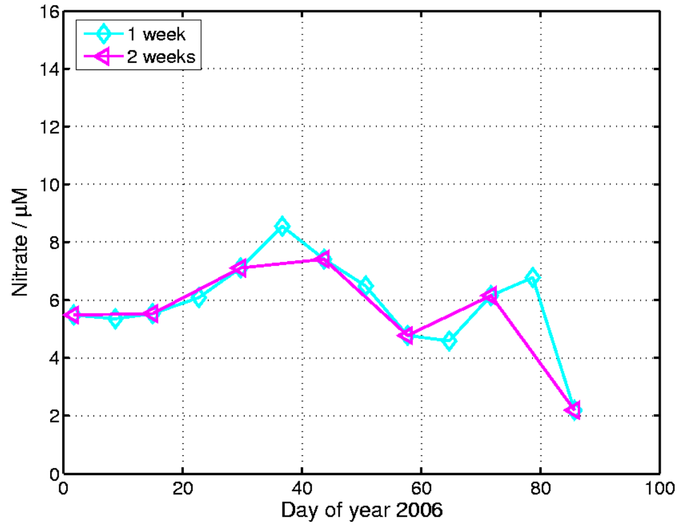
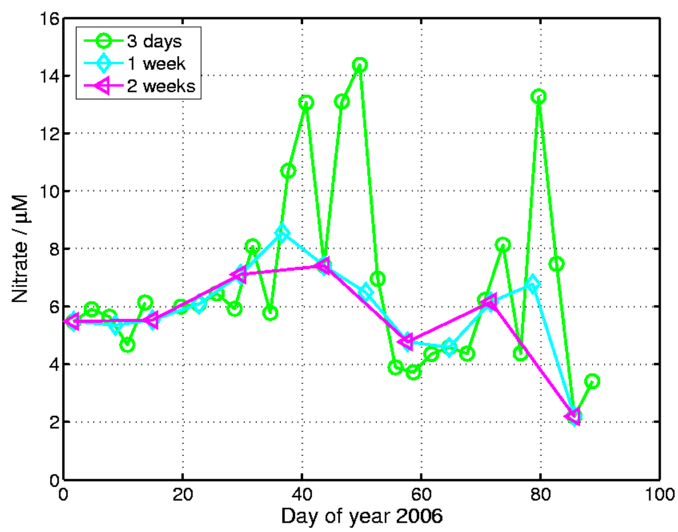
Temporal resolution: An example



Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

Environmental Sensors Conference - Biarritz

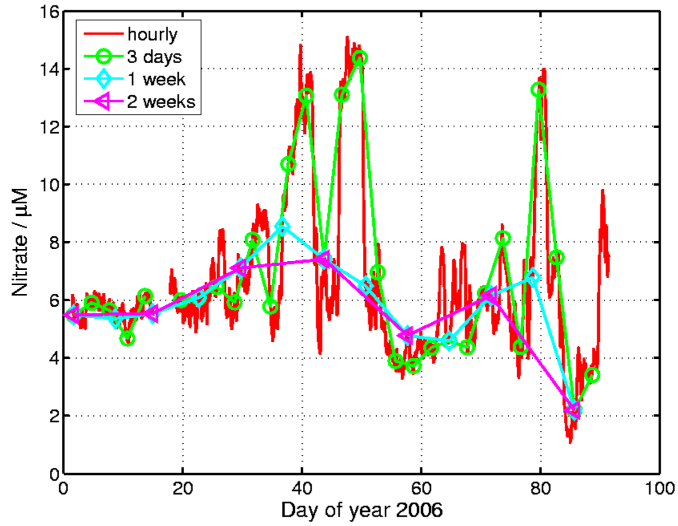
Temporal resolution: An example



Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

Environmental Sensors Conference - Biarritz

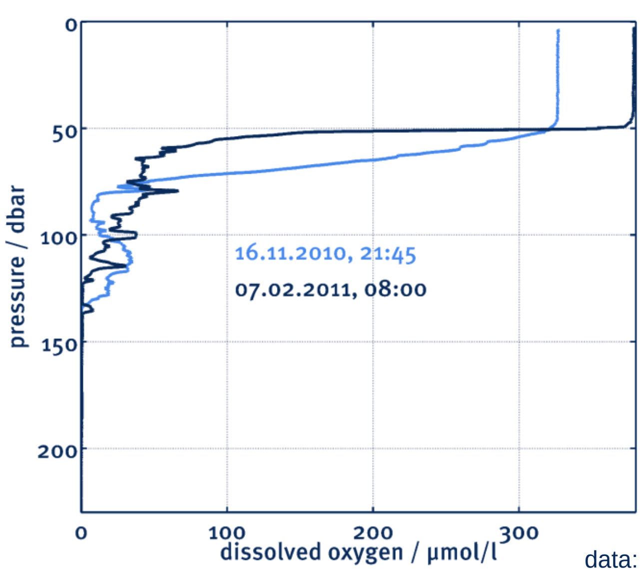
Temporal resolution: An example



Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

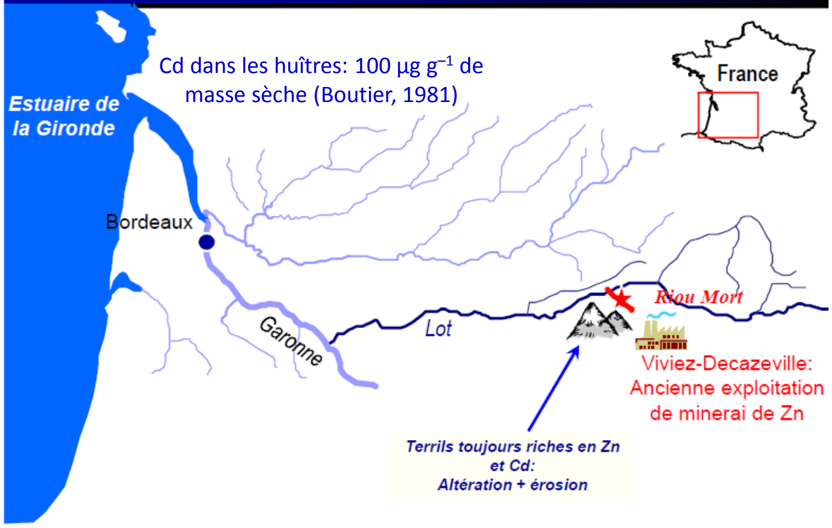
Environmental Sensors Conference - Biarritz

Temporal resolution: Another example



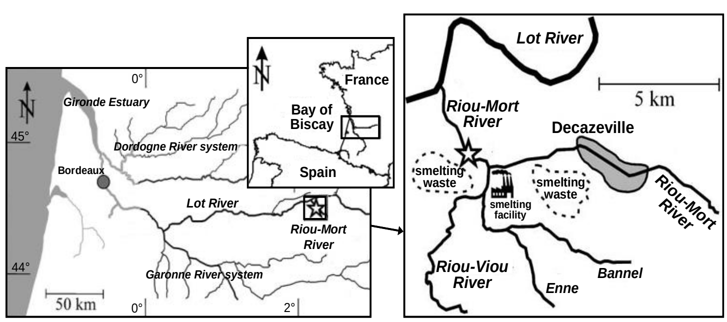
data: IOW monitoring

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:

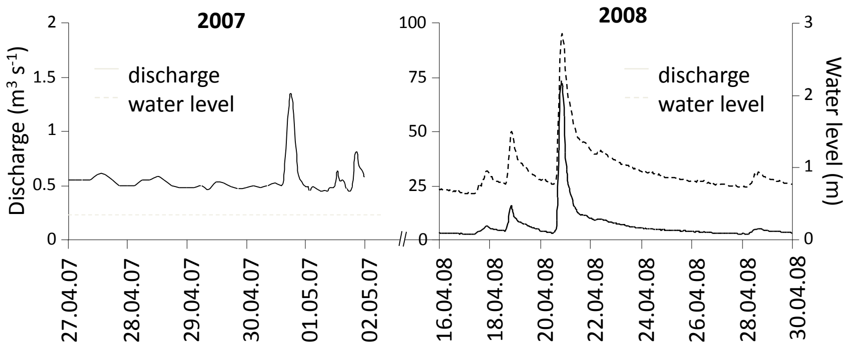
- affected by leaching and mechanical erosion of metallurgical wastes from former mining and ore smelting activities.
- known as the major source of the historical polymetallic pollution of the Lot-Garonne-Gironde fluvial-estuarine system

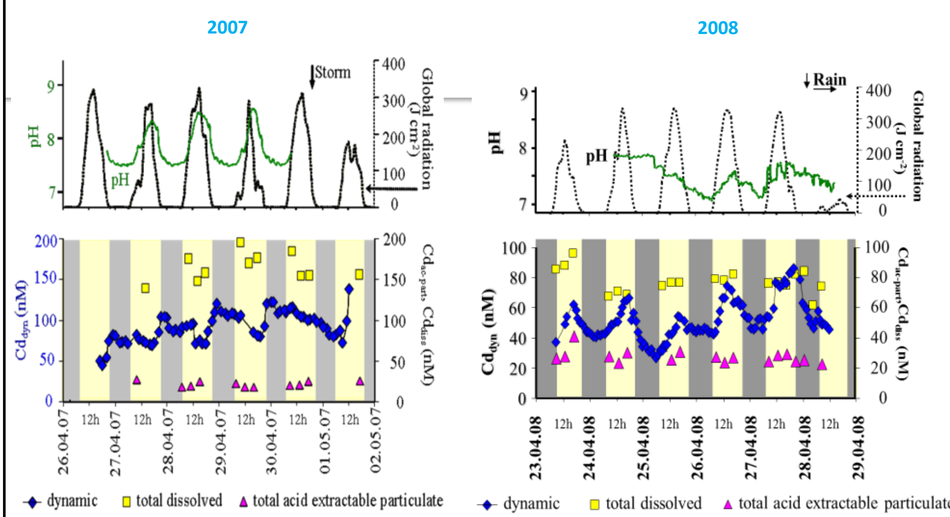
EU project ECODIS*: Dynamic sensing of chemical pollution disasters and predictive modelling of their spread and ecological impact (2005-2008)*

M.-L. Tercier-Waeber, Teddy Hezard, Matthieu Masson, Jörg Shäfer, Env. Sci. Tech. 2009*

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

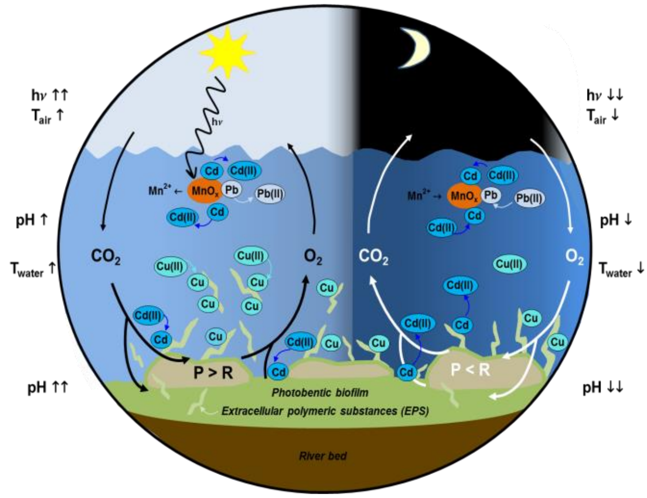
Surface Complexation

$$M^{2+} + \equiv S{-}OH \leftrightarrows \equiv S{-}OM^{+} + H^{+}$$

Photosynthesis-Respiration

$$6CO_{2(g)} + 6H_2O + \text{solar energy} \leftrightarrows \{CH_2O\}_6 + 6O_{2(g)}$$

(from Tercier-Waeber *et al.*, 2009)



Photosynthesis-respiration

$$6CO_{2(g)} + 6H_2O + \text{solar energy} \leftrightarrows \{CH_2O\}_6 + 6O_{2(g)}$$

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

FIELD

MODELLING

LABORATORY

$$106\ H_2CO_3^* + 16\ NO_3^- + HPO_4^{2-} + 16\ H_2O + 18\ H^+$$
$$+ \text{ trace elements (Fe, Mn, Mo, Si...)} + \text{solar energy}$$

Photosynthesis ⇆ Respiration

$$\{C_{106}H_{263}O_{110}N_{16}P_1\} + 138\ O_2$$

biomass

ANALYSES - MEASUREMENTS

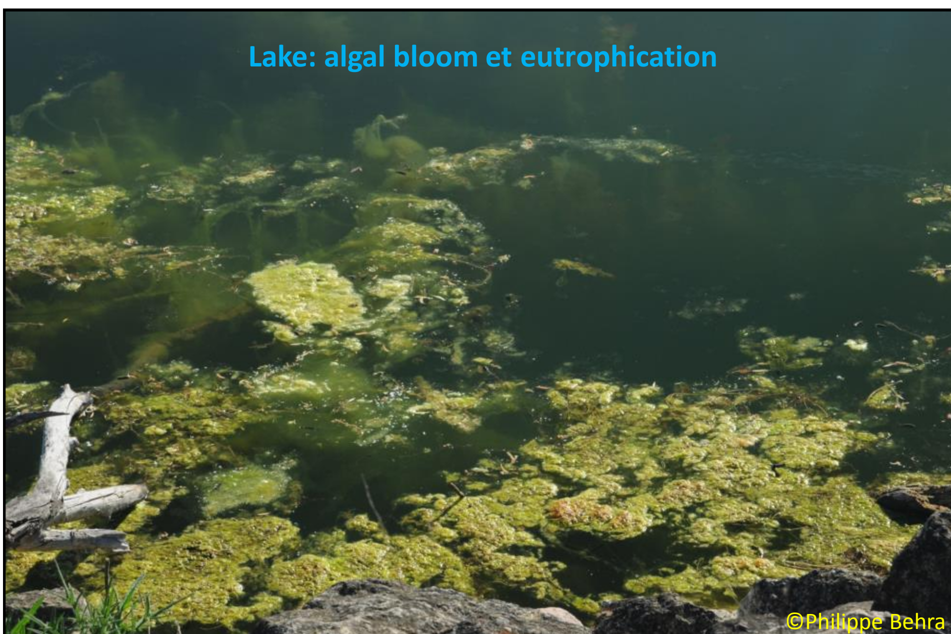
Analytical and physical-chemical chemistry

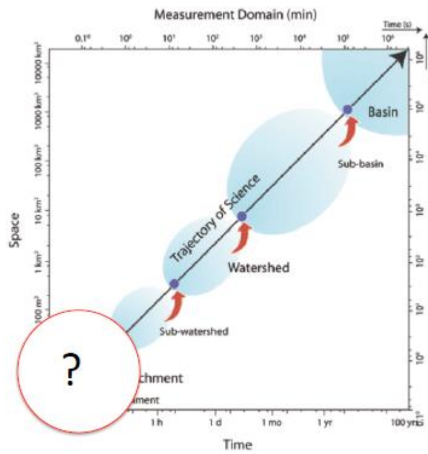
In situ *dynamic sensor development*

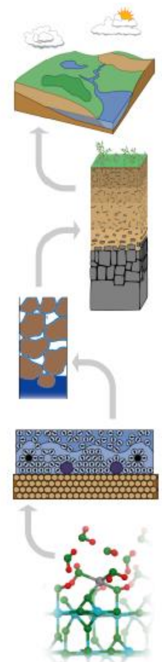
Speciation - (Micro)biology

(from Behra Ph., 2000, book, COST 67, COST, EUR 19248)

Lake: algal bloom et eutrophication







Coupling *in situ* physical, biological and chemical sensors to assess ecosystem health

George W. Luther, III and Daniel J. MacDonald
School of Marine Science & Policy,
University of Delaware, Lewes, DE, U.S.A.

With CTD (salinity, temperature, depth) **and *in-situ* solid state Au/Hg (micro)electrodes, define seasonally anoxic inland water columns** [stagnant canals Delaware]; O_2 **&** H_2S

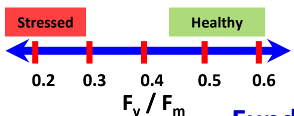
Add a biological sensor to indicate phytoplankton health

Role of the oxygen evolving centre (OEC) of photosystem II (PSII) being part of the complex biological machinery enabling photosynthesis in green plants and cyanobacteria

Fluorescence Induction and Relaxation system (FIRe) - Satlantic

F_v/F_m **reflecting physiological state of photosystem II (PSII)**

σ_{PSII} **reflecting community shift**



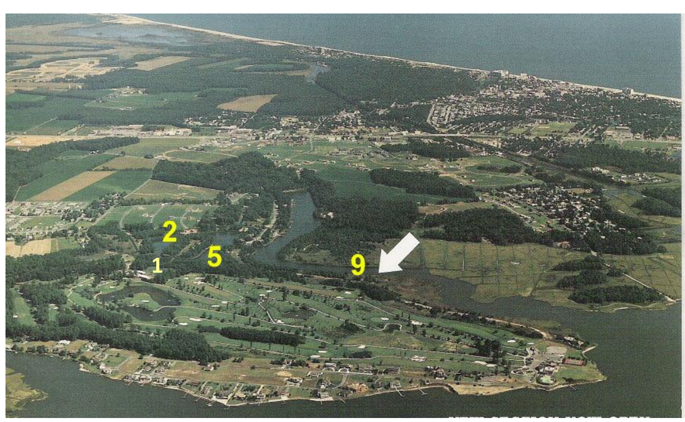
Diatoms 300-500 σ_{PSII}

HABS > 550-600 σ_{PSII}

(A^{o2} **quanta**$^{-1}$**)**

Funding sources

Torquay Canal/Bald Eagle Creek Sites



Torquay canal control sites = 1, 5

Torquay canal major hole = 2 (enclosed)

Bald Eagle Creek major hole = 9 (more open)

Torquay Canal DE – July 10, 2000 benthic processes at the worst?

Close-up

End of canal

2 m normal depth with
H_2S holes of 5 m deep

Electrodes on wire
for *in-situ* work

Menhaden - *Brevoortia tyrannus*

Feed on algae including HAB (harmful algal bloom) algae and are a bait fish for the recreational and commercial fishing industries

They are a major part of the trophic transfer in the western Atlantic Ocean and have been overfished –
now we also kill them with man made canals and holes containing H_2S and low O_2

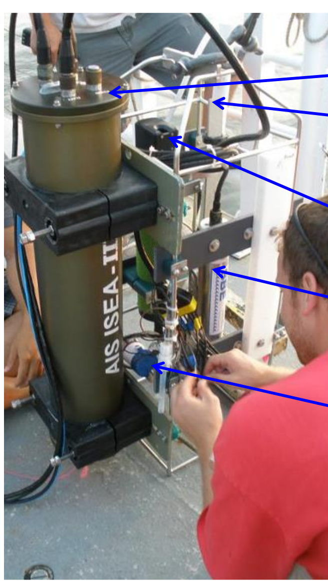
Other anoxic areas ARE present in our Inland Bays and elsewhere in the U.S.

These are ZONES OF DEATH for many organisms

Luther et al, 2004, *Estuaries*; Ma et al., 2006 *Aquat. Microbiol. Ecol.*

Blue crabs stressed: due to small amounts of O_2 in the surface waters along with H_2S

Sensor Package



ISEA ([O_2], [H_2S])

PAR (light, Photosynthetically active radiation**)**

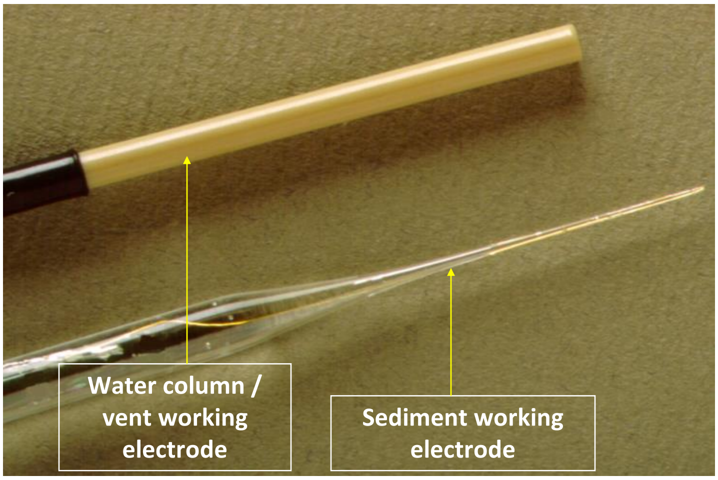
FIRe (F_v/F_m, σ_{PSII})

CTD (sal., temp., depth)

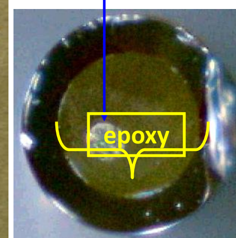
Pump (water collection) or to sensors in flow cells

- *e.g.*, SUNA ([NO_3])

PEEK & Glass encased electrodes in marine epoxy



100 µm diameter Au wire



Sanded, polished & plated with Hg film

O_2, Fe^{2+}, Mn^{2+}, H_2S, H_2O_2, I^-, S_x^{2-}, $S_2O_3^{2-}$, FeS_{aq}, Fe(III) are all measurable in one scan, if present

Tested to 5 000 m and 120 °C

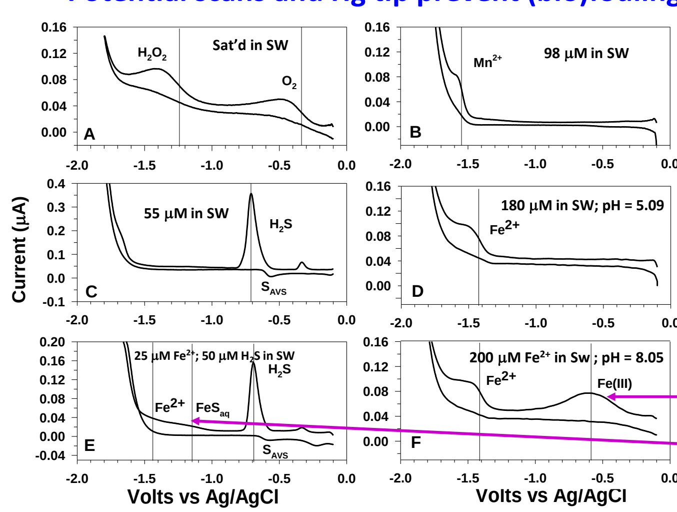
Brendel and Luther, 1995, *ES&T*

VOLTAMMETRY or I (current) vs E (voltage) plots

[similar to A vs λ or counts vs. Energy plots]

Vertical lines indicate the half-wave potential for the reduction of each analyte at the Au/Hg electrode

Potential scans and Hg tip prevent (bio)fouling



Detection limits:
3 µM for O_2
5 µM Mn^{2+}
10 µM Fe^{2+}
0.1 µM H_2S

Multi-analyte sensor

No standards for Fe(III) and FeS

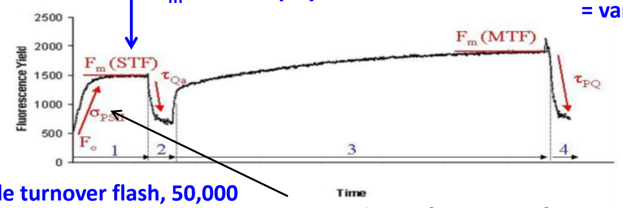
Luther et al 2008 Mar. Chem.

Variable Fluorescence method

F_m = chlorophyll-*a*

$F_v = F_m - F_0$
= variable fluorescence

F_v / F_m

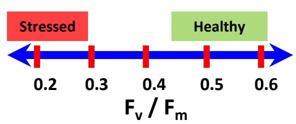


STF = single turnover flash, 50,000 μmol photons m^{-2} s^{-1} for 100 μs

σ_{PSII} = slope of transition from F_0 to F_m

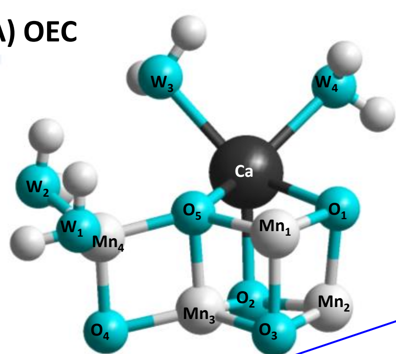
F_v/F_m of the photosystem center II (PSII): an indicator of how efficient a photosynthetic organism can utilize light energy to fix CO_2 and produce O_2

F_v/F_m affected by light intensity, water column stability, nutrient conc., & toxins, with lower values of F_v/F_m indicating organism stress.



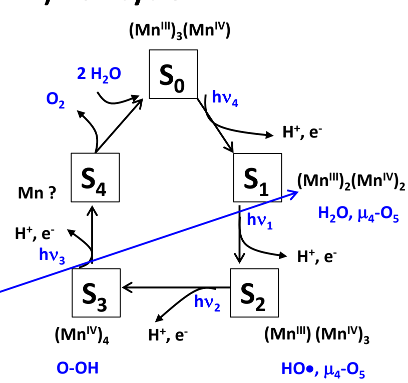
Diatoms 300-500 σ_{PSII}
HABS > 550-600 σ_{PSII} (A^{o2} quanta^{-1})

A) OEC



W = O atom from water

B) Kok cycle



S_1 is the native dark state. After 3 single flashes O_2 is produced. At S_3, O-O bond formation occurs, and this is where the efficiency is critical

If H_2S gets to the oxygen evolving centre (OEC) of photosystem II (PSII), then Mn(III,IV) can be reduced. More light is then needed to maintain Mn(III,IV) resulting in inefficient O-O bond formation (more H^+ and e^- needed) and thus stress.

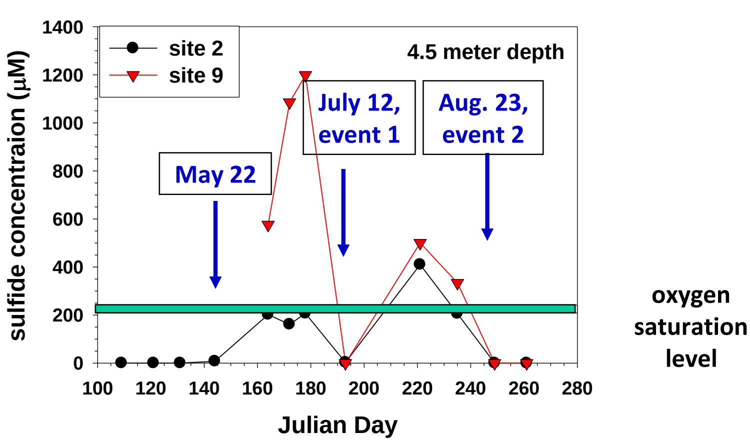
Solarbee circulator at Torquay Canal hole site #2

Sampling near the circulator –

0, 4, 8, 12 m samplings

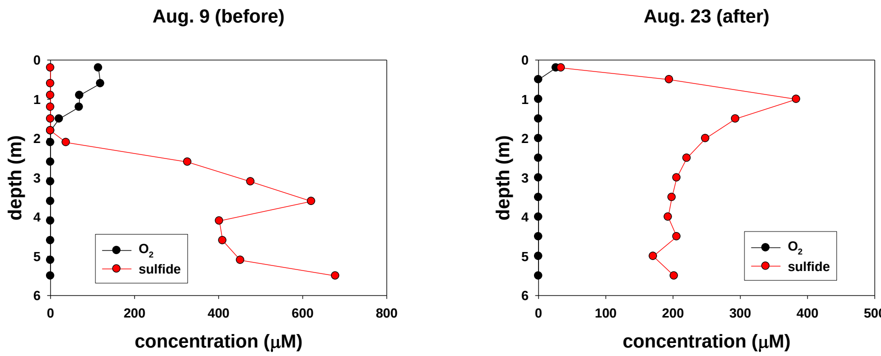
Interface disrupted with storm events

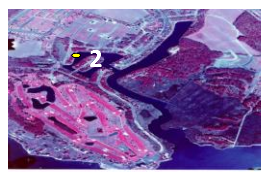
Sulfide change with season in waters at 4.5 m depth



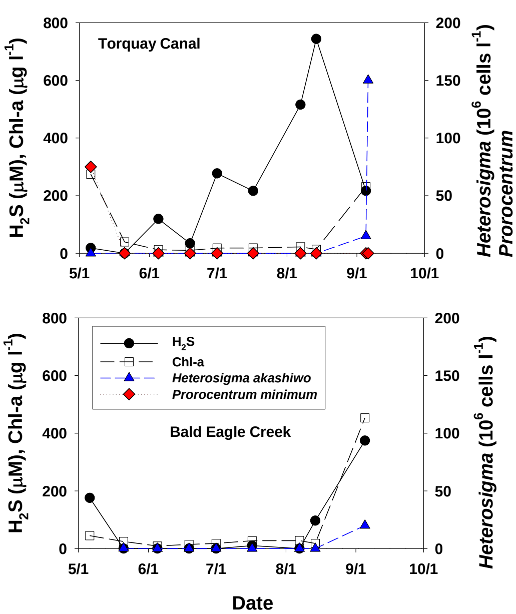
Sulfide levels are among the highest reported in anoxic basins

Site 2 Tourquay canal (Hole) – before and after storm event of another year





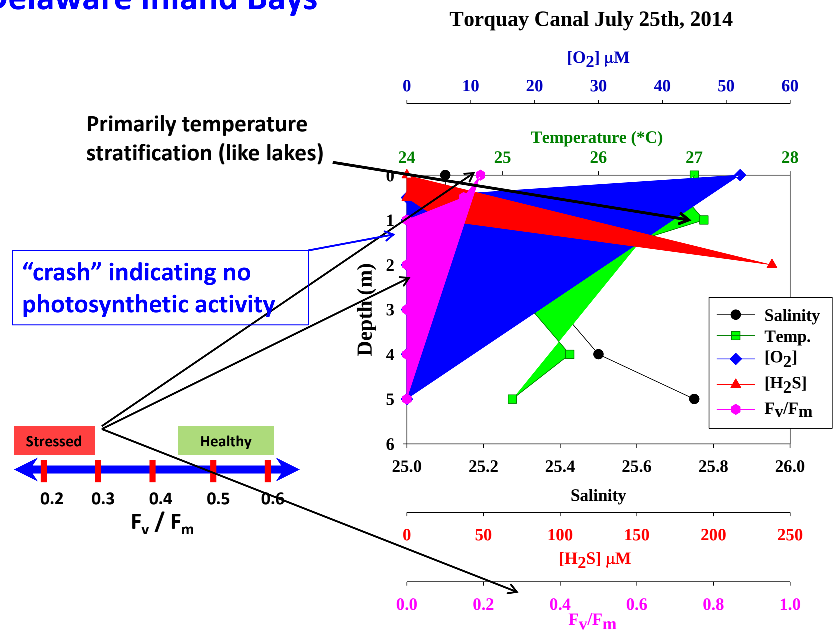
Increase of HABs over time



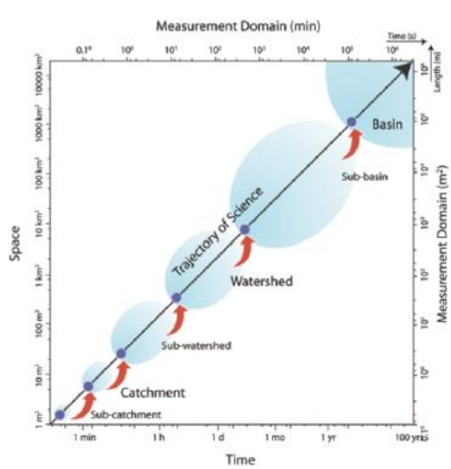
Enclosed canal; $[H_2S]$ buildup

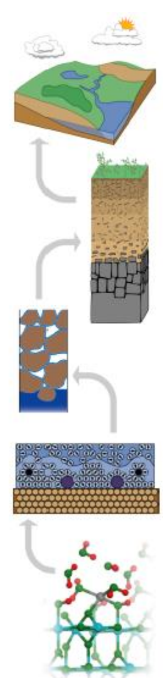
Waterway to canal; $[H_2S]$ buildup due to more exposure to winds

Delaware Inland Bays



Temporal series





Dynamic sensor for mercury speciation

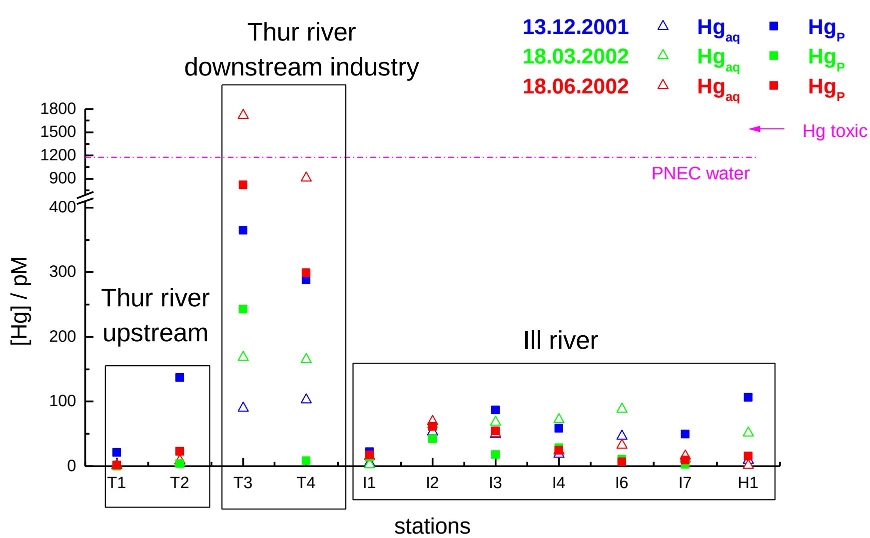
OBJECTIVES

Identifying and quantifying sources, fate and impact or toxic chemical at trace levels (European Water Framework directive):

Case of mercury

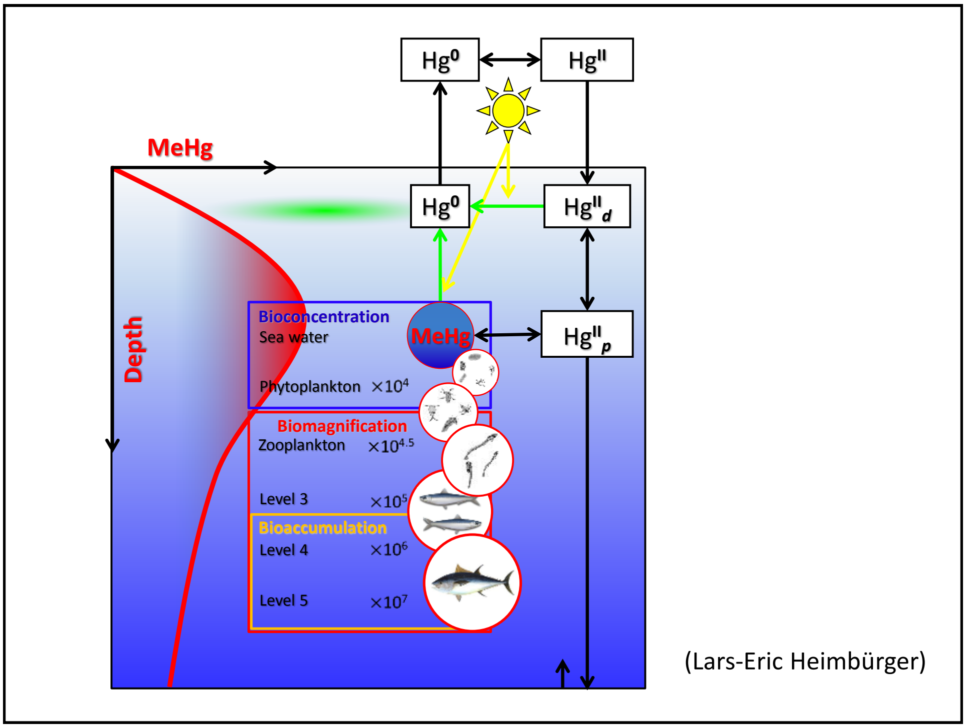
Identification of contamination sources and understanding the physico-chemical behavior of the different species (mechanisms of transport and transfer at interfaces, dynamic speciation in the water-sediment-soil system)

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

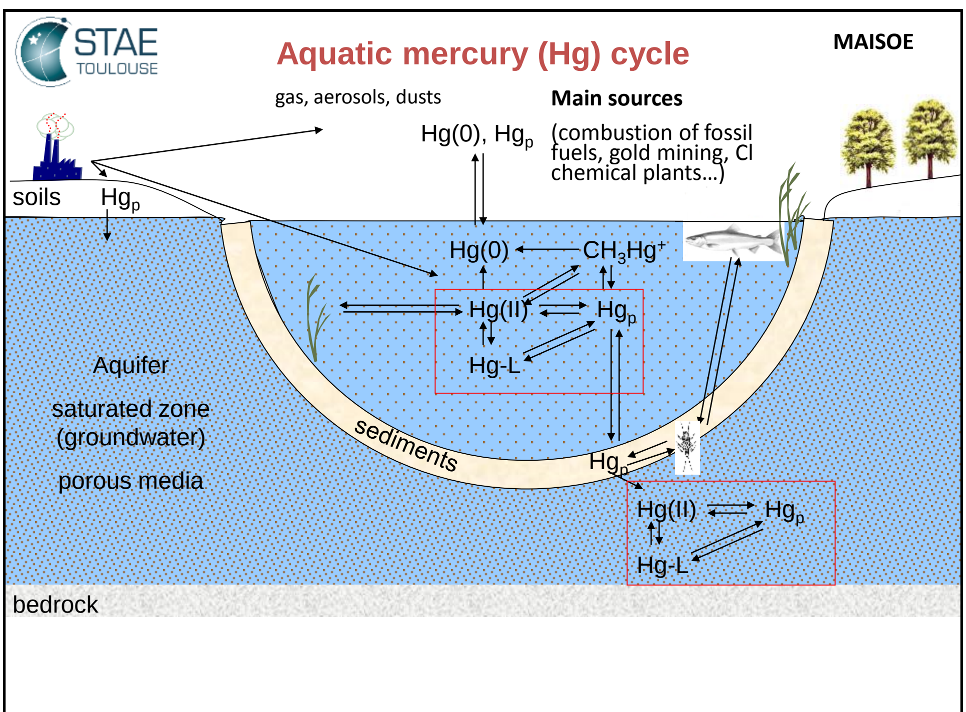


Hg transported either in the dissolved (0.8 pM - 1.7 nM) or particulate phases (0.1 - 819 pM)

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



Hg0
HgII
MeHg
Hg0
HgII d
Depth
Bioconcentration
Sea water
MeHg
HgII p
Phytoplankton ×10^4
Biomagnification
Zooplankton ×10^4.5
Level 3 ×10^5
Bioaccumulation
Level 4 ×10^6
Level 5 ×10^7
(Lars-Eric Heimbürger)



STAE
TOULOUSE
Aquatic mercury (Hg) cycle
MAISOE
gas, aerosols, dusts
Main sources
(combustion of fossil fuels, gold mining, Cl chemical plants...)
Hg(0), Hgp
soils
Hgp
Hg(0)
CH3Hg+
Hg(II)
Hgp
Hg-L
Aquifer
saturated zone (groundwater)
porous media
sediments
Hgp
Hg(II)
Hgp
Hg-L
bedrock

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

$\equiv SOH_2^+$

$\equiv SOH$

$\equiv SO^-$

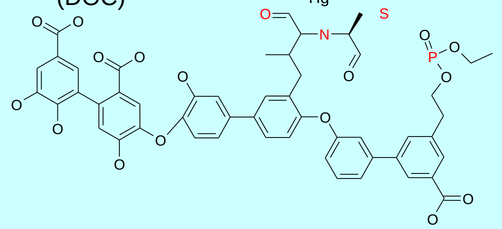
$\equiv S-L^{(y-1)-}$

$\equiv SO-Hg^+$

$\equiv S-OHg-L^{(1-y)+}$

$\equiv S-L-Hg^{(1-y)+}$

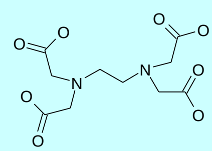
dissolved organic carbon (DOC)

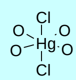


PO_4^{3-} CO_3^{2-}

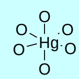
NO_3^- SO_4^{2-}

Cl^-

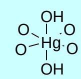




$HgCl_2$



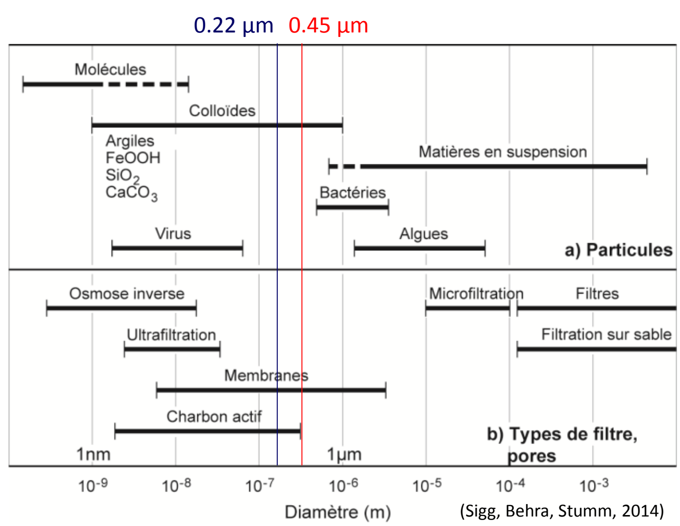
Hg^{2+}



$HgOH_2$

DDL **Aqueous phase**

What is the borderline between solid and liquid phases?



(Sigg, Behra, Stumm, 2014)

Spectrum of particle size in natural waters

Dynamic sensor for mercury speciation

Strategy: Implemented approach

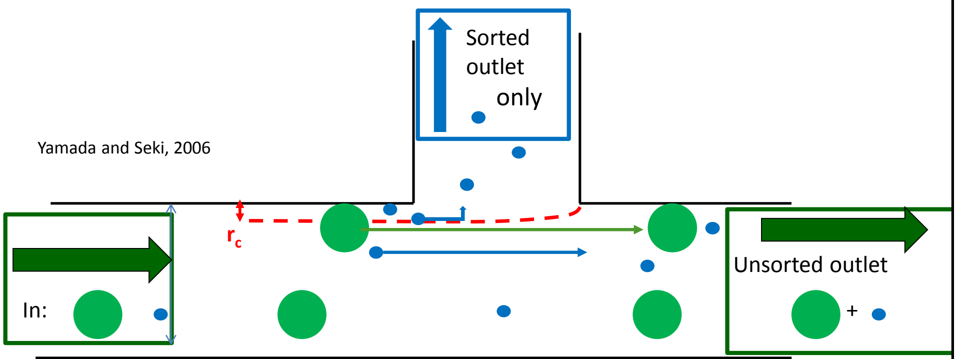
- **Fractionation of particulate phases (> 0,22 or 0,45 µm) and "dissolved" phase:** microfluidic
- **"Dissolved" phase (≤ 0,22 or 0,45 µm):** fractionation of colloids and "dissolved" phase strictly speaking (microfluidic)
- **"Dissolved" phase strictly speaking:** species separation (microfluidic)
- **Hg detection** by electrochemical method
- Development of a **microelectrode**
- Development of materials **against fouling** (biofilms), **corrosion**, interferences (transversal axis)…

Outline

Microfluidic Fractionation:

Preparation of the sample before detection

Approach: **hydrodynamic filtration**

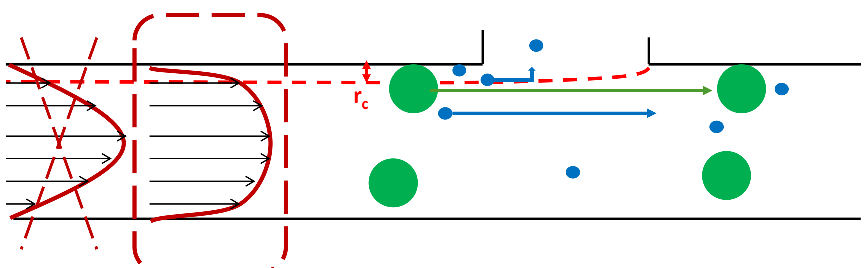


- Separation induced by: sterical exclusion
- Separation criterion: size in laminar flow
  [tool = hydrodynamic resistance]
- Advantage: robustness (r_c depends ONLY on the branching geometry)

Mader *et al.*, 2016. *Lab Chip* **16**, 720

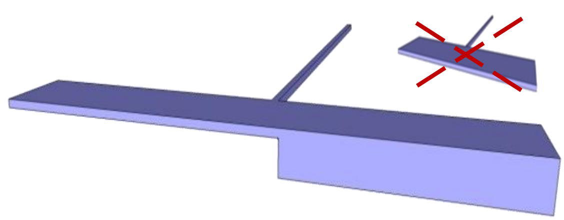
Hydrodynamic filtration: our contribution

(1) Rigorous analysis: real shape of the inlet velocity profile

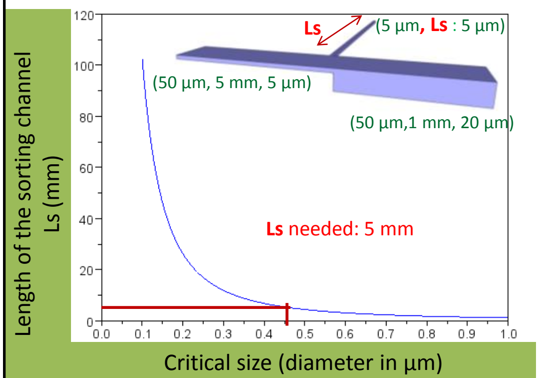


(2) Design trick : 2 levels devices

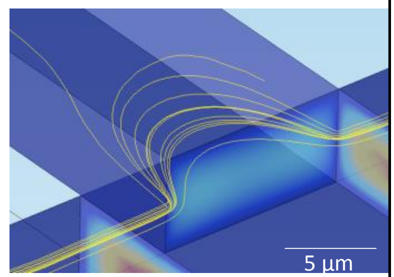
→Dramatical shortening
of the branches [$R_{hydro} \sim h^3$]



Exact model: design



Real shape at intersection



Simulation (Comsol)
→ Good agreement for $\mathbf{r_c}$

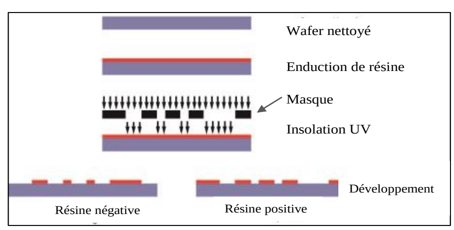
A 5 µm deep, 1 cm long channel can sort 0.45 µm particles in a few minutes

Orders of Magnitude:
- Pressure: 1 bar - Inlet velocity ~cm/s
- Velocity in sorting channel: ~10 µm/s
  →residence time ~ 10 min

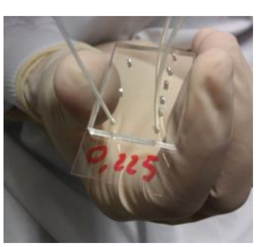
Prototyping and fabrication

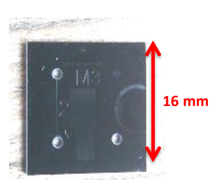
Clean room microtechnology (Photolithography, soft lithography)

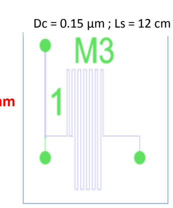
LAAS technological platform
[Renatech national program]



Polymers or silicon/glass devices





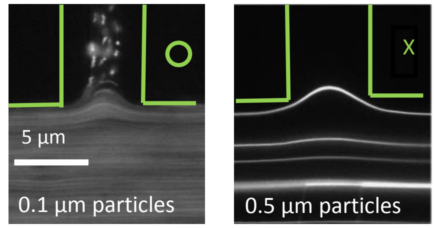


~ 20 devices for each fabrication run
Sorting sizes D_c 0.1 – 1 µm

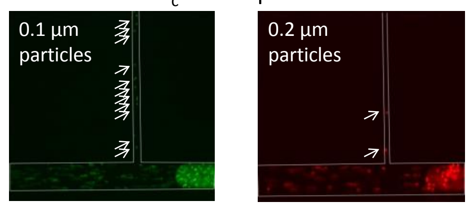
Experimental results

Setup

Sorting size $D_c = 0.32$ µm

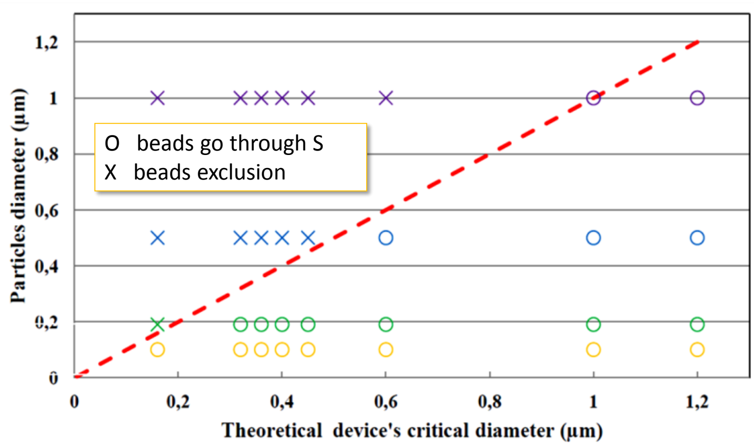


Simultaneous test: mixture of beads
$D_c = 0.15$ µm



- Fluorescent microbeads
- Pressure controled
- Test ≠ couples bead/sorting size

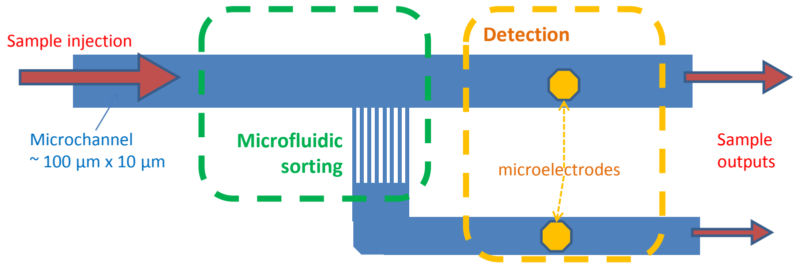
Experimental results: summary



Achievement: exclude particles > 200 nm
Good agreement prediction/experiment

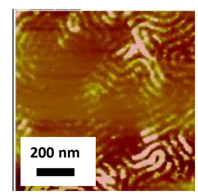
Perspectives

➢ **Integrate**: sorting + detection + antifouling treatment



➢ **Improve efficiency**: multi-outputs, hydrodynamic focusing

Technological route:
Nanochannels by self-assembly of bloc-copolymers



Environmental challenges

Bio-fouling

Trial in Southampton docks 2002

19. August (3 days) | 20. Sept. (35 days) | 25. Nov. (101 days)

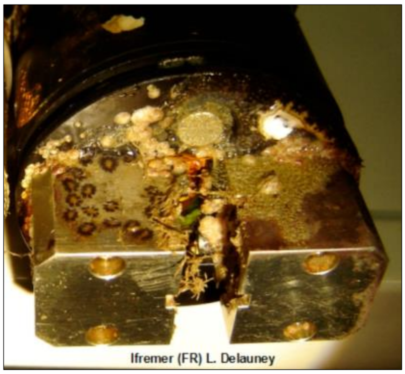
Oceanographic in situ sensors: Challenges and opportunities for nutrient analysis

Environmental Sensors Conference - Biarritz

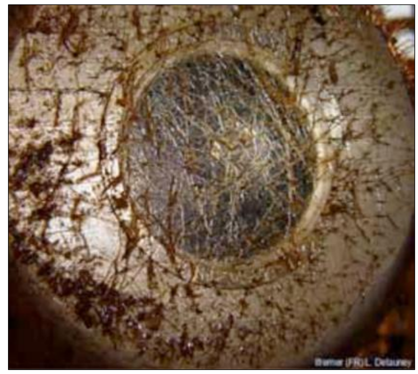
Environmental challenges

Bio-fouling

30 days Helgoland



40 days Trondheim



Photos: Laurent Delauney, Ifremer

From: Delauney et al., Biofouling protection for marine environmental sensors Ocean Sci., 6, 503-511, 2010. www.ocean-sci.net/6/503/2010

STAE TOULOUSE

fermat

Architectured coatings for the protection of immersed sensors in aqueous environments

superficial inlandwaters

MAISOE Project

PROCAPEN Project

Ana-Maria Lazar[1], Diane Samelor[2], Olivier Debieu[2], Elisabeth Leclerc[3], Aurélie Villeneuve[3], Claire Tendero[2], Constantin Vahlas[2]

[1]Fondation RTRA-STAE, [2]CIRIMAT, [3]ANDRA

112

Context

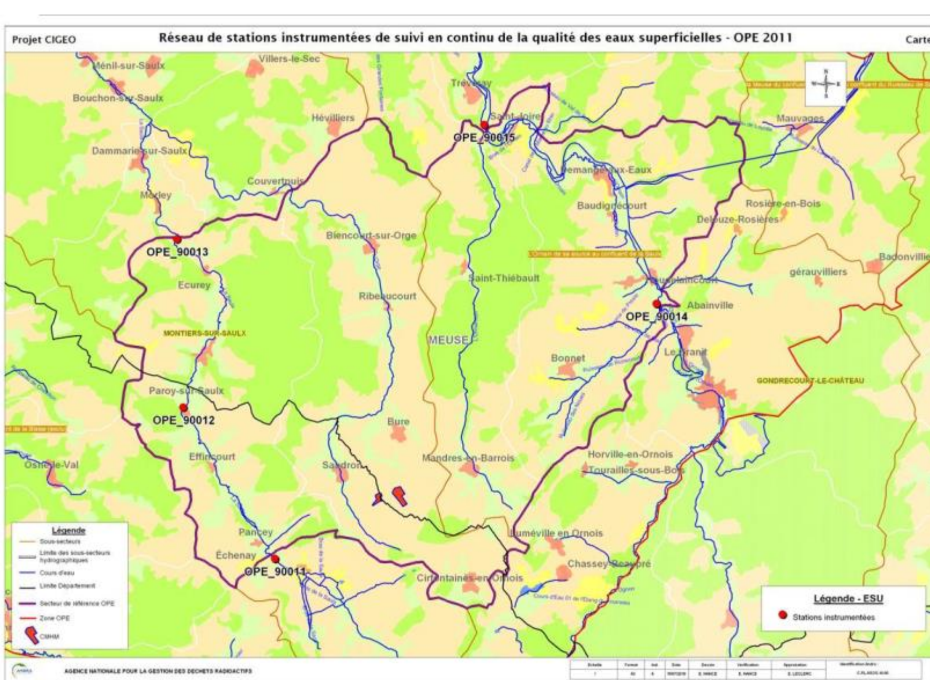
ANDRA → CIGEO project: future storage area for nuclear waste in Meuse

OPE: *Observatoire pérenne de l'environnement*
5 stations: Saulx, Orge, Ornain and Ormançon rivers

Goal: Characterization of the initial stage of the storage area and monitoring its evolution.

→ Monitoring of significant indicators for the evaluation of the quality of superficial continental waters (nitrates, phosphates, HAP, metals, pesticides…)

113

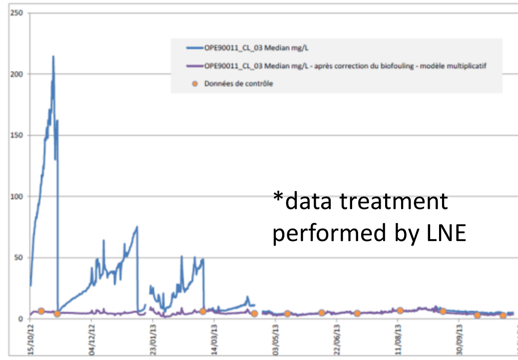


Context

Need in environmental immersed continuous sensors

Results from one-year immersion (collaboration with LNE, Paris)

Main issue: Biofouling
→ Instrumental deviation
→ Complex data post treatment - validity of measurements?



*data treatment performed by LNE

How is the antifouling issue managed?
mechanical cleaning + compressed air + human intervention (each week)

115

Context

Need
Slow down the biofouling to decrease the instrumental deviation as well as human intervention frequency

PROCAPEN project

BBE/Algae-Torch sensor to measure the chlorophyll and cyanobacteria amounts by fluorescence

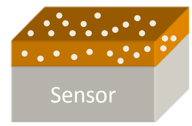
Wavelength of interest in the visible range
7 exciting LED: 470, 525, 610 nm
Detection in red: 680 nm

116

Context

Spec
- Protection of the active part of the BBE/Algae-Torch sensor.
- No interaction with the environment
- No interference with the measurement method

Multi-material solution
- Composite coatings : metallic NPs dispersion in a transparent matrix
- NPs : biocide effect
- matrix: NPs stabilization



Selection of materials conditioned by our know-how and specs: antifouling + transparent at 470, 525, 610, 680 nm

117

Context

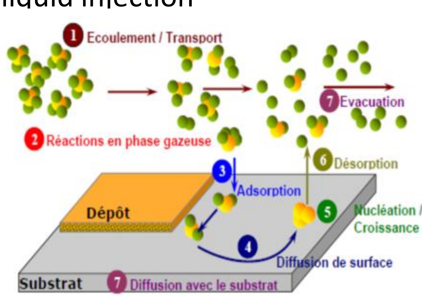
Know-how at the beginning of the project

☺ MOCVD technique

Chemical Vapor Deposition from organo-metallic precursors

Thermal activation

Precursor transport: sublimation, bubbling, liquid injection

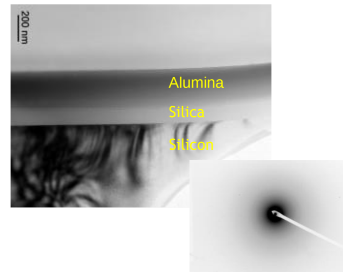


118

Context

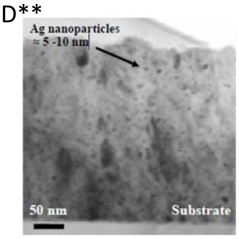
Know-how at the beginning of the project

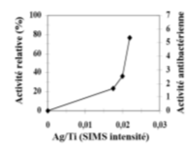
☺ Amorphous alumina on TA6V
Protection against corrosion
Aluminum precursor: $Al(O\text{-}i\text{-}Pr)_3$
$T_{deposition}$: 350°C – 650°C



☺ Biocide coatings
Ag NPs dispersion in titanium by DLI-MOCVD**

Silver precursor: (C_4H_9COOAg)
$T_{deposition}$: 350°C – 450°C





Norme JIS Z 2801
S. aureus

** Magda SOVAR, "Du tri-isopropoxyde aux oxydes d'aluminium par dépôt chimique en phase vapeur : procédé, composition et propriétés des revêtements obtenus", Thèse INPT, 2006*

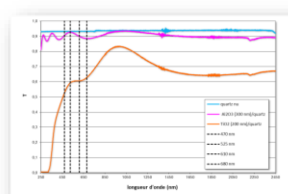
*** Jitti MUNGKALASIRI, "Elaboration par DLI-MOCVD de dépôts nanocomposités TiO2-M (M=Ag,Cu) et propriétés antibactériennes de ces surfaces solides", Thèse INPT/CEA, 2009*

119

Context

Spec

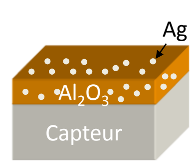
- Protection of the active part of the BBE/Algae-Torch sensor
- No interaction with the environment
- No interference with the measurement method



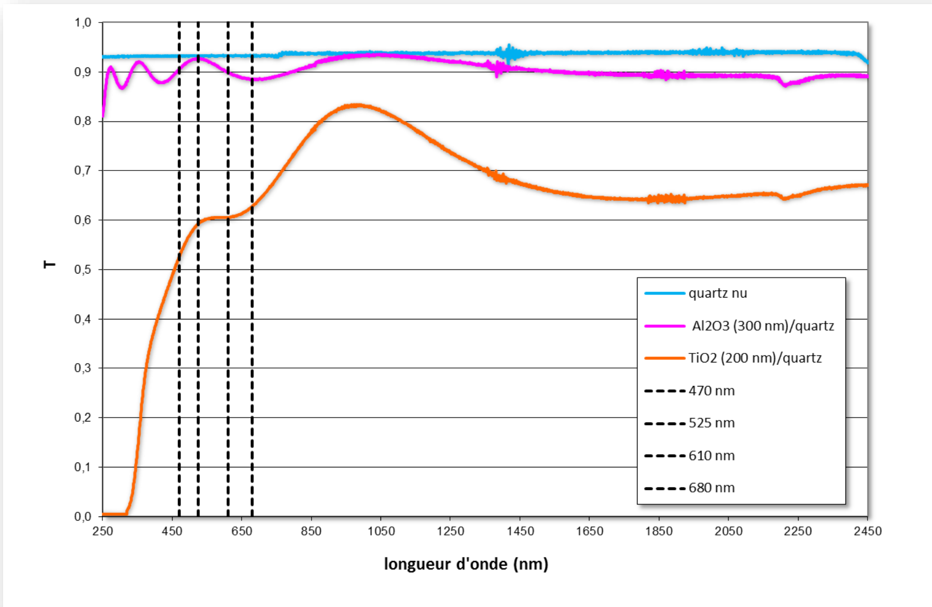
Multi-material solution

- Composite coatings: metallic NPs dispersion in a transparent matrix
- NPs: biocide effect
- matrix: NPs stabilization

Selection of materials conditioned by our know-how and specs: antifouling + transparent at 470, 525, 610, 680 nm



120



121

Approach

Steps

Elaboration of architectured coatings alumina / Ag NPs :
- Process control
- Structural characterizations

Functional properties:
- Optical
- Anti-biofouling

Challenges

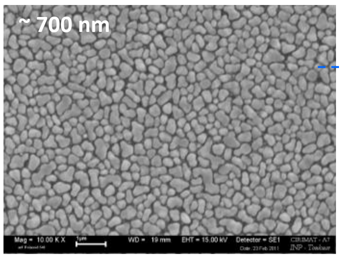
- Control of AgNPs
- Co-deposition alumina-AgNPs
- Control of architecture
- Coating integrity

- Complex environment
- Procedure
- Results interpretation
- Coating efficiency

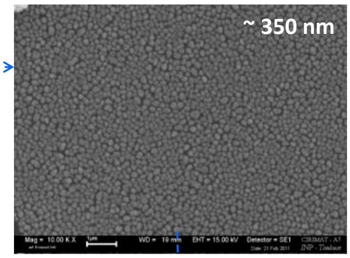
Results

Elaboration of the architectured coatings

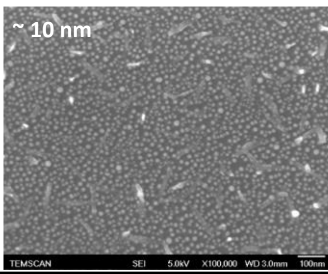
Control of injection parameters→ Control of AgNPs deposition



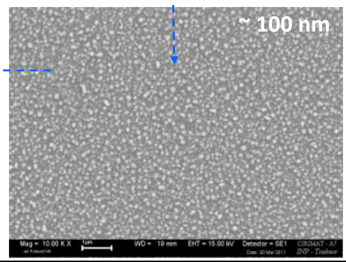
F = 3 Hz
TO = 20 ms
t = 20 min



F = 3 Hz
TO = 100 ms
t = 4.5 min



F = 1 Hz
TO = 10 ms
t = 5 min

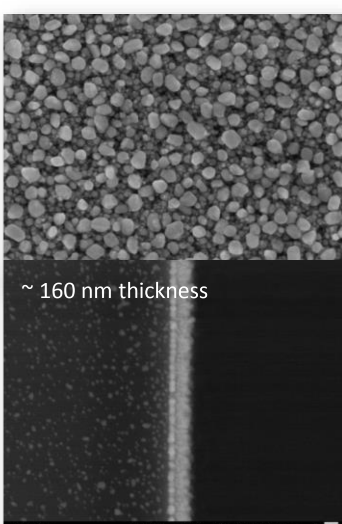


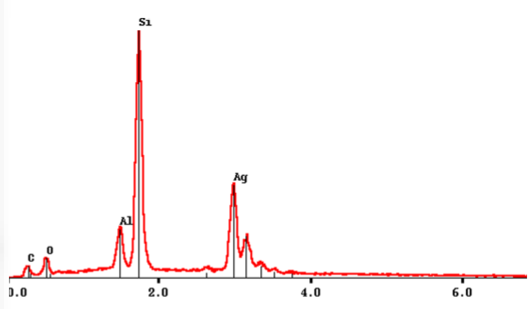
F = 1 Hz
TO = 10 ms
t = 30 min

Results

Elaboration of the architecture coatings

Co-deposition : 1 + 1 ≠ 2 !!!!





Operating conditions

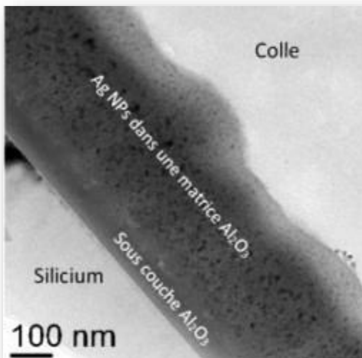
- $T_{co\text{-}deposition} = 450\ ^{\circ}C$
- t = 60 min
- $X_{Al2O3} / X_{Ag} = 11$

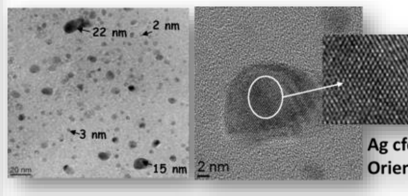
LISBP

Results

Elaboration of the architecture coatings

AgNPs dispersed in an amorphous alumina matrix



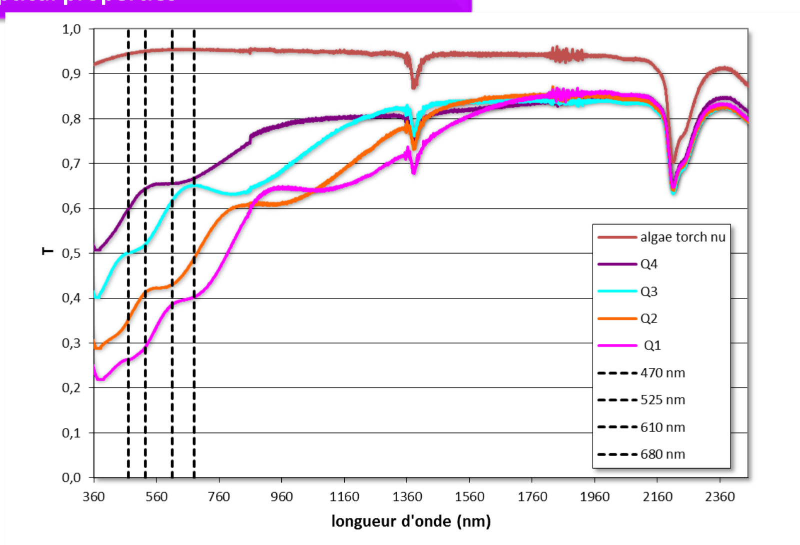


Ag cfc
Orientations [111]

LISBP

Results

Optical properties

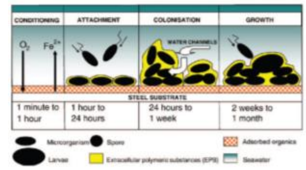


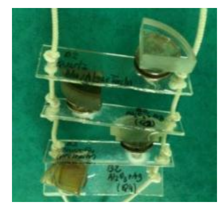
Results

Anti-fouling properties

Tests in natural environment:

☑ Reproducibility, control sample, procedure

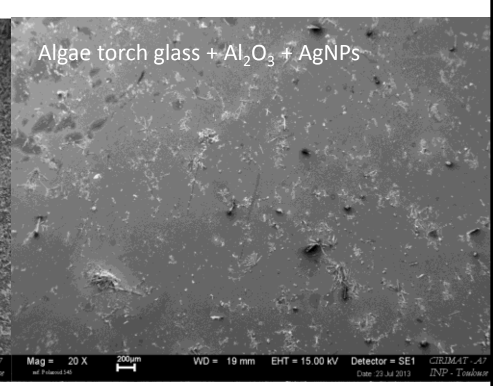




127

Results

Anti-fouling properties



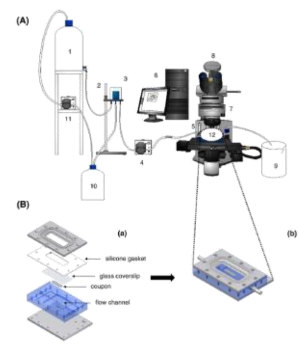
1 week immersion in the Meuse river

128

Further works

Understanding the influence of the substrate surface on the first steps of biofilm growth

- Adhesion of bacteria: shear stress flow chamber, optical tweezers, AFM, zetametry
- Matrix screening – functionalization with enzymes
- Complementary approaches: model environment + natural environment
- *Biocide effect of NPs + durability*



LISBP

Collaboration with LISBP: M. Castelain, P. Schmitz, D. Combes

129

Problems and needs due to sensor proliferation

Needs due to the **management of sensor networks** in order to overcome the very big data bases

Needs in **new algorithms artificial intelligence** for decision support, combining:

local measurement
and measurements at larger scales,
in time and space (example weather forecast)

in order to adjust, in real time, manufacturing processes or pollutant emissions

Needs of sensors at **very low cost**

Needs for Environmental Monitoring

Requirement of environmental monitoring for protecting the public and the environment from toxic contaminants and pathogens released possibly into a variety of media including air, soil, and water

Air pollutants: SO_2, CO, NO_2, and VOCs (volatile organic compounds), originated from sources such as vehicle emissions, power plants, refineries, and industrial and laboratory processes

Soil and water contaminants: microbiological (*e.g.*, coliform), radioactive (*e.g.*, tritium), inorganic (*e.g.*, arsenic), synthetic organic or xenobiotics (*e.g.*, pesticides), and VOCs (*e.g.*, benzene)

Application of pesticides and herbicides directly to plants and soils, and incidental releases of other contaminants from spills, leaking pipes, underground storage tanks, waste dumps, and waste repositories

Possible persistence of some of these contaminants for many years and migration through large regions of soil until reaching water resources, where present an ecological or human-health threat

Needs for Environmental Monitoring

Emerging sensor technologies being first evaluated and then used to monitor environmental contaminants, particularly for long-term environmental stewardship

Focus to four categories of contaminants:
- Metals
- Radioisotopes
- Volatile organic compounds
- Biological contaminants

For each contaminant, looking for portable sensors providing rapid responses (relative to current methods and technologies), ease of operation (for field use), and sufficient detection limits

Needs for Environmental Monitoring

Due to regulatory requirements, standards and policies

For drinking water: In Europe (European Framework Directive), in USA (National Primary Drinking Water Regulations) applied to public water systems and legally enforceable standards

Aims of these primary standards: intended to protect public health by limiting the levels of contaminants being found in drinking water, although applicable to public water systems (*i.e.*, at the tap), and often applied by remediation regulators in the aquifer (*i.e.*, at the monitoring wellhead)

See: European Official Journal for the European Framework Directive, and US Environmental Protection Agency for data

Needs for Environmental Monitoring

Due to regulatory requirements, standards and policies

Storm water monitoring

National pretreatment program monitoring

Ambient air quality

Sensor technologies for environmental monitoring

The purpose of this part: identifying and describing sensor technologies being applicable to monitoring various contaminants described previously

Classification of technologies according to analyte, including trace metals, radioisotopes, VOCs, and biological pathogens

Brief description of the sensor technologies followed by tables summarizing features and specifications (*e.g.*, sensitivity, size, speed, etc.) of each sensor technology

Sensor technologies for environmental monitoring

Trace metal sensors

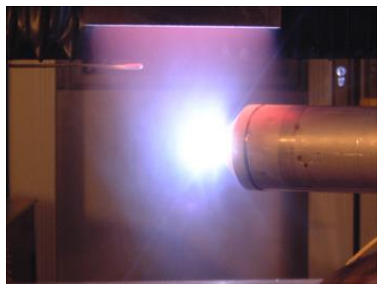
Nanoelectrode arrays fabricated to identify and quantify dissolved metals

- Signals from the electrodes obtained by monitoring current and voltage during application of an electrical potential
- Around 1 million individual electrodes placed on 1 cm^2 substrate using electron-beam lithography or chemical vapor deposition
- Sensing electrode integration with the reference electrode, eliminating need for buffers and permitting noncontaminating sensing in ultra-pure water
- Coupling the small electrode size with a very high density producing a signal with up to 103 times better signal-to-noise ratio than standard electrodes
- Using multiple electrodes, coatings, and electrochemical techniques, target analytes including toxic industrial chemicals and metals, such as trichloroethylene, As, Pb, Cr, Hg…

Sensor technologies for environmental monitoring

Laser-induced breakdown spectroscopy (LIBS)

- Use a laser to rapidly heat a very small area (usually solid or liquid), generating a plasma from the atomic constituents present at the focal point
- Radiative relaxation of the plasma then observed using sensitive spectroscopic instrumentation
- LIBS being also known as Laser Spark Spectroscopy (LASS)



Stand-off LIBS probe head
Laser ablation energy and spectroscopic collection occurring through fiber optics

Sensor technologies for environmental monitoring

Laser-induced breakdown spectroscopy (LIBS)

- Use of LIBS for rapid analysis of hazardous metals and other inorganic contaminants in water, soil, and mixed waste sites
- Use to detect almost all elements, though certain metals exhibit orders of magnitude greater emission
- Detection limits: function of each specific metal, and the spectroscopic and detector hardware
- Typical low trace levels for As, Be, Hg, Se, Pb, Cd, Cu, Zn, Ag, Cr, Fe, and Mn
- Extension of LIBS to biodetection by looking for rapid, temporal increases in the presence and/or ratios of Ca, Na, K

Sensor technologies for environmental monitoring

Radioisotope sensors

- RadFET (Radiation field-effect transistor): concept for measuring gamma radiation dose has been around for many years
- Cadmium zinc telluride (CZT) detectors: semiconductor gamma and neutron radiation detectors, producing current flow under the influence of a gate voltage, upon exposure to high energy radiation
- Low-energy pin diodes beta spectrometer
- Thermoluminescent dosimeter (TLD)
- Isotope identification gamma detector
- Neutron generator for nuclear material detection

Summary of specifications for **trace metal** sensors

Sensor Technology	Specifications							
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost
A) Nanoelectrode Array	low ppb	elemental in non-complex mixtures	long-term	seconds	1 square inch dip probe		personal computer	sensor:
B) Laser-Induced Breakdown Spectroscopy	low ppb	elemental	long-term	ms with intensified-CCD, minutes with scanning spectrometers or signal averaging	fiber-optics; lengths of 100+ meters possible	mW per pulse	personal computer	system: $50-150K

CCD: charge coupled device

Summary of specifications for **radioisotope** sensors

Sensor Technology	Specifications							
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost
A) RadFET	5 mV/rad	speciation with filters	> 1 year, 5% drift over 1000 hours after strong exposure	milliseconds, or cumulative expose can be read later	¼" with ASIC and dip	passive or mW bias	sensitive digital multimeter	< $1 in volume
B) Cadmium Zinc Telluride detectors (CZT)	0.8 mV/keV	very selective with spectroscopy	long-term	microseconds	3 mm^2 plus electronics	< 1 Watt	hand held or personal computer	$3000+ for system
C) Low-energy Pin Diodes Beta Spectrometer	single events > 1.4 keV. Above background noise, LOD is 0.1 disintegrations/cm^2/sec (3 rem/year)	very selective	long-term	20 ms	sensor: 13 mm^2, plus electronics	passive or mW bias	hand held or personal computer	$1000+ for photodiode
D) Thermoluminescent Dosimeter (TLD)	1 micro-rad/hour	non-specific to radiation source, but can employ filters or different crystal thicknesses and types	long-term	cumulative dose; nanoseconds per event	5 mm^2	passive	TLD Reader	low dollars for crystals; $1000+ for reader
E) Isotope Identification Gamma Detector	very high	very selective	long term	seconds	vehicle portal	110 AC	laptop	
F) Neutron Generator for Nuclear Material Detection	very high	very selective	long term	seconds	1 meter tall	110 AC	laptop	

Summary of specifications for **volatile organic compound (VOC)** sensors

Sensor Technology	Specifications							
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost
A) Fiber Optic Chemical Sensor	low ppm for hydrophobic organics	good selectivity with multivariate analysis in moderately complex environments; coating is non-specific for hydrophobic compounds	weekly calibration	20 minutes	fiber-optics; lengths up to kilometers possible	110 V, 5 amps	laptop	$0.25/meter $2500 for spectrometer
B) Grating Light Reflection Spectro-electrochemistry	ppm to ppb	multivariate analysis required for simple mixtures	long term	seconds to minutes	dip probe	5 Watts	laptop	<$500
C) Miniature Chemical Flow Probe Sensor	low ppb to low ppm, depending on analyte	good selectivity in moderately complex matrix	flow cell and fresh reagents ensure high reproducibility	1-2 minutes	2" probe diameter, up to 150 feet long; spectrometer and PC in 2 suitcases	110 AC when built (1995)	laptop	$10K for total system
D) SAW Chemical Sensor Arrays	ppm to ppb	good with multivariate analysis of mixtures that are not too complex	slow drift over time	tens of seconds	< 1 square inch sensor	mW	laptop or digital display	<$500
E) MicroChemLab (gas phase)	ppb	very good	slow drift over time	1-5 minutes	handheld	< 1 Watt	laptop or digital display	$10-20K
F) Gold Nanoparticle Chemiresistors	ppb	may be tailored to chemical classes	TBD	seconds	< 1 square inch sensor	mW	laptop or digital display	<$100
G) Electrical Impedance of Tethered Lipid Bilayers on Planar Electrodes	ppm to ppb	very high with antibody coatings; lower for non-specific receptors	weeks	minutes	cm^2	mW for sensor; 110 AC for whole instrument	laptop	<$1 per sensor
H) MicroHound	ppb	fairly high	days to weeks	seconds	handheld	battery	laptop or digital display	<$5K
I) Hyperspectral Imaging	ppm to ppb	good with multivariate analysis of mixtures that are not too complex	long term	seconds to minutes	handheld		laptop	$10K to $100K
J) Chemiresistor Arrays	~typically tens to hundreds of ppm; 0.1% of saturated vapor pressure	arrays can discriminate different classes of VOCs	slow drift over time	seconds to minutes, depending on concentration	several mm; package is ~2.5 cm diameter x~6 cm long	mW; battery powered	laptop or computer	<$100 for sensor array; package can be ~$500

SAW: surface acoustic wave; TBD: to be determined

Summary of specifications for **biological** sensors

Sensor Technology	Specifications							
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost
A) Fatty Acid Methyl Esters (FAME) Analyzer	low nanograms	highly selective	SAW sensor can irreversibly load	< 10 min.	handheld	< 5 Watts per analysis	syringe and keypad or laptop	potentially < $10K
B) iDEP (insulator-based dielectrophoresis)	preconcentration method for other sensors	non-selective	expected to be high	milliseconds	millimeters	< 1 W	Is a module for larger systems	< $1
C) Bio-SAW Sensor	picograms of proteins	highly selective	SAW can drift over time; analyte binding can be irreversible	minutes	several square cm	mW	system display plus some liquid handling; laptop	<$100 per sensor
D) µProLab	picograms	expected to be highly selective	acoustic sensors tend to drift with time; optical systems will be more stable	minutes	handheld	< 5 W	minimal fluid handling, system display or laptop	TBD
E) MicroChemLab (Liquid)	depending on analyte: 10-100 ppb for chemicals; sub-toxic (picomoles) for biotoxins	very high	hours	< 5 min	handheld	5 Watts	LCD display or laptop	< $10K

SAW: surface acoustic wave

Summary and comparison of relative requirements for different environmental monitoring applications

Requirements	Drinking Water	Storm Water	Pre-Treatment	Ambient Air
Concentration	Lowest concentrations (ppb to ppm in aqueous phase)	Higher concentrations than drinking water (e.g., arsenic is 160 ppb in storm water for wood preservers while drinking water is 10 ppb)	Concentration are higher than drinking water (e.g., TCE is 69 ppb (daily) compared to 5 ppb for drinking water); almost all biological except for a few industries that manufacture chemicals; INDUSTRY SPECIFIC	Air concentrations are typically in the ppm range
Sampling Frequency	Most frequent sampling of the three water applications (would like real time, continuous monitoring)	Only need to sample occasionally (during rain storms)	More frequent monitoring than for storm water but less than for drinking water	Continuous (current methods average over a period of time using continuous flow)
Sampling Method	On-line, continuous with remote telemetry	Can be hand-held for occasional sampling	On-line or hand-held	Continuous air monitoring with remote telemetry
Sample Phase	Aqueous	Aqueous	Aqueous	Gas

TCE: trichloroethylene

Summary of potential sensor technologies being able to address environmental monitoring needs

Sensor Technology	Application	Analyte	Comments
LIBS	Drinking Water, Storm Water, Pretreatment	Trace Metals	The cost of the laser and spectrometer are high. Additional development needs to bring the price down and package it for use in water applications. Could potentially be used to simultaneously identify 9 RCRA metals plus arsenic. Sampling interval ranges from 1 s to ~1 minute (for signal averaging). Can be run continuously.
Nanoelectrode Array	Drinking Water, Storm Water, Pretreatment	Trace Metals	Less selective than LIBS. Commercial company in Washington. Sampling interval on the order of seconds. Still under development to discern among multiple target analytes present.
Miniature Chemical Flow Probe Sensor	Drinking Water, Storm Water, Pretreatment	VOCs, Trace Metals	Expensive because of spectrometry (like LIBS). Reagents need to be supplied. Need to acquire sample to introduce reagent in a side-stream.
RadFET	Drinking Water	Radioisotopes	Need to use filters to allow speciation. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Low-energy Pin Diodes Beta Spectrometer	Drinking Water	Radioisotopes	Commercially available. May not need any additional development. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Cadmium Zinc Telluride Detectors	Drinking Water	Radioisotopes	Commercially available. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
SAWs	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity can get down to ~ppm, but fluctuations in environmental parameters (e.g., humidity, temperature) can reduce the sensitivity and accuracy. Sensor signal drifts over time. Cannot analyze more than three contaminants at once.
Chemiresistors	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity is limited (hundreds of ppm). Needs preconcentration. These can also be used to monitor in-situ remediation activities (patent pending: SD-7097 Automated Monitoring and Remediation System for Volatile Subsurface Contaminants).
MicroHound/Ion Mobility Spectrometer (IMS)	Drinking Water, Storm Water, Pretreatment, Air	Semi-Volatile Organic Compounds	Gas-phase detection; need to develop a sampling system to introduce water samples to IMS. Should be able to detect semi-volatile chlorinated hydrocarbons (e.g., polychlorinated biphenyls (PCBs)). Can detect pesticides, organic nitrates.
MicroChemLab (gas)	Drinking Water, Storm Water, Pretreatment, Air	VOCs	MCL is manufacturing these for ~$10K per unit. Additional development work is needed to adapt these systems for VOCs.
MicroChemLab (liquid)	Drinking Water	Biological	Cost is high.
FAME	Drinking Water	Biological	Sampling is currently done manually.

LIBS: laser-induced breakdown spectroscopy; RadFET: radiation field-effect transistor;
SAW: surface acoustic wave; FAME: fatty acids methyl esters; RCRA: Resource Conservation and Recovery Act

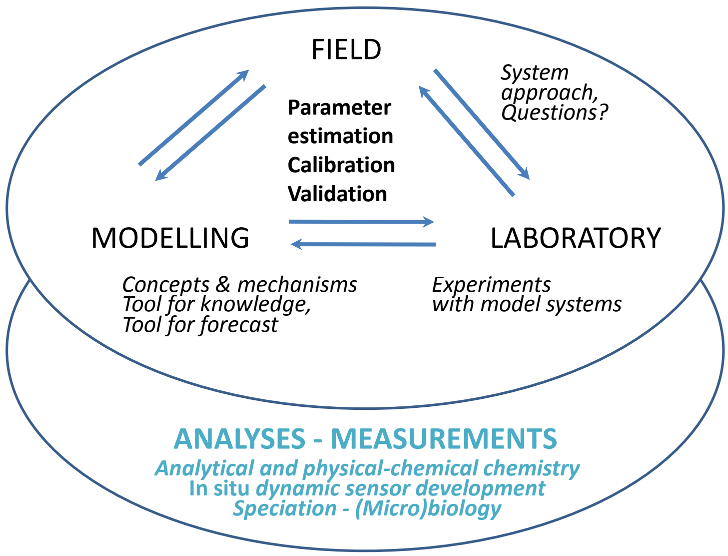
Summary of the most promising technologies for each analyte class that could benefit from further development

Sensor	Analyte	Future Development Required
LIBS	Trace Metals	LIBS systems employ diffraction gratings that must be scanned to cover the spectral range of metal contaminants with sufficient resolution for positive identification and quantification. Speed could be increased through the use of Sandia's programmable diffraction grating. Simultaneous determination could be made through the computer-aided design of holographic diffraction gratings.
CZT	Radioisotopes	These detectors are inexpensive and sensitive to regulated radiation levels. Commercial spectrometer systems are available. A low level effort could adapt the spectrometer for water monitoring. Alpha emitting contaminants in water can not be detected by radiation events as alpha radiation is nonpenetrating.
MicroChemLab, gas phase	VOCs	Due to the wide variety of organic contaminants that can be present in air or water, separation is essential for analysis. The MicroChemLab can be adapted to collect and analyze in both air and water. Leveraging funding could direct development towards specific targets.
MicroHound/Ion Mobility Specrometry	Semi-Volatiles	The ion mobility spectrometer behind this instrument can be used in positive mode for common semi-volatiles or negative mode for highly selective detection of pesticides and halogenated semivolatiles. The diffusion-based separation could benefit from a pre-separation using a chromatography column.
Bio-SAW Sensor	Biological Pathogens	Sensors with bioreceptors are highly selective, providing detection amplification over background contaminants. Still, biofouling can occur. Further development is needed to array significant numbers of sensors into a small area for multi-pathogen monitoring.

LIBS: laser-induced breakdown spectroscopy; CZT: cadmium zinc telluride;
SAW: surface acoustic wave

Chemodynamics of compounds

Methods for studying the critical zone as heterogeneous complex systems: flux study, scaling (in space and time) and inter-disciplinary approach



(from Behra Ph., 2000, book, COST 67, COST, EUR 19248)

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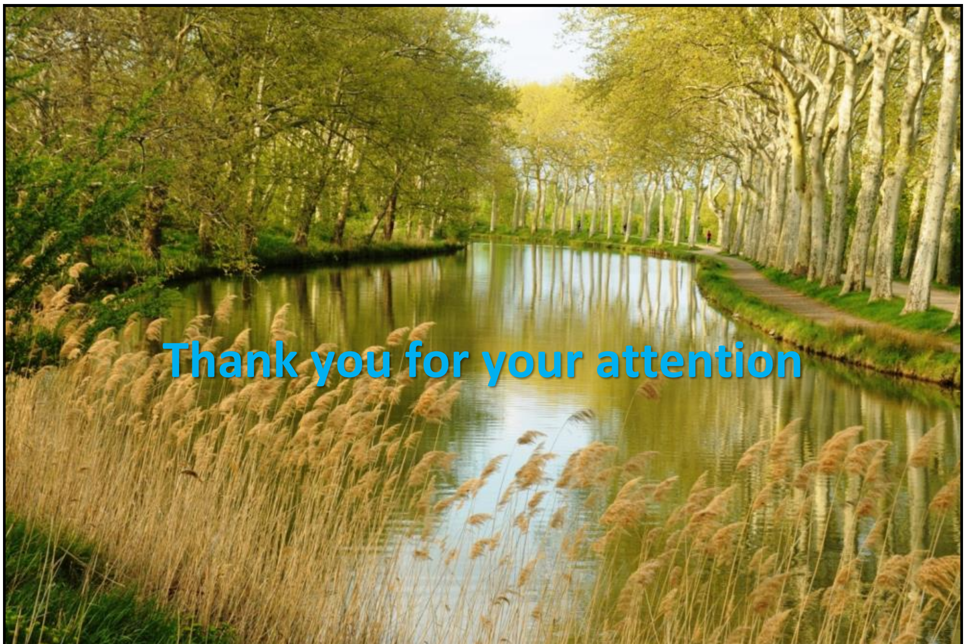
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