INNOVATIVE MODULAR SENSING SYSTEMS FOR AUTONOMOUS IN SITU MONITORING OF TRACE METALS AND (HARMFUL) ALGAE

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University of Geneva - Switzerland

AEI 2019 – 9 to 11 July 2019 - Lille (Polytech Lille) - France

Ocean monitoring and risk assessment

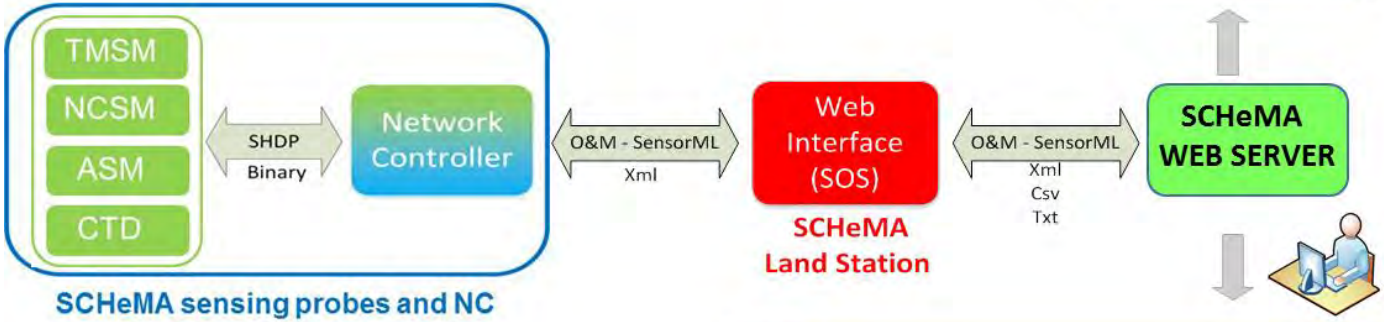
Integrated Multifunctional Autonomous In situ Sensor Observation System

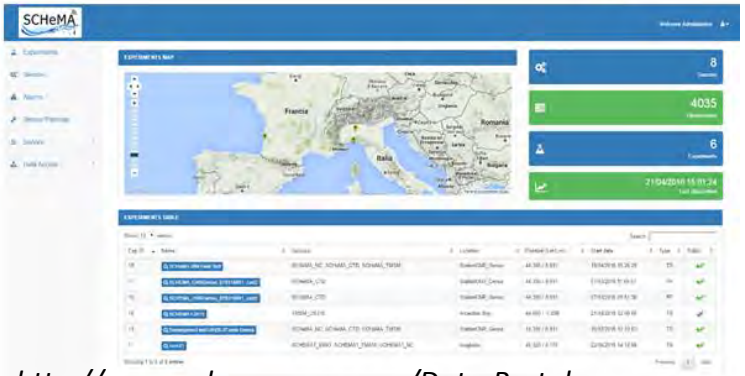
THE OCEAN OF TOMORROW

WEB information system

EMODnet · Copernicus · SeaDataNet · EuroGOOS European Global Ocean Observing System · The Global Ocean Observing System

WEB interfaces for wireless bi-directional interaction



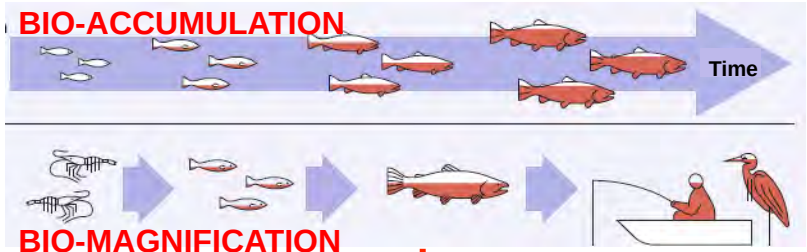


http://www.schema-ocean.eu/Data-Portal

UNIVERSITÉ DE GENÈVE FACULTÉ DES SCIENCES · IDRONAUT S.R.L. ITALY · uulm · TU Graz · EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE · nano myp · université de BORDEAUX · UNIVERSITÀ DEGLI STUDI DI GENOVA · ETT

Target analytes

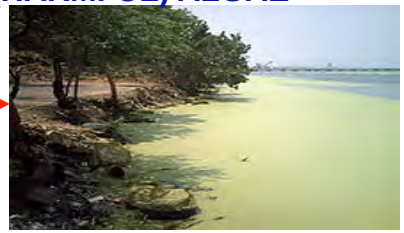
METALS



PHYCOTOXINS

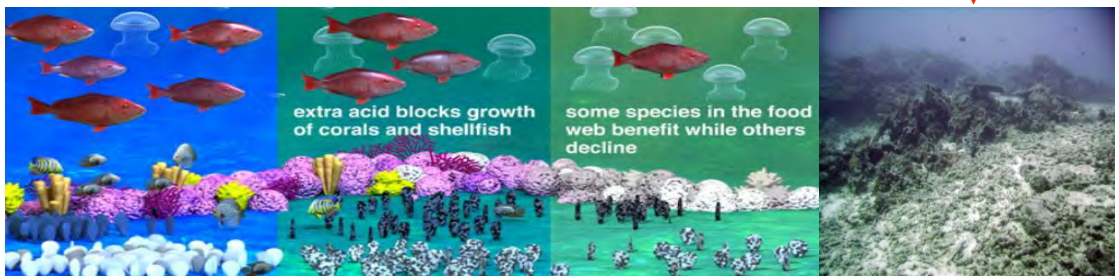
NUTRIENTS
NO_3^-, NO_2^-, Ca)

(HARMFUL) ALGAE



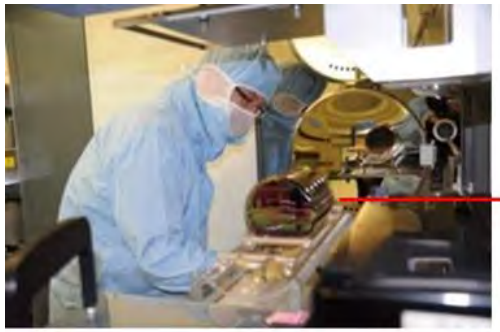
EUTROPHICATION
O_2
DEPLETION

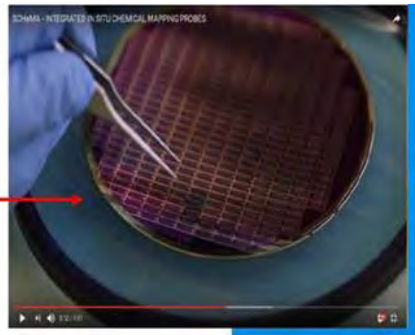
CARBONATE
CO_2
pH

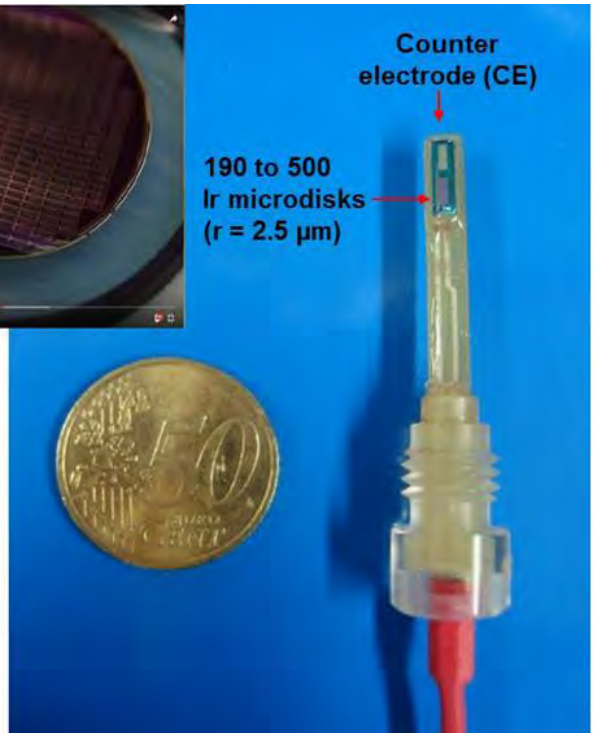


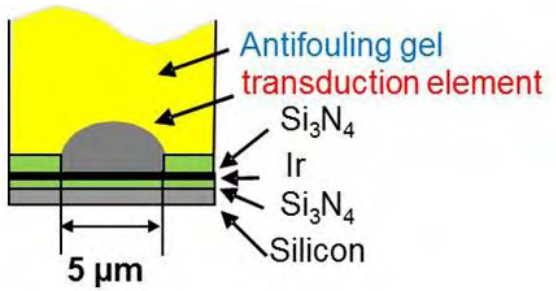
Sensors and probe for trace metals
(UNIGE, EPFL)

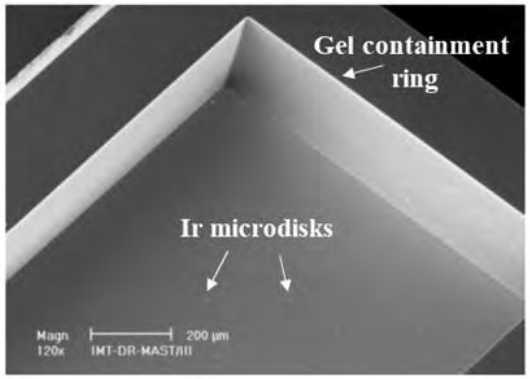
Analytical approach:



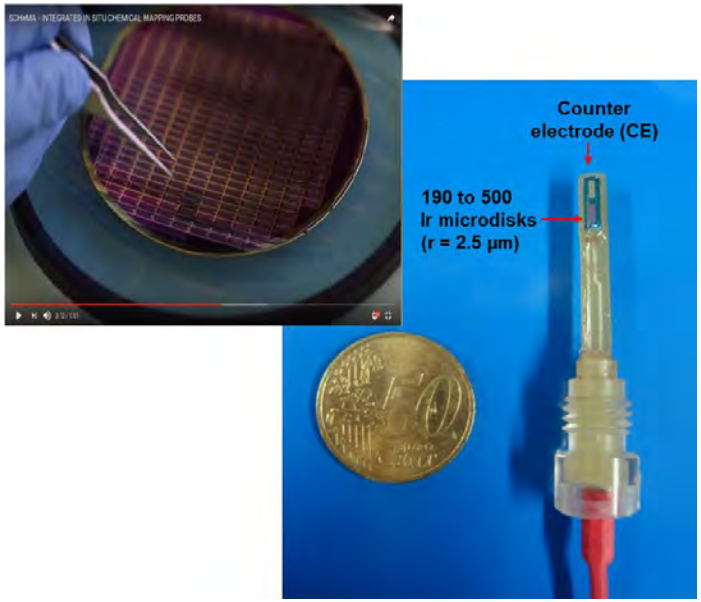


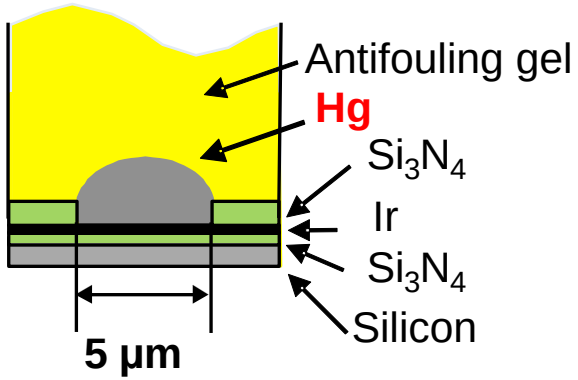






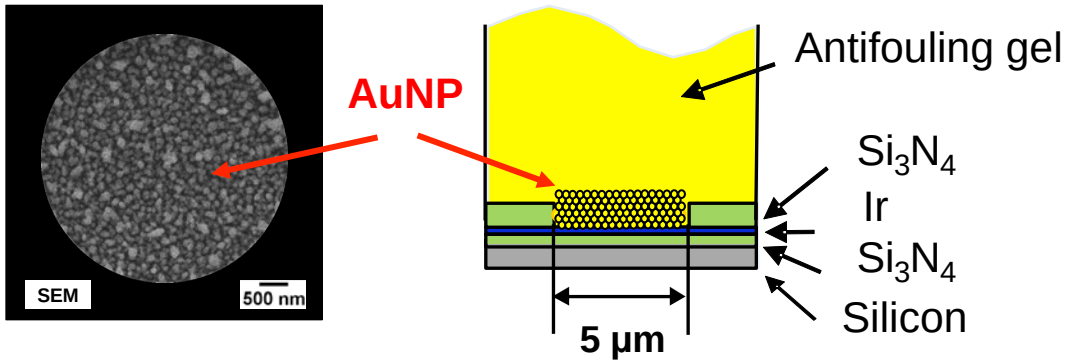
Sensors and probe for trace metals
(UNIGE, EPFL)





GIME: Cd(II), Pb(II), Cu(II), Zn(II)

AuNP-GIME: As(III), Hg(II)



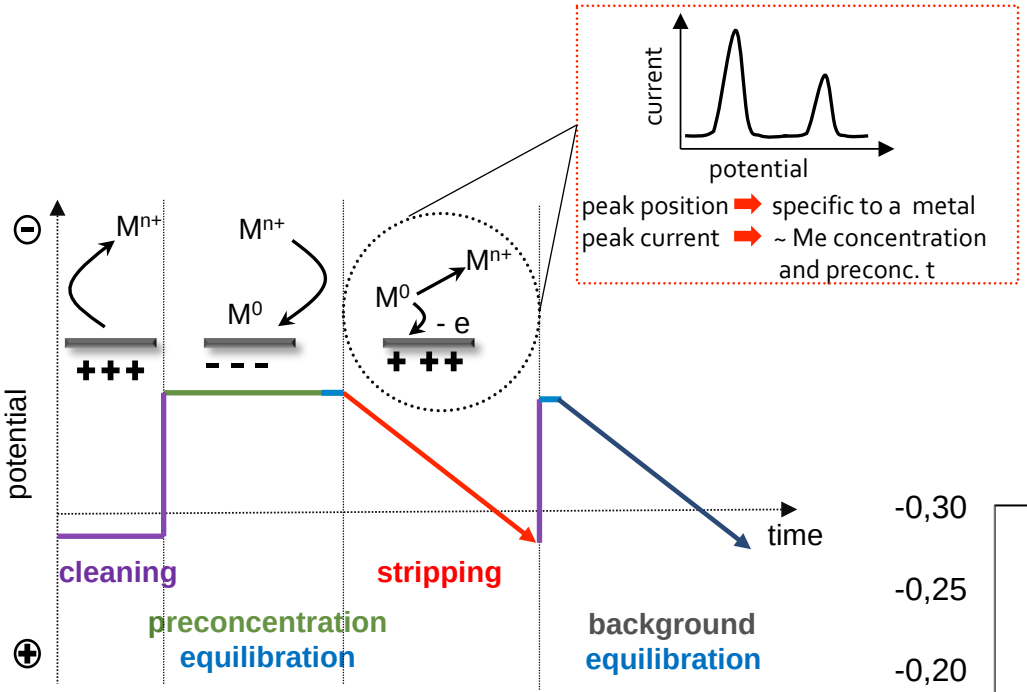
As tot = As(V)+As(III)

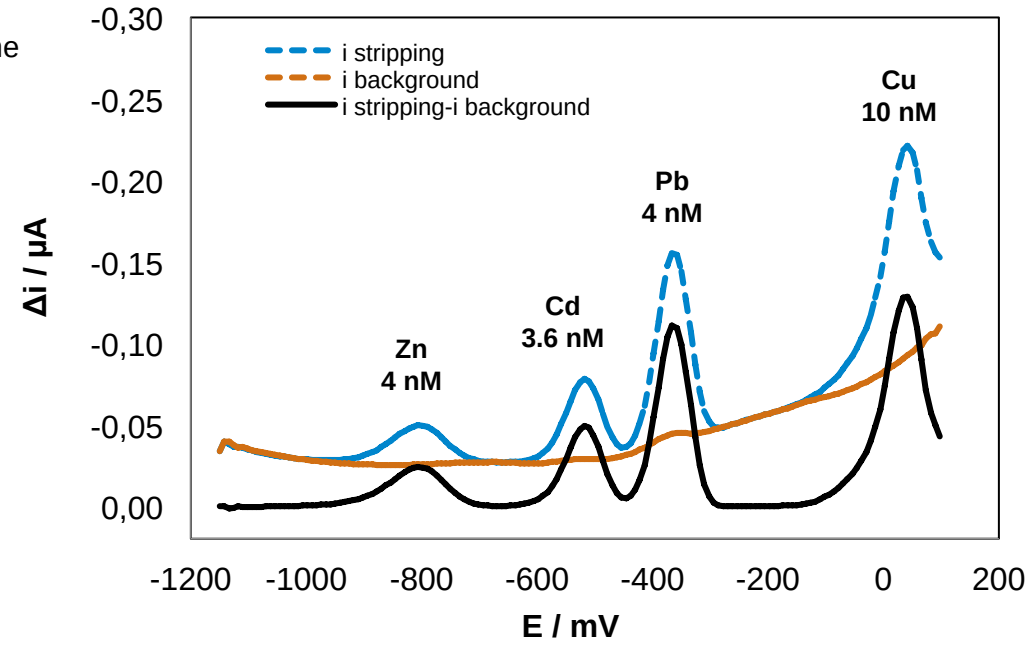
$$Mn(II) \xrightarrow{e^-} Mn(0)$$

$$As(V) + Mn(0) \longrightarrow As(III) + Mn(II)$$

Sensors and probe for trace metals

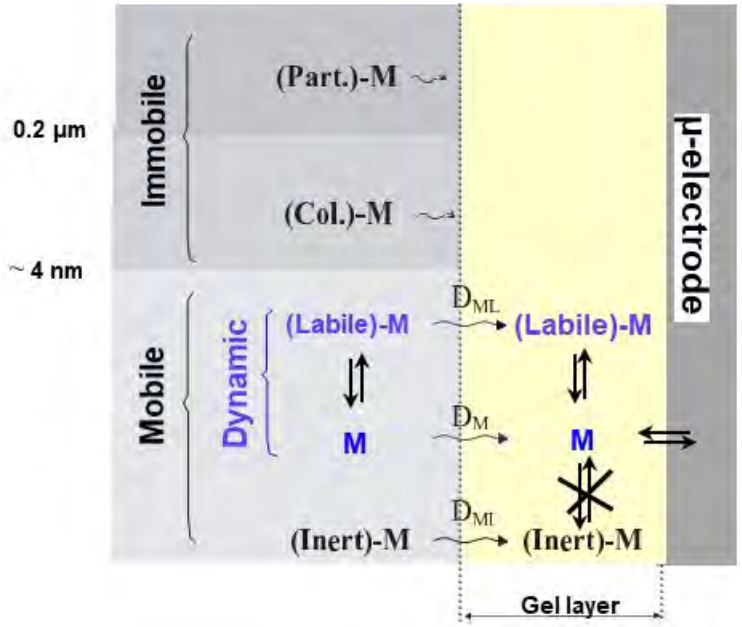
Detection technique: subtractive SWASV





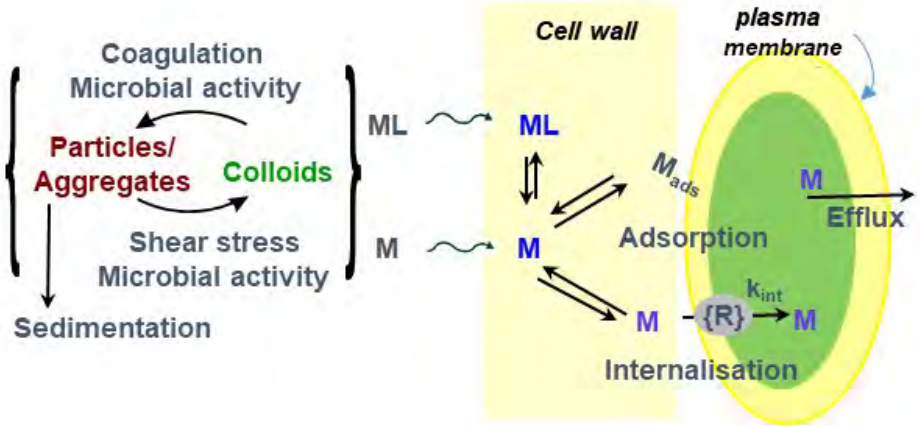
Sensors and probe for trace metals

GIME features



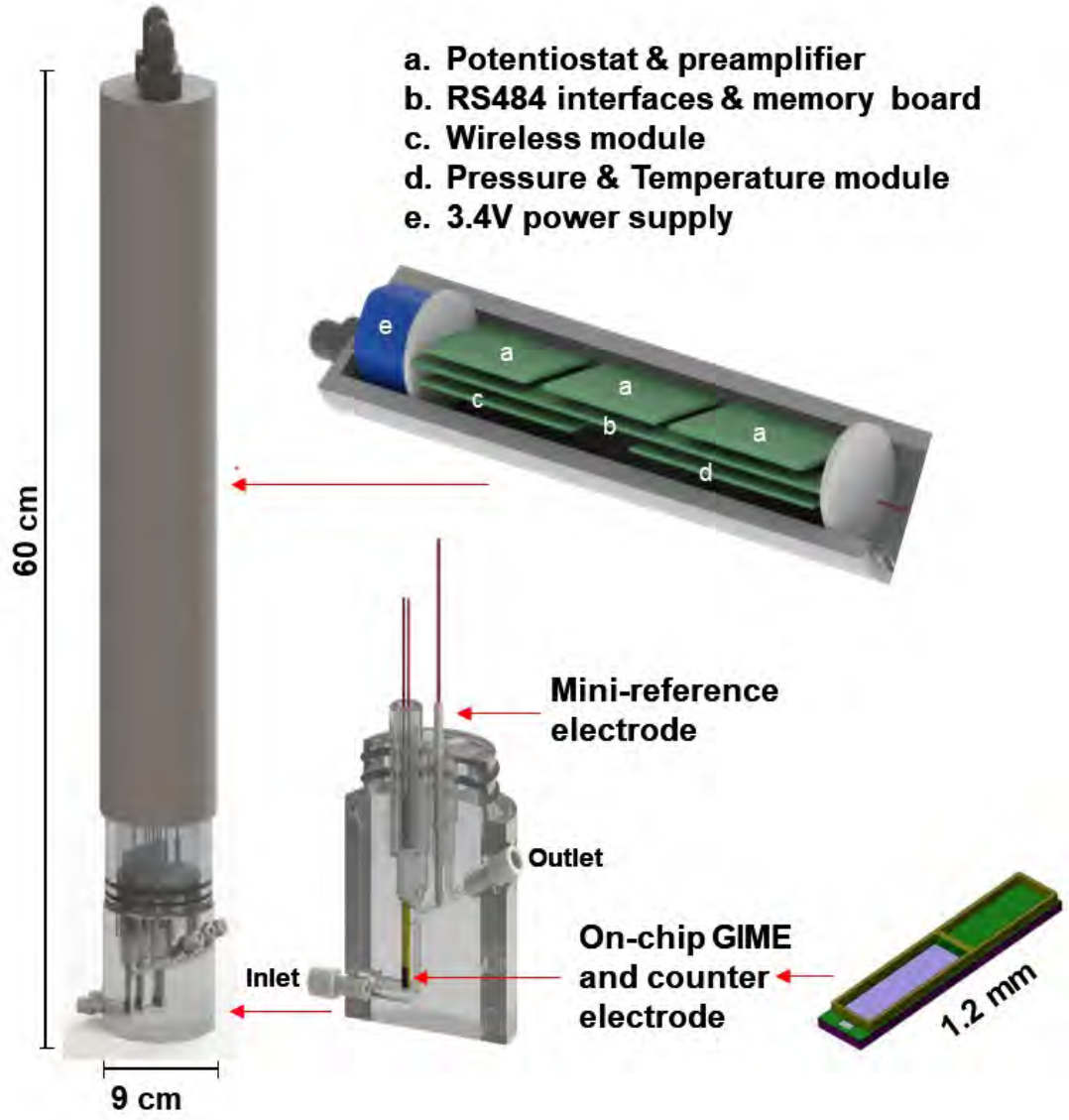
Main features related to the characteristics of micro-sized electrodes (r ≤ 10 µm)

Specific measurements of the dynamic M species **i.e. max conc. of M potentially available for bio-uptake**



J. Buffle, M.-L. Tercier-Waeber, Trends in Analytical Chemistry 24 (2005) 172-191.

Sensors and probe for trace metals
(UNIGE, IDRO, EPFL)

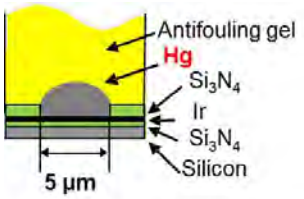


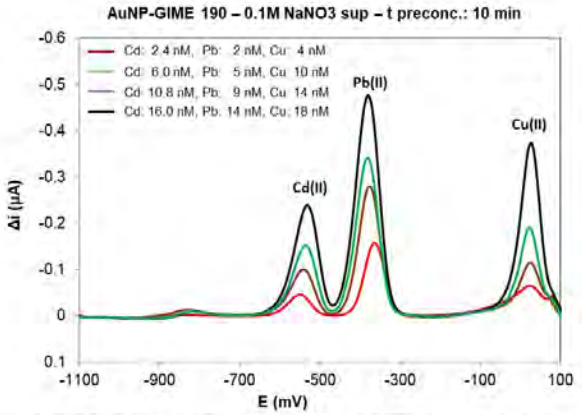
Sensors and probes for trace metals
(UNIGE, IDRO)

SCHeMA

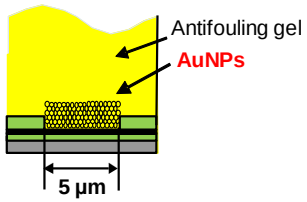
TMSM

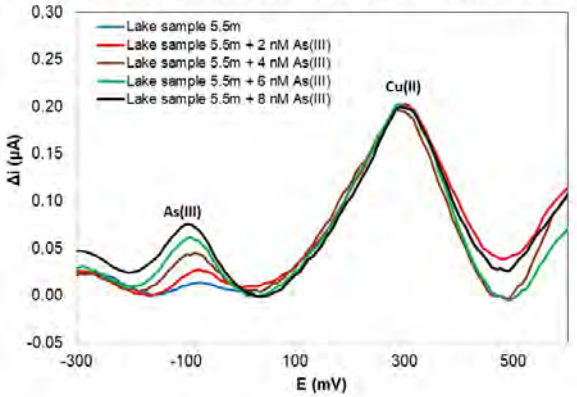
Channel 1



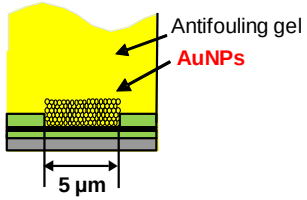


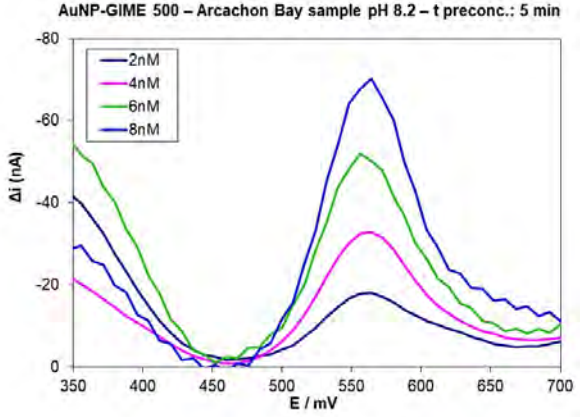
Channel 2





Channel 3





Raw signals

Sensors and probes for trace metals
(UNIGE, IDRO, EPFL)

- **TMSM analytical performance and potentiality for environmental and water quality monitoring**

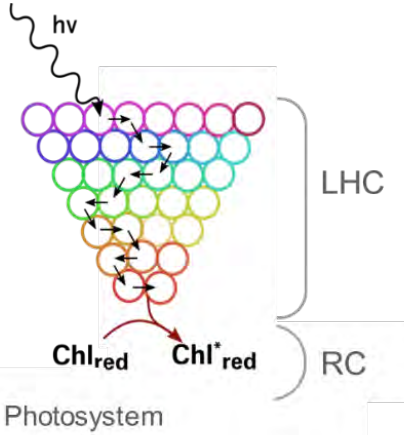
Me	LOD 190-GIME / nM (ng/L)		LOD 500-GIME / nM (ng/L)	
	Preconc.: 10 min	Preconc.: 30 min	Preconc.: 10 min	Preconc.: 30 min
Hg(II)	0.04 (8)	0.01 (2.5)	0.017 (3)	0.006 (1.2)
As(III)	0.50 (35)	0.20 (15)	0.20 (15)	0.08 (6)
Cu(II)	0.25 (15)	0.10 (6.3)	0.10 (6.3)	0.04 (2.5)
Pb(II)	0.02 (4)	0.01 (2)	0.01 (1.6)	0.005 (1)
Cd(II)	0.03 (3)	0.01 (1)	0.015 (1.5)	0.005 (0.6)
Zn(II)	0.40 (25)	0.15 (10)	0.15 (10)	0.05 (3)

Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz)

Analytical approach: Pigment-based taxonomic classification

The photosynthetic apparatus of algae consists of two types of pigment-protein complexes:

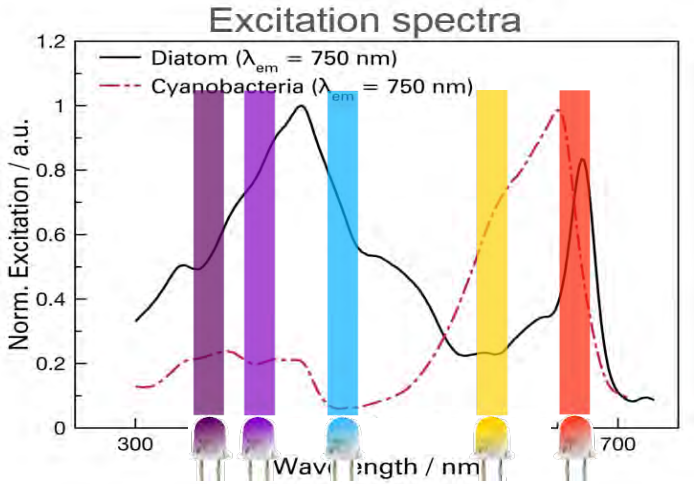
- *light-harvesting complexes*
- *reaction centers*



LHC contain pigments: absorb light, transferring it to photosystem *reaction centers*
Reaction centers: turn solar energy into chemical energy.

- Chlorophyll pigments omnipresent in all reaction centers (RC)
- Pigments of light-harvesting-complex (LHC) differs for different algal groups

➢ Combining LEDs with relevant wavelength ranges to signal deconvolution enable to detect the differencies in the algal group LHC relative pigment patterns



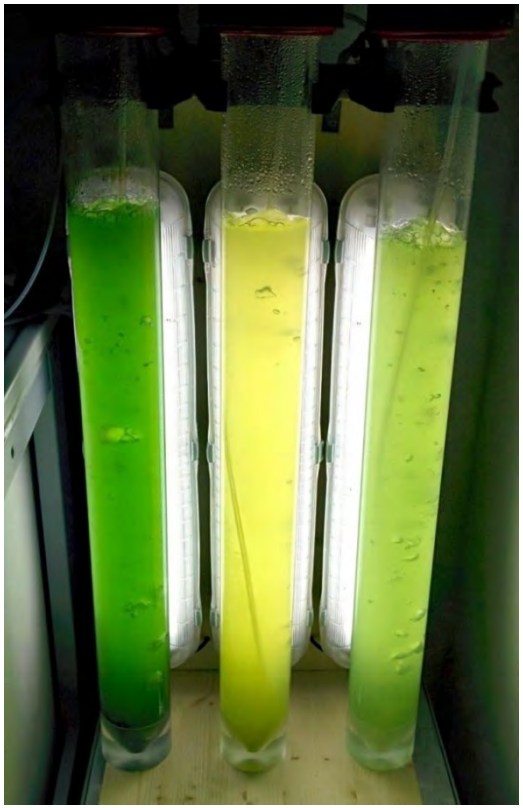
Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz)

Challenge: Lack of information about algal pigment pattern in literature

Analytical approach:

- Algae cultivation and characterization (fluorescence excitation spectra study; marker pigments analyzed via HPLC)

- Generation of data bank for signal analysis:
  - ✓ 76 coastal algae species belonging to 8 different phyla
  - Cyanobacteria → toxin productive algae
  - Dinophyta (Dinoflagellates) → toxin productive algae
  - Bacillariophyta (Diatoms)
  - Haptophyta
  - Chlorophyta
  - Ochrophyta
  - Cryptophyta
  - Euglenophyta.



- Selection of
  - ✓ Selection of optical components
  - ✓ Reference data matrix for data evaluation

Miniaturized fully Integrated Algal Detection Module - ASM (TUGraz)

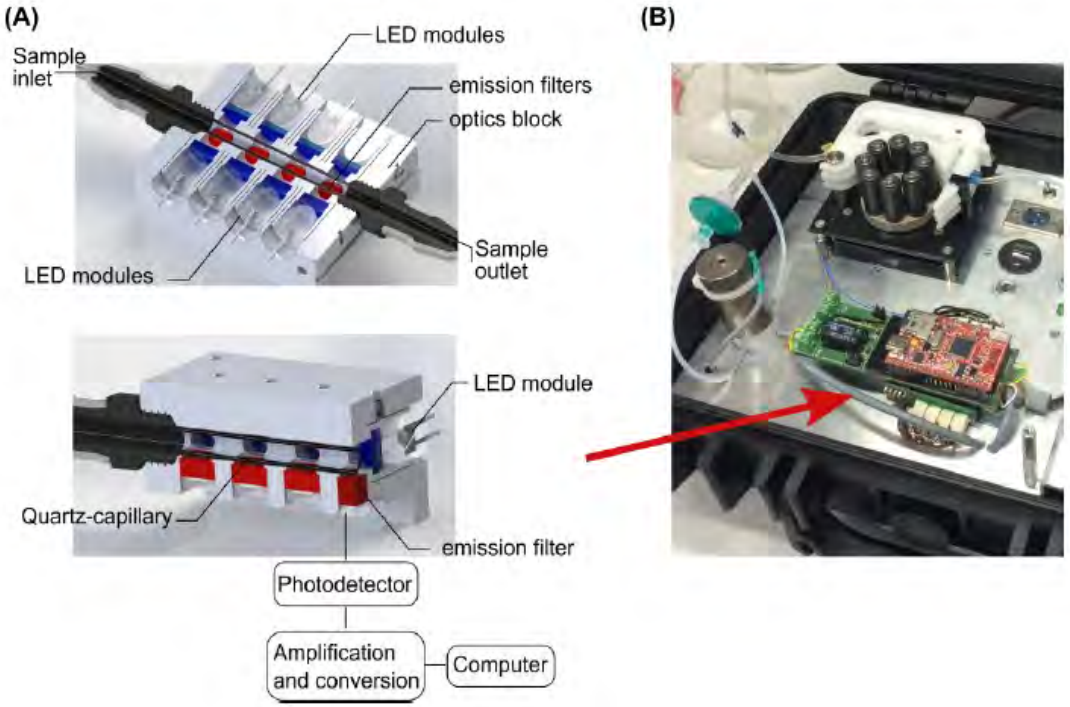
ASM detection module:

- **Material and Dimensions**

  Material: Aluminum
  Size : 28 x 34.8 x 15.8 mm^3
  Capillary: Quartz, ID = 1.94 mm, OD = 3 m
  Measurement volume: 5.91 µL

- **Optical components**

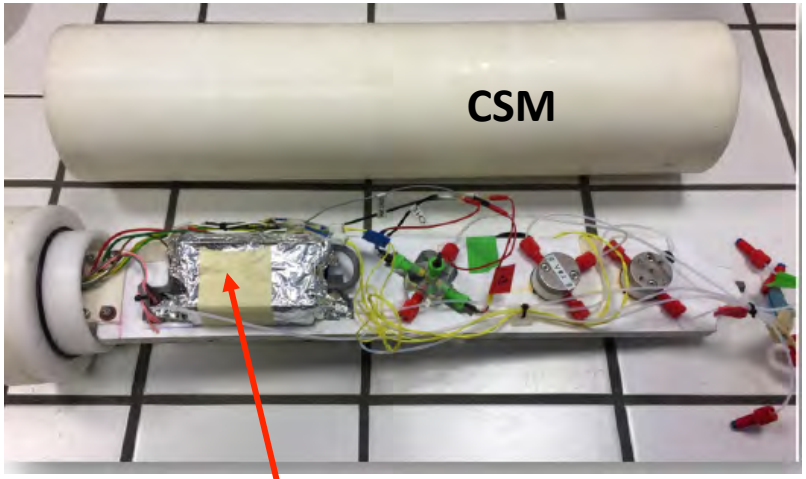
  8 Excitation sources : LEDs 380-650 nm
  4 Photodetectors: Silicon pin photodiode

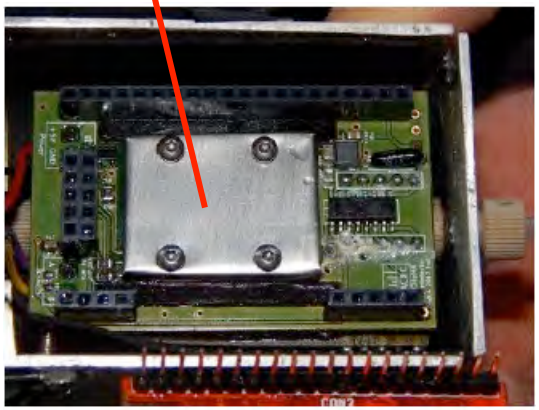


S. Zieger et all, Env. Sci. Tech., 2018

Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz, IDRO)

Algae detection system: portable and submersible

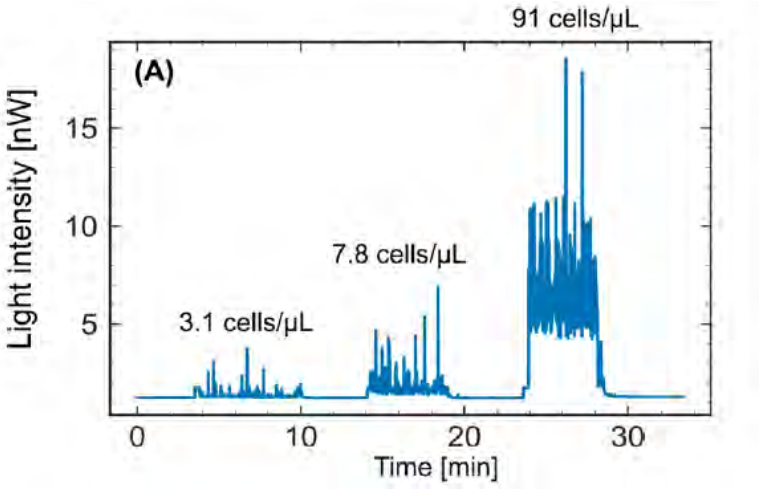


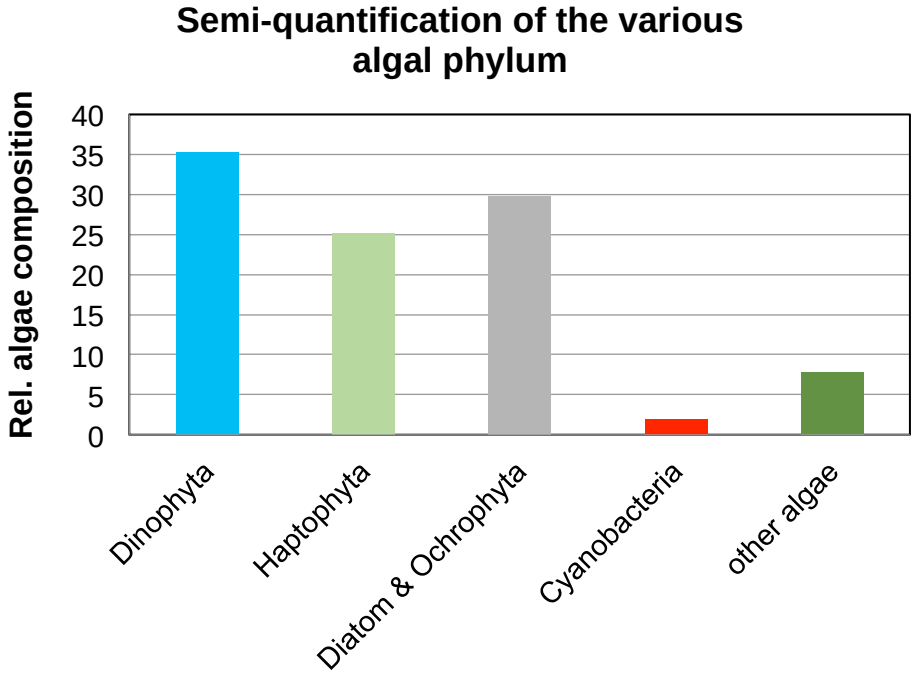


Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz)

Dedicated software

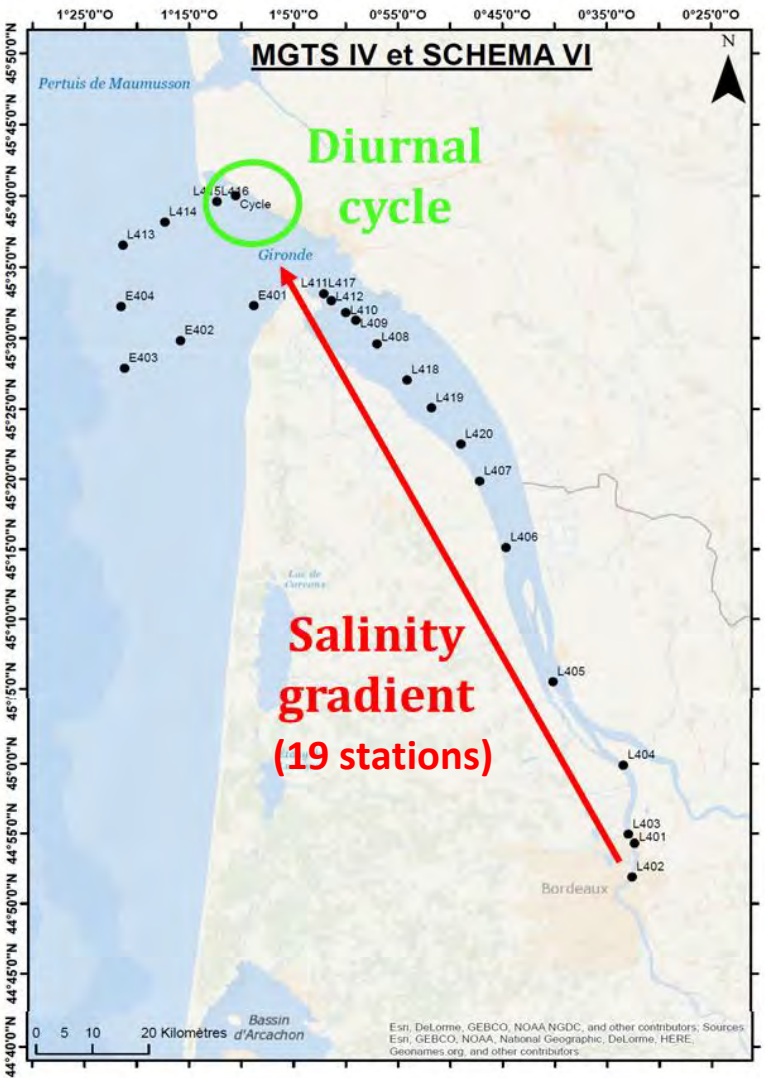
- ***Detection of single cell events***
  - quantification of average cell density





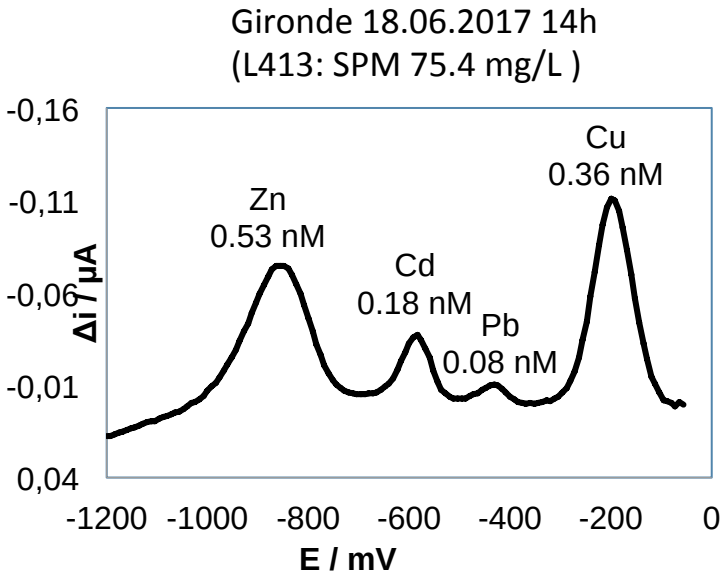
In situ application and validation (UNIGE, UBx, UNIGe-IT)

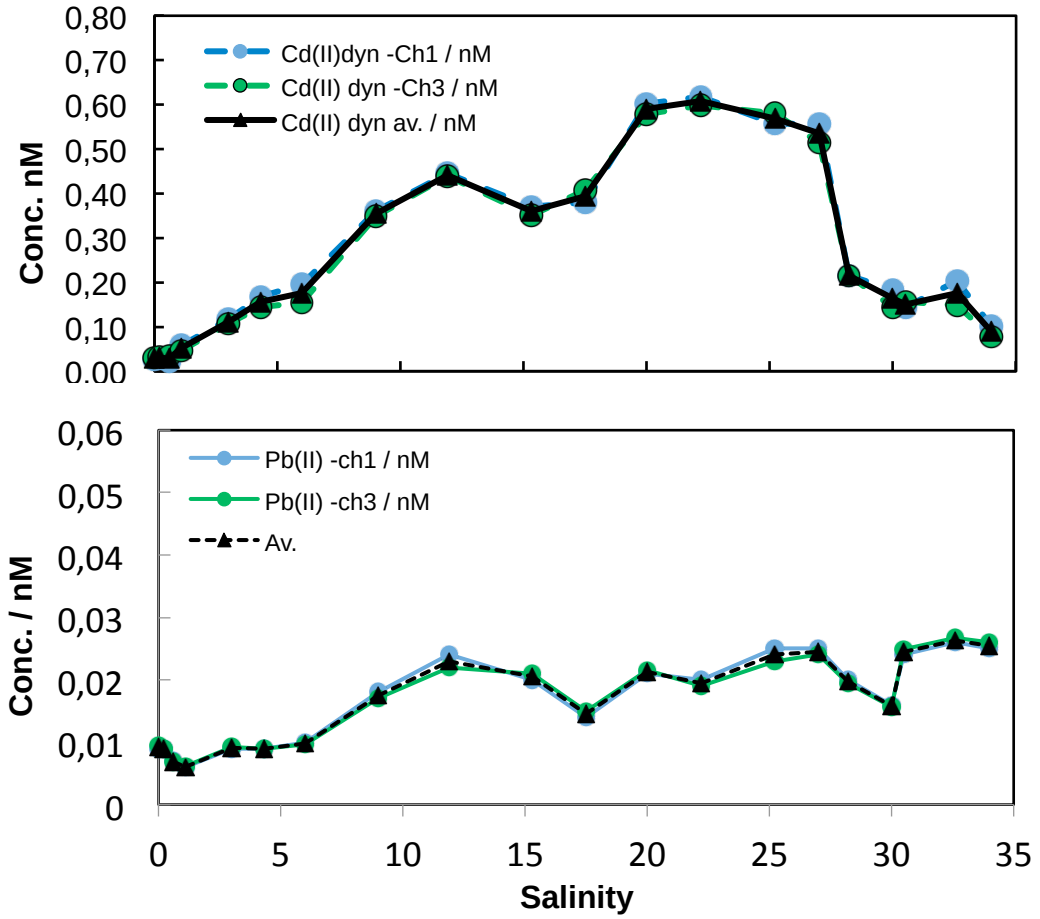
- **Gironde estuary – June 2017**
  - Reliability of measurements in salinity gradient and highly turbid system (SPM: 55 to 1600 mg/L)



GIME TMSM channels 1 and 3: copper, lead, cadmium, zinc

- **Gironde estuary – June 2017**
  - Reliability of GIME measurements in highly turbid systems



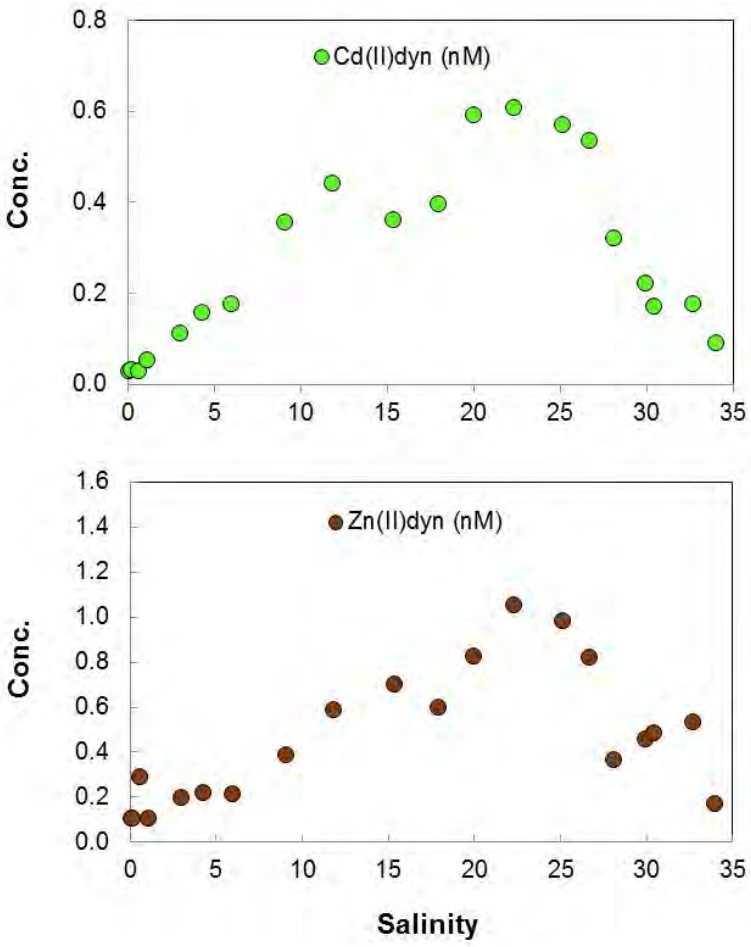


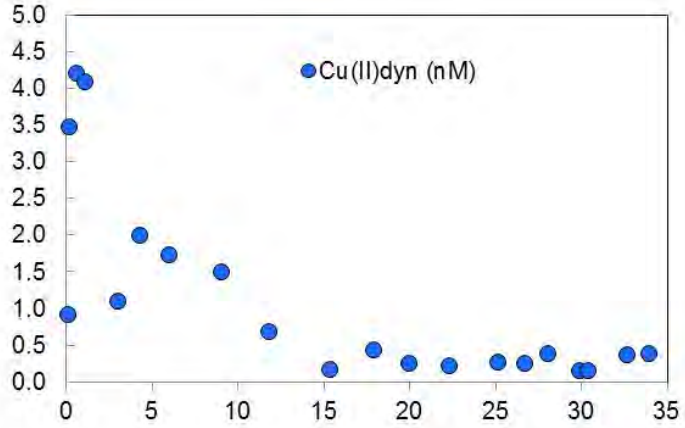
Sensors and probes for trace metals

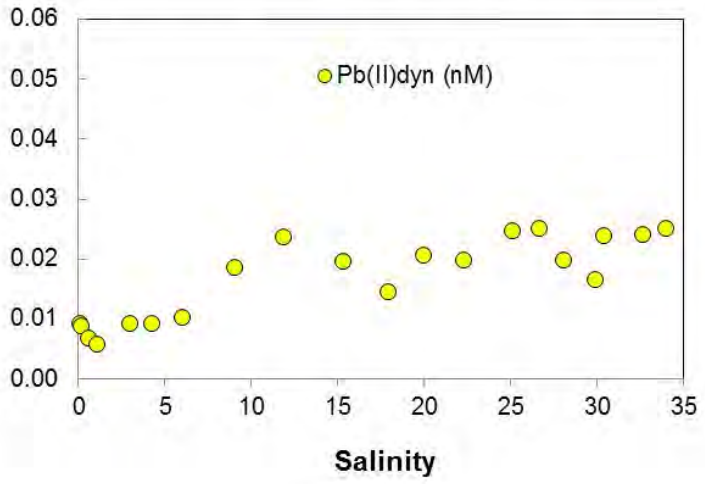
In situ application and validation (UNIGE, UBx)

Hg-GIME TMSM: copper, lead, cadmium, zinc

- **Gironde estuary – June 2017**
  - Variation of bioavailable fraction, under different trends, and up to one order of magnitude along the salinity gradient





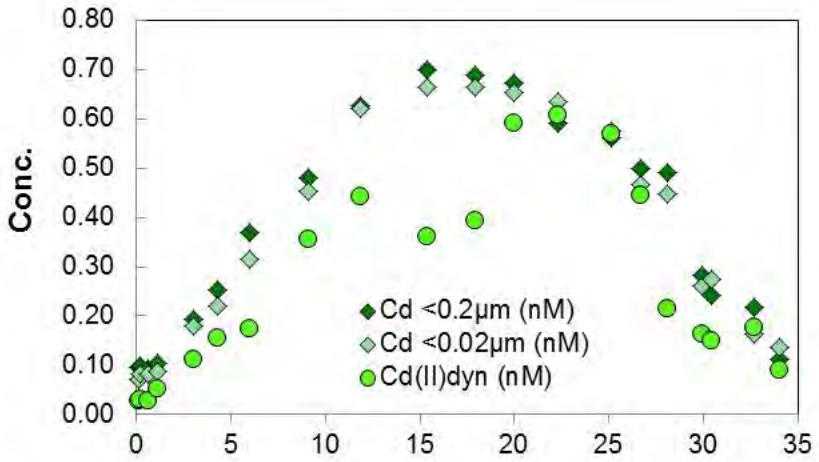


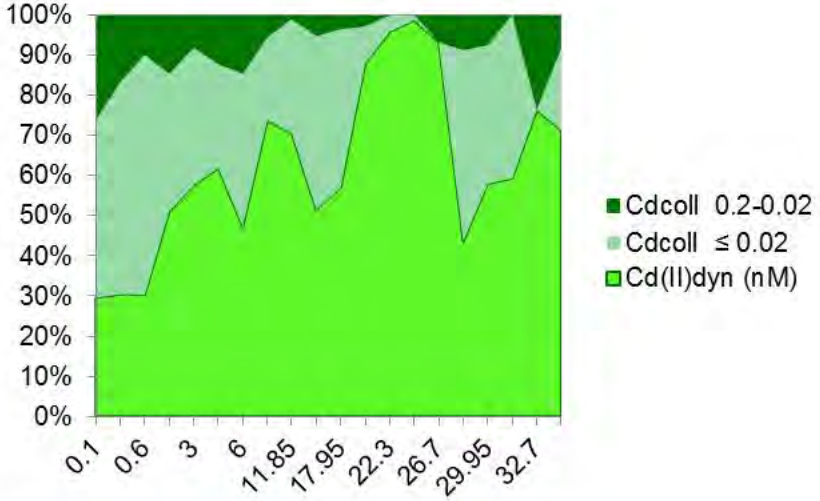
Sensors and probes for trace metals

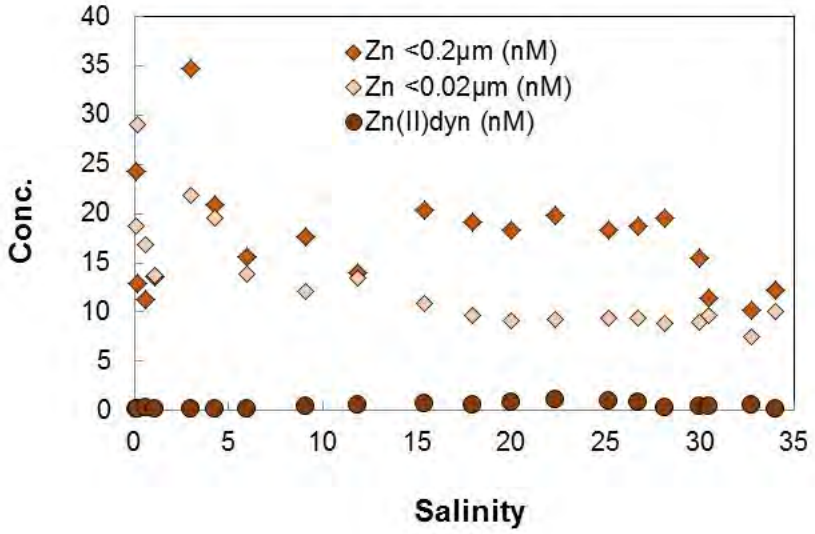
In situ application and validation (UNIGE, UBx)

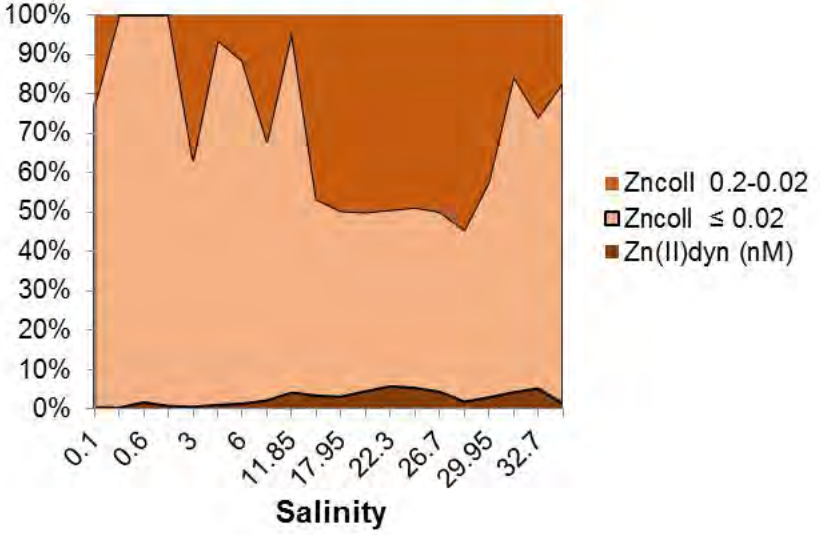
Hg-GIME TMSM: copper, lead, cadmium, zinc

- **Me speciation - Gironde estuary – June 2017**





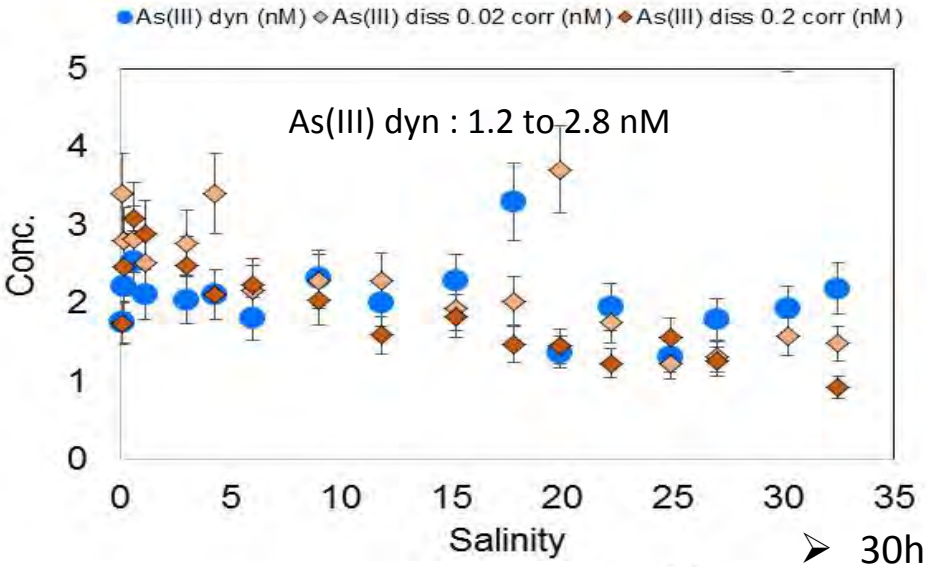


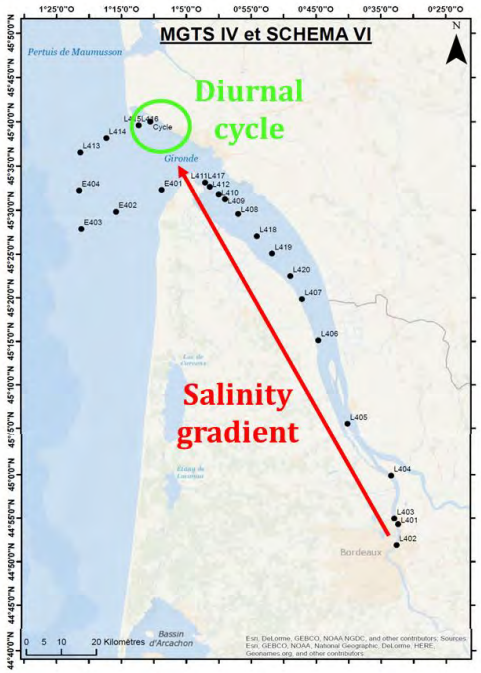


Sensors and probes for trace metals
In situ application and validation (UNIGE, UBx)

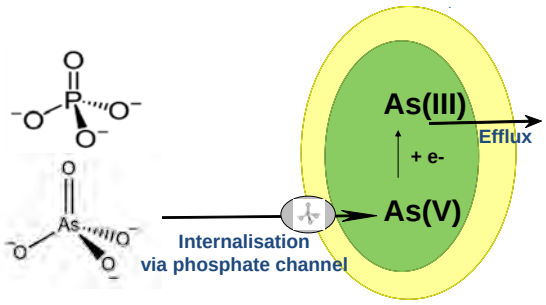
AuNP-GIME TMSM: As(III) Gironde Estuary – June 2017

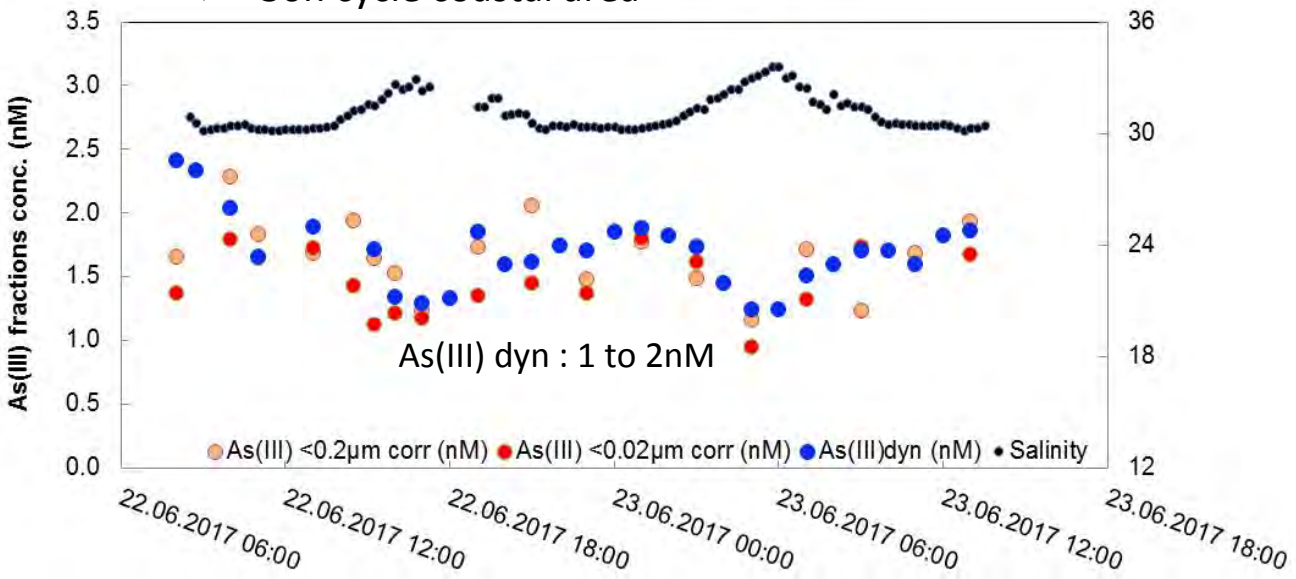
- Salinity gradient





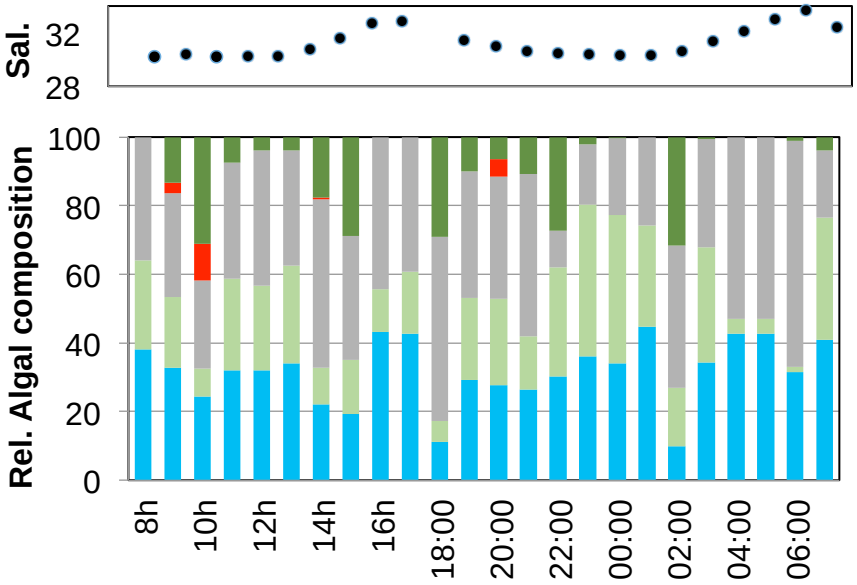
- 30h cycle coastal area





Miniaturized fully Integrated Algae Detection Module - ASM
In situ application and validation (TUGraz, UNIGe-IT, ETT)

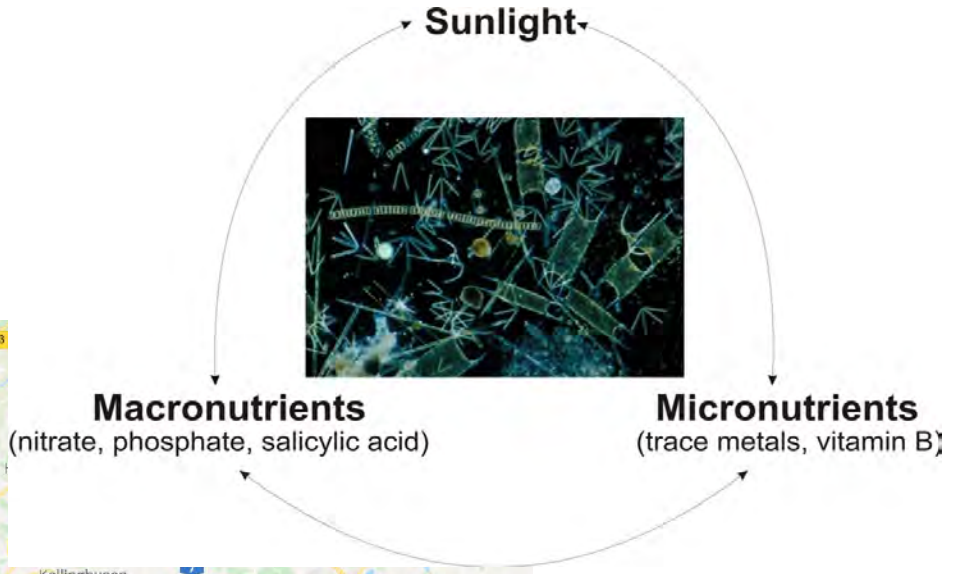
Gironde coastal area
24h cycle – June 2017



Deviation from microscope analysis < 15%

In situ application and validation (UNIGE, UBx, ETT)

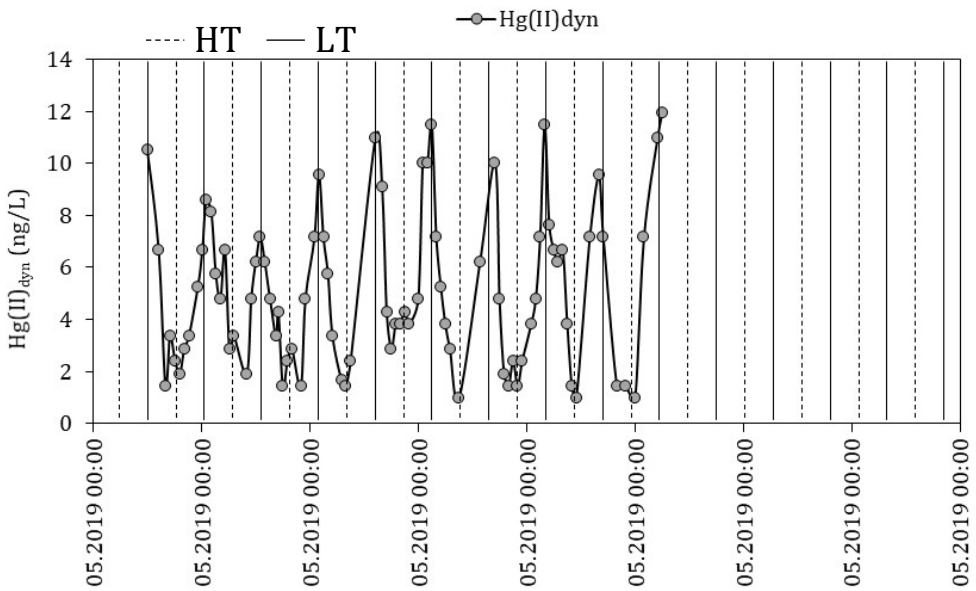
- **Elbe Estuary mouth: 7-16 May 2019**

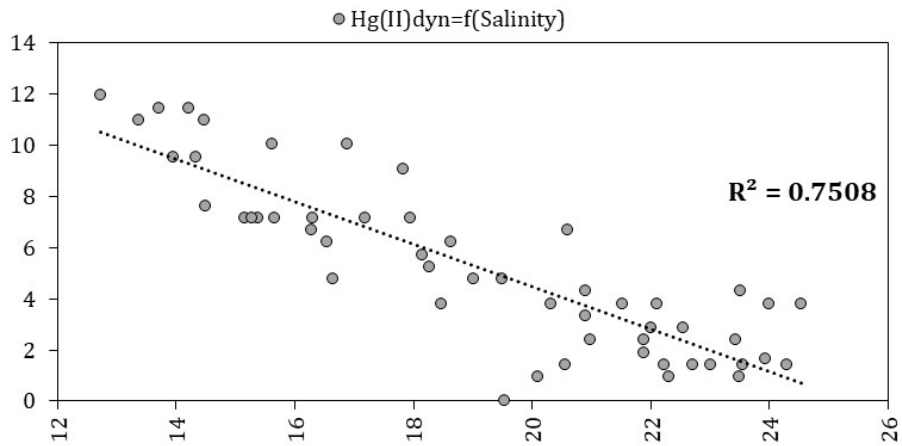


Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

In situ application and validation (UNIGE, UBx, ETT)

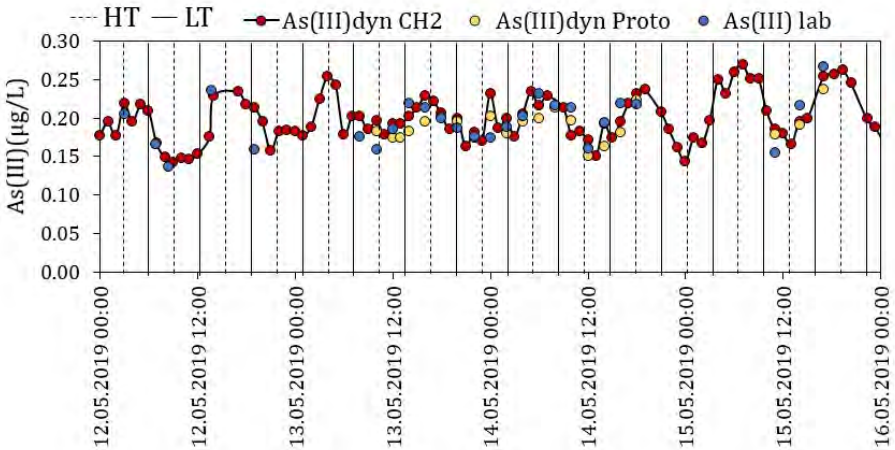
AuNP-GIME TMSM channel 3: 95 measurements without renewal of the AuNP layers

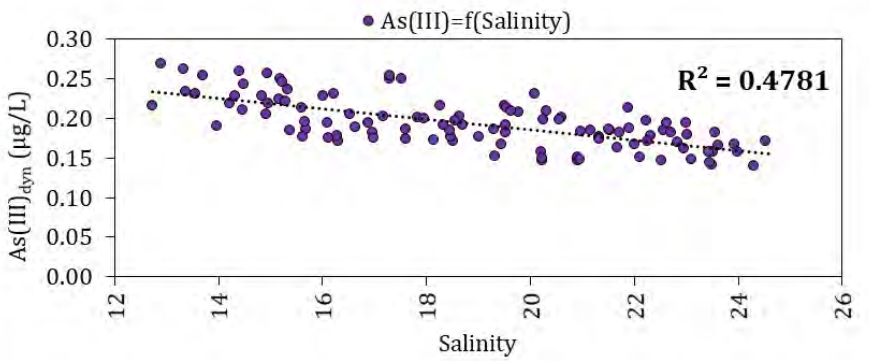




In situ application and validation (UNIGE, UBx, ETT)

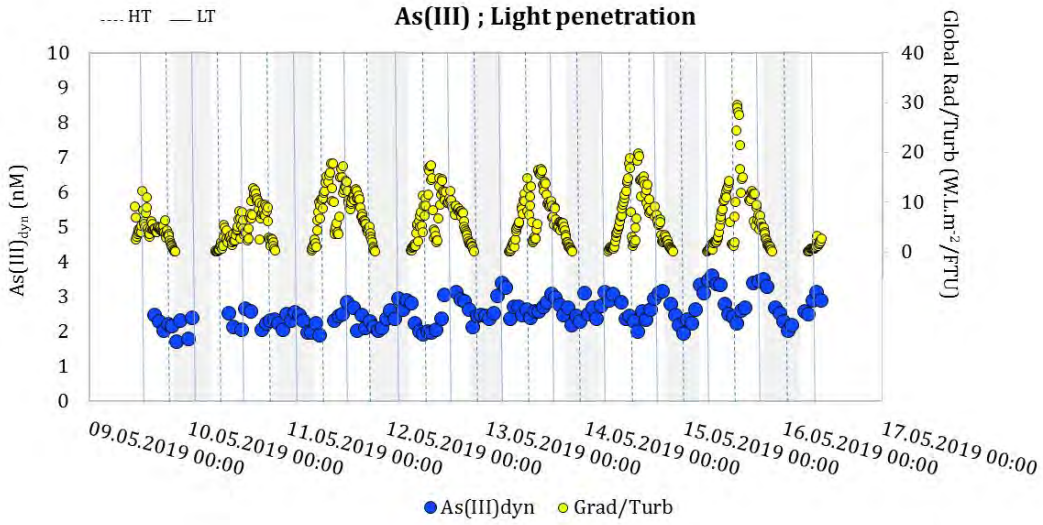
AuNP-GIME TMSM channel 2: 150 measurements without renewal of the AuNP layers

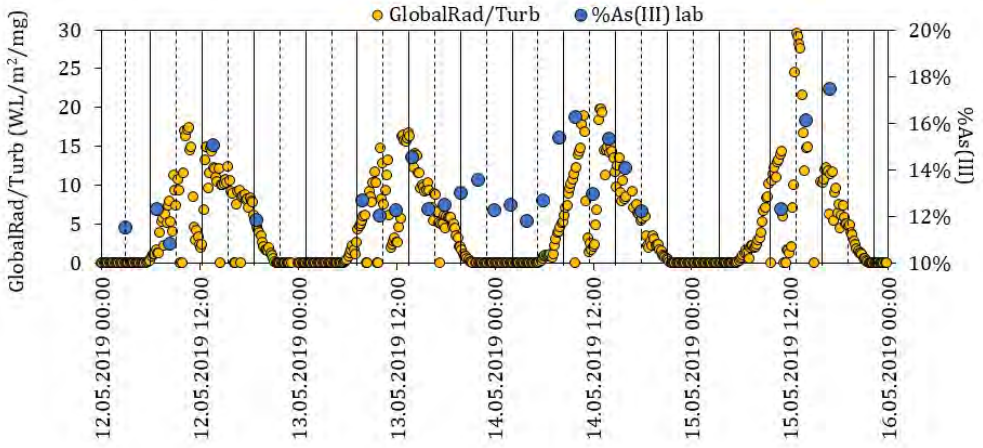




In situ application and validation (UNIGE, UBx, ETT)

AuNP-GIME TMSM channel 2: 150 measurements without renewal of the AuNP layers



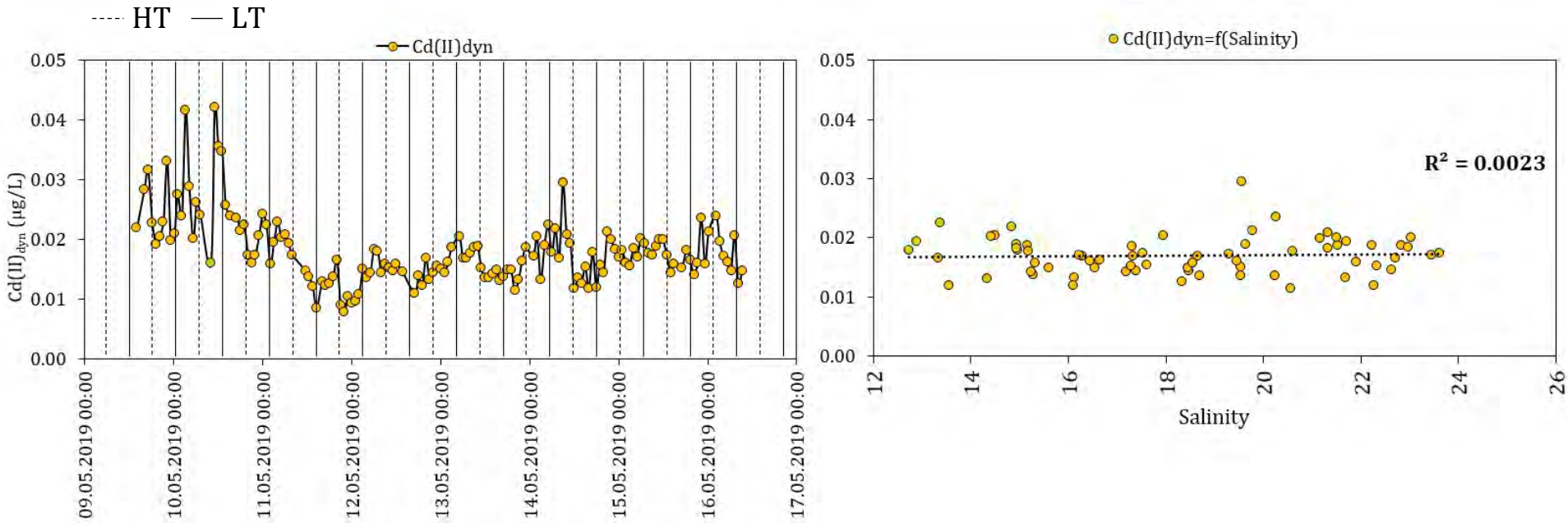


✓ **Bioavailable $As(III)_{dyn}$ and $As(III)_{dyn}/As_{tot}$ ratio ↗ with effective light penetration**

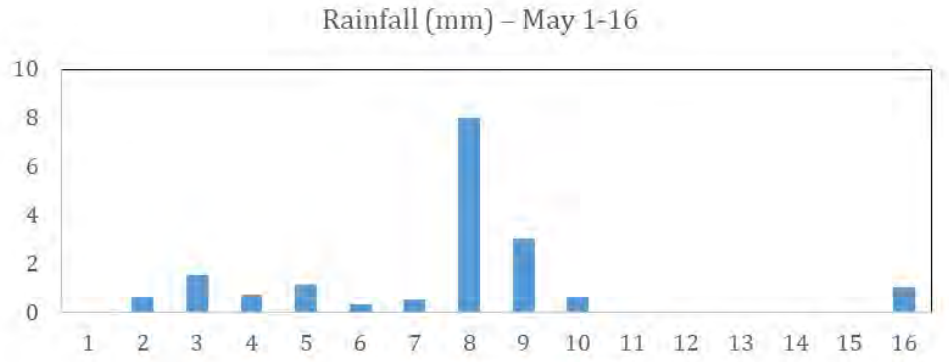
→ As(III) in oxygen saturated water related to As(V) uptake (chemically similar to phosphate) and subsequent biotransformation and excretion of As(III)

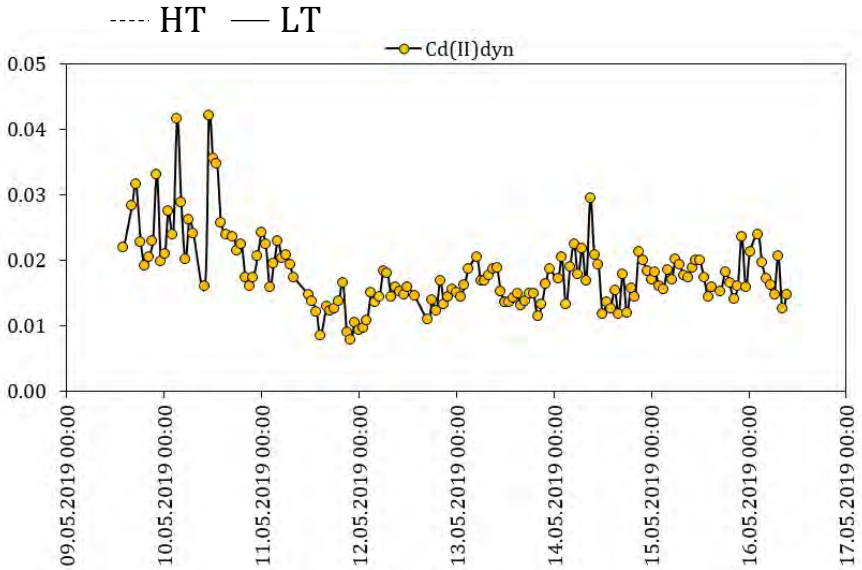
In situ application and validation (UNIGE, UBx, ETT)

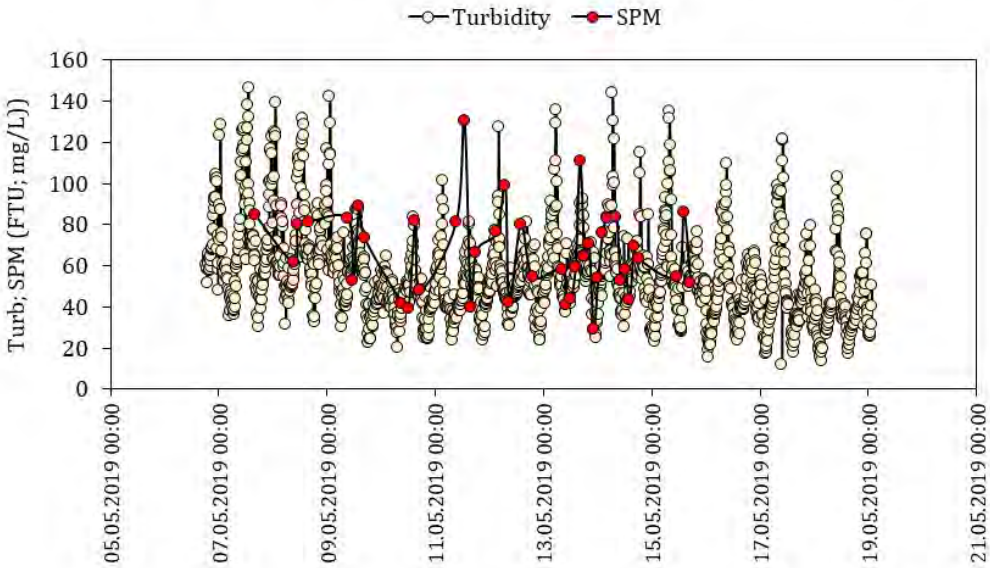
GIME TMSM channel 1 : 150 measurements without renewal of the Hg layers



In situ application and validation (UNIGE, UBx, ETT)

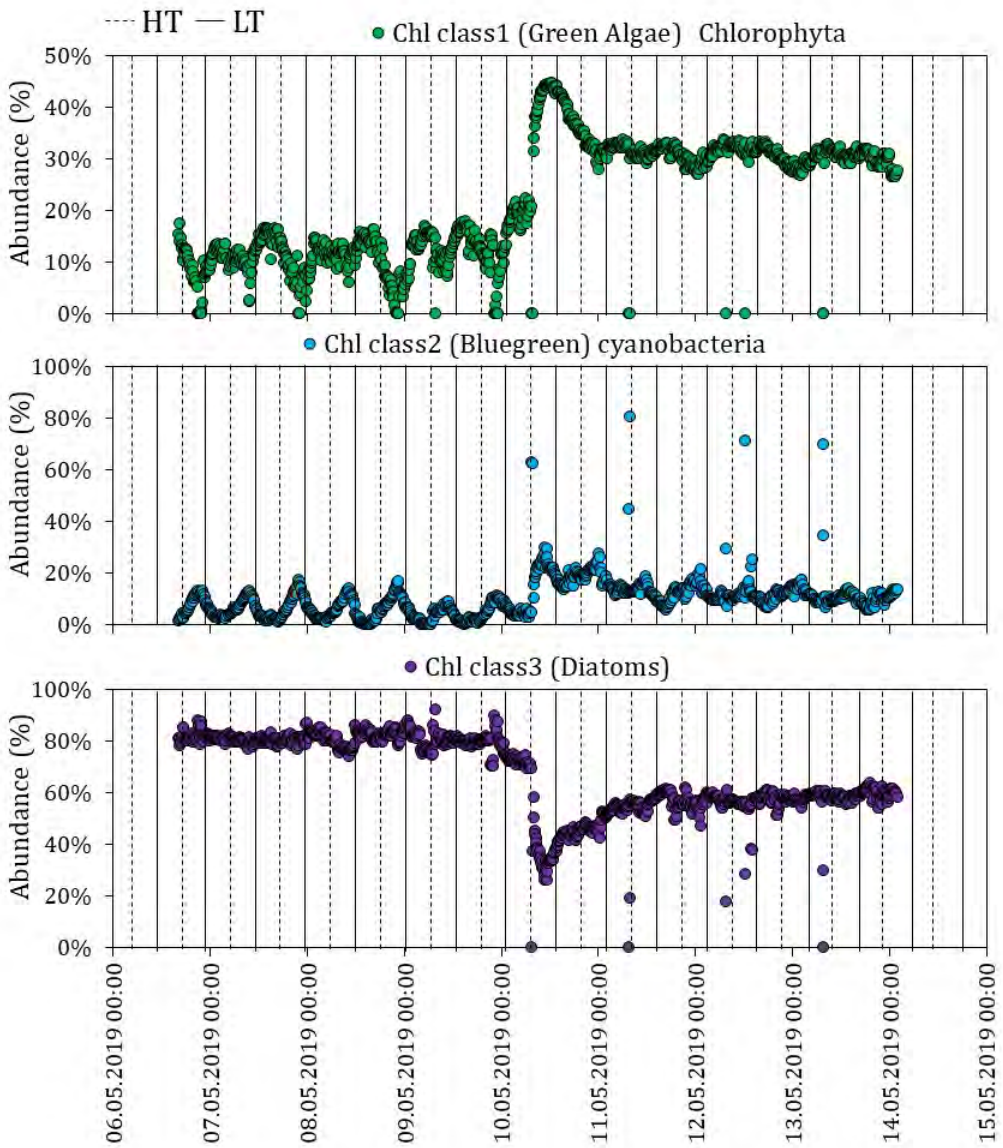






In situ application and validation (UNIGE, UBx, ETT)

Phytoplankton communities



For more information

THE OCEAN OF TOMORROW

- **Visit the SCHeMA web site**

http://www.schema-ocean.eu

Maritime Sensor Technologies for the European Market:
Research, Development and Implementation.
Good practice guide.

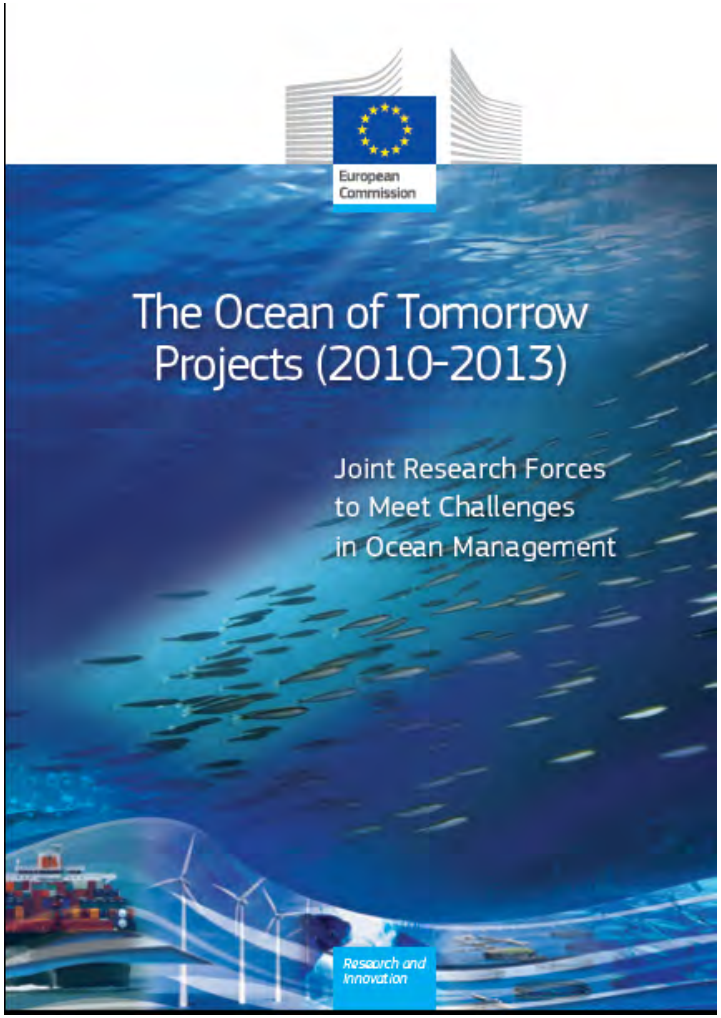
Horizon 2020: COLUMBUS and Atlantos projects
FP7: Ocean of Tomorrow projects

UNIVERSITÉ DE GENÈVE FACULTÉ DES SCIENCES · IDRONAUT S.r.l. ITALY · TU Graz · EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE · nano myp · université de BORDEAUX Collège Sciences et technologies · Università degli Studi di Genova · ETT

For more information

THE OCEAN OF TOMORROW

EU publications



The ocean of tomorrow projects (2010-2013) Joint research forces to meet challenges in ocean management

Main contributors

Development TMSM sensors and probe

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Financial support European Commission:

SCHeMA (FP7 – Ocean of Tomorrow)

SCHeMA

THE OCEAN OF TOMORROW

MEPHY (FP7 – JERICO-NEXT NTA

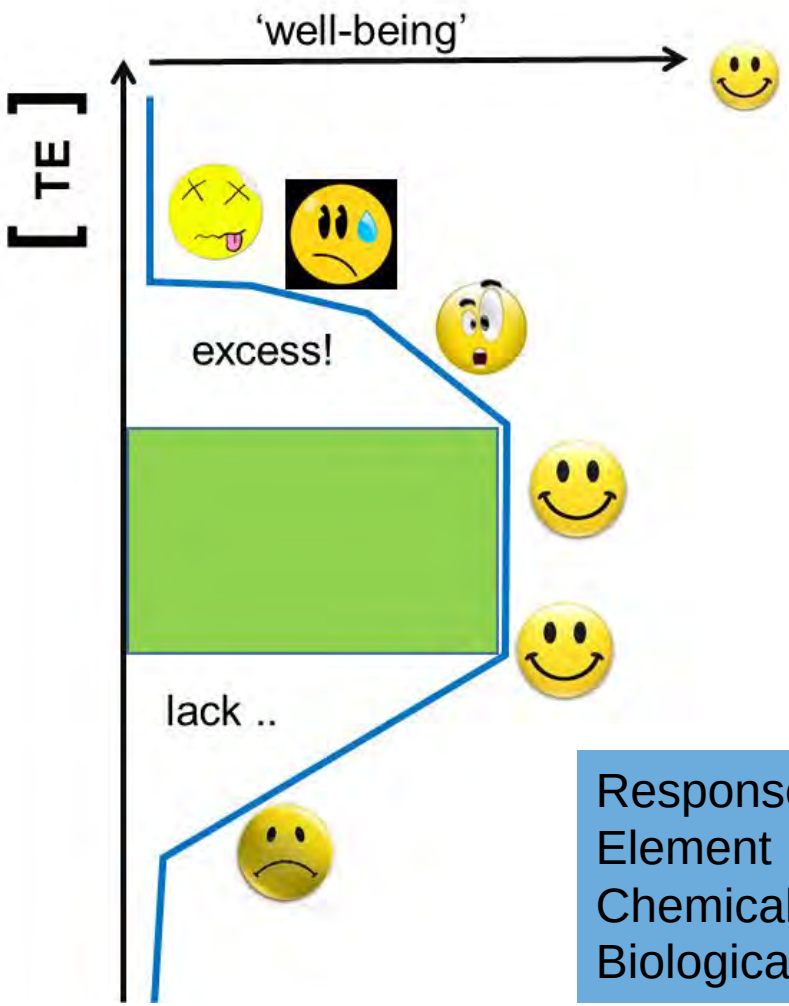
MEPHY

JERICO next

Sensors and probe for trace metals

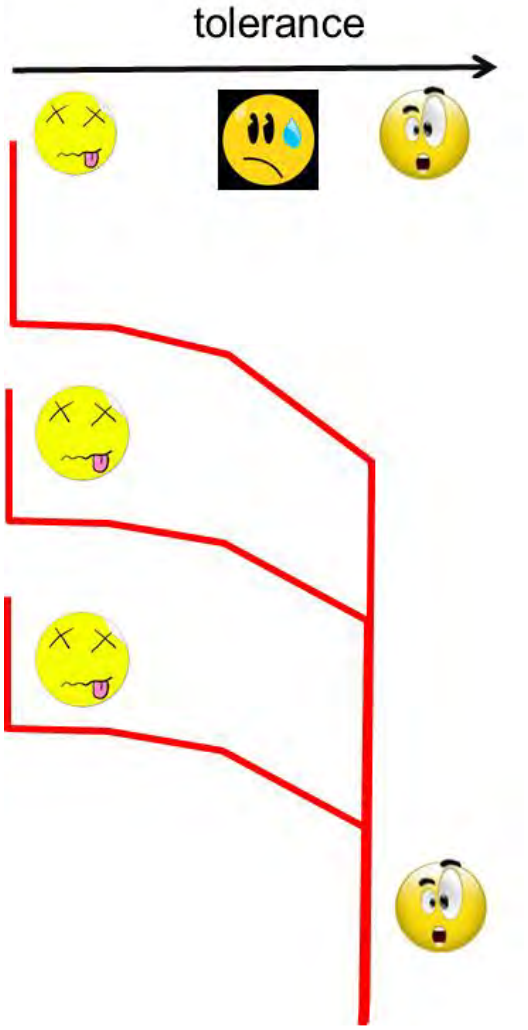
Motivation and Challenges:

Oligoelements, i.e. essential to living organisms, or toxic depending on their concentrations



Response depends on:
Element
Chemical species
Biological target

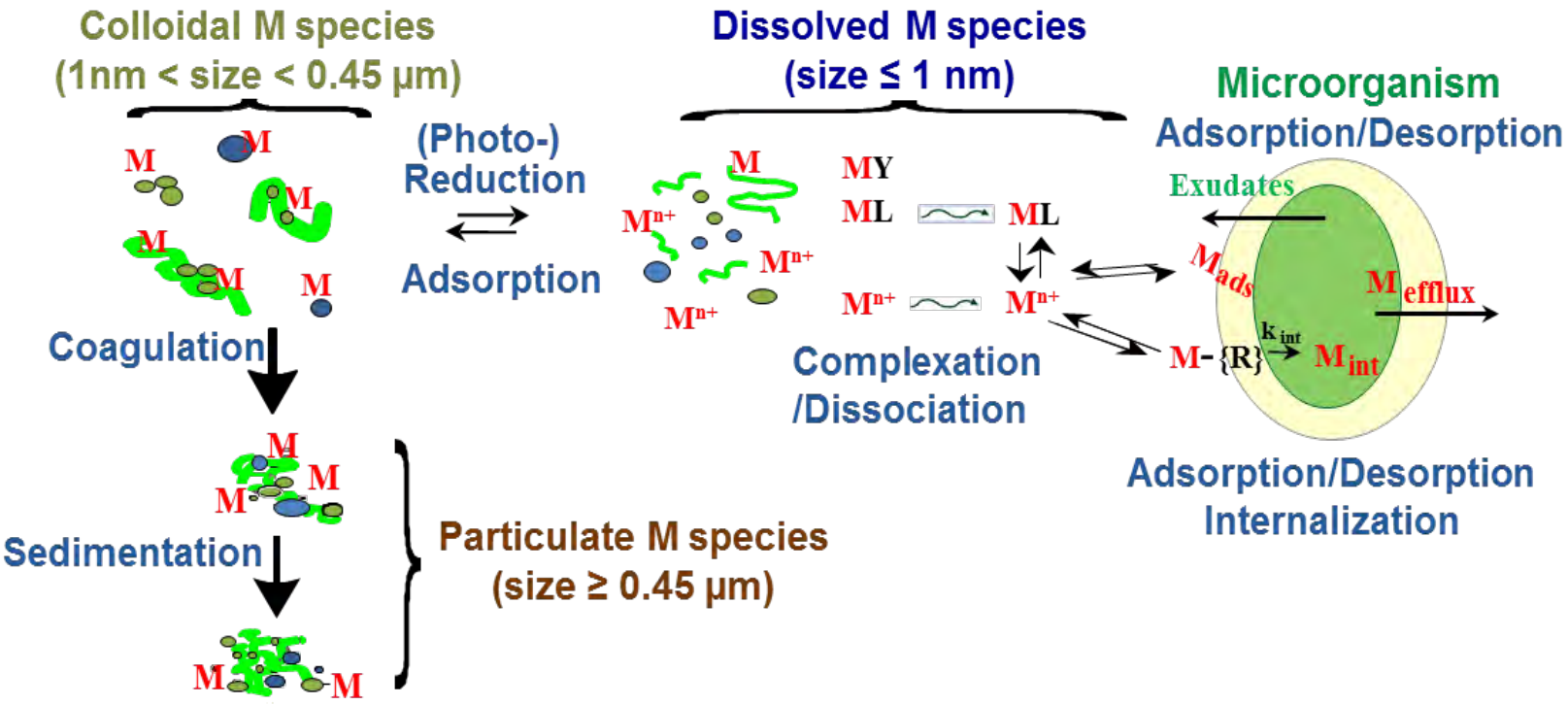
Toxic even at very low conc. (Hg, As, Pb, U, Tl)



Sensors and probe for trace metals

Motivation and Challenges:

- Direct monitoring at natural pH and in presence fouling materials and oxygen
- Detection limit: nM to pM
- Selectivity to relevant, in term of toxicity, metal species



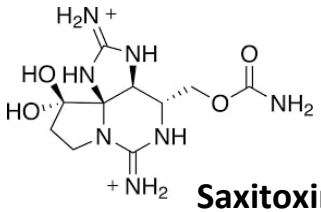
M.-L. Tercier-Waeber, M. Taillefert, J. Environ. Monit., 10, 2008, 30-54.

Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz)

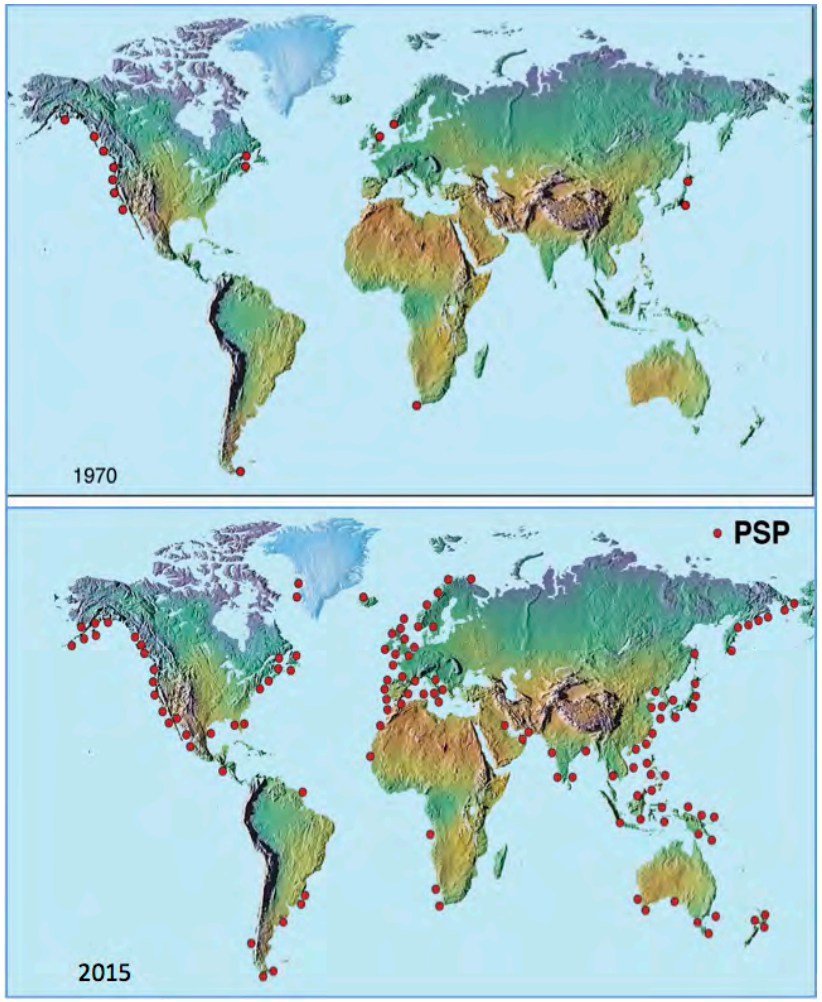
Motivation and Challenges:

- Occurrence and intensity increase
- Production of various toxins
  - Physical threat to fish and human
  - Fish and shellfish poisoning
- Relevant as screening and alarm system for:
  - Recreational facilities
  - Fish farming industry

Dinoflagellates (Dynophyta)



Saxitoxin (STX)



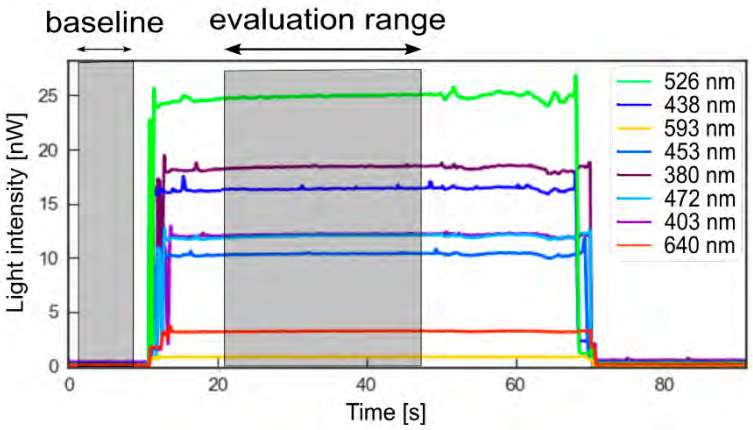
https://www.whoi.edu/website/redtide/regions/world-distribution/

Miniaturized fully Integrated Algae Detection Module - ASM (TUGraz)

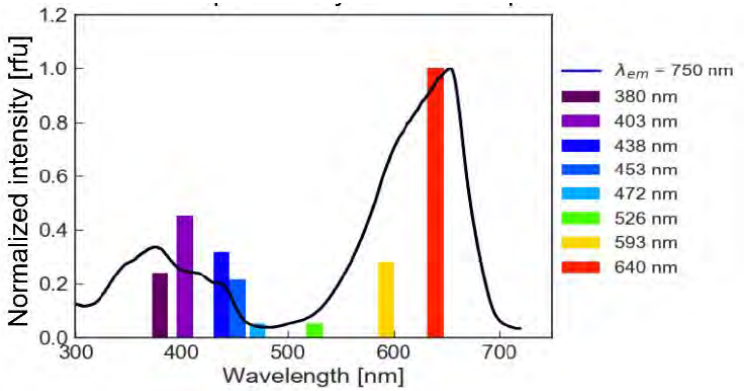
Dedicated software:

- identification/classification of the various algae
- clear separation of common toxin producing Cyanobacteria and Dinophyta (Fisher's linear discriminant analysis)

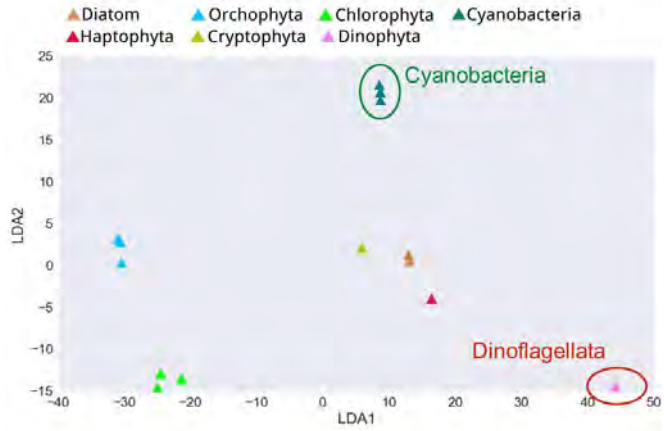
Light intensity spectra



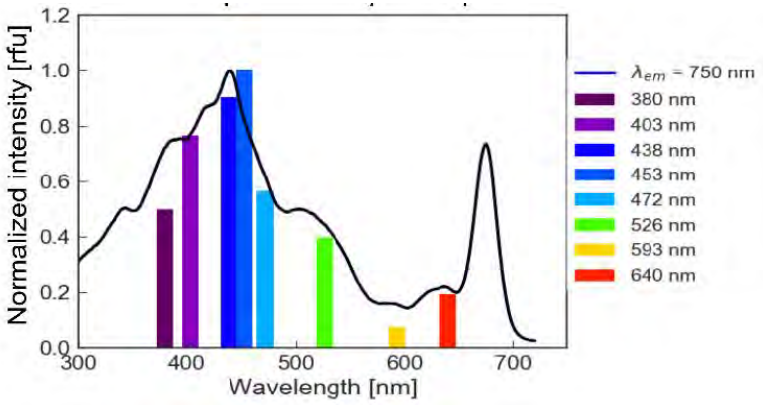
Excitation spectrum Cyanobacteria sp.



Separation in the LDA subspace

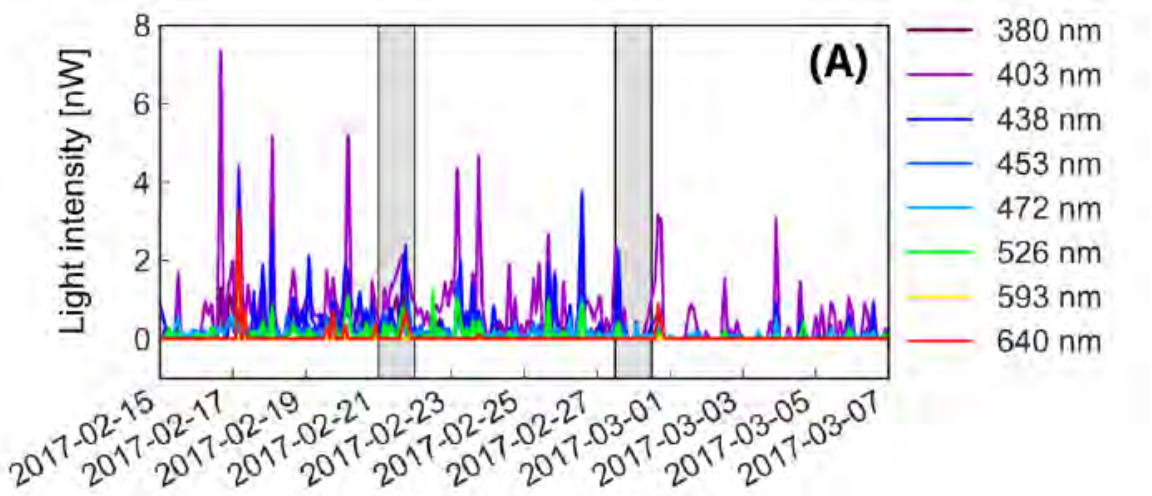


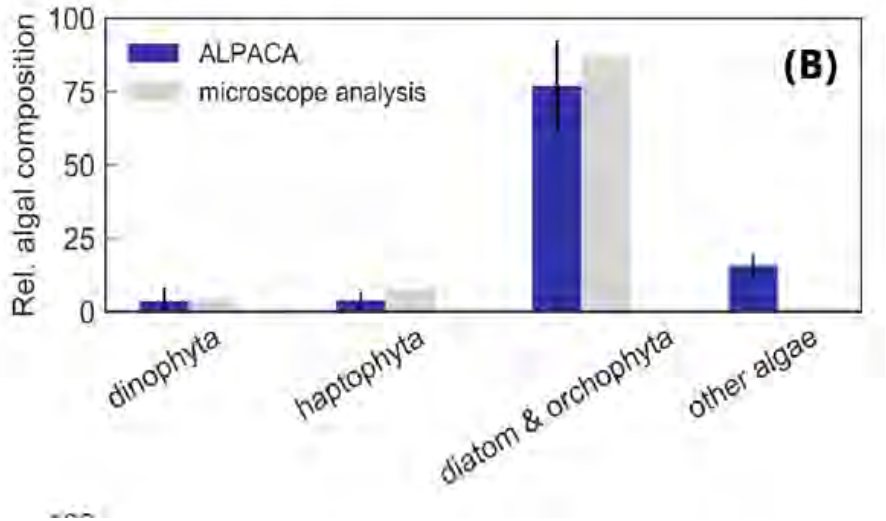
Excitation spectrum Amphora sp.

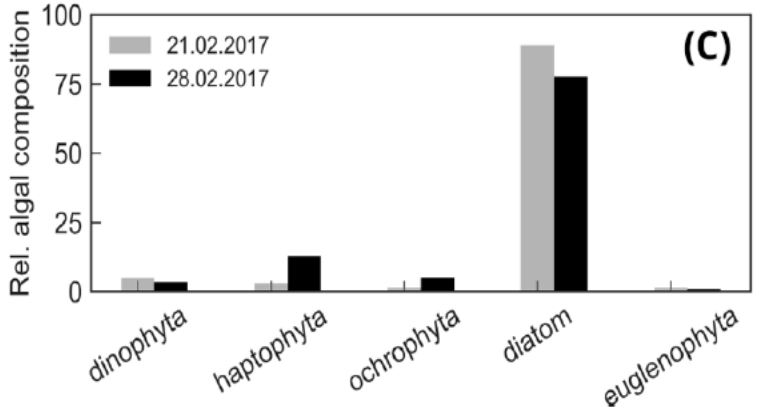


Miniaturized fully Integrated Algae Detection Module - ASM
In situ evaluation and validation (TUGraz, UNIGe-IT, ETT)

➢ **Evaluation: Genoa long-term field tests (15 February - 7 March 2017)**

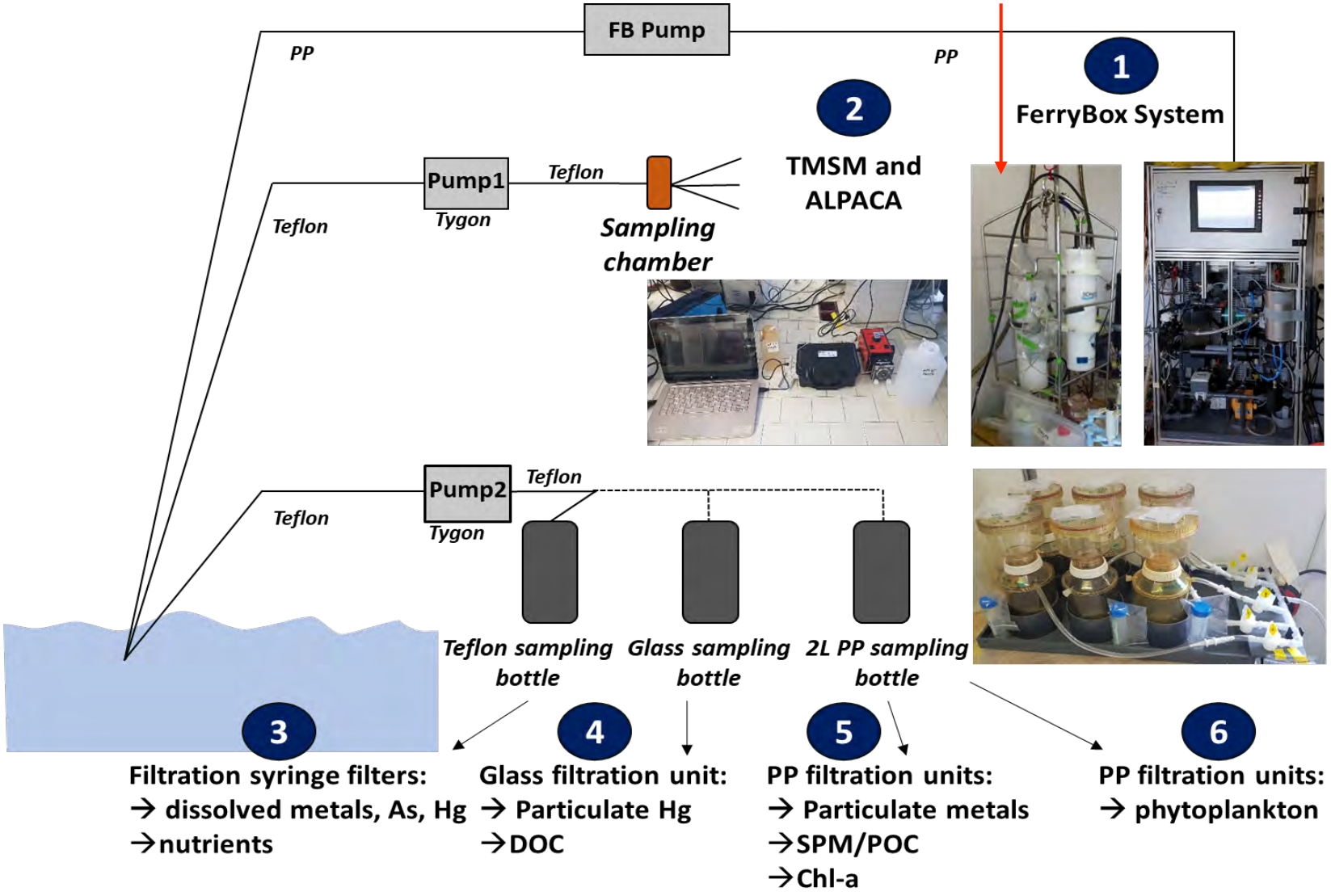






In situ application and validation (UNIGE, UBx, ETT, HZG)

(TMSM: 1 GIMEs; 2 AuNP-GIMEs)



M. Abdou[a], P. Groc[a*],
J. Schäfer[b], M. Labassa[b*], T. Devanne[b*],
A. Novellino[c], S. Alloisio[c], L. Bonofiglio[c],
B. W. Petersen[d], D. Blandfort[d]

Field tests Elbe (MEPHY)

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ETT Luca Bonofiglio
Susanna Alloisio

HZG Willi Petersen
Daniel Blandfort

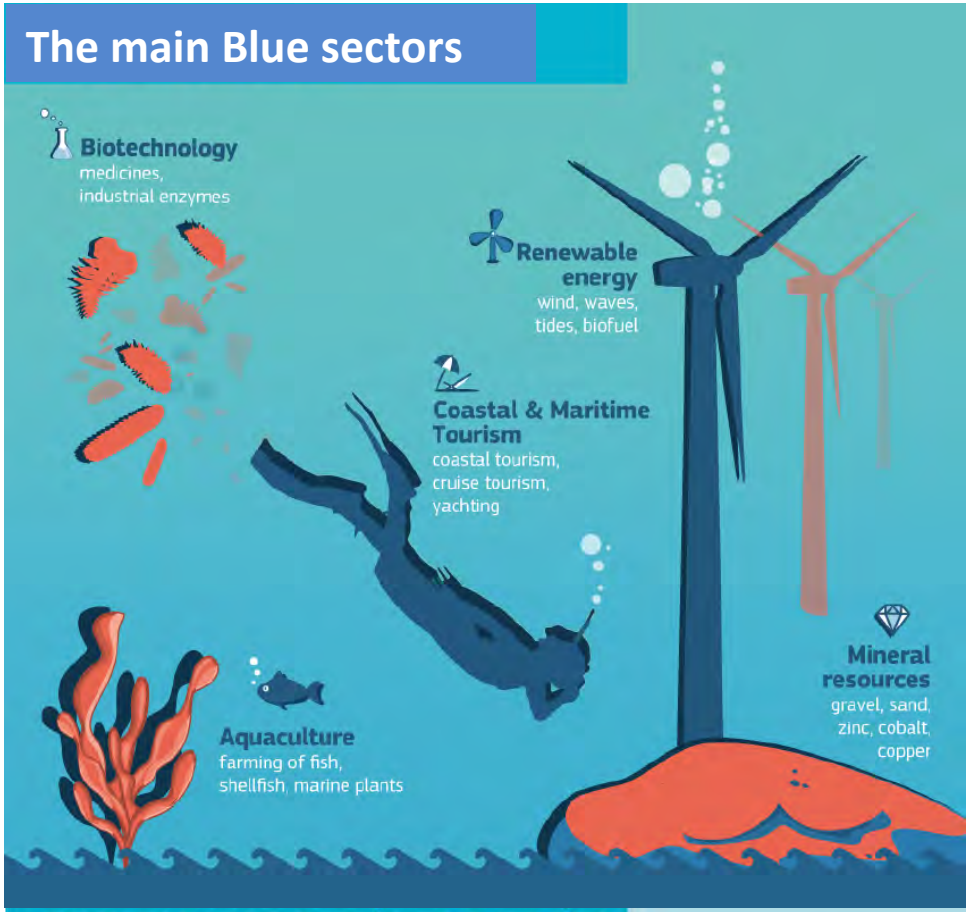
**Master students*

Marine ecosystems: cradle of life on the Earth

- 94 percent of life on Earth is aquatic

Ocean resources and contribution to economy : Well being of billions of people

The main Blue sectors



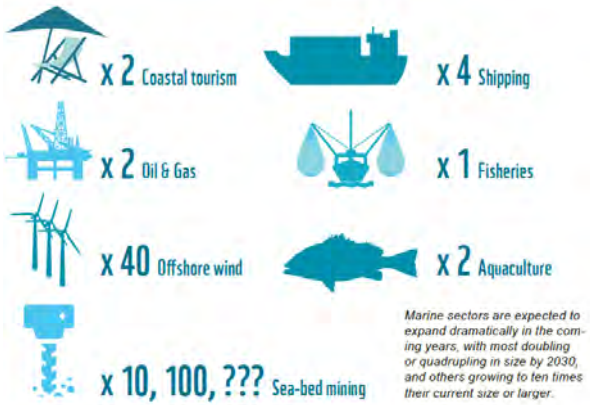
http://ec.europa.eu/maritimeaffairs/policy/blue_growth/index_en.htm

The EU 'blue' economy represents roughly **5.4 million jobs** and generates a gross added value of almost **€500 billion a year**.

Global economic output of the World's oceans and seas, per year

TYPE OF OUTPUT	BILLION US$
Direct output (fishing, aquaculture, etc.)	400 – 420
Services (tourism, education etc.)	365 – 400
Trade and transportation (shipping)	700 – 750
Adjacent benefits (carbon sequestration, biotechnology etc.)	890 – 1,000
Other intangible benefits*	nonquantifiable
TOTAL	**US$2.4 – 2.6 TN**

Estimated Global Blue Growth until 2030



Source: "Restoring the Ocean Economy – Action Agenda 2015," WWF

Ocean monitoring and risk assessment

- **Detailed spatial and temporal measurements required for efficient**
  - ✓ ***water quality monitoring***
  - ✓ ***risk assessment***
  - ✓ ***to define appropriate action to ensure further sustainable management and therefore Blue Growth Economy***

Chemical sensor probe network development: Criteria of current R&D

- ✓ ***Innovative sensors with improved:***
  - sensitivity, selectivity and reliability
  - robustness
- ✓ ***Miniaturization***
- ✓ ***Minimum reagents requirements***
- ✓ ***Low power consumption and cost***
- ✓ ***Standardization of :***
  - wired and wireless networking solutions
  - web-based data information system

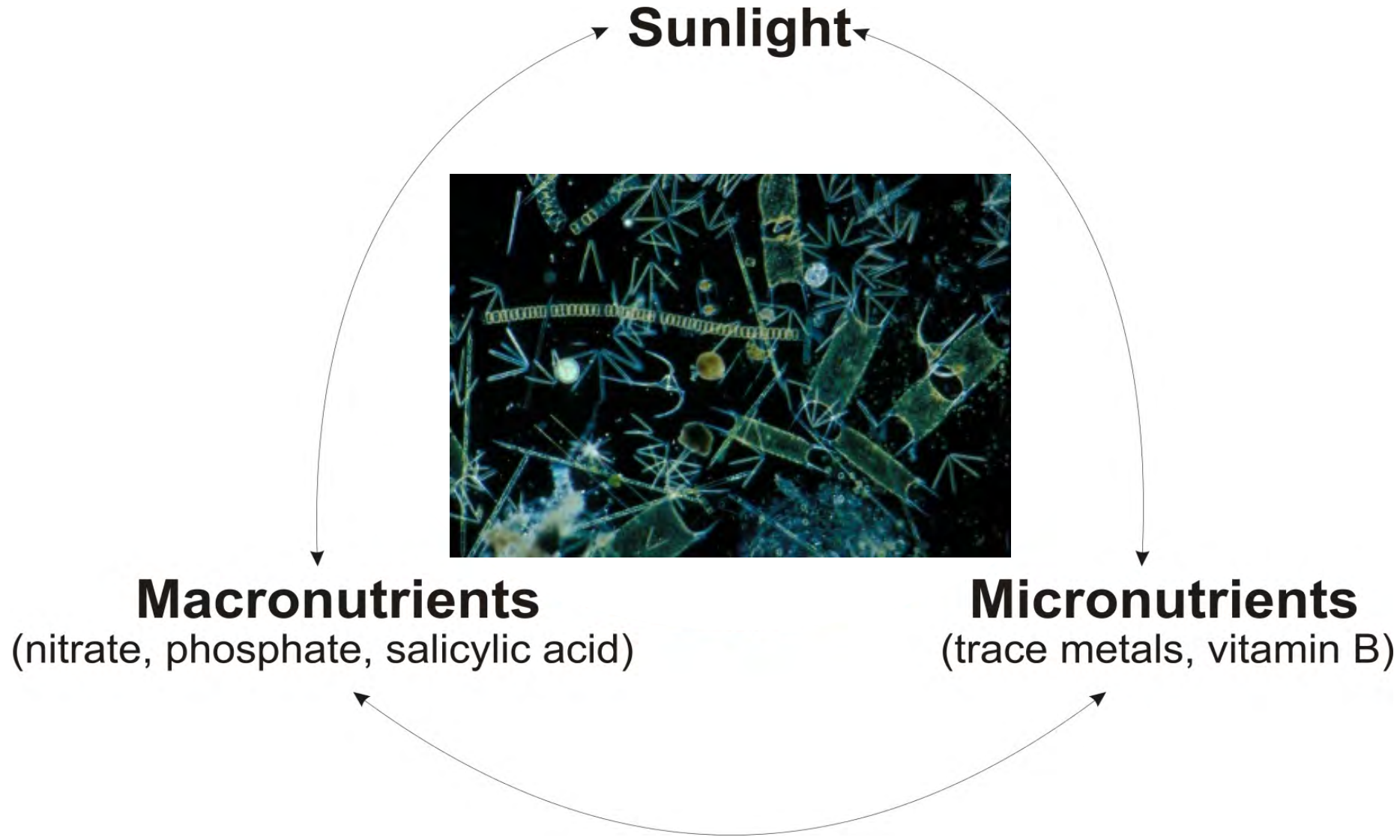
Sensors and probes for trace metals
(UNIGE, IDRO, EPFL)

- **TMSM analytical performance and potentiality for environmental and water quality monitoring**

Me	LOD 190-GIME / nM (ng/L)		LOD 500-GIME / nM (ng/L)	
	Preconc.: 10 min	Preconc.: 30 min	Preconc.: 10 min	Preconc.: 30 min
Hg(II)	0.04 (8)	0.01 (2.5)	0.017 (3)	0.006 (1.2)
As(III)	0.50 (35)	0.20 (15)	0.20 (15)	0.08 (6)
Cu(II)	0.25 (15)	0.10 (6.3)	0.10 (6.3)	0.04 (2.5)
Pb(II)	0.02 (4)	0.01 (2)	0.01 (1.6)	0.005 (1)
Cd(II)	0.03 (3)	0.01 (1)	0.015 (1.5)	0.005 (0.6)
Zn(II)	0.40 (25)	0.15 (10)	0.15 (10)	0.05 (3)

Parameter	Units	Open Sea	Coastal / surface water	AA-WQS
Dissolved Inorganic **Mercury (II)**	nM	0.0002-0.0015	0.001 - 15	1.50
Dissolved Inorganic **Arsenic (III)**	nM	0.3-0.6	1 - 500	130.00
Dissolved **Copper (Cu)**	nM	0.5-5	1 - 235	80.00
Dissolved **Lead (Pb)**	nM	0.005-0.09	0.03 - 200	120.00
Dissolved **Cadmium (Cd)**	nM	0.001-1.2	0.005 - 25	22.00
Dissolved **Zinc (Zn)**	nM	0.1 - 8	0.3 - 680	610.00

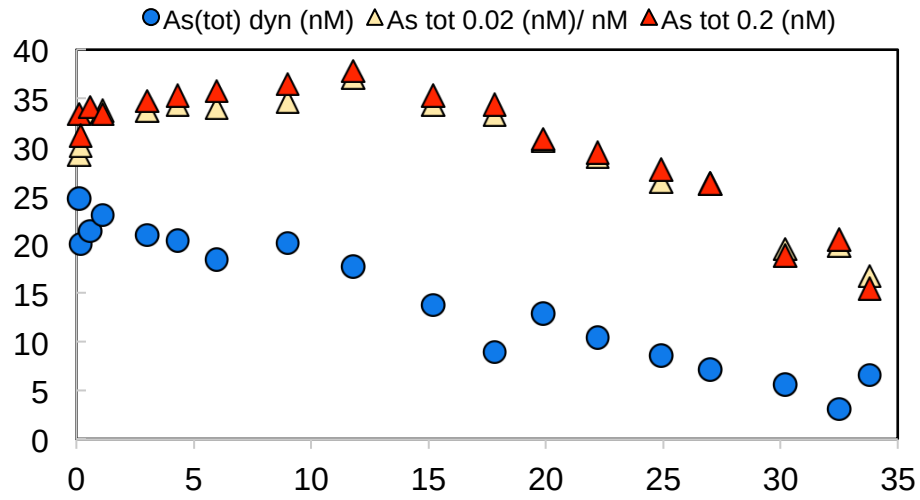
Macro / micronutrients and light: parameters that ensure or limit the development and maintenance of life in aquatic environments

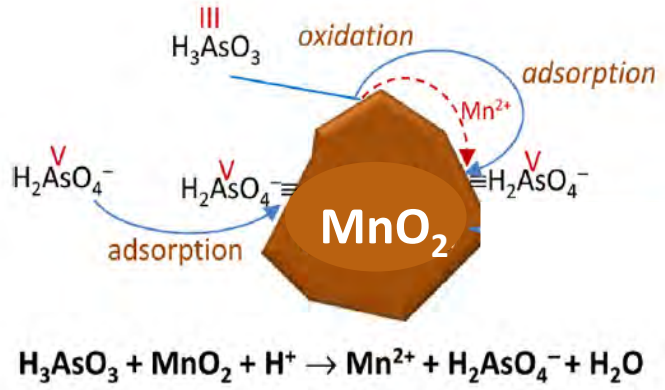


Sensors and probes for trace metals

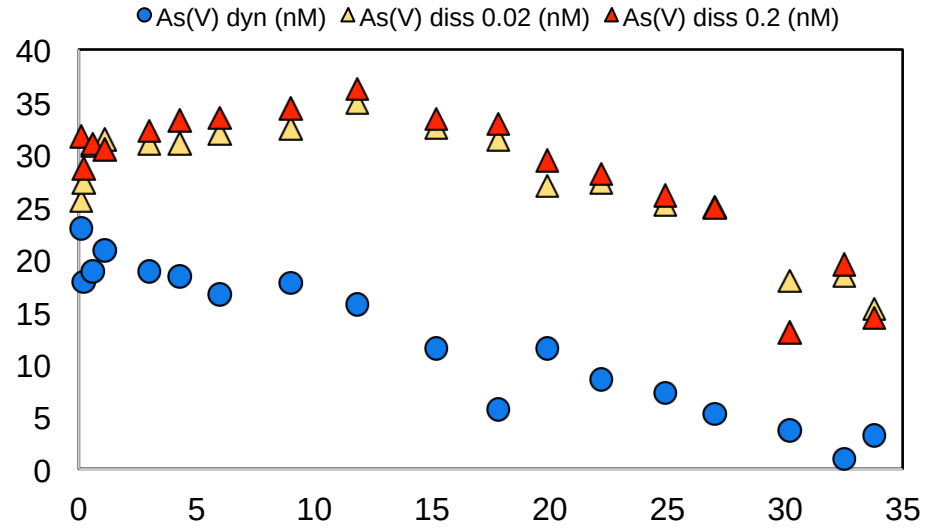
In situ application and validation (UNIGE, UBx)

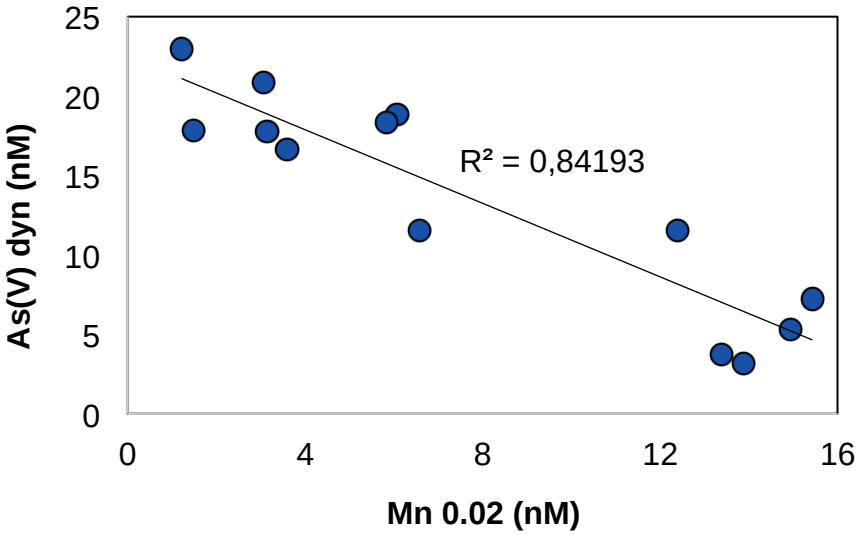
AuNP-GIME TMSM: As(V), As_{tot} - Gironde Estuary – June 2017





$$H_3AsO_3 + MnO_2 + H^+ \rightarrow Mn^{2+} + H_2AsO_4^- + H_2O$$





Integrated Multifunctional Intonomous In situ Sensor Observation System

Miniaturized fluorometer:

+ Low-cost and miniaturized device

+ *In situ* applications possible

+ Cyanobacteria vs. algae

- No further identification of relevant algal classes
- Interferences from ambient light

Flow cytometer:

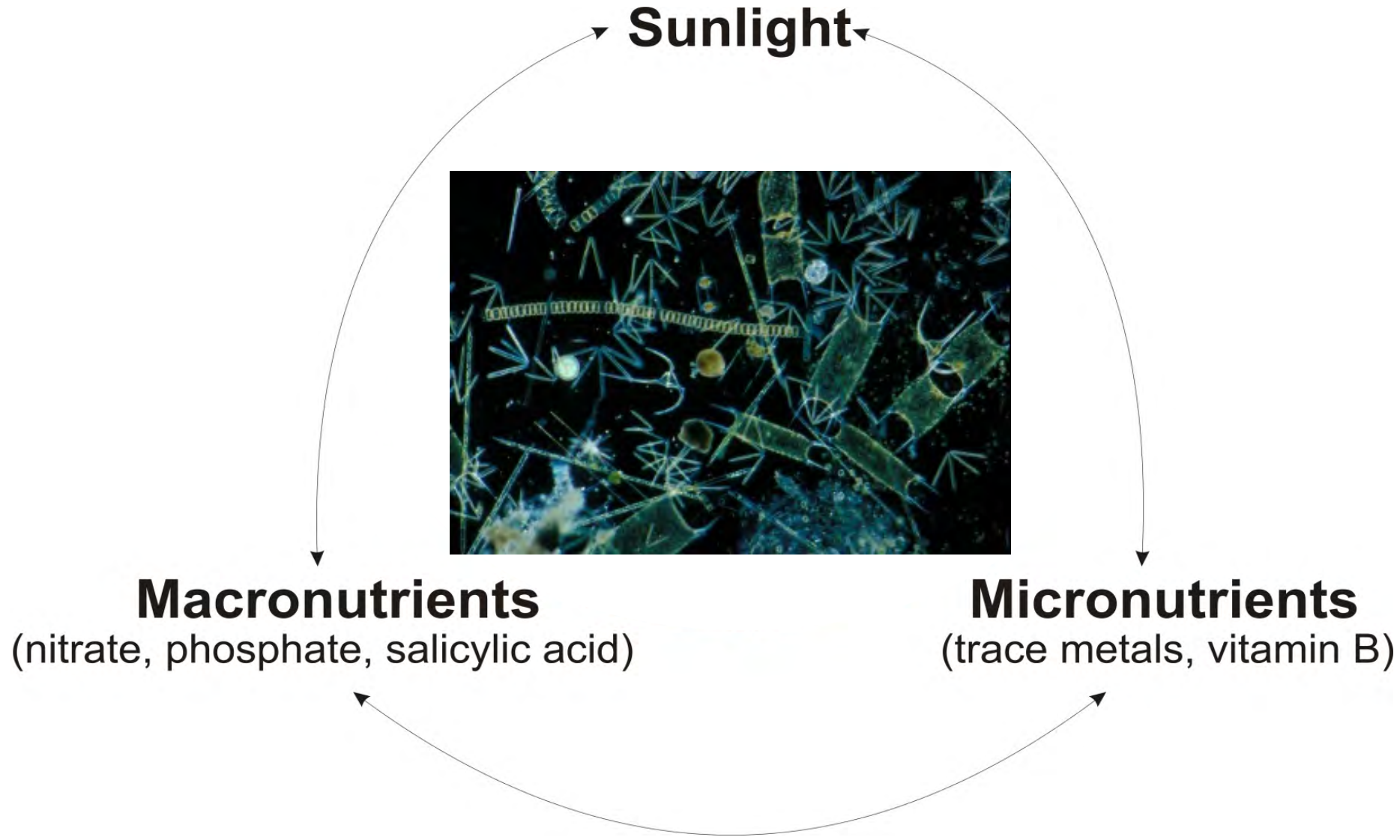
+ Single cell detection

+ Distinct species identification

+ Highly selective

- High fabrication costs
- Time and energy consuming
- Not submersible

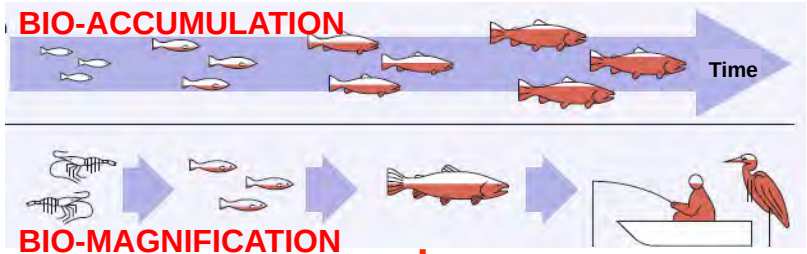
Sources, behaviour, fate and synergic interaction



Target analytes

METALS

NUTRIENTS

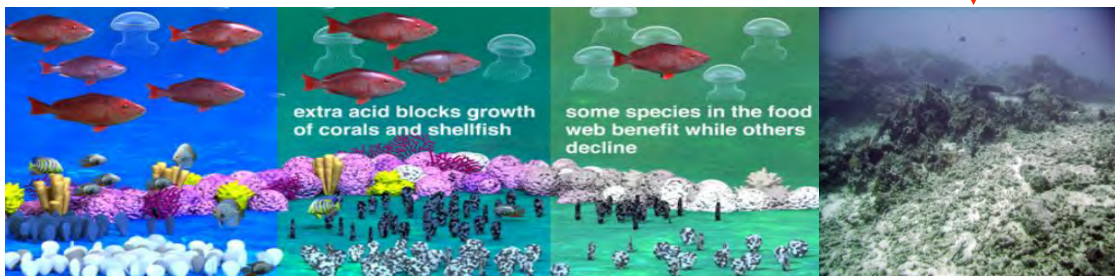


(HARMFUL) ALGAE

PHYCOTOXINS

EUTROPHICATION

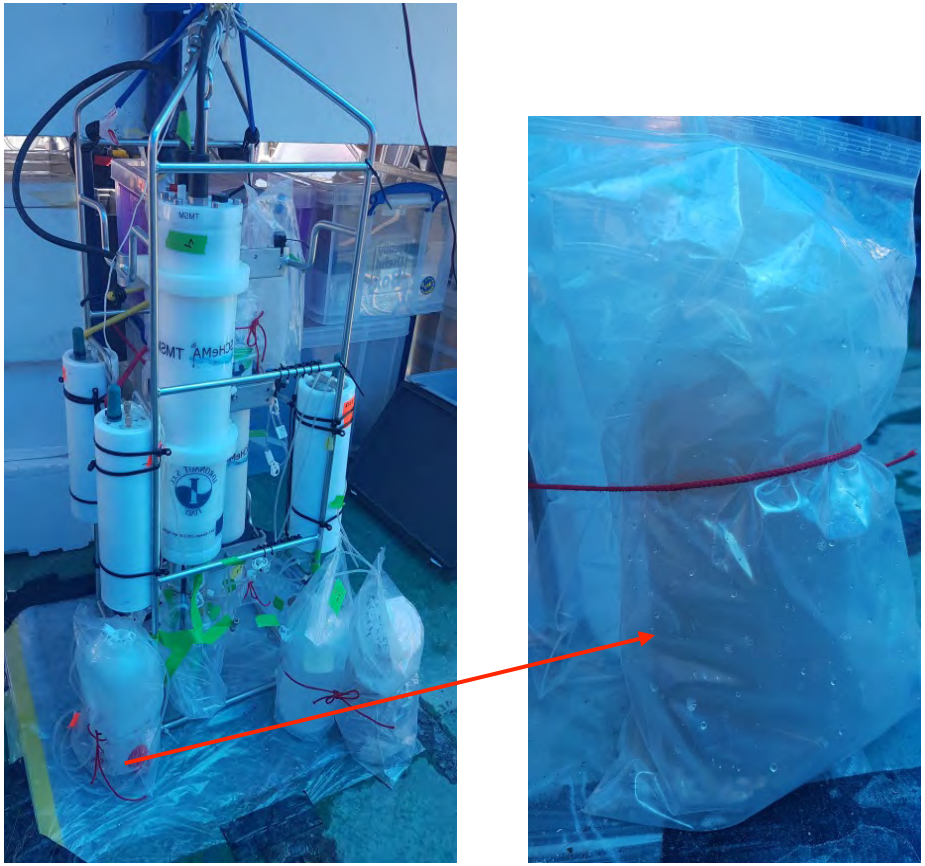
O_2 DEPLETION



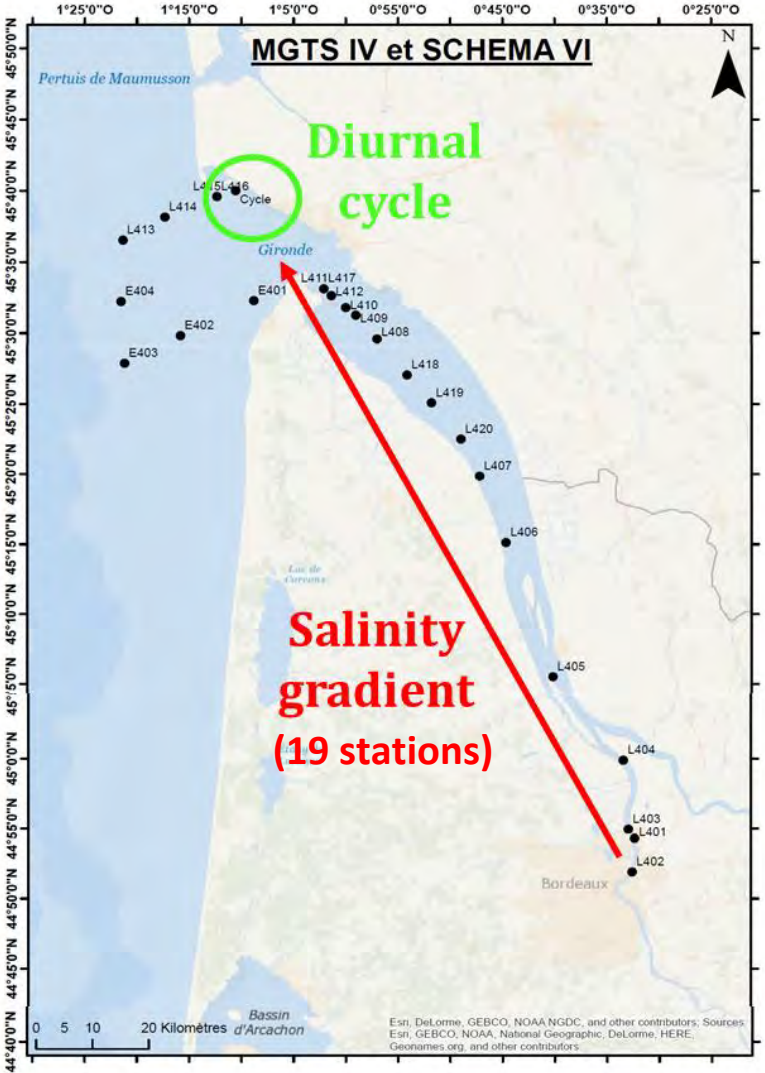
In situ application and validation (UNIGE, UBx, UNIGe-IT)

➢ **Gironde estuary – June 2017**

- Reliability of GIME measurement in salinity gradient and highly turbid system (SPM: 55 to 1600 mg/L)



(2 Hg-GIMEs; 1 AuNP-GIME)



FP7: Ocean of Tomorrow projects

- **9 Partners from 6 different countries (*5 Universities, 3 SMEs, 1 Federal Institute of Technology)***

University of Geneva
Switzerland

Idronaut S.r.l
Italy

University of Ulm
Germany

Graz University of Technology
Austria

EPFL
Switzerland

NanoMyP
Spain

University of Bordeaux
France

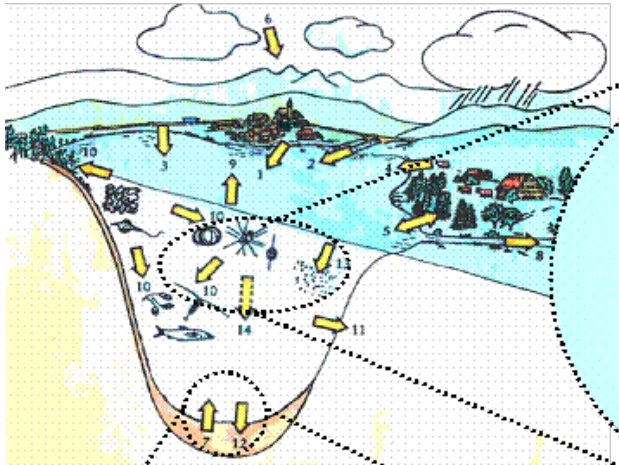
University of Genoa
Italy

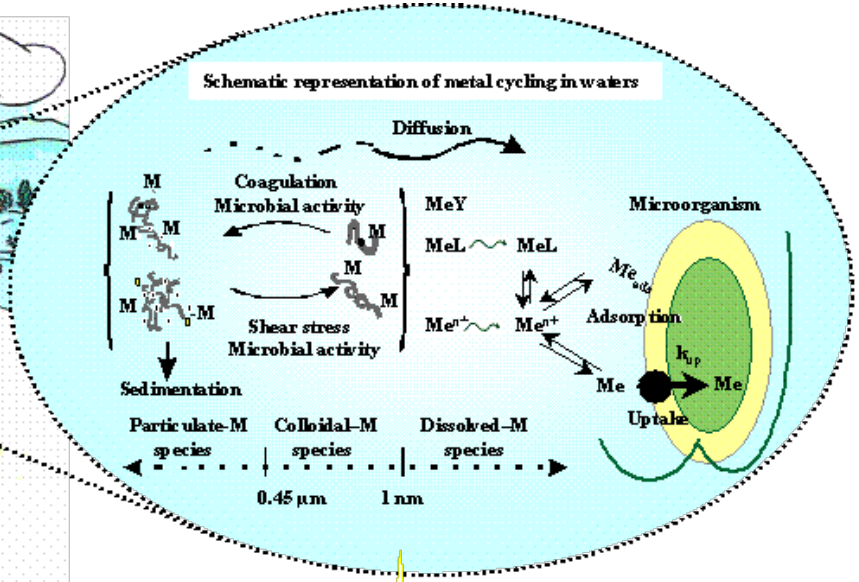
ETT S.p.a.
Italy

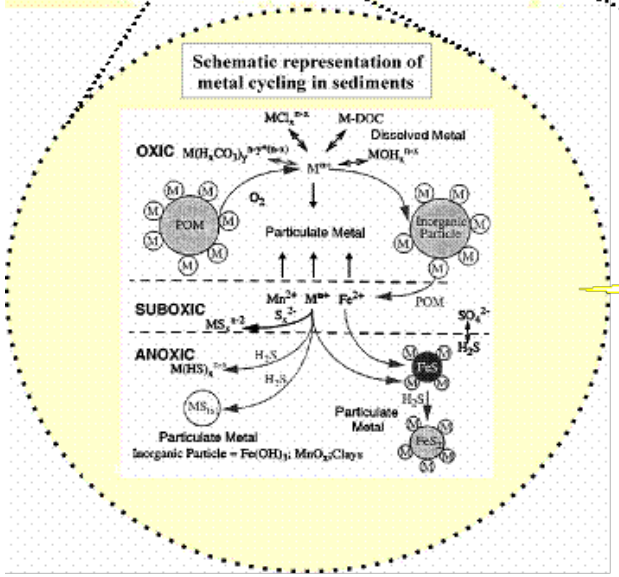
- **Starting date:** 1st October 2013 (48 months)
- **Total budget:** € 6.74 Million
- **EU contribution:** € 5.2 Million

Metal role, behavior and fate are very complex:

- inherently persistent (i.e. non bio-degradable)
- involved in bio-geochemical processes







Free Me ions
Simple inorganic Me species
Organic Me complexes
Me adsorbed on colloids/particles

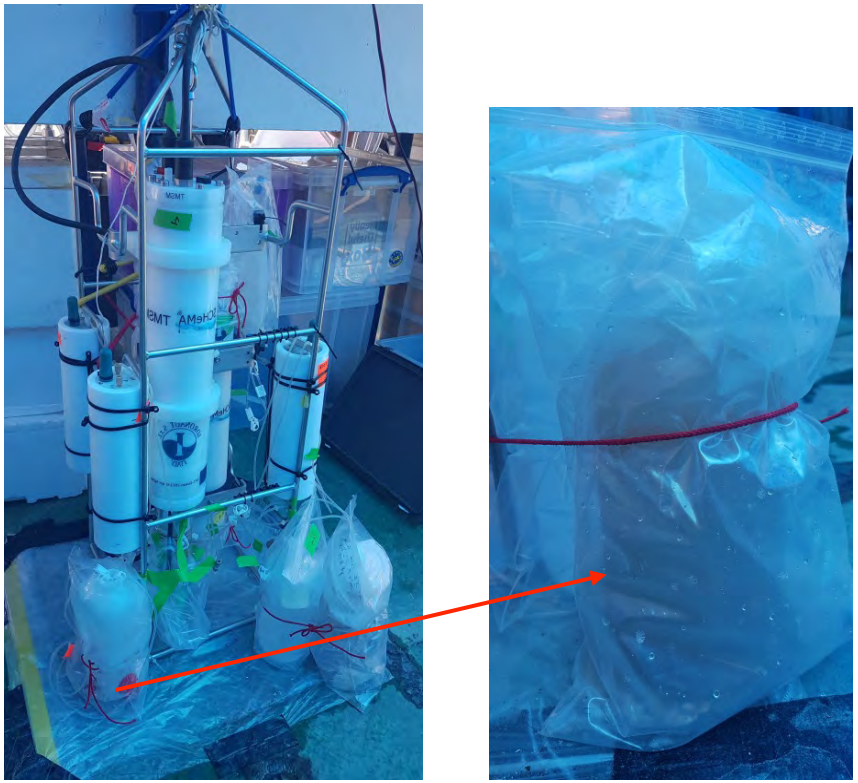
Réactivité ?
Biodisponibility ?
Ecotoxicité ?
Propagation?

Sensors and probes for trace metals

In situ application and validation (UNIGE, UBx, UNIGe-IT)

Hg-GIME TMSM: copper, lead cadmium, zinc

- **Gironde estuary – June 2017**
  - Reliability of GIME measurement in salinity gradient and highly turbid system (SPM: 55 to 1600 mg/L)



(2 GIMEs; 1 AuNP-GIME)