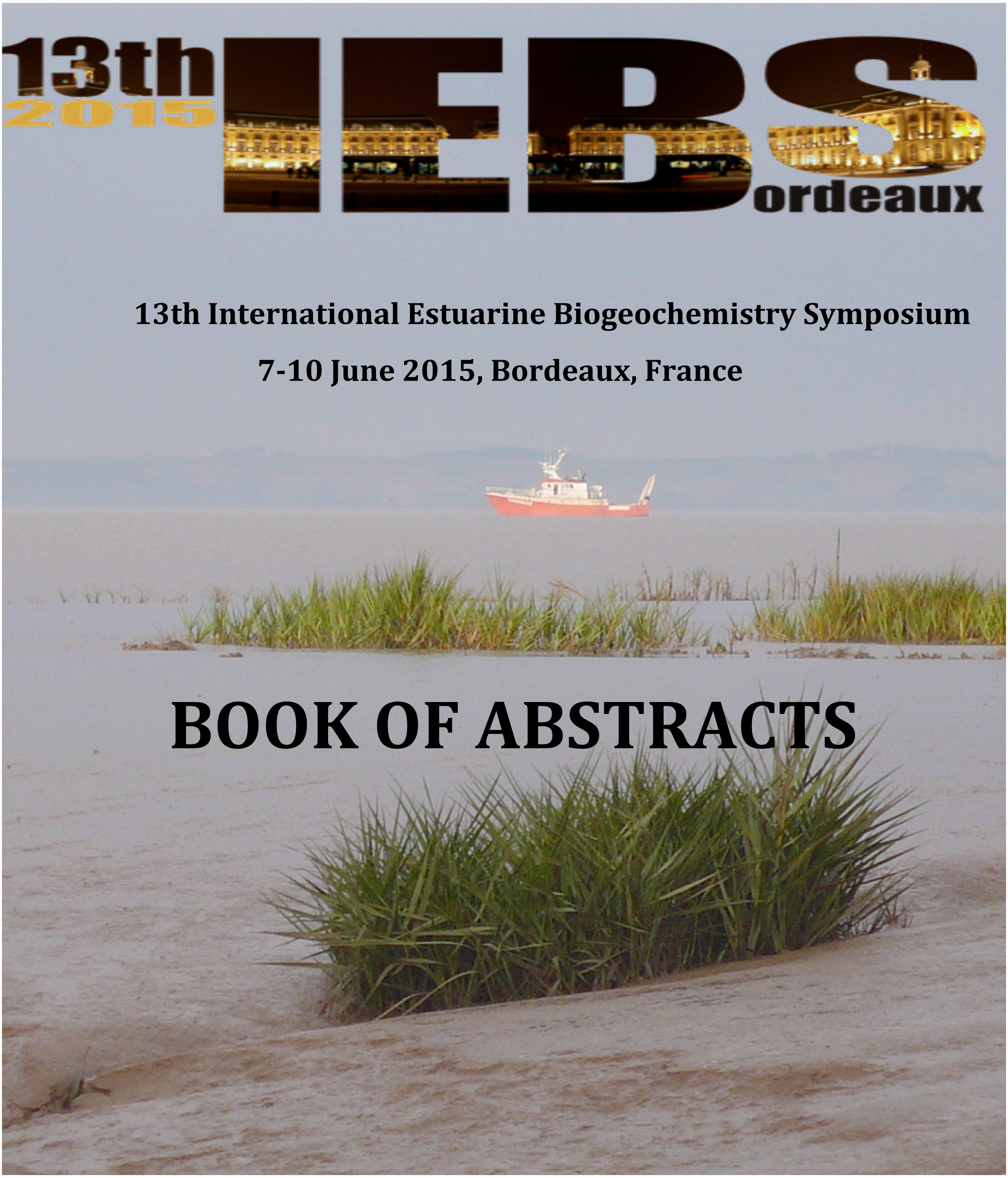

# 13th IEBS 2015 Bordeaux

## 13th International Estuarine Biogeochemistry Symposium

7-10 June 2015, Bordeaux, France

# BOOK OF ABSTRACTS

SCHeMA Integrated in Situ CHemical MApping probes

SEVENTH FRAMEWORK PROGRAMME

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# PROGRAMME

## International Scientific Committee:

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**Minhan Dai**
**Johan Ingri**
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## *Monday, June 8:*

### *Oral session 1:* ***Past, present and future anthropogenic pressure – how do environmental changes affect nutrient and Organic Matter cycles, eutrophication, contaminant fate, coastal ocean acidification and ecosystem functions?***

08:30 ***Registration***

09:00 Symposium opening
*Jörg Schäfer*

09:15 ***Opening lecture:***
Reconstructing the past, predicting the future: geochemical records of estuarine change
*Andrew Cundy*

09:40 The International Estuarine Biogeochemistry Conference: A prospectus on meeting goals with progress
*Thomas Church*

10:00 Historical records and geographical distribution of metallic pollution in sediments of the estuary of the Nerbioi-Ibaizabal Estuary (Bilbao, Basque Coutry)
*Azibar Rodriguez-Iruretagoiena, Nerea Elejoste, Ainara Gredilla, Silvia Fernandez-Ortiz de Vallejuelo, Gorka Arana, Juan Manuel Madariaga, Alberto de Diego Rodriguez*

10:20 Natural radionuclides enhanced by industrial activities: a 50 years sediment record in the upper Seine Estuary
*Dominique Boust, Patrick Lesueur, Luc Solier, Marianne Rozet, Carole Dubrulle-Brunaud*

10:40 ***Coffee Break***

11:05 Anthropogenic tritium in the Loire River estuary
*Olivier Péron, Claire Gégout, Benjamin Reeves, Gilles Montavon, Catherine Landesman*

11:25 Mercury speciation in waters from the Aveiro Lagoon (Portugal)
*Teodor Stoichev, Emmanuel Tessier, Marisa Almeida, David Amouroux, Maria Clara Basto, Vitor Vasconcelos, Olivier Donard*

11:45 ***Poster flash presentations***

12:25 ***Lunch Time & Poster Session***

14:00 Contrasting geochemical behavior and sources of Osmium and Platinum in the environment as revealed from intertidal sediments
*Clara Almecija, Antonio Cobelo-Garcia, Mukul Sharma, Juan Santos-Echeandia, Miguel Caetano*

14:20 Occurence, sources and fate of pesticides in Gironde estuary (France)
*Justine Cruz, Patrick Pardon, Karyn Le Ménach, Marie-Hélène Dévier, Hélène Budzinski*

14:40 Occurrence of synthetic musk compounds in the Adour estuary (SW France) and their fate during treatment processes
*Laurent Lanceleur, Joana Cavalheiro, Thierry Pigot, Mathilde Monperrus*

15:00 Dynamics and pathways of glutathione-like and thioacetamide-like compounds in temperate macrotidal estuary (Brittany-France)
*Lauriane Marie, Benoit Pernet-Coudrer, Matthieu Waeles, Ricardo Riso*

15:20 Past and present carbon dynamics in the Scheldt estuary as traced by changes in C speciation and isotopes
*Natacha Brion, Marc Elskens, Loreto De Brabandere, Frank Dehairs*

15:40 ***Coffee Break***

16:05 Biogeochemical characterisation of 200 years local changes in a transitional environment – What is the foraminifera's message?
*Fabio Francescangeli, Eric Armynot du Chatelet, Alain Trentesaux, Thorbjørn Andersen, Vincent Bouchet*

16:20 The freshwater estuaries of the Three Gorges Reservoir in China-Insights from in situ and online monitoring with a MINIBAT multisensor system
*Andreas Holbach, Yonghong Bi, Lijing Wang, Yijun Yuan, Hao Chen, Binghui Zheng, Stefan Norra*

16:40 Approaching environmental Cu and Ag bioaccumulation in oysters (*Crassostrea gigas*) from Gironde Estuary by stable isotope spiking in-vivo experimentations
*Mathilde Mikolaczyk, Ane Rementeria, Laurent Lanceleur, Jörg Schäfer, Jérome Petit, Benat Zaldibar, Jean-François Chiffoleau, Manu Soto, Ionan Marigomez, Gérard Blanc*

17:00 Geochemical patterns applied to Corbicula fluminea as a tool for Acid Mine Drainage Pollution Assessment in Sediment from the Iberian Pyrite Belt: North-American Shale Composite (NASC)-normalized Rare Earth Element patterns application.
*Bonnail Estefania, Sarmiento Aguasanta M., Pérez-López Rafael, Del Valls Casillas T. Angel , Nieto Liñán José Miguel*

17:20 Origin, Transport and Fate of Particulate Organic Carbon and Nitrogen along the Land-Sea Interface of the São Francisco River-Estuary, NE-Brazil
*Bastiaan Knoppers, Paulo Medeiros, Tim Jennerjahn, Luiz da S. Fontes, Marcileia do Carmo, W de Souza, M Messias, M Arguelho, I Carvalho, M Silva, M Carneiro*

17:40 ***End of Session 1***

## *Tuesday, June 9:*

### *Oral session 2: Physical and chemical factors influencing biogeochemistry and exchanges at estuarine boundaries (sediment-water-air, urban areas, subterranean estuaries).*

08:50 Introduction to the Session 2
*Jörg Schäfer*

09:00 Influence of environmental variables on the early diagenesis of Fe and Mn in the Laurentian Trough - one of the world's largest estuaries
*Qiang Chen, Alfonso Mucci, Bjorn Sundby*

09:20 Trace metal cycling in the Baltic Sea: role of suspended Mn and Fe particles
*Johan Ingri, Susanne Bauer*

09:40 Fe isotopes in the near-shore environment - fractionation in the sediments and the water column
*Michael Staubwasser, Susann Henkel, Sabine Kasten, Simon Poulton*

10:00 Natural and anthropogenic processes controlling trace metals dynamics in a highly stratified estuary: the Krka River estuary (Adriatic, Croatia)
*Ana-Marija Cindric, Cédric Garnier, Benjamin Oursel, Ivanka Pizeta, Dario Omanovic*

10:20 Influence of seasonal diminishing of river discharge on the trace metals distribution and fluxes in estuaries
*Vladimir Shulkin, Pavel Tishchenko*

10:40 ***Coffee Break***

11:05 Spatial and seasonal variability of reactive metals in surface sediments of the Morbihan coast (South Brittany)
*Joselyn Jimenez, Evelyne Goubert, Laurent Labeyrie, Alexandra Coynel, David Menier*

11:25 ***Poster flash presentations***

12:25 ***Lunch Time & Poster Session***

14:00 Conservative or Reactive? Permafrost-derived organic matter in the Lena River Delta
*Boris Koch, Ivan Dubinenkov, Ruth Flerus, Philippe Schmitt-Kopplin, Gerhard Kattner*

14:20 Evolution of molecular weight and type of dissolved organic matter in the Gironde Estuary using asymmetrical field flow fractionation
*Jérémie Parot, Edith Parlanti, Céline Guéguen*

14:40 Nutrient cycling along a subterranean estuary and the discharge zone
*Mathilde Couturier, Gwénaëlle Chaillou, Christian Nozais*

15:00 Nutrient flux through the subterranean estuary of the 240 km-long Aquitanian coast
*Pierre Anschutz, Céline Charbonnier, Loris Deirmendjian, Damien Buquet, Pascal Lecroart*

15:20 Carbon mitigation: a salt marsh ecosystem service in times of change
*Isabel Caçador, Bernardo Duarte, João Marques, Noomene Sleimi*

15:40 ***Coffee Break***

16:05 A large annual $CO_2$ sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil)
*Luiz Carlos Cotovicz Jr, Bastiaan Knoppers, Nilva BRANDINI, Suzan Da Costa Santos, Gwenaël Abril*

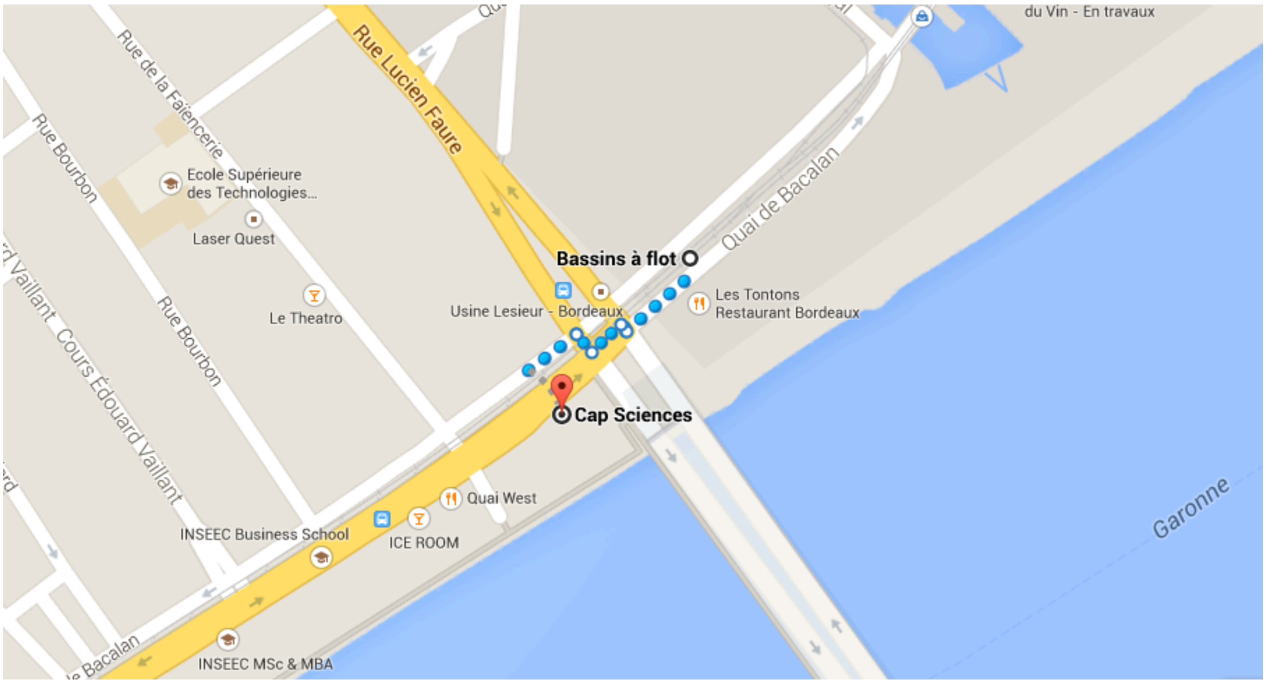
16:25 Effects of $CO_2$ leakage from CCS technology using a mixed marine microalgae population
*Esther Bautista Chamizo, Manoela Romanó de Orte, Inmaculada Riba López, T. Angel del Valls Casillas*

16:45 ***End of Session 2***

19:30 ***Conference Dinner: CapSciences***

**Location:** CapSciences - 20 Quai de Bacalan, 33300 Bordeaux

The building is at 1 min. walk from the “Bassins à flot” tramway station of the B Line.



## ***Wednesday, June 10:***

### ***Oral session 3:* New experimental techniques and technologies for in-situ high-resolution monitoring and modelling of element cycles in coastal environments.**

09:00 Introduction to the Session 3, supported by the SChemA project

09:20 ***Keynote speaker:***
Interconnections between Estuaries, Human Health and Wellbeing
*Michael Depledge*

10:00 Nutrient and Carbon Cyclingin Coastal Tropical Waters of Hawaii: effects of land- derived inputs, reef biogeochemistry, and physical forcing.
*Eric Heinen De Carlo, Gerianne Terlouw, Patrick Drupp, Fred Mackenzie, Sylvia Musielewicz, Adrienne Sutton, Christopher Sabine*

10:20 Modelling nutrient budgets in the Elbe Estuary (Germany)–role of phytoplanktonas sink and source term
*Andreas Schöl*

10:40 ***Coffee Break***

11:10 Connectivity and fate of nutrients in the Derwent and Huon Estuaries in southeast Tasmania
*Karen Wild-Allen, John Andrewartha*

11:30 Study of water-sediment interface: coupled approach biogeochemistry-modeling for nutrient fluxes evaluation (C, P, N)
*Arnaud Vennin, Valérie Mesnage, Nicolas Lecoq*

11:50 ***Poster flash presentations***

12:30 ***Lunch Time & Poster Session***

14:00 The environmental constraints on faunal distribution: biogeochemical interaction as underlined by geostatistical tools
*Eric Armynot du Chatelet, Viviane Bout-Roumazeilles, Rodolfo Coccioni, Fabrizio Frontalini, Fabio Francescangeli, Giulia Margaritelli, Roberto Rettori, Federico Spagnoli, Federica Semprucci, Alain Trentesaux, Nicolas Tribovillard*

14:20 Geochemical rates estimated from two-dimensional distributions of dissolved iron and phosphate from an intertidal estuarine mudflat
*Aubin Thibault de Chanvalon, Edouard Metzger, Emmanuelle Geslin, Florian Cesbron, Joel Knoery, Aurelia Mouret, Sebastiaan van de Velde, Filip Meysman*

14:40 Lab-on-chip analysers for high resolution in situ analysis of nutrients in estuaries and rivers
*Alexander Beaton, Anouska Panton, Duncan Purdie, Matthew Mowlem*

15:00 The Biofish – an underwater insitu and on line measuring multi-sensor system
*Stefan Norra, Andreas Holbach, Lijing Wang, Hao Chen, Yanwen Qin, Binghui Zheng, Yonghong Bi, Peter Haushahn*

15:20 ***Coffee Break***

15:45 Defining benchmark values for nutrients in twelve Portuguese estuaries under the Water Framework Directive
*Miguel Caetano*

16:05 Abandoned boats as a source of metal contamination of estuarine sediments
*Andrew Turner, Aldous Rees*

16:25 Modelling summer hypoxia in the Gironde estuary, using a 3D model coupling hydrodynamics, sediment transport and biogeochemical processes.
*Katixa Lajaunie Salla, Aldo Sottolichio, Bénédicte Thouvenin, Xavier Litrico, Gwenael Abril*

16:45 ***Awards for the best student oral and poster presentation***

16:55 ***Announcements***

17:00 ***Closing***

***The Organizing Committee greatly acknowledges support by:***

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# ABSTRACTS

# The International Estuarine Biogeochemistry Conference: A prospectus on meeting goals with progress.

Church Thomas [1*]

1: School of Marine Science and Policy (SMSP/CEOE) University of Delaware, Newark, DE 19716-3501 http://www.ceoe.udel.edu
*: Corresponding author

For many decades, changing climate and population growth have had major impacts, particularly in estuarine and coastal regions. Manifest has been alterations to watersheds, freshwater runoff and sea-level rise and. These have led to significant changes in estuarine circulation, chemical input, sedimentary storage and ecology.

Biogeochemical processes have been represented by property-property (salinity) parameterization and end member mixing experiments. This revealed how scavenging via « flocculation» of humic material affect primarily nutrients and trace elements, many of pollutant interest. Estuarine reaction zones have been envisioned as more «geochemical» in upper turbid areas and more «biochemical» in productive photic zones of lower areas.

By the end of the 1980's, estuarine chemists from North America and Europe conceived better international cooperation in the study of the estuarine biogeochemistry. A series of symposia was proposed to be convened every 2 years to present results to compare different estuarine systems. They identified processes where specific characteristic(s) may dominate regional biogeochemistry. As such, comparison of 'model estuaries' could lead to fundamental understanding of estuarine biogeochemical processes.

Thus the First International Symposium on the Biogeochemistry of Model Estuaries was held in Primosten, the former Yugoslavia, May 1989 (Marine Chemistry; 32, 2-4, 1991). The second symposium was held in May 1991 at Jekyll Island, Georgia, USA with the overall goal of evaluating estuarine processes in global change. As many themes went beyond this scope, continued use of «model» in the series title was discontinued. However, estuarine models have progressed beyond property/property evidence of estuarine sources and sinks. Now there has been the introduction of numerical models and quantification of scavenging rates with the use of natural radionuclides. Discovered are new important inputs such as ground water in the subterranean estuary.

# Historical records and geographical distribution of metallic pollution in sediments of the estuary of the Nerbioi- Ibaizabal Estuary (Bilbao, Basque Country).

Rodriguez-Iruretagoiena Azibar [1*], Elejoste Nerea [1], Gredilla Ainara [1], Fernandez-Ortiz De Vallejuelo Silvia [1], Arana Gorka [1], Madariaga Juan Manuel [1], De Diego Rodriguez Alberto [1]

1: Department of Analytical Chemistry; Faculty of Science and Technology; University of the Basque Country PoBox 644; 48080 Bilbao, Basque Country
http://www.ehu.es/eu/web/ibea/home
*: Corresponding author

Pollution in estuaries is an issue of high concern for scientists, and local stakeholders and authorities. Sediments have been frequently used as sentinels of chemical pollution, including metals and metalloids. The estuary of the Nerbioi-Ibaizabal River was subjected to an important input of metals since the late XIXth century until about 1975. Afterwards, a significant decrease in chemical pollution has occurred due to a progressive closure of the most polluting activities and the pre-treatment of waste waters. However, an important actuation, including a large movement of highly polluted sediments, has recently started in order to reduce the effects of floods and improve the urban image of the city. It is therefore of interest to have a precise description of the situation in terms of chemical pollution, in order to make feasible a future quantification of the effects derived from the above-mentioned actuation. With this aim, we collected sediments at about 50 sites in the inter-tidal part of the estuary in January 2009, 2010, 2011 and 2014, and the concentration of fourteen elements (Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn) in the acidic extract of the samples was simultaneously measured by ICP/MS. Geoaccumulation indexes to estimate the metal fraction of anthropogenic origin, Normalized and Weighed Average Concentrations (NWAC's) to identify areas of higher concern and mean Effect-Range-Median quotients (mERMq's) to estimate the toxicity associated to the samples were computed. The results show that i) the geographical distribution of metals is rather heterogeneous within the estuary with relatively high concentrations only in a few points (docks of Axpe and Udondo, channel of Deustu, and the surroundings of the Galindo WWTP), ii) the toxicological risk associated to these sediments goes from slight to moderate and, iii) the situation remains fairly constant over the period investigated.

Acknowledgements: This work has been financially supported by the SUDOE Interreg IV B Programme through the ORQUE SUDOE (Ref. SOE3/P2/F591/5) project and the Basque Government through the Consolidated Research Group Project 2013-2018 (Ref. IT-742-13). A. Rodriguez-Iruretagoiena is grateful to the UPV/EHU for his pre-doctoral fellowship.

# Natural radionuclides enhanced by industrial activities: a 50 years sediment record in the upper Seine estuary.

Boust Dominique[1], Lesueur Patrick, Solier Luc, Rozet Marianne, Dubrulle-Brunaud Carole

1: Laboratoire de Radioécologie de Cherbourg-Octeville (IRSN) Institut de Radioprotection et de Sûreté Nucléaire (IRSN); BP10 50130 CHERBOURG-OCTEVILLE

Long-term sediment records allow to reconstruct the history of past contamination and, deciphering the response of catchment areas, to predict how anthropogenized rivers and estuaries are liable to recover from former discharges and fallout. We report data from two sediment cores collected (1) in the lower Seine river (a flood plain) and (2) in the upper tidal estuary (a Rouen harbour basin). Both cores were successfully dated using artificial radionuclides yielding an accurate and reliable age model over the last 50 years.

Numerous geochemical data were produced on these unique sediment records. Among them, we will focus on the naturally-occurring radionuclides, as most of them display huge concentrations from mid-1960s to mid-1980s, and only in the core collected in the Rouen harbour. Indeed, between 1965 and 1987, considerable amounts (up to 2.106 tons per year) of phosphogypsum (also referred to, more generically, as TNORM, for Technologically Naturally Occurring enhanced Radioactive Material) were discharged in the upper estuary either by direct discharge or via losses during loading or transportation operations.

The phosphogypsym is a by-product of the wet-process fertilizer production from phosphate ores that are naturally uranium-enriched ($^{235}$U and $^{238}$U and radionuclides of their decay chain up to some thousands of Bq.Kg$^{-1}$). In the course of the phosphoric acid production, the raw material is dissolved by sulphuric acid and the radionuclides released in solution react in accordance to their relative affinity to phosphate or sulphate phases. Consequently, U and Th series in the phosphogypsum are far from being in a state of secular equilibrium, that is to say that they display very different activities: e.g. 1500 Bq.kg$^{-1}$ for $^{226}$Ra versus 200 Bq.kg$^{-1}$ for $^{232}$Th, in the same sample. Disequilibria observed in the U and Th series will be presented and interpreted, taking into account radionuclide chemical properties and post-process equilibration of the short lived radionuclides. Contribution of this industrial source versus time can be accurately deciphered by comparison to the core collected at the upstream site which is out of reach of this contamination, due to a weir located some 40 km upstream of the Rouen harbour.

# Anthropogenic tritium in the Loire River estuary.

Péron Olivier [1]*, Gégout Claire, Reeves Benjamin, Montavon Gilles, Landesman Catherine

1: Laboratoire de physique subatomique et des technologies associées (Subatech)
CNRS: UMR6457Université de Nantes
Ecole des Mines de Nantes 4, rue Alfred Kastler La Chantrerie BP 20722 44307 Nantes cedex 3
*: Corresponding author

The aim of radioecology is to understand the transfer of radionuclides through the ecosystem. It relies strongly on field studies which can provide useful information on the presence of radionuclides in the environment, and their origins (natural and anthropogenic). In this study, the radioactive isotope of hydrogen, i.e. tritium (3H or T), is considered. Tritium is a beta emitter with a radioactive half life of 12.3 years. It is present in the environment in three principal forms: tritiated water (HTO or free water tririum), organically bound tritium (OBT) and tritiated gas (HT). Tritiated water is the most abundant chemical form of tritium in the aquatic and terrestrial environment.
Within the scope of radioecological monitoring of anthropogenic tritium, mud, sediment core and water samples were recovered from upstream and downstream of several nuclear power plants on the Loire River to the estuary. The Loire estuary is the outlet of a watershed where several nuclear power plants are located. Mud and sediment core samples were subjected to freeze-drying and combustion as pre treatment in order to recover free HTO and total OBT respectively. Free HTO (lyophilisation water) and total OBT (combustion water) activities from mud samples range from 3.9 ± 0.6 to 26.1 ± 3.2 $Bq.L^{-1}$ and from 10.3 ± 2.8 to 22.9 ± 3.4 $Bq. L^{-1}$, respectively. 3H activity concentrations of a sediment core were also analysed. Free HTO and total OBT activities from sediment core sections range from 2.6 ± 0.5 to 4.1 ± 0.7 $Bq.L^{-1}$ and from 1.3 ± 1.4 to 13.0 ± 0.4 $Bq.L^{-1}$, respectively.

# Mercury speciation in waters from the Aveiro Lagoon (Portugal).

Stoichev Teodor [1], Tessier Emmanuel [2], Almeida Marisa [1], Amouroux David [2], Basto Maria Clara [1], Vasconcelos Vitor [1], Donard Olivier [2]

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HELIOPARC - 2 Avenue du Président Angot 64000 PAU
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Aveiro lagoon (Ria de Aveiro) is a shallow coastal lagoon in the North of Portugal which has suffered from industrial mercury pollution. In Laranjo Bay and Estareja channel previously important gradients of total Hg (HgTOT) concentrations in water have been observed. This is the first report of methylmercury (MeHg) concentrations in the waters from the Laranjo Bay and Estareja Channel (Aveiro Lagoon).

Water from four selected sites, at high and low tides, were collected during five sampling campaigns. Hg species from suspended particles were extracted with 6M nitric acid using microwave irradiation. Hg speciation analyses in filtered water samples and the extracts were carried out by propylation of the Hg species and gas chromatography (GC) coupled to inductively coupled plasma mass spectrometry (ICPMS) using species-specific isotope dilution analysis. The speciation and distribution of Hg was studied for different hydrological, meteorological, chemical and biological conditions in the Aveiro Lagoon.

This work was partially supported by Observatório de Investigação sobre a Qualidade do Meio Ambiente do grande Sudoeste Europeu (Orque-Sudoe project) and by FCT - Foundation for Science and Technology in Portugal through the fellowship of T. Stoichev (SFRH/ BPD/88675/2012), co-financed by POPH/FSE.

# Contrasting geochemical behavior and sources of osmium and platinum in the environment as revealed from intertidal sediments.

Almecija Clara [1], Cobelo-Garcia Antonio [2], Sharma Mukul [3], Santos-Echeandia Juan [1], Caetano Miguel [4]

1: Instituto de Investigacions Mariñas (IIM-CSIC) Eduardo Cabello 6. 36208 Vigo
2: Instituto de Investigacións Mariñas (IIM-CSIC) Eduardo Cabello 6. 36208 Vigo www.iim.csic.e
3: Radiogenic Isotope Geochemistry Laboratory, Department of Earth Sciences, Dartmouth College Hanover, New Hampshire 03755
4: Portuguese Institute of Sea and Atmosphere (IPMA) Av. Brasilia, 1449-006, Lisbon

The use of catalytic converters in automobiles has significantly increased the release of platinum group elements to the environment. It has been invoked that common sources and similar geochemical behavior control the environmental distribution of these elements. In order to check this hypothesis intertidal salt marsh sediment cores were sampled in two sites of the Tagus Estuary (SW Europe) affected by different traffic pressure. Platinum and Os concentrations and $^{187}Os/^{188}Os$ isotopic ratios were determined in sediments and interstitial waters. Concentration of Pt in surface sediments nearby a high traffic zone (up to 40 $ng{\cdot}g^{-1}$) indicated severe contamination. However, surface sediments did not show Os enrichment and $^{187}Os/^{188}Os$ ratios, ranging from 0.908 to 1.178, indicating the existence of other source besides vehicles. Concentrations of dissolved Pt and Os in interstitial waters, 0.1-0.7 pg $g^{-1}$ for Pt and 30-100 fg $g^{-1}$ for Os, were higher than typical values for uncontaminated waters. Based on the obtained results, two sources of Pt and Os into the Tagus Estuary salt marshes were identified: a regional input linked with industrial activities affected by fossil oils combustions and regional traffic, and a local source associated with the nearby traffic density. Estimations of Os and Pt released by catalytic converters support this two-source model. Besides the different sources, ability of dispersion (Pt is released as particles and Os as gaseous $OsO_4$) and different dissolution/mobility processes reinforce the decoupled behavior between Pt and Os; these findings question the use of Os isotopes as a proxy of platinum group elements sources to the environment.

# Occurence, sources and fate of pesticides in Gironde estuary (France).

Cruz Justine [1], Pardon Patrick [1], Le Ménach Karyn [1], Dévier Marie-Hélène [1], Budzinski Hélène [1*]

1: Environnements et Paléoenvironnements OCéaniques (EPOC-LPTC)
INSUCNRS: UMR5805École Pratique des Hautes Études [EPHE], Université de Bordeaux Sciences et Technologies – Observatoire Aquitain des Sciences de l'Univers
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*: Corresponding author

Pesticides are significant components widely used in intensive agriculture all around the world in order to improve agricultural yields, but they are also used in urban areas (material protection, gardening...). This leads to a global contamination of environmental compartments, and given to the known toxicity of these micropollutants, they are nowadays recognized as a major public health issue. In this context, the aim of this study was to investigate the contamination of the Gironde estuary, one of the largest European estuaries located in southwest of France, by pesticides from agricultural but also urban use.

Sensitive methods (LOQs below 5 ng/L) based on active and passive sampling were applied in order to target a wide range of 58 pesticides (herbicides, insecticides, fungicides and metabolites) in the two major Gironde estuary rivers (Garonne and Dordogne rivers) and in a Garonne river tributary, the Jalle of Blanquefort, which receives a wastewater treatment plant (WWTP) effluent from one of the major WWTPs of Bordeaux city.

Both active and passive sampling methods have been applied to monitor pesticides over one year. They have shown that inputs into the Gironde estuary are very variable (1000-10000 $g.d^{-1}$) originating mainly from Garonne river (90 %) and are characterized by the predominance of S-metolachlor and its metabolites (applied for maize cultivation) which represents 70 % (12000 $g.d^{-1}$) of total inputs. Those typical from WWTP input such as diuron, imidacloprid and fipronil were lower (50-300 $g.d^{-1}$). They however cannot be neglected as fipronil for instance is a toxic molecule even at low concentration. It was indeed detected at concentrations sometimes exceeding its predicted no effect concentration (0.77 $ng.L^{-1}$).

This underlines pesticide ubiquity and the importance of molecule selection for environmental risk assessment as not only most used pesticides must be targeted, but also those with potential high toxicity.

# Occurrence of synthetic musk compounds in the Adour estuary (SW France) and their fate during treatment processes.

Lanceleur Laurent [1], Cavalheiro Joana [1], Pigot Thierry [2], Monperrus Mathilde [1]*

1: Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE-IPREM) CNRS: UMR5254Université de Pau et des Pays de l'Adour [UPPA]
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CNRS: UMR5254Université de Pau et des Pays de l'Adour [UPPA]
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Synthetic musk compounds are the dominant artificial fragrance compounds used as substitutes for natural musks. Due to their extensive use in personal care and household products, they are produced at the tonnage scale, which placed them on the list of chemicals for priority action (OSPAR, 2000). Recently, synthetic musks have raised considerable attention due to their persistence in the environment and hazardous potential to ecosystems even at low concentrations. Wastewater treatment plants (WWTPs) represent the major route of musk contamination into the aquatic environment. It has been recognized that these substances are only partially degraded during treatment process, and little is known about their transformation products that should be included in all assessments concerning musks' fate and toxicity.
The aim of this work was to investigate the occurrence of synthetic musk compounds and their degradation products in WWTPs and surface water of the Adour Estuary (SW of France) and to evaluate their fate during treatment processes. Influents and effluents of three WWTPs with different treatment processes including activated sludges and biofiltration have been analysed as well as estuarine surface waters. The total capacity of the investigated WWTPs was 170,000 inhabitant equivalents for a 30,000 to 70,000 m3.day-1 average flow rate. Synthetic musk compounds were detected in all samples and ranged between 40 ng.L$^{-1}$ to 2,900 ng.L$^{-1}$. Removal efficiencies estimations indicated a potential release of musk compounds toward the dissolved phase during the treatment process. Estimated musk fluxes into the estuary were in the range of 7 to 30 kg.year $^{-1.}$
Experimentally, new advanced oxidation processes have been also evaluated for the degradation of the main synthetic musk compound (HHCB,Galaxolide®). Several treatments combining oxidative and photochemical processes have been tested and the formation/degradation of products were investigated using time series experiments. The reactivity of HHCB towards different Reactive Oxygen Species (singlet oxygen, superoxide anion, hydroxyl radical) has been investigated and will be discussed. The results have identified efficient degradation pathways for wastewater treatment and highlight the need to focus on degradation products and their potential (eco)toxicological effects.

# Dynamics and pathways of glutathione-like and thioacetamide-like compounds in temperate macrotidal estuary (Brittany-France).

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A fraction of dissolved organic matter (DOM), the reduced sulfur substances (RSSs), such as thiols, are widely suspected to play major roles in aquatic environment, due to their detoxifying effect as metal ligands and reactive oxygen species scavengers. However, although their important roles, identification, detection and understanding of these substances have been poorly studied due to the lack of specific analytic methods and the trace level concentrations in natural waters. Estuaries are an important place where DOM is transferred from soils and rivers to the ocean. This study focuses on the sources and the dynamics of two RSSs over one year in a macrotidal estuarine system (Aulne, France). For the first time, glutathione-like (GSH-like) and thioacetamide-like (TA-like) compounds were simultaneously measured along the whole salinity gradient during one hydrological year with the new differential pulse cathodic stripping voltammetry method(1). Results reveal a riverine major source of each compound in this estuary. Annual variations of GSH-like compounds may result from different sources: allochtone origins, primary productivity and bacterial degradation. GSH-like compounds are slightly not conservative along the estuary with less than 20 % of loss. TA-like compounds clearly do not behave conservatively with 64% loss maybe due to degradation processes. Furthermore, TA-like annual flux is mainly transferred (77 %) to the ocean during the flood (February) due to the high discharge and also the high concentrations which may be explained by the sediment removal. (1) Pernet-Coudrier, B., Waeles, M., Filella, M., Quentel, F. and D.R., Riso, 2013. Science of The Total Environment, 463-464, 997-1005

# Past and present carbon dynamics in the Scheldt estuary as traced by changes in C speciation and isotopes.

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The Scheldt Estuary (Belgium-The Netherlands), located in one of the most densely populated areas of Europe (over 500 inh./km$^2$), is a highly eutrophic system currently recovering from hyper-eutrophication thanks to improved waste water treatment efforts. Consequently, the carbon cycle in the Scheldt estuary underwent a series of consecutive changes. We analyzed the evolution of organic carbon content and carbon-to-nitrogen ratio in suspended particulate matter, of inorganic carbon speciation (carbon dioxide, bicarbonates and carbonates) and of the $^{13}C/^{12}C$ isotopic composition of particulate organic and dissolved inorganic carbon, at monthly resolution over the past 20 years. Results show a long term trend superimposed on seasonal patterns. Since the nineties, allochtonous organic carbon inputs decreased progressively in the upstream river basin of the estuary with the reduction of untreated sewage releases, while a simultaneous increase of oxygen and pH, a decrease of DIC (and especially of $CO_2$), and an increase of $\delta^{13}C$-DIC are observed. These all point to reduced respiration and increased primary production in the estuary. Consequences of changes on the global C budget of the estuary are estimated and discussed.

# Biogeochemical characterisation of 200 years local changes in a transitional environment ? What is the foraminifera's message?

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Transitional environments are deeply affected by global and local changes. These changes can be monitored by sedimentological, physicochemical, geochemical and biological parameters. Moreover a clear separation between naturally-induced changes and anthropogenically-induced changes is often a difficult task. We suggest that biological and geochemical parameters should be used together since they offer greater potential for linking cause-and-effect relationships. The European Marine Strategy Framework Directive (MSFD: Directive 2008/56/EC), which aims at the achievement of good ecological status (GES) in all marine water bodies by 2020, enforces the need to assess the aforementioned changes. According to this, Ecological Quality Status assessment needs a «reference condition» with which to compare the present-day condition. The fossil record has a potential to reconstruct PaleoEcoQS and thereby establish in situ reference conditions from pre-impact times.

The objective of the current study is to use microfaunal (benthic foraminifera), geochemical (major and trace elements, organic matter) and physical (sediment grain-size, clay mineralogy) proxies to investigate environmental transformations in a coastal area, over the last 200 years. A 33-cm long core has been sampled in an intertidal area of the Boulogne-sur-Mer harbour (Pas de Calais, Northern France). The age-depth model was based on $^{210}$Pb and $^{137}$Cs activities. The evolutionary trends of the benthic community (based on ecological criteria) and sediment grain-size, testify to a shallowing upward tendency, with the decrease of epiphytic species. Along the sedimentary record, the interaction between microfaunal and geochemical elements has allowed a pre-impacted phase to be distinguished from an industrial one. The upper part of the core seems to reflect better ecological conditions: could this be evidence of a move toward environmental recovery?

# The freshwater estuaries of the Three Gorges Reservoir in China-Insights from in situ and online monitoring with a MINIBAT multisensor system.

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Estuaries represent unique ecosystems of partially enclosed water bodies at the interface between rivers and large tidal water bodies such as the sea or the Great Lakes in USA. The huge Three Gorges Reservoir (TGR) has been impounded on the Yangtze River in China since 2003. One third of the reservoir water surface area is formed by flooded dendritic tributary valleys now forming artificial freshwater estuaries. These partially isolated water bodies have very different characteristics than the Yangtze River main stream along the TGR center. ‘Tides' in the TGR are controlled by the artificial management of the Three Gorges Dam and the Yangtze River discharge. Annually, there is a ‘tidal' sequence of 30 m amplitude. 93% of the daily water level fluctuations are below 1 m/day, whilst, flood events in the Yangtze River can raise TGR water levels more than 4 m/day and dam sluicing can make them drop by more than 2 m/day. During several fieldtrips, we have performed in situ and online monitoring with a ‘MINIBAT' multisensor system to study spatial and temporal distributions of water quality patterns in two major estuaries of the TGR. Their water masses originate from both their tributary headwaters and the Yangtze River main stream. Interactions with the Yangtze River main stream are mainly controlled by reservoir ‘tides' and density pump effects due to differing thermal properties. In turn the resulting lateral flows are responsible for pollutant/nutrient transport and destabilization of stratification. During non-‘tidal' periods when strong thermal stratification can establish, excess nutrient loads frequently lead to harmful algal blooms, a primary environmental threat in the TGR. The observed patterns and processes are specific to the TGR but have much in common with classical estuaries. ‘MINIBAT' monitoring techniques can also be applied in any estuarine water body for similar studies.

# Approaching environmental Cu and Ag bioaccumulation in oysters (*Crassostrea gigas*) from Gironde Estuary by stable isotope spiking in-vivo experimentations.

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Analysis of a databank on Cu and Ag concentrations measured in oysters from 13 sites on the French Atlantic Coast during 2003-2012 period (french biomonitoring program RNO/ROCCH, IFREMER) have shown site-specific spatial and temporal variations reflecting local contaminant pressure. Oysters from the Gironde Estuary systematically showed highest Cu and Ag concentrations (Cu: 220-2200 $mg.kg^{-1}dw$; Ag: 8-100 $mg.kg^{-1}dw$) compared to those in oysters from the other studied French sites. Despite different and variable concentrations, Cu/Ag ratios in oysters from Gironde sites remained rather stable in space and time over the observation period. The Cu/Ag ratios in oysters increased with salinity and lower dissolved Ag, suggesting that Ag bioaccumulation reflects levels observed in water. These observations supported (i) common physiological processes involved in Cu and Ag accumulation in oysters reflecting (ii) estuarine processes and (iii) anthropogenic sources. A short-term in-vivo experiment (during 4 weeks) consisted in a combine exposure of uncontaminated oysters to dissolved Cu and Ag to detect potential synergy or antagonism effects on bioaccumulation kinetics. Oysters were exposed by direct pathway to close-to-real contaminant levels using stable metal isotope spikes ($^{63}$Cu, 1000 $ng.L^{-1}$ and 2000 $ng.L^{-1}$; $^{107}$Ag, 50 $ng.L^{-1}$ and 500 $ng.L^{-1}$). Results showed (i) a synergy effect on the Ag accumulation increasing in the presence of higher Cu exposure and (ii) antagonism resulting in lower Cu accumulation at a given Cu exposure when Ag exposure levels increase. The net accumulation of $^{65}$Cu ($^{65}Cu_{acc}$) and $^{107}$Ag ($^{107}Ag_{acc}$) showed rapid decrease in $^{65}Cu_{acc}/^{107}Ag_{acc}$ ratios at higher Ag exposure with final values reaching a plateau after 21 days, close to Cu/Ag ratios in wild oysters provided by the biomonitoring program.

# Origin, Transport and Fate of Particulate Organic Carbon and Nitrogen along the Land-Sea Interface of the São Francisco River-Estuary, NE-Brazil.

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The origin, transport and fate of POC and PON of the São Francisco estuary, NE-Brazil (SFR; Lat. 10°36'S and Long. 36°23'W) was assessed. The behavior of TSS, POC, PON, $\delta^{13}C$ and $\delta^{15}N$, and Chl.a from the river to the margin of the shelf was discerned over a year in 2001/2002, with a monthly sampling frequency of around 23 stations. Sediment facies and sedimentation rates ($^{210}$ Pb/ CIC method) of the SFR pro-delta and shelf were established in 2008/2009. Impacts by dams, reduced the TSS load by 95%, nutrients by 90% and river flow by 35% to the estuary. It is now oligotrophic, and river flow is constant (QR of $\approx 1760 m^3.s^{-1}$). The average river and marine concentrations were 5.2 ± 2.3 and 6.6 ± 7.7$mg.dm^3$ for TSS, 373 ± 32 and 186 ± 56$\mu g.dm^3$ for POC, 39.4 ± 4 and 21.4$\mu g.dm^3$ for PON and 1.6 ± 1.1 and 0.4 ± 0.3$\mu g.dm^3$ for Chl. a, respectively. All parameters exhibited a slight non-conservative behavior. Slight increases of TSS and POC at the pro-delta were driven by erosion and resuspension of bottom sediments. The ratios of POC:PONwt of 10.2 ± 2 and 7 ± 2 and POC:Chl awt of 305 ±50 and 612 ± 565 between the river and the sea, resp. and a gain of POC against a loss of Chl.a over the pro-delta and along the plume, showed that the shelf was being enriched by detrital POC from the river and resuspension processes (i.e.river $\delta^{13}C$ -24.84 ± 0.99 and marine $\delta^{13}C$ -21.05 ± 0.77; river $\delta^{15}N$ 6.43 ± 0.71 and marine 7.65 ± 0.47). Shelf sediment POC levels varied from 0.2 to 2 % and sedimentation rates from 0.1 to 0.7$cm.year^{-1}$. POC river loads, dilution during plume dispersal, primary production and accumulation rates are presented.

# Influence of environmental variables on the early diagenesis of Fe and Mn in the Laurentian Trough - one of the world's largest estuaries.

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The circulation in the 1200 km long, 300-600 m deep, permanently stratified Laurentian Trough is estuarine with seaward flow in the surface layer and landward flow in the bottom layer. As a result, the bottom sediments are subjected to a spatial gradient in environmental variables, such as organic matter supply, sediment accumulation rate, and bottom water oxygenation, that influence diagenesis. The diagenesis of Mn and Fe is sensitive to these environmental variables but it is not clear how it responds to combinations of variables. This study presents data on the vertical distributions of dissolved as well as solid phase ascorbate-extractable Mn and Fe in six sediment cores recovered on a transect along the Laurentian Trough. At all sites, the sediment surface layer is enriched in extractable Mn and Fe. Manganese cycles both within the sediment column and across the sediment-water interface, which leads to a net loss of Mn to the overlying waters. In contrast, Fe cycles entirely within the sediment column at all sites, without loss. The inventories of solid extractable Fe and porewater Fe as well as the diffusive fluxes of Fe and Mn across the oxic-anoxic boundary strongly correlate with the reactivity of the sedimentary organic matter, which is a function of the water depth, bottom water oxygenation, and the length of time that organic matter is exposed to oxygen. Despite a seaward increase in the relative supply of marine organic matter to the seafloor, the correlations and the strength of the diagenetic cycles of Mn and Fe nearly follow the seaward decreasing sedimentation rate and decreasing oxygen levels in the bottom waters along the transect.

# Trace metal cycling in the Baltic Sea: role of suspended Mn and Fe particles.

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Suspended particles have been sampled at the Landsort deep, southern Baltic, and the Bothnian Bay, northern Baltic, using membrane filtration with a 0.2µm cut-off. The Landsort Deep show a 10-15 m thick suboxic zone at approximately 70-90 m depth, and the Bothnian Bay is strongly influenced by freshwater input.

Iron-rich particles dominate close to the coast, whereas manganese rich particles dominate in the open Baltic Sea. Suspended Fe particles can be divided into two groups, Fe(II,III)-OC (light Fe isotope signature) and Fe(III)-OH (with a heavy Fe isotope signature). Particles and colloids with negative Fe isotope signatures are mobilised in forested areas during spring flood discharge. Suspended Fe aggregates with a light signature are labile and transform during transport, forming Fe(III)-OH colloids and particles with a heavy iron isotope signature. Phosphorus and organic carbon are to different extent associated to these two suspended iron aggregates during transport. Trace metals associated with the Fe(II,III)-OC particles are rapidly transferred to the sediment during estuarine mixing. Most of the Fe(II,III)-OC particles are removed from the water column below 1psu. The pelagic suboxic zone in the Baltic Sea is a producer of Mn-rich particles. These particles remove dissolved oxyanions, Mo, U, W, and cations Co, Ce, Ba, Cd, and Cu from the suboxic zone. Arsenic, Cd, Cu, Mo, Sb, Tl, U, and Zn are enriched in particles in the sulfidic zone.

# Fe isotopes in the near-shore environment - fractionation in the sediments and the water column.

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Fe discharged from rivers is largely lost from solution during particle coagulation and sedimentation in estuaries and on the shelf. However, after settlement those Fe-particles constitute a significant reservoir of highly reactive Fe that may be remobilized by microbially driven redox reactions during marine early diagenesis. Fe isotope fractionation during early diagenesis is thought to be potentially useful in tracing such remobilized Fe, but the fractionation process is still poorly understood. Fe isotope results from selectively leached marine sediments from the North Sea and from the Potter Cove Estuary (King George Island, Antarctica) demonstrate, that downcore Fe isotope variability in reducible Fe-(oxyhydr)oxides is almost exclusively the result of fractionation of surface-bound reactive Fe. The various Fe-(oxyhydr)oxide minerals themselves show virtually no systematic change with progressing early diagenesis. This result, together with previously published isotope trends from water profiles across redox gradients in principle outlines the underlying systematic and thus likely predictable fractionation of Fe isotopes during early diagenesis and subsequent release into the water column. Understanding and quantification of isotope fractionation during these processes are necessary requirements if Fe-isotopes were to be used to trace and monitor the evolution and intensification of water column hypoxia and suboxia in the near-shore environment.

# Natural and anthropogenic processes controlling trace metals dynamic in a highly stratified estuary: the Krka River estuary (Adriatic, Croatia).

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Distributions of trace metals (TM), organic carbon, SPM and physico-chemical parameters were studied in the highly stratified and pristine Krka River estuary in winter/summer periods. Along the surface layer, TM behave non-conservatively (Zn, Cd, Pb, Cu) especially in summer, mainly due to the inputs from nautical marina and harbour (e.g. release from antifouling paints), as evidenced by Šibenik bay mapping. Contrarily, Ni and Co essentially followed near-conservative line. The extremely low river SPM discharge led all TM to exist mainly in dissolved fraction (>80%), except Pb. However, upstream increase of bottom seawater residence time coupled with vertical TM scavenging induced the accumulation and progressive increase of all TM and SPM. Downstream decrease of distribution coefficient (KD) for all TM in surface water for winter period was ascribed to the change of SPM nature (terrestrial vs. biogenic), whereas in summer, a variable and largely biogenic SPM caused less defined KDs.

# Influence of seasonal diminishing of river discharge on the trace metals distribution and fluxes in estuaries.

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Estuaries are broadly recognized as a multifaceted biogeochemical barrier for the riverine matter runoff to the sea. The action of this barrier has been used to explain the low concentration and prevailing of dissolved forms of many trace elements in sea water. It is true for the suspended solids delivered by rivers, and for dissolved forms of elements prone to hydrolysis (Fe, Al, Ti, LREEs). For other elements (e.g. Mn, Cd, Zn, Ni, Pb) the increase of dissolved forms often occurs in the waters of intermediate salinity, and therefore some estuaries act as an additional source of dissolved trace metals. The factors controlling the distribution and fluxes of trace metals are still poor estimated for many estuaries. The seasonality of river discharge determines many features of river end-member and properties of estuary itself. The estuary of Razdolnaya River and adjacent sea area in northwestern part of the Sea of Japan were studied to elucidate this aspect. Diminished river discharge in autumn was accompanied by the hypoxia (down to 13.7 uM DO) in the near bottom more saline waters of upper estuary. The elevated concentration of dissolved Mn, Ni, Zn and even Fe were observed in oxygen depleted estuarine waters, but dissolved Cu, Cd and Pb has not shown any increase. In the aerated upper layer the dissolved Mn raises up to 15000 nM Dissolved Zn, Ni and especially Cu show semi-linear decline in the upper layer of estuary along salinity gradient, and dissolved Fe usual non-linear drop at the salinity less than 5 psu. Dissolved Cd demonstrates increase trend along salinity gradient in accordance with low river end-member and seasonally elevated Cd content in sea water. The possible influence of seasonal variations of estuarine processes on the trace metal fluxes in the adjacent sea areas will be discussed.

# Spatial and seasonal variability of reactive metals in surface sediments of the Morbihan coast (South Brittany).

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The aim of this study is to evaluate the mobility (Spatial and seasonal) of MTE in surface coastal sediments of the Bay of Quiberon and the Gulf of Morbihan (South Brittany, France) in relation to anthropic forcing (harbor pollution). Local coastal sediment is composed of a matrix of low reactivity old eroded minerals from the Hercynian chain (over 300 Million years old) and clays accumulated from coastal transport. Recent development of agriculture and yachting contaminated surface sediments with MTE from paint coatings and other pollutions. Organic matter accumulates also in harbors and protected areas. To evidence potential geochemical interactions between these components, we analyzed 52 samples distributed over the area using multiple single extractions.

The chemical partitioning is divided in five operationally defined fractions (exchangeable/ carbonate, Fe/Mn oxides, organic matter/sulfide, acid soluble, residual). Principal component analysis on the results of each leaching method would indicate mixed sources for MTE distribution, depending on the location: yachting paint pollution, organic matter content, sediment anaeroby (traced by U enrichment) and sediment size fractionation.

The detailed MTE distribution analysis is in progress. Preliminary interpretation would indicate a high sensitivity of leachable elements distribution to environmental parameter. A preliminary distinction is apparent between mobile and bioavalable elements such as As, Cd and Zn and unreactive metals such as Sn possibly associated with heavy minerals.

# Conservative or Reactive? Permafrost-derived organic matter in the Lena River Delta.

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The impact of global warming on organic carbon budgets in permafrost systems are not well constrained. Changes in organic carbon fluxes caused by permafrost thaw depend on microbial activity, coastal erosion, mobilization of organic matter by increased porewater fluxes, and the inherent chemical stability of organic matter in permafrost soils. Here we aim at the identification and molecular characterization of active and inactive dissolved organic matter (DOM) components within the river-ocean transition. We studied four transects in the coastal Laptev Sea characterized by steep physico-chemical gradients. Molecular information on solid-phase extracted DOM was derived from ultrahigh resolution mass spectrometry. Changes of the chemical composition with salinity were used as a measure for DOM reactivity. Although changes of dissolved organic carbon (DOC) in the estuary suggested conservative mixing, only 27% of the identified molecular formulas behaved conservatively, 32% were moderately affected, and 41% were actively involved in estuarine processes. The molecular complexity in the DOM samples increased with growing marine influence and the average elemental composition (i.e. relative contribution of organic nitrogen and oxygen compounds) changed significantly with increasing salinity. These chemical changes were consistent with the results of a 20-day microbial incubation experiment, during which more than half of the permafrost-derived DOC was mineralized. We conclude that, although the DOC gradient in the estuary suggests conservative behavior, terrestrial DOM is substantially affected by estuarine processes which in turn also impact organic carbon budgets in the Lena Delta.

# Evolution of molecular weight and type of dissolved organic matter in the Gironde Estuary using asymmetrical field flow fractionation.

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Aquatic dissolved organic matter (DOM) is a mixture of ill-defined macromolecules from different origins. The removal of DOM by flocculation is of fundamental importance to understanding its reactivity and mobility in natural waters, more precisely in a salinity gradient like an estuary. In this study, asymmetrical flow field flow fractionation (AF4) and spectrophotometry were used to determine the molecular size and optical properties of DOM collected in the Gironde estuary (France). The objectives of this study were (1) to determine the change in DOM molecular weight (MW) and optical properties from low to high salinity (0 to 35) in the Gironde estuary and (2) to determine the flocculation effect at different salinity ranges. The influence of river inputs on DOM molecular weight was also investigated at high salinity. DOM MW decreased from 1057 to 1524 Da with increasing salinity. A significant reduction in MW was also noticed at intermediate salinity, suggesting colloidal removal and flocculation during estuarine mixing. The low salinity samples were enriched in high MW molecules with a more aromatic character relative to the high salinity DOM samples. A comparison of three marine sites submitted to different riverine inputs showed noticeable differences in MW as well as in optical properties of DOM.

Collectively, these results demonstrated that the composition and nature of DOM were highly dynamic in transitional zones.

# Nutrient cycling along a subterranean estuary and the discharge zone.

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Groundwater is an important pathway for derived nutrients from land to enter the coastal ocean. In coastal aquifers, groundwater transits through subterranean estuary, a mixing between seawater and groundwater and where sharp gradient occur. Transports and transformations pathways from coastal aquifers to the ocean are still poorly constrained, particularly in permeable sandy beaches which are recognized as significant biogeochemical reactive zones. Hydrogeochemical conditions as residence time, flow velocity, mixing between groundwater and saltwater control nutrient transformations. In this presentation we will focus on nitrogen biochemistry over three spring period when water table level is high. Vertical and horizontal profiles of $NH_4^+$, $NO_3^-$, $NO_2$, C/N, DOC, were analyzed in a subterranean estuary and the associated discharging zone of a sandy beach to provide an overview of transformations of the potentially exported nutrients. This study takes place in Magdalen Island (St Lawrence Gulf, Quebec) where unconfined aquifers are experiencing, and are expected to experience, important anthropic pressures and hydroclimatic changes. Groundwater velocity (2 to 7 $cm.d^{-1}$), low oxygen conditions (20%), microbial activity and redox oscillations induced by hydrodynamic condition at the beach surface provide an environment highly suitable for important nutrient transformations such as nitrification and denitrification. Elevated $NH_4^+$ (>80µM) were observed along the subterranean estuary and in the discharge zone potentially due to organic matter degradation and ammonification.

# Nutrient flux through the subterranean estuary of the 240 km-long Aquitanian coast.

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A subterranean estuary takes place in the 240 km-long coastal aquifer of the south-west France Atlantic coast. The aquifer consists of sandy dune sediments. The estuary located in intertidal beach sands is a mixing between saline pore waters and fresh waters from the dune watershed. In a subterranean estuary, a strong redox gradient overlaps the salinity gradient. The objective of our study was to quantify flux of nutrients from the coastal fresh water aquifer to the coastal zone, and to determine the processes that impact these fluxes. For that, we collected samples from sea water, beach pore waters, groundwater, and rain water in order to determine the flux of inorganic dissolved nitrogen (DIN), phosphorus and silica from submarine groundwater discharge (SGD). The flux of fresh groundwater was obtained from a water balance calculation based on precipitation and evapotranspiration and assessment of the coastal watershed from hydrograph separation. Waters with intermediate salinities between sea water and fresh waters are found all along the 240-km long coast, indicating that SGD are ubiquitous. The mean fresh water flux is 2.25 $m^3$/d/m longshore. Fresh SGD provides a DIN flux of 9 megamoles each year to the adjacent coastal zone. This flux is low because the upland land use consists almost exclusively of pine forest. Dissolved iron, phosphorus and silica have much higher concentrations in the anoxic forest aquifer than in the fresh-water end-member of the subterranean estuary sampled in the upper beach aquifer. This suggests that the salinity gradient of the estuary does not correspond to a redox gradient. The redox front between anoxic groundwater and fresh oxic waters occurs below the soil-depleted foredune. This study points out the role of the sandy foredune aquifer in biogeochemical fluxes from SGD. It dilutes and oxidizes waters from the unconfined surficial upland aquifer.

# Carbon mitigation: a salt marsh ecosystem service in times of change.

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Salt marshes have great ecological value for the ecosystem, namely in nutrient regeneration, primary production, habitat for wildlife species and as shoreline stabilizers. Multiple services of wetlands and its value are already well known. As it is now known the major carbon sink of the planet are the oceans, followed by the terrestrial zones. Considering the terrestrial sink, the more productive and more important zones retaining carbon are the wetlands retaining about 1/2 to 1/3 of the carbon. Vascular plants in salt marshes are crucial to the dynamics of the estuarine ecosystem, strongly influencing the processes of retention of heavy metals, reduction of eutrophication and mitigation of carbon. External stresses driven by warming, like nutrient balances disturbances, may lead to the successful rise up of less competitive species. $CO_2$ can be another key factor altering plant dynamics, favoring the species with higher aerial biomass production and increasing competition for light. These differences in plant biomass production strategy are also to consider in terms of plant dominance as an important part of interspecific competition. With $CO_2$ increase, the dynamics of plant distribution may be affected, as the differences in the photosynthetic metabolisms will provide some species conditions of higher production, and therefore competitive advantage. The opposite point of view is also important to be accounted for. How can salt marshes contribute for reducing $CO_2$ rising? And more important from the holistic point of view how will these changes affect the services provided to the ecosystem? Integrating the fact that these ecosystems are very productive with the generally accepted knowledge that global atmospheric $CO_2$ is rising, becomes important to know the present status salt marsh systems and how their important services to the ecosystem overall will behave in a climate change scenario with increasing atmospheric $CO_2$.

# A large annual $CO_2$ sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil).

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In contrast to its small surface area, the coastal zone plays a disproportionate role in the global carbon cycle. Carbon production, transformation, emission and burial at land-ocean interface are still poorly known quantitatively. Surface water $pCO_2$ and ancillary parameters were monitored during ten field campaigns between April 2013 and April 2014 in Guanabara Bay (Rio de Janeiro, SE-Brazil), a tropical eutrophic to hypertrophic semi-enclosed estuarine embayment. Water $pCO_2$ varied between 22 and 3715 ppmv in the Bay showing spatial, diurnal and seasonal trends that mirrored those of dissolved oxygen (DO) and Chlorophyll a (Chl a). A marked $pCO_2$ undersaturation was prevalent in the shallow, confined and thermally stratified waters, whereas $pCO_2$ oversaturation was restricted to sites close to the small river mouths and small sewage channels, which covered only 10 % of the bay´s area. Important daily variations in $pCO_2$ (up to 395 ppmv between dawn and dusk) were also registered and could be integrated for the establishment of net diurnal, seasonal and annual $CO_2$ fluxes. In contrast to other estuaries worldwide, Guanabara Bay behaved as a net sink of atmospheric $CO_2$, a property enhanced by the concomitant effects of strong radiation intensity, thermal stratification, and high availability of nutrients, which promotes phytoplankton development and net autotrophy. In the inner part of the bay, the calculated annual $CO_2$ sink (-19.6 mol C m2 yr $^{-1}$) matched the organic carbon burial in the sediments reported in the literature. The carbon sink and autotrophy of Guanabara Bay was driven by planktonic primary production promoted by eutrophication, and by its typology of marine embayment, in contrast to river-dominated estuarine systems, which are generally net heterotrophic and $CO_2$ emitters. Our results show that global $CO_2$ budgetary assertions still lack information on tropical estuarine embayments and lagoons.

# Effects of CO2 leakage from CCS technology using a mixed marine microalgae population.

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Ocean acidification has been unequivocally associated with climate change. This acidification means changes on the physicochemical characteristics of the ocean, and it has increased from preindustrial time to nowadays due to the wide rise of anthropogenic greenhouse gases (GHG). With the aim of mitigating this process, the Carbon Capture and Storage (CCS) technology has been developed, with a present storage capacity around 40 million tons per year. Despite of the low probability of a $CO_2$ leakage from sub-seabed storage sites, is necessary to set up the ecological impact of a potential release. In this sense, growth-inhibition tests were developed with a mixed culture of three marine microalgae (Pleurochrysis roscoffensis, Cyclotella sp. and Andifinium sp.) being exposed to four selected pH values (5.5, 6, 6.5 and 7). Laboratory-scale experiments were carried out during 10 days. A full inhibition of these marine microalgae were experimented at pH 5.5. In contrast, Pleurochrysis roscoffensis showed an enhanced growth at pH 6, featuring a smaller sensitivity under acidification conditions respect with the other two species in the mixed culture. The proposed methodology contributes to the knowledge in order to stablish future risk assessment guides of this technology applied into the aquatic environment.

# Nutrient and Carbon Cycling in Coastal Tropical Waters of Hawaii: Effects of Land-derived Inputs, Reef biogeochemistry, and Physical Forcing.

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We describe studies of nutrient and carbon cycling in coastal waters of Oahu, Hawaii. Our work involves continuous monitoring using a network of buoys, which allow us to characterize how nearshore tropical waters of Hawaii respond to the combination of land-derived nutrient inputs, reef processes, and physical forcing. We have focused on lagoonal and back-reef settings, and fringing reefs exposed to the open ocean. The sites vary in physical characteristics (e.g., residence time), proximity to riverine input and urban development and show a highly variable response to system perturbations. Nutrient inputs from terrestrial runoff to lagoons rapidly increase the molar N:P ratio from N-limited oligotrophic conditions to values near 48, and drive phytoplankton growth as well as sharp declines in the $pCO_2$ of seawater. Conditions return to baseline over time scales ranging from a few days to several weeks, depending on the settings and proximity to sources of runoff. Fringing reef sites which differ in their proximity to riverine input also show rapid response to perturbations but rapid flushing causes rapid recovery of the system to baseline conditions. Annualized CO2 air-sea fluxes at our sites vary widely and range from as low as -0.03 mol C $m^{-2}$ $yr^{-1}$ on a fringing reef in Honolulu exposed to the open ocean to +1.63 mol C m-2 $yr^{-1}$ on a barrier reef flat in Kaneohe Bay, and +2.50 mol C m-2 $yr^{-1}$ in the southern lagoon of Kaneohe Bay. We also discuss the climatology of these settings and how they have evolved over the last six years.. We place special attention on elucidating whether OA is evidenced in our data or whether longer term trends are locally driven. Our work demonstrates the utility of high frequency autonomous observations to study changes in estuarine and coastal waters over a broad range of time.

# Modelling nutrient budgets in the Elbe Estuary (Germany) - role of phytoplankton as sink and source term.

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The Elbe Estuary is a mesotidal estuary located at the southern coast of the North Sea. The total length is about 140 km from its upper boundary at the weir of Geesthacht (km 586) down to the North Sea at Cuxhaven (km 727). The extended freshwater region (FR) reaches from km 586 to km 655 including the Hamburg Harbour. The tidal range in the FR at the gauge St. Pauli (km 620) is about 3.6 m.

In summer, the FR of the Elbe estuary is loaded by high inputs of algal biomass from the highly productive middle reach of the river. In the Hamburg Harbour area (km 610 - 630), a strong decline of algal biomass can be observed. In parallel, a strong depletion of oxygen lowers the ecological state of the Elbe estuary dramatically.

The one-dimensional, mechanistic water quality model QSim of the German Federal Institute of Hydrology was applied to the FR of the Elbe estuary and the middle part of the Elbe River as well using simplifications concerning river morphology and hydrodynamic conditions. Based on the model results, the different sink and source processes of the organic carbon and nitrogen budget were quantified. The strong linkage of these budgets to the fate of phytoplankton is shown. The seasonal cycle of phytoplankton as well as the nutrients is strongly dependent on the water residence time, which is determined by the river discharge. For verification, the model results are compared with measured longitudinal profiles of algal biomass (chlorophyll) and nutrients.

# Connectivity and fate of nutrients in the Derwent and Huon Estuaries in southeast Tasmania.

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We use a 3D coupled hydrodynamic, sediment and biogeochemical model to investigate the fine-scale (<100 m; <1 day) nutrient dynamics of the temperate Huon and Derwent estuaries in southeast Tasmania, which are connected by the D'Entrecasteaux Channel. The Huon estuary drains a principally rural catchment with relatively low nutrient loading, augmented by numerous finfish farms in the lower reaches and adjacent marine channel. The Derwent estuary is highly modified urban estuary with a history of elevated sewerage and industrial nutrient loads. We use the model to demonstrate the connectivity between the 2 estuaries and explore the fate of marine, catchment and anthropogenic nutrient loads in the system. Model skill is assessed against monthly water quality observations throughout the region and nutrient budgets are evaluated for each sub-region. Results demonstrate strong seasonality in estuarine flushing with persistent anthropogenic sources augmenting phytoplankton production in summer months. In conjunction with resource managers, alternate locations for future sewerage discharge were explored. Scenario simulations showed contrasting retention of wastewater in the estuary and are helping managers optimise future discharge infrastructure.

# Study of water-sediment interface: coupled approach biogeochemistry-modeling for nutrient fluxes evaluation (C, P, N).

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In the nutrient cycle the estuary has a major importance due to its position at the interface between a river and the ocean and the hydrodynamic which results from phenomena such as tide and swell trap and concentrate the nutrient within the area. Therefore estuarine mudflats play a major role by being simultaneously a sink and a source of nutrient. The direction of the fluxes at the water/sediment interface depends on the environmental condition. This interface can be studied using in situ methods such as dialysis porewater sampler (DPS). This method consists of vials included in a Plexiglas plate fill in with distilled water which will equilibrate with the sediment porewater in surrounding. It can also been studied using diffusion models. To do so the model considers several phenomena such as diffusion, advection/convection, bioturbation, sediment porosity and compaction with depth and can give estimation of the nutrient profile in the sediment. Those parameters can be put in a model to help predict the equilibration time of the DPS.

The subject of our study is at first to develop a diffusion model to predict the equilibration of the DPS used in the Seine River mudflat. It is implemented using parameters which come from the diagenesis models, specially the bioturbation which occurs in the first centimeters of the sediment and the adsorption/desorption phenomenon which concerned nutrients such as phoshorus. Results show up that the model works but should be improved to better integrate the latter parameters. It have been chose to do so using stochastic diffusion model namely the CTRW which has been used to study bioturbation but to our knowledge never used to model adsorption in mudflat. The ultimate goal would be to implement those CTRW parameters in a diagenesis model and compare the results with the existing models.

# The environmental constraints on faunal distribution: biogeochemical interaction as underlined by geostatistical tools.

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Due to their location on the border between the sea and the land, transitional environments are influenced by strong spatial and temporal variability in terms of sedimentological, physicochemical and geochemical parameters. An increasing number of studies suggest the use of benthic foraminifera and meiofauna for environmental monitoring purposes. However, sensitivity to these environmental parameters is often tested separately, even though it is known that interactions are numerous within this complex ecosystem.

An integrated biogeochemical study was conducted in Lake Varano (Italy). Based on 45 samples spatially distributed throughout the area, the impact of environmental parameters (characterized by trace elements, organic matter, clay mineralogy, sediment grain size and water characteristics) on benthic foraminifera and meiobenthos was tested. Four orders of impact were distinguished: (1) the Lake Varano ecosystem is dominantly affected by terrigenous inputs and only the enrichment of Cd and As could be interpreted as moderate pollution; (2) the organic content is high and may contribute to seasonal eutrophication. The transitional environment fauna that develop here are perfectly adapted and reflect these characteristics; (3) water characteristics may show that foraminifera might tolerate low oxygen levels; and (4) the grain size distribution have no impact on the fauna. Overall, this study illustrates that, prior to any examination of ecological status (possible occurrences of sources of pollution), integrated research, including a detailed sedimentological study, should be conducted to clearly describe the natural functioning of the area.

# Geochemical rates estimated from two-dimensional distributions of dissolved iron and phosphate from an intertidal estuarine mudflat.

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Sediment diagenesis generates chemical fluxes through the sediment-water interface which can strongly impact the water column. The reductive dissolution of iron (hydr)oxides in the Loire estuary sediment is an important diagenetic process in the first 20 cm depth, and forms a possible source of dissolved phosphate and trace metals to the river. Here we propose a new numerical model technique to estimate the production rates of ferrous iron and other solutes from two- dimensional (2D) concentration distributions. Based on the Savitzky Golay filter approach, this model approach suitably «denoises» the measured concentration data and allows to calculate the first order derivative (providing the flux) and the second order derivative (providing the production rate) in a numeral robust way. The new approach was applied to test one-dimensional depth profiles and compared to the widely used «profile» software[1]. Subsequently, we applied the new technique to estimate the production rates from a 2D pore water data set obtained by a combined DET-gel/colorimetry technique[2]. Two mains sources of heterogeneity are described: the bioirrigation of sediment by macrofauna and the patchiness of labile organic carbon. By coupling dissolved iron with dissolved phosphate data set, followed by inverse production rate modeling, we are able, for the first time, to study the impact of this heterogeneity on iron cycle and its consequences on phosphorus mobilization.

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[2] Florian Cesbron et al., « Simultaneous 2D Imaging of Dissolved Iron and Reactive Phosphorus in Sediment Porewaters by Thin-Film and Hyperspectral Methods », Environmental Science & Technology 48, no 5 (4 mars 2014): 2816-26, doi:10.1021/es404724r.

# Lab-on-chip analysers for high resolution in situ analysis of nutrients in estuaries and rivers.

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We present a new generation of miniaturised submersible in situ nutrient analysers that are based on lab-on-chip technology. Lab-on-chip allows us to minimise power and reagent consumption, allowing high quality colourimetric nutrient analysis to be performed for long periods in remote locations that are difficult to service regularly and do not have mains power. The analysers have been deployed alongside multiparameter sondes to measure nitrate at high temporal resolution for several months in multiple rivers and estuaries in the south of England. We present long term high resolution (one measurement per hour) datasets from Christchurch Harbour, Southampton Water, the Hampshire Avon and the River Stour (Dorset). The analysers can also be configured to measure phosphate, silicate, pH and dissolve iron, and have been shown to operate in a range of aquatic environments, including rivers, estuaries, glacial meltwater and the deep sea. The analysers have exciting potential for future applications in estuarine science.

# The Biofish - an underwater insitu and on line measuring multi-sensor system.

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In situ measurements of three dimensional distributions of physico-bio-chemical parameters in various water bodies in high spatial resolution are acutely demanded for monitoring, investigation and assessment purposes. Today's hydrodynamic and water quality models provide highly resolved information on physical and biochemical properties of water bodies. Those models visualize temporal developments of e.g. flow fields or algae blooms. But very often it is difficult to verify the highly resolved spatial results of those models. Furthermore, highly resolved spatial investigations of water bodies are needed to reveal distributions of water quality parameters such as temperature, electrical conductivity or $O_2$. For this purpose, the Biofish was developed on basis of the former sensor system Minibat.

The Biofish is a towed underwater multisensor system dragged by an appropriate vessel. Equipped with steerable wings, the Biofish can be navigated during the cruise from water surface to 60 m depth. Larger depths such as 200 m can be investigated by using the Biofish as probe when the vessel is not moving. The Biofish carries sensors permanently recording pressure, temperature, $O_2$, electrical conductivity, colored dissolved organic matter, photosynthetic active radiation, chlorophyll a, turbidity and $H_2S$. Furthermore, the Biofish is equipped with a remotely controlled sampling system for six samples with 50 mL volume each. The recorded data are sent via the dragging cable to the computer on board of the vessel. According to the online visualized measurement results, the operator specifically can select locations/depths of interest where to release the sampling mechanism. Three dimensional maps of spatially distributed data are generated by geostatistical modeling. Thus, the Biofish is able e.g. to identify pollution sources, stratification dynamics or mixtures of different water bodies. Although examples from fieldwork in the Yangtze Three Gorges Reservoir will be presented here, the system is deployable in marine and brackish waters as well.

# Defining benchmark values for nutrients in twelve portuguese estuaries under the water framework directive.

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The Water Framework Directive requires the assessment of the chemical quality of water bodies. To achieve this estimation, water samples were collected in 90 sites located at 42 water bodies from 12 transitional systems in Portugal. Nitrate, nitrite, phosphate and silicate concentrations were measured in surface and near-bottom water samples, at high tide and low tide in autumn/ winter and spring/summer of 2009 and 2010. The water bodies were defined along the salinity gradient, including the tidal fresh water end-member. The influence of salinity, biological consumption, morphology, and river basin inputs was examined. Results showed that nutrient variability in transitional waters is estuary and site specific. To overcome these inter-specificity complexity benchmark values for nutrients were estimated for five salinity classes on the basis of nutrient concentrations along 12 Portuguese meso-tidal estuaries with different morphology, fresh water inputs and human impacts.

This methodology allowed classifying the chemical status of 42 water bodies of the surveyed systems. Water bodies of Tagus, Ave, Cávado and Douro showed the poorer chemical status, and ammonium was often above the corresponding benchmark value. Comparatively, nutrients in almost all WBs of Minho, Sado, Arade and Guadiana were lower than the benchmark values and therefore a classification of high is proposed.

# Abandoned boats as a source of metal contamination of estuarine sediments.

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Abandoned boats are a common site on the foreshores of estuaries and pose hazards to navigation, human health and the local sediment. In this study, fragments of boat paint have been sampled from derelict sailing barges, houseboats, yachts and trawlers on the intertidal mudflats of two estuaries in eastern England. Samples were analysed for Cu, Pb and Zn by field portable X-ray fluorescence (XRF) spectroscopy. Lead was detected in all cases (430 analyses of 155 fragments) and median concentrations on each boat ranged from about 350 to 35,000 mg $g^{-1}$, with individual concentrations exceeding 20% in several cases. Zinc was detected in most samples with median concentrations ranging from about 50 to 10,000 mg $g^{-1}$ and a maximum individual concentration of 24%. Copper was detected in fewest (277) cases and mainly on samples taken from the outer hulls, with median concentrations on each boat ranging from about 50 to 1900 mg $g^{-1}$ and an individual maximum concentration of 17%.

The relatively high abundance and persistence of Pb in the paints resulted in greatest contamination of local sediment by this metal, with concentrations exceeding quality guidelines (of 112 mg $g^{-1}$) in several instances. Among the metals considered, therefore, Pb is of greatest concern from both environmental and human health perspectives. Contamination arising from peeling paint on abandoned craft is likely to be a general, albeit localised problem, whose significance depends on the size, age, condition and nature of the boat. Although further research into the problem is required, including an assessment of the aquatic toxicities of metals in old paints, immediate recommendations are clear legislation preventing the abandonment of boats and the creation of facilities designed to assist boat owners with the disposal of end-of-life vessels.

# Modelling summer hypoxia in the Gironde estuary, using a 3D model coupling hydrodynamics, sediment transport and biogeochemical processes.

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Estuarine ecosystems commonly experience hypoxia problems. The macrotidal Gironde estuary is mainly characterized by the presence of a highly-concentrated Turbidity Maximum Zone (TMZ). In the past years late-summer hypoxic events occurred, particularly around the city of Bordeaux in the upper estuary. Summer hypoxia occurs in the TMZ, under conditions of low river flow, increasing water temperature, during the spring to neap tide transition, and in the presence of urban effluents. These multiple factors act together, and therefore it is essential to understand and grade respective contributions to the temporal and spatial variations of dissolved oxygen in the estuary.

In order to investigate these mechanisms, a three-dimensional dissolved oxygen model was developed by coupling hydrodynamics, sediment transport and biogeochemical processes. The aim is to reproduce the depletion of dissolved oxygen in the TMZ and under the influence of an urban effluent. Our model describes the transport of solutes and suspended material, and the major biogeochemical mechanisms: primary production, degradation of natural and anthropogenic organic matter, nitrification and re-aeration. The parameter values are based on experimental data on the study site.

This work presents simulations covering 9 months from winter to late summer. Simulations were performed in the absence or presence of urban effluent, and under increasing water temperature and decreasing summer river flow. The model reproduced in satisfactory way a decrease of dissolved oxygen saturation in the TMZ, and showed the influence of urban effluent. We compare the different situations and evaluate the relative impact of the biogeochemical processes and of natural and anthropogenic forcing on the quantity of dissolved oxygen.

# Impact of anthropogenic inputs from Marseille agglomeration on the vulnerability of the Mediterranean Sea.

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Progressive anthropization of coastal areas over the world results in changes in the biology and chemistry of the coastal seawaters. Sources of marine pollutions are various but large coastal cities are one of the most worrying, especially in the Mediterranean Sea: e.g. Marseille (~1.7 million inhabitants). The originality of the Marseille system is that the river waters are mixed with the city WWTPs effluents then rapidly discharged into the open sea, without passing through an estuary. Objectives were (1) to quantify the contaminants brought to the sea under different weather conditions and (2) to study their dynamics in the plume. Various sampling campaigns were carried out during dry and wet periods in the main Marseille tributaries (rivers, WWTP, outlet and mixing zone). A monitoring of outlet waters was also conducted during 24h in dry conditions (150mL/10min/1h). Remobilization batch experiments of outlet particles in different salinity ratios were also managed in lab to better apprehend the metal partitioning kinetics between dissolved and particulate fractions in the plume. Two techniques of sample filtrations were also conducted. Dissolved trace metals were quantified by voltammetry and particulate metals were measured by HR-ICP-MS. Organic carbon was determined in both dissolved and particulate fraction. Results of the monitoring showed that in dry conditions, dynamic of elements at the outlet was controlled by WWTPs effluents. After laboratory filtration (~3-4h after sampling) results showed a quasi-conservative behavior of the studied elements along the salinity gradient. Contrarily, results obtained after immediate on-field filtration showed that dissolved/particulate metal distributions were not at equilibrium when discharged at sea, resulting in an important and rapid metal desorption in the salinity gradient. Such a phenomenon, confirmed by lab remobilization experiments, was undetectable using the classical sample treatment protocol. It indicates that contamination of organisms along the coast can be higher than expected.

# Dynamic and variability of Organically Bound Tritium activities within Mediterranean coastal and continental water systems.

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Naturally occurring in the atmosphere due to its cosmogenic origin, tritium has been massively released in the environment by atmospheric nuclear weapons testing from 1945 to 1980 leading to activities in rains around two hundred times higher than natural levels (UNSCEAR, 2000). Today, this hydrogen isotope is currently one of the most emitted by nuclear facilities and unlike main trace elements tritium integrates both into the water and carbon cycles.

Naturally encountered in gaseous form, it is also largely present as tritiated water form (HTO) in rainfall fostering its integration into the biomass. Thus, it can be bound to the organic matter in two specific ways, according to the kind of bind, to form Exchangeable or Non-Exchangeable Organically Bound Tritium (E-OBT and NE-OBT). Tritium integration into organic matter is governed mainly by photosynthesis process but also through metabolic reactions without bright conditions (Diabaté and Strack, 1997). Once incorporated, this radionuclide is closely linked to the biodegradation cycle of organic compound (Eyrolle-Boyer et al., 2014). A recent assessment of OBT activity data into different aquatic matrices, from areas located outside industrial influence indicates an important range of variability between bind and free forms activities within the same compartment and points to the fundamental role of the quality and origin of organic matter. The delayed transfer of terrigenous organic matter, marked by previous atmospheric fallout, to estuarine and coastal areas seems to explain disequilibrium registered in some marine organisms as observed in coastal areas of the Mediterranean Sea.

This presentation aims to provide the preliminary results obtained regarding OBT concentrations in sampling waters, sediments and coastal organisms of several areas in the south of France which could enable to verify these hypotheses.

# Occurence of phthalate esters in Rhone River estuary (Mediterranean coastal Sea).

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Phthalic acid esters (PAEs) are widely used as additives in plastics to improve their softness and flexibility. As PAEs are not chemically bind in the polymeric matrix, discharge of phthalates into the environment can occur during the production of plastic and plastic material or after disposal from urban runoff, industrial wastewater or municipal sewage. Recent investigations have shown that several PAEs have endocrine disrupting effects, which are toxic and harmful to human health, although little is known about the impact on marine ecosystems. This study reports the first data on the concentrations of DMP, DEP, DiBP, DnBP, BzBP and DEHP in the Rhone River and in the Mediterranean coastal Sea. Fresh and seawater samples were collected in the Rhone Estuary at Arles and Port Saint Louis stations as well as in the River Plume in Mediterreanean coastal Sea during 2014-2015. PAEs were extracted from the dissolved phase from 500 mL - 1L of sample using Solid Phase Extraction (SPE) (Oasis HLB sorbent) in a clean room and detected by gas chromatography and mass spectrometry (GC/MS). The results showed that PAEs were detected in all the samples, ranging from 2 to 1300 ng/L with concentration decreasing from the River to the coastal Sea. DEHP and DiBP were the most abundant phthalate followed by DnBP and DEP. DEHP was characterized by the highest concentration (1302.6 ng/L) at Arles and a decreasing at Port Saint Louis (406.8 ng/L) and in plume (104-59 ng/L). DiBP was characterized by a different trend, with the lowest concentration at Arles (66.4 ng/L) and an increasing at Port Saint Louis (125.9 ng/L) and decreasing in the plume (49-67 ng/L).

# A seasonal study of three estuaries from the biscay coast with different pollution levels.

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A study of the seasonal variation of the contents of some nutrients as well as some physico- chemical parameters has been made in three different estuaries of Biscay (North of Spain). These estuaries are close together (The measured analytes have been nitrate, ammonia, phosphate, silicate and dissolved oxygen. Also, a multiparametric probe has been used to measure other physico-chemical parameters such as temperature, conductivity, salinity, total dissolved solids, fluorescent dissolved organic matter, pH and oxidation-reduction potential.

This work has been carried out with two main objectives in mind. The first one was to perform a study during a whole year in which samples have been taken each season in different sampling stations located along and outside the tidal zones in order to see the seasonal variation of the investigated parameters in each estuary. The second one is to analyze the differences in the nutrient content and in the physico-chemical characteristics of the three estuaries which, despite their proximity, have a very different history and environmental pressure resulting in very distinct pollution levels. These levels range from a clean biosphere reserve such as the Urdaibai estuary to a historically polluted estuary, due to the heavy industrialization from the 19th century in the Bilbao area, as the Nerbioi-Ibaizabal, with the Butroi estuary which might be considered an intermediate situation among the the other two.

# Long-term records of platinum contamination and sources in sediments and oysters from a fluvial-estuarine system (Gironde Estuary, SW France).

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Platinum (Pt), one of the rarest elements in the Earth crust, is considered as an emerging pollutant for which it is necessary to develop innovative techniques providing insights into its environmental behavior, speciation, and concentrations. Improvement of signal processing in stripping voltammetry allowed for accurate determinations of Pt in historical records of river sediments and estuarine oysters from the Gironde fluvial-estuarine continuum (SW France) comprising the Lot River. Sediment cores from the Lot River revealed a historical Pt contamination with Thorium (Th) - normalized values of $9.04.10^{-5} \pm 0.66.10^{-5}$ for the deepest part of the core which is clearly greater than the regional geochemical background value ($Pt/Th \sim 1.6.10^{-5} \pm 0.32.10^{-5}$). These samples, dated from 1952 to 2001, showed past Pt contamination which was related to former industrial activities in the Lot River watershed. Wild oyster samples from the mouth of the Gironde Estuary collected from 1981 to 2013 showed Pt concentrations ranging from $0.16 \pm 0.002$ $ng.g^{-1}$ to $0.61 \pm 0.027$ $ng.g^{-1}$. Oyster samples recorded historical industrial Pt contamination and empirical modelling suggests the recent rise of a new source of Pt to the system. Temporal variations of Pt in oysters attributed to this recent source reflect the exponential increase of Pt demand for car catalytic converters, pointing towards the increasing importance of this emerging source to the aquatic system. Estuarine oysters prove to be suitable bioindicators for Pt contamination providing sensitive monitoring of emission variations over time. Furthermore, oysters may bioconcentrate Pt and introduce this trace metal pollution to the higher food chain (Bioconcentration Factor, $BCF \sim 10^3$). This highlights the need for deeper understanding of environmental Pt contamination, processes and possible adverse effects to biota.

# The estuarine geochemical reactivity of Zn isotopes: implications for the biomonitoring (RNO/ROCCH oysters) of regional metal contaminations in the Gironde system and for global oceanic budget.

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High precision measurements (MC-ICP-MS) provide new constraints for the use of Zn stable isotopes as environmental tracer. We have studied Zn isotope signals (i) covering the long range (400 km) transport and phasing out of the metal contamination from the Decazeville Zn-refining district (Lot Watershed), (ii) across the estuarine system, and (iii) recorded by the 30-years oysters sample bank (RNO/ROCCH, Ifremer) from the Gironde Estuary mouth. Constant d$^{66}$Zn values of 0.35 ± 0.03 ‰ (1SD, n=15) in recent particles (2003-2011) are similar to the regional natural background and contrast with those of dissolved Zn (ZnD). In the estuary, ZnD shows a strong removal by adsorption onto particles, due to increasing total available sorption sites in the turbidity gradient. This subtraction goes along with a progressive enrichment in heavy isotopes in the dissolved phase, varying from d$^{66}$ZnD =-0.02 ‰ to 0.9 ‰, strongly related to SPM concentrations. This fractionation mechanism is confirmed by Seine River data. Oysters show d66Zn values varying from =1.43 ‰ in 1983 to 1.18 ‰ in 2010, heavier by 0.5 ‰ compared to typical seawater and oysters from other French coastal sites with more marine influence. Zinc isotopes signatures in oysters, rather than being only driven by the phasing out of the Decazeville signal, are strongly reflecting the geochemical reactivity of Zn isotopes in the estuary. Variations of d$^{66}$ZnD in the Gironde Estuary cover the whole range of values reported from World Rivers and World Surface Ocean, indicating that the geochemical reactivity of Zn in estuarine systems has been overlooked and probably requires re-assessing the global oceanic budget for Zn isotopes.

# Decadal trends of mercury levels, behavior and speciation in a macrotidal estuary: the Loire River (France).

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The RS2E project allowed to examine the distribution and speciation of mercury (Hg) and other trace-metals under contrasted river flow and tidal regimes. This study focused on mercury (Hg) is carried out based on a series of 4 cruises taking place between 2012 and 2015. Over the last three years, results from the Camelia cruises confirm that the riverine levels are in the low pM range, that concentrations decrease progressively during mixing with seawater, and the oceanic end-member concentrations are near 0.5pM. Concentration variations depend on concentration of suspended solids, on estuarine biological activity and riverine hydrological regime. Also, an on-going (2014-2015) monitoring of mercury levels and speciation in the upper reaches of the estuary and upriver at the Montjean bridge concur that these Hg properties fluctuate with water flow and areal flooding upstream.

In the early 1990's, a similar set of observations had already been conducted by our research team. For Hg, it showed estuarine levels between 1 and 6pM, also with a strong dependency on the hydrological regime (Coquery et al., 1997 Mar. Chem.).

These repeated observations at a twenty years interval, but using comparable and traceable analytical procedures, allow to reliably compare the changes that occurred for Hg, and to discuss the causes of the observed evolution. In particular, we will recall the sampling and analytical practices that have been used, and place the current observations in the context of changes in land-use and in environmental regulation.

Use of the N/O Thalia for the Camelia estuarine cruises, and financial support from the RS2E project and from Ifremer are gratefully acknowledged.

# Distribution of trace metals in superficial sediments of the Bay of Algiers in function of bathymetry.

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The study of the evolution of the contamination by trace metals in marine sediments according to bathymetry was carried out in the Bay of Algiers. The superficial sediment samples were performed using a grab at depths between 10 and 140 m during an oceanographic campaign in March 2009. The samples were taken along a radial which begin at the mouth of Oued El Harrach, the most important source of pollution in the Bay of Algiers

The samples were processed and analyzed by atomic absorption spectrophotometry with Zeeman effect for the determination of the concentration of trace metals: Cr, Cu, Zn, Mn, Ni, and Fe.

The distribution of the metals studied in the superficial sediment shows some anomalies in the coastal samples (Almost all metals), in the port (Zn, Cu, and Cr) and the station (17) the deepest (Ni, and Mn). Disregarding the anomaly observed in the coastal sediment, and in general, almost all of metals exhibits a concentration gradient decreasing in function of the depth.

# Sources and historical record of tin and butyl-tin species in a Mediterranean bay (Toulon Bay; France).

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Concentrations of inorganic tin (Sn), Tributyltin (TBT), Dibutyltin (DBT) and Monobutyltin (MBT) were measured in sediments of the Toulon Bay, hosting the major French military harbour. In marine environments these species mainly derive from antifouling paints used in various naval domains including military, trade, tourism and leisure. In the past, butyl-Sn contamination has severely impacted bivalve and gastropod populations (mortality, deformations, imposex, etc.) and they are known to accumulate in the aquatic food chain. Anticipating planned dredging, the aim of the present work is to map and evaluate for the first time the recent and historic contamination of these sediments by inorganic and organic Sn species. Surface sediments from 29 sites covering the entire Toulon Bay and two cores from a military area and mussel production zone were analyzed by ICP-MS and GC-ICP-MS using species-specific isotope dilution (TBT, DBT and MBT enriched in $^{119}$Sn) to determine concentrations of inorganic Sn and butyl-Sn.

Tin and butyl-Sn concentrations in the bay varied over 4 orders of magnitude, depending on the distance to the shipyards. The common spatial distribution of total Sn (1300 to 112000 µg/kg), TBT (<0.5 to 2700 µg/kg), DBT (<0.5 to 1800 µg/kg) and MBT (0.5 to 1000 µg/kg), similar to that of other contaminants in the Bay (e.g. Hg, Pb, Cu), the Enrichment Factors, the low degradation and the historical records of butyl-Sn species, support the scenario of a strongly polluted marine environment with exportation of polluted sediment to the open Mediterranean. Low degradation and the historical records of butyl-Sn species in two $^{210}$Pb-dated sediment cores, representative of the Northern Bay, are consistent with the relatively recent use of TBT by military shipyards and confirm maximum pollution during the 1970s, which will persist in the anoxic sediments for several centuries. Resuspension of extremely contaminated subsurface sediments by the scheduled dredging will probably result in mobilization of important amounts of butyl-Sn species in the water column, highlighting the need for thorough monitoring with respect to existing French dredging guidelines (GEODE). All these results suggest that the contaminant cocktail in the Toulon Bay presents a severe risk for this coastal ecosystem.

# Historical records of heavy metal concentrations along a river-estuarine-coastal gradient using sediment cores: an example from the Garonne-Gironde System (France).

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The Garonne-Gironde System is known for its high metal contamination (Zn, Cd, Pb, Cu, Ag) originating from industrial sources, with mining and smelting activities in the Decazeville watershed since the late 19th century. Furthermore, agricultural (e.g. Cu used in vineyards) and urban sources (e.g. Ag due to Bordeaux urban area) have impacted sediment quality. The temporal variability of heavy metal concentrations was examined in 2 sediment cores (GirHistoII and III; 450 cm long) collected in the Gironde Estuary (Macau Inlet). Ad- ditionally, the spatial distribution of Zn, Cd, Cu, Pb and Ag along the river-estuarine-coastal (REC) gradient was investigated, by comparison with published metal records obtained in the Garonne-Gironde system (e.g. Grousset et al., 1999; Audry et al. 2004).Both cores pro- vided information on regional geochemical background levels (RGB). Metal depth profiles showed similar low concentrations in the bottom and marked increasing trends towards the surface sediments. Qualitative correlation with historical metal contamination in the area allows assuming the sediments below 390cm as pre-industrial RGB for the Garonne-Gironde System (Zn/Th=11.9; Cd/Th=0.02; Cu/Th=2.07 Pb/Th=3.39; Ag/Th=0.04). Estimated maximum enrichment factors (EF) in the sediments revealed moderate to severe enrichment in Zn and Cd (EF=4.8 and 20, respectively), and low to moderate enrichments in Pb (EF˜4), Cu (EF $\sim$ 2) and Ag (EF $\sim$ 2) compared to RGB levels. Along the REC gradient, EF val- ues decrease from the upstream highly contaminated fluvial site (Cajarc in the Lot; e.g. Zn=40x; Cd=500x) to the poorly polluted coastal site (West Gironde Mud Patch; EF Zn, Cd=1.5), suggesting a consistent metal dilution and/or significant biogeochemical processes in the physico-chemical gradient. This work provides information on the impact of past and present human activities and in the evaluation of the effects along the Garonne-Gironde System of management strategies for contamination reduction in the upstream sediments.

# Depositional variability and metal contamination in estuarine intertidal sediments from Moreton Bay, Australia.

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Moreton Bay, southeast Queensland, is an estuarine/marine environment recognized by its ecological significance. In the last decades the catchment area has been subjected to increased anthropogenic pressure. In this work the spatial and temporal variability of trace metals contamination was investigated in thirteen sediment cores from the intertidal areas across the shores of Moreton Bay. Short-lived radionuclides ($^{210}$Pb and $^{137}$Cs), grain size, major and trace element analyses (Zn, Pb, Cd, Cu, Cr, Co, Ni, As) revealed that intertidal sedimentation has a high spatial variability. Sedimentation rates at four sites ranged between 0.16 and 0.71 $g/cm^2/y$ over the last 100 years and increased accretion rates were correlated to land use modifications after European settlement (1824). In the other sites sediments were mixed up to 80 cm depth. Increasing temporal trends of Pb, Zn, and Cu correlated to the major development of the catchment area and metal enrichment were 1.5-3 times the regional background calculated for Moreton Bay. Where sediment mixing occurred, vertical variations of metal concentrations were associated to both anthropogenic contribution and post - depositional processes, showing that local hydrologic conditions in the intertidal areas (e.g. tide, waves) play a controlling role on the spatial and temporal distribution of metals in Moreton Bay. According to sediment quality guidelines Cr, Cu, Ni and As were the main contributors to sediment contamination. The environmental risks posed by metals potential bioavailability in the surface sediments were also evaluated ffollowing the Risk Assessment Code (RAC). At the investigated sites Zn, Cd and Co may pose high to very high risk to the aquatic environment, while Ni, As, Cu, Pb and Cr may pose medium risk.

# Assessment of pollution and eutrophication status in louros and arachthos estuaries (amvrakikos gulf, n. W. Greece).

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Water and sediment samples in Arachthos and Louros estuaries at the north-western and north-eastern part of Amvrakikos gulf, respectively, have been collected in order to assess the status of pollution and eutrophication in relation to the anthropogenic pressures in the area. It is known that estuarine systems being biologically productive and receiving considerable pollutant inputs from land-based sources via river runoff, act as a transit zone in which contaminants are transported to the sea. For this reason the distribution and sources of nutrients, methane and organic pollutants in the estuaries were investigated, by using a molecular marker approach and several diagnostic criteria and indices. The study region is protected by the international convention of Ramsar. However, eutrophication phenomena have been observed in the past. High nutrient concentrations were recorded at the near-bottom layer of the estuaries, especially during wet period with high freshwater discharge (winter-spring), reaching values of 5.00 μmol/L for nitrate+nitrite; 66 μmol/L for silicate; 1.68 μmol/L for phosphate and 1.83 μmol/L for ammonium. Additionally, the main organic pollutants recorded in the water column were some low molecular weight polycyclic aromatic hydrocarbons (PAHs). High concentrations of methane in the near bottom layer (0.9 μmol/L in Louros estuary and 1.4 μmol/L in Arachthos estuary) were recorded during September 2014, whereas the methane concentrations at the surface layer were 0.2 μmol/L. Hydrogen sulfide was not detected, as DO concentrations were relatively high in the near-bottom layer of the estuaries (3.12 and 3.42 mL/Lat Louros and Arachthos estuaries, respectively). Relatively high PAH concentrations were measured in Arachthos and Louros estuaries (600ng/g and 319ng/g, respectively). Phenanthrene compounds and various methylated PAH predominated evidencing an influence of petrogenic sources. Perylene, considered as an indicator of terrestrial influence, was also determined in high quantities in Louros.

# Evaluation of the Trophic State of Guanabara Bay, SE- Brazil, with the TRIX and O´Boyle Indices.

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This study addresses the trophic state of Guanabara Bay (GB) with the TRIX (Vollenweider et al. 1998) and O'Boyle (O´Boyle 2013) Indices. The GB estuary (As = 384m$^2$; Zm = 5,7m; AB = 4080 km$^2$; QR = 100 ±59 m$^3$s$^{-1}$) is set at the SE-coast of Brazil (23o 45'S 44°45'W). It is prone to manifold sewage point and diffuse sources from the City of Rio de Janeiro and other municipalities. The study involved nine surveys (2013/2014) with continuous In Situ measurements along trajectories between the fresh and marine end-members and across the bay and also sampling at 15 to 19 stations along the runs. The parameters were: T (°C), S, pH, DO (mg.l$^{-1}$), nutrients (DIN and DIP in uM), Chl.a (µg/l). The hydro-geomorphological configuration, current regime and the parameters measured, permitted the division of the bay into five sectors (S): 1) the bay´s entrance, 2) the lateral polluted harbor area, 3) the central channel, 4) a mangrove reserve and 5) which receives the largest sewage inputs of the GB. S 4 and 5 compose the upper estuary. The TRIX Index (i.e.NID, PID, OD% and Chl.a) detected seasonal and spatial variability of the trophic state. S 1 (marine) was mesotrophic and S 2 and 5 eutrophic throughout the year. S 3 and 4 oscillated between mesotrophic and eutrophic. The TRIX Index, does unfortunately not include a hypertrophic category, which in fact should be allotted to S 2 and 5, due to their high ammonia and Chl.a concentrations. The application of the O'Boyle Index (i.e. pH and OD % saturation) was less successful due to the paucity of further studies in tropical systems. On a relative basis however, it managed to detect the discrepancies of the trophic state between the sectors.

# Surface water $pCO_2$ in the tropical oligotrophic São Francisco estuary (NE-Brazil), impacted by dams.

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This study reports on water $pCO_2$ measurements and associated air-water $CO_2$ fluxes along continuous trajectories with the equilibrator system coupled to a Li-Cor 800 detector within the tropical and oligotrophic São Francisco river estuary, NE of Brazil (Lat. 10°36'S; Long. 36°23'W). Dam impacts from up-river, lead to a reduction of the TSS load by 95%, DIN and DIP by 90% and river flow by 35% to the estuary. It is now transparent (TSS < 5 $mg.L^{-1}$), oligotrophic (DIN < 5mM, DIP < 0.2mM, Chl.a < $2mg.L^{-1}$), river flow is constant with a QR of ≈ $1800m3.s^{-1}$ and mean atmospheric $pCO_2$ of 376ppmv. The primary channel exhibited $pCO_2$ range between 224 and 1351ppmv. The 1st compartment (L = 20.5km), the tidal river portion, acted as a source with an average $pCO_2$ of 669 ± 136 ppmv. The 2nd compartment, the estuarine proper (L = 11.5km), varied spatially as a source or a sink of $CO_2$ ($pCO_2$ average of 523 ± 275ppmv). The 3rd compartment, the secondary channel (L = 27.4km), was subdivided into three sectors: A- affected by waters from the estuary, with a $pCO_2$ average of 548 ± 140ppmv, B- the mangrove portion, with $pCO_2$ of 510 ± 226ppmv and C - the channels marine portion with $pCO_2$ of 466 ± 145ppmv. Low nutrient and Chlorophyll a concentrations indicated that $pCO_2$ in the primary channel was governed by physical processes, including land-sea breezes, dominating NE-winds, tidal pumping and associated currents, and alternation between homogeneous and partially stratified waters. In the secondary channel water exchange with the mangroves slightly increased water $pCO_2$ and its spatial variability, whereas in the lower marine portion the salinity increased it and phytoplankton biomass decreased it. In spite of the substantial spatial variability, both channels acted as a source of $CO_2$ to the atmosphere.

# Mid-Infrared Optical Sensors for the Detection of VOCs in Sea Water.

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Volatile organic compounds (VOCs) in water including chlorinated aliphatic hydrocarbons and chlorinated aromatic hydrocarbons (CHCs), as well as benzene, xylene, and toluene (BTX) are considered harmful to the aqueous ecosystem. Nonetheless, they are found in all kinds of environmental aqueous phases, and may affect the human health and the ecological system. Due to industrialization and continuously increasing population across coastal areas, an increase of VOC discharge into the marine environment can be observed[1]. Therefore, monitoring of VOCs in marine ecosystems is a relevant task for protecting ecological systems, and human as well as animal health.

The direct detection of volatile organic constituents in water remains a difficult task. Conventionally, lossy sampling procedures are followed by complex sample pre-treatment strategies and subsequent instrumental analysis. These steps are time consuming, error prone, and cost extensive due to the fact that the samples have to be collected, transported, stored, and prepared[1,2]. Hence, direct chemical sensing techniques providing a molecular selective quantitative feedback on the presence of VOC contaminants during in-situ studies as developed in the currently ongoing SCHeMA project (http://www.schema-ocean.eu) are in significant demand, in particular for applications in harsh environmental scenarios such as coastal/marine ecosystems.

A submersible chemical sensor system for the online determination of VOCs in water based on evanescent field infrared absorption spectroscopy is currently in development operating at 3-15 μ m wavelength. A miniaturized FTIR spectrometer is coupled to an IR-transparent planar silver halide optical fiber sensor serving as active transducer. The sensing segment of the silver halide fiber is coated with a hydrophobic polymer excluding water from the analytical volume probed by the evanescent field along the fiber surface, while simultaneously enriching non-polar analytes such as VOCs into the polymer layer. In addition, this enrichment effect lowers the achievable limits of detection to the ppb (μg/L) concentration regime for CHCs as well as BTX constituents. Progress on the development of a submersible IR sensing system for in-field detection in marine environments is reported in this contribution[1,3,4].

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# The isotopic geochemistry of lead in the Scheldt continuum and the Belgian coastal zone.

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Now that Australian ore-based alkyllead gasoline has vanished in NW Europe, secondary anthropogenic Pb sources of more similar isotopic compositions have become prevalent. Unraveling isotopic signals to identify Pb sources, qualify transfer processes and quantify mixing proportions in multi-source dynamic systems such as rivers and estuaries remain a challenging task. Pb isotopes is a powerful tracer, but is limited by covarying ratios, allowing for only two sources to be discriminated along the typical ESPL trend line. High precision measurements provide substantial improvements, revealing subtle uranogenic and thorogenic compositions of Pb isotopes, allowing a better discrimination of sources and extrapolation of mixing trends. We report the first consistent geochemical dataset (140 samples) with high precision Pb isotopes measurements (MC-ICP-MS using thallium-doping for mass bias correction and resin chromatography on AG1-X8) for surface sediments (SS) and suspended particulate matter (SPM) from the Belgian coastal zone, the Scheldt Estuary (6 cruises on board of the Belgica R.V.) and its six major tributaries (1 year monthly surveys) in contrasted freshwater discharges.

Pb isotopes in SS and SPM show sub-parallel conservative-like profiles in the salinity gradient, with a higher radiogenicity for sediments due to mineralogical/grain-size controls. Pb isotopes signatures in SPM entering the estuary are mostly dependent on the relative contributions of the two major rivers due to the differential mobilisation of natural and anthropogenic Pb sources from watersheds, owing to their contrasted hydrosedimentary regimes. Smaller tributaries with more homogenous land use show more specific Pb signatures and mixing trends shifted from the typical ESPL. Pb isotopes also document a coastal contamination isotopically distinct from contaminated particles of the estuary reaching the North Sea. As a whole, five source components of variable relative contributions in function of time and space give rise to different mixing trends and explain the variability of Pb isotopes in the Scheldt system: (1) geochemical background (Pb-poor and more radiogenic), (2) urban/household activities (Pb-rich and radiogenic), (3) « historical» metallurgy (Pb-rich and less radiogenic), (4) coal/fuel (more uranogenic) and (5) fertilizers (more thorogenic).

The complex interplay of sources often evocated in environmental studies related to metal contamination are perfectly illustrated with Pb isotope data in the Scheldt system.

# Copper isotopic composition in the sediments of a contaminated marina (Port-Camargue, South France).

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The sediments of Mediterranean marina are contaminated with Cu. For the port users the contamination would be linked to the used of Cu sulfate for vine treatment. For others the contamination would be due to the intensive use of Cu as a biocide in antifouling paints. Numerous studies have shown that the variations of stable isotope composition of Cu in the environment was linked to biogeochemical processes (Zhu et al., 2000; Markle et al., 2006; Baliestrieri et al., 2008). However some studies have shown that variations of the Cu stable isotope ratio could at least partially reflect the mixing of different sources (ElAzzi et al., 2013; Mathur et al., 2014). Surface sediments of the marina of Port-Camargue are heavily contaminated in Cu with concentrations reaching 1500µg $g^{-1}$ near the yacht maintenance area. In absence of vine on the basin, the pollution is mainly due to antifouling paints. In this relatively simple environment with two Cu sources (natural/antifouling paints), the variations of the isotopic composition of Cu has been studied in the sediments and in the antifouling paint in order to test the capacity of Cu isotope composition to trace Cu sources. Results obtained in sediment cores indicate a decrease of the stable Cu isotope ratio ($\partial^{65}$Cu) from surface sediment, which is the most strongly contaminated to the deep sediment which reflects the local background Cu concentration. Nevertheless the relation between concentrations and $\partial^{65}$Cu cannot be accounted for by a simple mixing between two end-members. In addition to source mixing, biogeochemical processes as Cu reduction and sulfide precipitation must be taken into account to explain the variations of the isotopic composition of Cu.

# Geochemical patterns applied to Corbicula fluminea as a tool for Acid Mine Drainage Pollution Assessment in Sediment from the Iberian Pyrite Belt: North-American Shale Composite (NASC)-normalized Rare Earth Element patterns application.

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The Asian clam Corbicula fluminea is one of the most invasive species in aquatic ecosystems; widely spread by shipping, becoming the major component of the benthic macrofauna in upstream reaches of estuaries in America and Europe. Therefore, studies use it to monitor different inputs of pollution, especially for metals. However, in extremely metal-polluted environments, e.g. affected by rock acid pollution, the scope of new research includes monitoring through rare earth elements (REE) to determine petrological influences. The normalized REE patterns to these minoritary elements allow to determine the origin of the contamination. In the current study, geochemical patterns were applied to REE bioaccumulated in the clam.

Results showed a REE enrichment, displaying a particular acid mine drainage pattern, observed in the clam tissue. This might be an innovative technique for biogeochemical monitoring of pollution inputs to determine the origins of contamination in rivers, estuaries and bays by means of using these organisms collected in-situ.

# Sedimentary organic matter in the Admiralty Bay (King George Island, Antarctic Peninsula).

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The characterization of links between the diversity of benthic fauna, sediment bioturbation processes, and biogeochemical fluxes at the sediment-water interface is essential to better understand the consequences of a change in benthic biodiversity resulting from global changes on the ecological and biogeochemical functioning of Antarctic coastal ecosystems. The first part of this approach was aimed at assessing the spatial variability of the main features of sedimentary OM and its lability. Organic carbon and total nitrogen, total and enzymatically hydrolysable amino acids, chloropigments (and their degradation products), mean grain size and $\delta^{13}C_{OC}$ were measured in the top sediment layer of sediments cores collected during the 2012 austral summer at 53 stations located within the three inlets of Admiralty Bay (King George Island, South Shetland Islands, Antarctic Peninsula). Results clearly show an important spatial variability of OM descriptors throughout the Admiralty Bay. Based on the main features of sedimentary organics, the inlets are significantly different. Organic C contents were quite low in the different inlets of Admiralty Bay as observed in other Antarctic areas although the highest contents were measured in areas enriched in macroalgae and close to the Brazilian Scientific Station. Total N had a similar pattern with levels 3-fold higher close to the Brazilian Station. Sediments consisted mainly of silty muds but fine sands have also been found in some areas in the vicinity of glaciers or at the entrance of inlets. However, the differences in OM descriptors cannot be only explained by sediment grain size. The C/N ratios and $\delta^{13}C_{OC}$ values suggest the occurrence of marine OM although a contribution of continental inputs and/or degraded material can be locally observed. This is coherent with the high values of qualitative descriptors, which indicate a high lability of sedimentary OM, and spatial variability associated to its origin.

# Influence of Loire estuary's hydrology on diagenetic processes of an intertidal mudflat: focus on iron remobilization.

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Brillantes is the largest mudflat of the Loire estuary. Sedimentary regime and primary production are mainly driven by the hydrology of the Loire River. Nutrients runoff and sedimentation/ resuspension processes are variable at different spatial and temporal scales. In this study we choose to investigate processes associated to organic carbon mineralization at contrasted hydrological situations (late summer low flow, winter flow and spring descending flow) between September 2012 and February 2014, for two sites along a cross-shore transect. Analysing both pore water (DET-probe sampling, microprofiling) and sediment chemistry at a millimetre scale resolution over the first ten centimeters, we documented the impact of a rapid deposition of sediment on iron recycling and its slow evolution towards solid/dissolved equilibrium. Sediment at Brillantes is an iron-oxydes-rich fine silt containing a relatively high amount of organic carbon (3% dry weight on the top core during the peak flood of winter). Therefore, organic carbon mineralization processes are intense and dissimilatory iron reduction plays a major role. The impact of flood on deposition was stronger close to the shore. The more distal station was more subjected to repetitive resuspension due to tides that smoothed a more seasonal signal on deposition and recycling of metals.

# Two dimensional relations between solid and dissolved phases of iron and phosphorus in the Loire estuary's sediments.

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Sediment diagenesis generates chemical fluxes through the sediment-water interface which can strongly impact the water column. The reductive dissolution of iron (hydr)oxides in the Loire estuary sediment is an important diagenetic process in the first 20 cm depth, and forms a possible source of dissolved phosphate and trace metals to the river. A two dimension sampling of the dissolved phase by a combined DET-gel/colorimetry technique[1] showed the strong effect of macrofauna bioturbation on dissolved iron and phosphate flux. Nevertheless, this picture illustrated a relative short-term variability, which can change according to the variations of macrofauna activity. As sediment solid phase integrates more long-term diagenetic reactions, we compared reactive solid phase with dissolved phase in two dimensions to understand the long-term effect of macrofauna on diagenetic processes. The sampling system allowed recovering simultaneously the gel plate and the sediment facing it. Reactive Fe and P were obtained by ascorbate extraction from the sediment sliced at a centimetre-scale (sample of 1 $cm^3$). The lateral homogeneity of the solid phase strongly contrasted with the heterogeneity of the dissolved phase. This result seems to show that bioturbation has limited impact on solid phase transformation through long-term diagenesis.

[1] Florian Cesbron et al., « Simultaneous 2D Imaging of Dissolved Iron and Reactive Phosphorus in Sediment Porewaters by Thin-Film and Hyperspectral Methods », Environmental Science & Technology 48, no 5 (4 mars 2014): 2816-26, doi:10.1021/es404724r.

# Porewater biogeochemistry in a sandy beach influenced by a subterranean estuary (Yeu Island, French Atlantic coast).

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Porewater biogeochemistry was investigated along a tidal cross-shore transect of a sandy beach of Yeu Island. In situ sediment porewaters were sampled and salinity, dissolved oxygen, nitrate, nitrite, ammonium, phosphate, dissolved iron and manganese, and sulphide were measured. Salinity measurements highlight the existence of a subterranean estuary resulting of a mixing between a small fresh groundwater aquifer and recirculating seawater in the beach. Oxygen and nutrient concentrations of porewaters suggest that mineralization of organic matter occurs in the beach sediments. During flood tide, oxic and nutrient-depleted seawater penetrates the upper beach coarse sediments, which are water-unsaturated down to 80 cm at low tide. In the lower beach, the sediment remains always water-saturated and the sand is finer and less permeable. During high tide, the upper 25-cm of porewaters of the lower beach are replaced by new seawater supplied by breaking waves. During ebb tide, the downslope drainage from the berm to the lower beach induces percolation of porewaters through the sand. Thus, porewaters become older in seaward direction across the beach cross-shore profile. The renewal and the flow of porewaters depend on slope and sand permeability, which are not homogeneous along this beach. Our results show that porewater composition is progressively modified along the tidal cross-shore transect because of the production and consumption of chemical components due to organic matter mineralization. Inorganic nitrogen concentrations (ammonium, nitrite, nitrate) suggest that denitrification process probably takes place in the lower part of the beach where suboxic conditions are found. Nitrification seems to occur at the interface between the upper and lower parts of the beach, where high abundances of sand worms are found in oxic conditions.

# Microbial metabolism of transparent exopolymer particles (TEP) during the summer months along a eutrophic estuary system.

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This study explores the role of transparent exopolymer particles (TEP) as an additional carbon source for heterotrophic microbial activity in the eutrophic Qishon estuary. From the coastal station and upstream the estuary; TEP concentrations, β-glucosidase activity, bacterial production and abundance have gradually increased. TEP were often found as bio-aggregates, scaffolding algae, detritus matter and bacteria that likely formed “hotspots” for enhance microbial activity. To further demonstrate the link between TEP and heterotrophic bacterial activity, confined incubations with ambient and polysaccharide-enriched estuary water were carried out. Following polysaccharide addition, elevated (~50%) β-glucosidase activity rates were observed, leading to TEP hydrolysis. This newly formed bioavailable carbon resulted in significantly higher growth rates, with up to a 5-fold increase in heterotrophic bacterial biomass, comprising mostly high nucleic acid content bacteria. Taking together the findings from this research, we conclude that even in highly eutrophic environments heterotrophic bacteria may still be carbon limited. It is possible that once carbon is available other nutrient become limiting, then specialized heterotrophic bacteria such as diazotrophs could utilize these new conditions (e.g. high C > N) and prevail. Further, TEP as a polysaccharide matrix can act as a metabolic surrogate, adding fresh bioavailable carbon through tight associations with bacteria in eutrophic ecosystems such as the Qishon estuary.

# The influence of ph and waterborne metals on egg fertilization of *Paracentrotus lividus*, *Crassostrea gigas* and *Mytilus edulis.*

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The study evaluated the combined effect of pH and metals on the egg fertilization process of two estuarine species, blue mussel Mytilus edulis, oyster Crassostrea gigas and sea urchin Paracentrotus lividus. The success of egg fertilization was examined after two-hour exposure to environmental sediment extracts of various degrees of contamination at pH 6.0, 6.5, 7.0, 7.5, 8.0. The results revealed that egg fertilization was almost completely inhibited at pH 6.0 for all species; however, at higher pH levels (6.5, 7.0, 8.0) eggs of the different species demonstrated different sensitivity to metal and/or acidic exposure. In general, the eggs of sea urchin demonstrated concentration-dependent response, whilst the eggs of blue mussel were the least sensitive to the exposure. Acidity, while increasing the concentration of metal ions, may reduce availability of these ions to organisms. This could be related to any of the following: reactivity of the metal chemical form, competition among metals and other waterborne constituents for binding sites in the biological surface or organismal specifics. The results of this study add to our knowledge of adverse effects of acidification in aquatic animals and acidity-metal interactions.

# Sediment contamination and toxicity in the Guadalquivir Estuary (SW, Spain).

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This report assesses environmental quality in an estuarine environment in the upper area with a high influence of fresh water conditions, as the Guadalquivir river course between the Alcalá del Río´s dam and Seville. This assessment was developed through the determination of metals in sediment samples and toxicity under laboratory conditions applying a battery of bioassays with different animal groups (the amphipod Ampelisca brevicornis, the bacteria Vibrio fischeri, the sea urchin Paracentrotus lividus, and the oligochaete Tubifex tubifex). The objective of this work was to determine the potential risk associated with sediment contamination under an integrative point of view in a complex area such us the estuarine environment. Different species either fresh water, sea water and brackish were used to address the potential effect of the sediment contamination. An increasing toxicity gradient was shown downstream using the bioassays with the amphipod A. brevicornis, the fertilization test using the sea urchin P. lividus, and the fresh water worm growth T. tubifex. Conversely, an increasing toxicity gradient was shown upstream in the embryo-larval P. lividus development. The stations located close to the city of Seville (AL and SE) showed an important alteration related to metals, while the other station AR has accumulated metals from upstream the dam with different origins (agriculture, urban and industrial). The three stations considered in this study in the Guadalquivir estuary showed adverse effect to the organism used in the study. Lastly, a Sediment Quality Guideline (SQG) for different metal concentrations was made to be applied in riverine management plans.

# Influence of river discharge on the dissolved organic matter dynamics in the French South Coastal Zone of the Bay of Biscay.

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Dissolved organic matter (DOM) is a heterogeneous, complex mixture of macromolecular compounds, including humic-like substances, extracellular polymeric substances (EPS), proteins or lipids, with wide ranging chemical properties and size. DOM can interact with pollutants, affecting their transport and their fate in aquatic environments. It is thus of fundamental importance to understand their dynamics in aquatic ecosystems and especially in coastal zones submitted to river inputs. The national French research program «LIGA» focuses on tracing colloidal DOM sources and cycling in the Bay of Biscay (South Western French coast).

A one-year intensive monitoring survey of DOM optical properties was undertaken by using UV/visible absorbance and excitation emission matrix (EEM) fluorescence spectroscopy. From April 2013 until June 2014, water samples were monthly collected from the Adour River (main freshwater inputs) and from 2 coastal marine sites in the Bay of Biscay at 3 depths of the water column (surface water, at the maximum of chlorophyll-a, and deep water). Furthermore, intensified samplings took place twice a week during 4 weeks from the appearance in waters of marine mucilage. Environmental parameters such as precipitations, the Adour River discharge, swell and temperature, were acquired simultaneously to DOM monitoring. The EEM fluorescence data set was analyzed using PARAFAC DOMFluor toolbox in Matlab which decomposes the complex data matrix into its main components. PCA analysis was run on the optical spectroscopic dataset of the samples and the environmental parameters.

The application of UV/visible absorbance and EEM fluorescence spectroscopy coupled to PARAFAC and PCA analyses appears thus to be a very powerful tool for the long term monitoring of DOM properties and is very useful for a better understanding of the biogeochemical processes in marine environments and of the marine colloidal DOM ecodynamics.

# Dynamics of Dissolved Organic Matter at the Arno river mouth.

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Estuaries are the primary interface between land and sea where most of the organic carbon undergoes physical, chemical and biological transformation before it enters into the marine environment. Arno river (Tuscany, Italy) has a low discharge (2.6 $Km^3/y$), compared to the main Mediterranean Sea rivers, however it represents an important source of dissolved organic carbon (DOC) to the coastal area. The average DOC concentration in the river is almost twice the concentration measured in Rhone and Po rivers. The main goal of this work is to assess what are the main processes affecting DOM dynamics at the Arno river mouth. This study will contribute to assess the role of coastal areas impacted by river inputs as sinks or sources of $CO_2$ to the atmosphere. DOC concentration and CDOM optical properties (absorption and fluorescence) were measured weekly at one station located in the Arno river (S=0) and along transects from the river to the coastal area impacted by its plume. DOC and CDOM varied notably (169 – 480 µM) during the year. Peaks in DOC and CDOM were observed during flood events, followed by a rapid decrease, as well as in summer, when river discharge was at its minimum. A direct correlation with temperature was also observed, suggesting that in situ biological processes are responsible for the observed DOC accumulation in spring. The relationship between DOC and salinity at the river mouth showed that, although dilution is the main factor controlling the input of riverine DOM to the coastal area, other processes play a role in shaping DOM distribution and concentration. Long term incubations used to estimate mineralization rates at the mouth of the river showed DOC removal and CDOM release. Bacterial abundances suggested that these are able to consume labile DOC and responsible for the release of CDOM.

# Carbon Capture and Storage (CCS) strategy: a risk assessment overview focused on marine bacteria.

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Scientific community has focused on several aspects related to the ocean acidification in the water column due to an increase of $CO_2$ in the atmosphere, such as pH variations, seawater chemistry and negative effects on diverse marine organisms. Ocean acidification term has to be extended because a pH decrease may also occur in deep water as a consequence of a $CO_2$ leak from a stable geological formation (carbon, capture and storage, CCS) or natural $CO_2$ escapes. CCS is one of the best options to storage carbon dioxide to mitigate the negative effects of the climate change. However, this strategy may have associated some risks such as $CO_2$ leakages due to an escape from the reservoir. It is necessary to improve the knowledge about the chemistry, nutrients fluxes, pollutants mobilization and effects in benthic organisms. In this context, marine bacteria, and all the processes which they are involved in, have been underestimated. In order to figure out the gaps and the lack of knowledge, this work summarizes different studies on the potential effects on the marine bacteria related to an acidification caused by $CO_2$ leak from CSS. Moreover, this contribution proposes a strategy for laboratory protocols using Pseudomona stanieri (CECT7076) as a case of study and analyzes the response of the strain under different $CO_2$ conditions. Results showed significant differences in the growth rate under six/diluted enriched mediums and differences about the days in the exponential growth phase. Best mediums were selected to expose P. stanieri under several acidification conditions. The results of this work will provide an essential tool to understand and develop a management strategy to improve future works related to possible effects produced by potential $CO_2$ leaks.

# Seasonal Variability of Carbonate System Parameters in the Razdolnaya River and Its Estuary (Amursky Bay, Sea of Japan).

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It was suggested the approach for accurate study of carbonate system in river waters and estuaries. This approach includes: a) knowledge of apparent dissociation constants which measured from 1.5 - 40 salinity range of seawater and calculated dissociation constants by means of Pitzer method for given composition of river waters; b) measurements of pH by means of cell without liquid junction using Pitzer pH scale; c) measurements of total alkalinity (TA) by means of Bruevich method; d) measurements of humic substances concentrations by means of spectrophotometric method and taking into account of organic alkalinity caused by existence of humic substances in the river and estuarine waters. Suggested approach was applied to study carbonate system of Razdolnaya River and its estuary for four seasons.

Amursky Bay area is characterized by a monsoon climate. Winter season here is cold and dry and the northern part of the bay and Razdolnaya River are covered by ice. Summer is mild and wet. In winter season the $pCO_2$ reaches maximum values (up to 6000 uatm) because there is not any air/water exchange. TA and DIC have highest contents (up to 3000 umol/kg). In summer season, when River has high water, the $pCO_2$ in riverine part of estuary is high (up to 2000 uatm) and low in marine part of estuary. In this case TA content of river waters is low (about 500 umol/ kg). In spring and autumn seasons the River and its estuary is a sink for atmospheric $CO_2$ as rule. The «concave" character of TA vs salinity dependence for Razdolnaya River is rather apparent non-conservative behavior which is caused by temporal variability of TA content in river water. It was estimated that annual fluxes of total alkalinity and humic substances supplied by the River into Amursky Bay are 15400 moles and 115 kgC, respectively.

# Analysis of metals bioavailability from resuspension test the Sepetiba Bay superficial sediments, Rio de Janeiro, Brazil.

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The resuspension of sediments due to natural processes or anthropogenic activities (such as dredging) can influence the trace metal bioavailability. This hypothesis was tested in an area of Sepetiba Bay (RJ) affected by elevated contamination by Cd and Zn.Therefore, the main objective of this study was to evaluate the effects of resuspension of sediments from the region affected by Saco do Engenho (Baía de Sepetiba) on the bioavailability of potentially-toxic trace metals (Cd, Cu, Ni, Pb and Zn), by performing laboratory assays, as a strategy to subside the environmental risks associated to dredging. Samples from 12 sampling points were collected near the Saco do Engenho creek and the Itaguaí Harbor, being submitted to two resuspension time intervals (1 hour and 24 hours). With the exception of Ni, trace metals exceeded local background values. There was predominance of weakly-bound fraction (extracted in 1 mol/L HCl), except for Ni, occurring a tendency of decrease in the potential bioavailability with the distance from the source in relation to Cd, Cu, Pb and Zn. Changes in the weakly-bound concentrations of Cd and Zn after re-suspension were above the Level 1 for two samples only. It was evidenced that Fe and Mn compounds are important factors affecting the weakly-bound fraction, while total organic carbon (TOC) showed correlations with Cd, Zn and Cu strongly- bound fraction (extracted in concentrated $HNO_3$), demonstrating the importance of organic matter for the preservation of these metals in such fraction less susceptible to biological incorporation. Results evidence that re-suspension affects the bioavailability of different metals, principally in the first time interval (1 hour), reflecting abrupt changes due to exposure to oxidizing conditions.

# Evaluation of trace elements remobilisation during polluted sediments resuspension: insight from batch experiments and kinetic modelling.

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Toulon bay (NW Mediterranean Sea), a semi-closed area with a low sedimentation rate (0.2 cm $yr^{-1}$), is presenting a high sedimentary multi-contamination (metals/metalloids/organometallics/ organics). This study aims at apprehending the risk of dredging operation upon seawater quality through batch simulations on surface/suboxic and deep/anoxic polluted sediment. Core sediments, sampled in various sites were sliced every 2 cm under inert atmosphere. Porewaters and solid fractions were recovered and characterized for their physical-chemical parameters, total concentration of major, minor, trace elements, as well as dissolved/particulate organic matter content. Surface (0-2 cm) and deep (20-22 or 30-32 cm) sediments were stored under inert atmosphere until their mixing with seawater (sampled at the same site) at different solid/liquid ratios (0.1, 1 and 10 g $L^{-1}$) in Teflon bottles. The mixture was shaken head-over-head at 15 rpm, and exposed at least daily to ambient air to maintain the oxic conditions. Aliquots were collected at 10 contact times, ranging from 5 min to 2 weeks. Physical-chemical parameters (pH, Eh, $O_2$ ...) were recorded, major/minor/trace elements and dissolved organic/inorganic carbon concentrations were analyzed. The batch simulation results showed a continuous acidification of seawater (up to 1 unity of pH over 2 weeks of contact time) whose amplitude was mainly dependent on the solid/liquid ratio but less on the initial redox status of the sediment. Concerning trace elements, As was characterized by a rapid mobilization, right away followed by a readsorption. A similar, but even more pronounced, behaviour was demonstrated for Pb and Cd whereas Cu showed an inverse trend. Many processes controlled these alternative adsorption/ desorption steps, as porewater Fe/Mn precipitation or sulfide oxidation, ... . For all cases, the trace element concentrations reached at the maximum of remobilization exceeded the toxicity levels for microorganisms. Kinetic modelling efficiently reproduced the observed trace metals behavior indicating a possible predictive use.

# Salinity and redox gradients control carbon, nutrient and trace metal cycling in high-energy beach pore waters.

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Intertidal permeable beach sediments represent major transition zones (land-sea, freshwater- saltwater, oxic-anoxic), which play an important role in coastal carbon, nutrient and trace metal cycling. Seawater enters the sediment during flood tide and pore water drains out during ebb tide. This pore water advection continuously supplies fresh organic substrate to the sediment. Remineralization products of microbial degradation processes are enriched in the pore water compared to open seawater concentrations. Terrestrially-derived fresh groundwater modifies the marine-dominated pore water composition. We investigated the spatial distribution of dissolved organic carbon, inorganic nutrients, trace metals and sulfate. High nitrate concentrations indicate that redox conditions are oxic within the duneward freshwater part, while ammonification, denitrification, manganese and iron reduction seem to prevail in the seawater circulation zone. We can show that salinity and redox gradients influence the composition of pore waters, which discharge into coastal surface seawaters, where they may trigger primary production.

# Impacts of anthropogenic pressure on metal contamination in the Danshui fluvio-estuarine System from the Urban Agglomeration of Taipei (NE Taiwan)

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Estuaries are important interface between continent and ocean and deliver invaluable ecosystem services. However, these vital systems are facing different degrees of anthropogenic pressure, especially for trace metals. The evaluation of geochemical risks for estuarine water quality due to urban pressures are of particular concern as world population are projected to increase from 7.1 to 8.4 billion in 2030 and 60% will live in urban areas. The Danshui River is the major water system in North Taiwan. It shows a quite undisturbed section in upstream but drains the Taipei-Keelung-Taoyuan Metropolitan area (9 million inhabitants) in downstream. A snapshot sampling campaign was performed in March 2015 for characterizing the spatial distribution of dissolved and particulate trace metal (Zn, Cu, Cd, As, Ag and Sn) concentrations in water and sediments collected in the Danshui and its major tributaries (Xindian, Keelung). Additionally, road sediments were also collected in Taipei conurbation. The objective is to establish local geochemical background (LGB), localize geochemical anomalies compared to LGB values and identify sources. Particulate metal Enrichment Factors (EF) are calculated using LGB and indicate that trace metal concentrations display a high spatial variability depending on the studied element. For example, the EF sequence for maximal values obtained are 11>Ag>Sn>Cu>Cd>Zn>As>2 for river sediments and 55>Cu>Sn>Cd>Ag>Zn>As>3 for road sediments. Finally, our findings confirm that Ag is a good tracer for urban sources and runoff of road sediments may contribute to additional sources in the Danshui. However, due to the high mechanical erosion and sediment supply entering in the estuary, this impact may be low during extreme rainy events (e.g. typhoons). This system is less deteriorated than other urban systems (e.g. Gironde Estuary). These results could suggest significant effects of remediation procedure involved in the recent years in the Danshui System.

# Spatiotemporal distribution of dissolved and particulate inorganic antimony along the Gironde fluvial-estuarine continuum: a preliminary approach to regional nuclear accident scenarios.

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The nuclear power plant accident of Fukushima Dai-ichi (Japan, 2011), has raised concern on radionuclide behaviour and dispersal in aquatic systems. Antimony (Sb) is a fission product in nuclear power plants, presenting non-negligible radioactive intensities at relatively long term exposure conditions (i.e., $^{125}$Sb isotope: half-life of 2.76 y). Antimony is also considered a dangerous substance by the European Community (Directive 2006/11/EC) due to its high toxicity, comparable to that of lead (Pb). The fate of radioactive elements can be extrapolated from their natural stable isotopes due to their analogous biogeochemical behaviour. We present dissolved and particulate Sb concentrations and fluxes entering the Gironde Estuary via the Garonne River (from 2003 to 2014) and its distribution along the salinity and turbidity gradients of the Gironde Estuary (flood periods in March 2013 and 2014). The first data on particulate Sb (SbP) concentrations suggest constant values along the Gironde salinity gradient, with higher concentrations (2.05 ± 0.31 mg kg$^{-1}$) during a flood compared to 1.58 ± 0.30 mg kg$^{-1}$ during intermediate discharge. This and the generally 2-fold higher concentrations of $Sb_P$ in the Garonne River may suggest physical dilution and/or Sb mobilisation in the saline estuary. Dissolved Sb concentrations increased with salinity from 0.25 µg L$^{-1}$ at S=0 to 1.01 µg L$^{-1}$ at S=27, i.e. clearly higher than expected values for North Atlantic coastal waters (~0.3-0.5 µg L$^{-1}$), supporting the idea of non-conservative Sb behaviour in the hyperturbid Gironde Estuary. Distribution coefficients (Kd ≈ 103 - 104 L kg-1) indicate that in the Maximum Turbidity Zone (MTZ; SPM ~1000 mg L$^{-1}$) ~90% of the total Sb is associated with particles, whereas low Suspended Particulate Matter (SPM ~ <100 mg L$^{-1}$) favour Sb solubility, with only ~10% of total Sb in the particulate phase. This means that freshwater discharge and the resulting position and dynamics of the MTZ, both controlling water and particle residence times in the Gironde fluvial-estuarine system will be of major importance for radioprotection scenarios in case of a crisis in one of the two nuclear power plants in its watershed.

# In situ voltammetric As (III) sensing in natural waters.

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Arsenic in the environment is of a global concern because of the widespread, chronic poisoning, found in a number of countries and affecting large populations. Inorganic As(III) and As(V) species are predominant in the water column, while organic forms are the main arsenic species in aquatic organisms. Inorganic arsenic has been classified by the International Agency for Research on Cancer (IARC) as a group 1 human carcinogen. As(III) species are 60 times as toxic as the pentavalent salts and several hundred times as toxic as methylated arsenicals. The proportions of the inorganic species in the media are function of the bio-physicochemical conditions and thus may varies continuously in space and time [1]. Robust and sensitive analytical tools capable of direct, continuous in-situ As(III) sensing is therefore of prime interest for As health risk assessment. The characteristics of voltammetric techniques make them particularly well suited for the development of such tools [2].
This will be illustrated by the development of a gel integrated gold nanoparticles plated Ir-based microelectrode arrays (AuNPs-GIME). The AuNPs-GIME and analytical protocol have been specially developed to minimize fouling problem [2] and to enable continuous and reliable direct measurements of As(III) in complex media. The characteristics and the analytical performances of this novel microsensor will be presented. Environmental features of this sensor integrated in a submersible voltammetric in situ profiling system (VIP) will be illustrated with examples of laboratory measurements and field applications.

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# Interconnected microelectrode arrays for trace metal detection in natural waters: fabrication and electrochemical characterization.

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We report here on the fabrication and preliminary electrochemical characterization of new designed interconnected microelectrode arrays for trace metal detection in natural waters. The devices have a total size of 2.4 x 6 mm and consist of an array of 19 x 10 interconnected iridium microdiscs of 5µm diameter separated by center-to-center spacing of 155 µm (columns) and 190 µm (rows). These sensors have been fabricated on silicon wafers coated with a 200 nm thick $Si_3N_4$ layer. An Ir layer of 100 nm was deposited by sputtering and patterned by Ion Beam Etching thus defining Ir bands, while a $Si_3N_4$ layer of 200 nm was deposited by Plasma-Enhanced Chemical Vapor Deposition and then patterned by Deep Reactive Ion Etching to define the microelectrode discs and the bonding pads. The individual devices were mounted on a printed circuit board, wire bonded and encapsulated with epoxy resin.

The electrochemical behavior of the Ir-based microdisc arrays has been characterized by cyclic voltammetry in 1 mM potassium ferricyanide solution. The observed S-shaped response proved the absence of shielding effect and diffusion layer overlapping. The diffusion controlled steady- state current measured was found to be in good agreement with the theoretical value calculated for a recessed geometry. The fabricated Ir-based microdisc arrays were then electrochemically plated with either Hg-hemispheres or gold nanoparticles (AuNPs) and applied to the Square Wave Anodic Stripping Voltammetry (SWASV) detection of respectively 10 nM Pb(II) and 12 nM Cd(II) or 50 nM As(III) in synthetic solutions. The results obtained demonstrated a significant increase in sensitivity compared to the ones obtained previously using 5x20 Hg-plated Ir-based microelectrode arrays for the detection of Pb(II) and Cd(II) [1] and a AuNPs plated Ir-based single microelectrode [2].

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# Detection of Volatile Organic Constituents in Seawater using Mid-Infrared Spectroscopy.

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Volatile organic compounds (VOCs) are toxic and in part carcinogenic contaminants in seawater. Pollutants such as chlorinated aliphatic or aromatic hydrocarbons (CHCs), and benzene, toluene and xylene (BTX) were detected in seawater[1,2]. As such, they pose a potential risk to humans, animals, and the marine ecosystem. Most pollutants originate from insufficiently treated wastewater discharged by industrial or municipal sites into the coastal or estuary regions[3]. As a result, on-line continuous monitoring of the water quality pertaining VOCs is in substantial demand.
Detection of VOCs in seawater is conventionally performed using chromatographic methods, e. g., gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled with a variety of detection schemes[1,2]. However, such measurements are challenging, as seawater is a complex matrix. Furthermore, these methods are time- and cost-extensive and by far and large limited to laboratory conditions. Hence, water samples have to be collected in the field, stored, and transported to appropriately equipped laboratories for analysis. The desired alternative is to determine VOCs directly onsite and in-situ, i.e., in the marine environment, as proposed within the currently ongoing SCHeMA project (http://www.schema-ocean.eu). Infrared evanescent field absorption sensors based on compact FTIR spectrometers combined with a planar silver halide fiber sensing element provide an innovative concept for in-situ optical chemical sensing[4]. The actively transducing part of the fiber was coated with a thin hydrophobic polymer membrane (i.e., ethylene/propylene copolymer; E/P-co). Then, hydrophobic VOCs were enriched into the membrane, while water was effectively excluded from the analytical volume (few µL) probed by the evanescent field[5]. This contribution focuses on recent laboratory results investigating various strategies and sensing configurations for VOC analysis in seawater.

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# Innovative approaches for the sampling and determination of emerging contaminants in water.

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Human health and ecosystems are threatened by the releasing and the accumulation of emerging pollutants in the aquatic environment, which needs to be constantly monitored. Recently, the focus of research has been partly shifted from the conventional priority pollutants to the analysis of compounds used in everyday life, like pharmacologically active substances which are not entirely absorbed by human body and excreted, reaching the aquatic compartment through the effluents mainly from wastewater treatment plants and hospital and pharmaceutical production facility effluents.

The main analytical problems related to the determination of these compounds are represented by their very low concentration levels and the presence of potential interferents; then, highly sensitive and selective detection techniques must be preceded by accurate sampling and preconcentration steps.

Two innovative analytical approaches for sampling and preconcentrating analytes in water are SBSE (stir bar sorptive extraction) and passive sampling by using POCIS (Polar Organic Chemical Integrative Sampler). The first one is a sample preparation technique based upon sorptive extraction on a polymeric phase covering a magnetic bar. The second one is based on the integrative sampling of the analytes by the exposition of the sampler in the water environment to be studied during a period of several days or weeks.

We developed different methods based on these approaches for the determination of nonsteroidal anti-inflammatorydrugs (NSAIDs), pesticides and non-target analytes in water by electrospray ionization liquid chromatography-tandem mass spectrometry (LC-ESI-MS/MS). In particular, SBSE was developed by comparing EG-Silicone and PDMS stir bars and optimizing main parameters to attain high recovery, sensitivity and specificity. The developed methods were successfully applied to the analysis of wastewater, river and tap water samples from different Italian regions. Preliminary data regarding the application of these approaches for the study of marine ecosystems (coastal areas in Liguria and Antarctica) are also presented.

# Toward in-situ monitoring of the dynamic fraction of inorganic mercury.

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Mercury is one of the most toxic elements impacting on ecosystem, and ultimately human, health. This is related to its bio-accumulation and bio-magnification along the food chain. As for the other trace metals, the chemical form of mercury controls its bioavailability, transport, persistence and impact. Speciation analysis provides therefore more useful information that the measurement of total mercury concentration. In aquatic fresh and marine coastal waters, the main mercury species are inorganic Hg(II) and mercury-organic species, in particular methylmercury. Inorganic Hg(II)forms complexes or compounds with inorganic and/or organic species (e.g. hydroxide, chloride, sulphide, FA/HA) under proportion which dependent on the local physicochemical conditions. Mercury-organic species originates from bio-methylation of bio-available inorganic Hg(II) compounds.

Recent developments in analytical techniques have made the separation of Hg species and their quantification in collected natural samples possible at the pg·L$^{-1}$ level. Nevertheless, the determination of Hg species in natural waters is still a challenge due to the high risk of contamination, analyte losses, and inter-species conversion during sampling, storage, and pre- treatment. The development of easy to use, in-situ, reagent-free pre-concentration devices, and ultimately in-situ quantification methods, for routine monitoring is therefore of prime interest. In the frame of the collaborative EU project SCHeMA (www.schema-ocean.eu), we are exploring the development of gel integrated gold nanoparticles-plated microelectrode arrays (AuNPs- GIME) and (bio-) polymer functionalized AuNPs-GIME for selective, highly sensitive, in-situ voltammetric quantification of the bioavailable fraction of inorganic Hg(II). We report here on the characteristics of these sensors and the analytical approaches used for their development. The present analytical performances of these microsensors are illustrated by examples of results obtained in synthetic solutions and collected natural samples.

# Highly sensitive monitoring of fipronil and its metabolites in the Gironde estuary (France).

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Performing appropriate monitoring is a relevant issue, particularly in diluted waters such as estuaries, where pollutants can be present at trace levels. In this respect a good example of the interest of developing highly sensitive monitoring methodology is illustrated by Fipronil which is an insecticide registered for limited agricultural applications in France but which is used for flea and termite control. Fipronil has been found in Bordeaux (southwest of France) wastewater treatment plant influents (≈ 50 $ng.L^{-1}$). As it is not removed by waste water treatments, it is discharged into the receiving environment (≈ $g.d^{-1}$), the Garonne river, which is one of the two rivers forming the Gironde estuary (with the Dordogne river). Fipronil has been searched in Garonne river but has not been detected. This molecule is however toxic at very low levels of concentration as its predicted no effect concentration (PNEC) is 0.77 $ng.L^{-1}$ and the initial method was not sensitive enough to reach such levels (LOQ between 2 and 5 $ng.L^{-1}$). Taking into consideration the ecotoxicological relevance of its determination, it was then necessary to develop a new technique able to monitor Fipronil in the Garonne river at relevant level, with LOQ below PNEC. Stir-bar sportive extraction (SBSE) appeared to be a good approach as this semi-automated technique allows to easily analyze pollutants at trace levels. After optimization, the developed method was very sensitive with limits of quantification under 0.2 $ng.L^{-1}$. Its application to real samples from the Garonne estuary has revealed the presence of Fipronil at ultra-trace levels (≈1 $ng.L^{-1}$) but however of concern as sometimes concentrations exceeded the PNEC level. This feature illustrates the interest of sensitive environmental monitoring as a new compound of interest for Garonne river risk assessment has been highlighted which moreover justifies further and deeper investigations especially regarding its sources.

# Estuarine biogeochemistry modeling of scavenging rates using the natural radionuclides $^{210}$Po and $^{210}$Pb in the Delaware and Chesapeake Bays.

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The natural radionuclide $^{210}$Po ($t_{1/2}$= 138.4 d) and its grandparent $^{210}$Pb ($T_{1/2}$ = 22.3 y) may be used to identify and quantify trace element processing in the estuarine environment. The upper Delaware Bay is characterized by large metropolitan inputs, turbidity maximum, and with the greatest production found in the estuarine portion. The upper Chesapeake Bay estuary is a drowned river valley hosting seasonally anoxic deep waters. During the spring and summer months of 2012 dissolved and particulate $^{210}$Po and $^{210}$Pb particulate activities were found to be dominant in the upper reaches, and gradually decreasing further seaward.

In the upper Delaware, the dissolved $^{210}$Po/ $^{210}$Pb activity ratio was deficient (<1) due to excess $^{210}$Pb from spring run-off and the differential scavenging of Pb within the turbidity maximum. Seaward the surface $^{210}$Po/ $^{210}$Pb ratio was in excess (1-2), along with increased nutrients and POC. At depth the $^{210}$Po/ $^{210}$Pb ratio was larger (>2) from the regeneration of POC enriched with $^{210}$Po.

In the upper Chesapeake, the $^{210}$Po/ $^{210}$Pb activity ratio was largely in excess (1-5) enhanced by plankton production. Deeper in the suboxic basin, both dissolved $^{210}$Po and $^{210}$Pb increased at the pycnocline from POC regeneration, decreasing within the deeper suboxic zone during particulate extraction by iron, manganese, and sulphide precipitates.

A mass balance box model predicts nuclide scavenging residence times. In the Delaware these times decreased seaward from several to less than one week, less than that of hydrological mixing. The $^{210}$Po times were greater in the upper more bioactive Chesapeake, almost twice that of $^{210}$Pb. These two nuclides may be used as proxies to estimate scavenging residence times of Type B biogenic trace elements such as $^{210}$Po and Type A lithogenic trace elements such as $^{210}$Pb.

# Biomacromolecules based detection of pollution in marine aquatic environments.

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The function of natural biomacromolecules is inherent to their remarkable recognition properties. For instance, complementary nucleotide sequences undergo hybridization according to Watson Crick base paring to assemble the DNA double helix, which carries the universal genetic information. Suitable synthetic peptide or nucleotide sequences might interact as well with high specificity with a target moiety. Aptamers for instance are synthetic short single-stranded nucleotide sequences that bind to a wide variety of targets from single molecules to complex mixtures or whole organisms with binding affinities comparable to those achieved with antibodies. Biomimetic approaches in the field of polymer science proved successful as demonstrated through the efficient grafting of a polymer to the aptamer against immunoglobulin E (IgE), an allergy biomarker, to assemble functional sub-micrometer size capsules with potential for sensing or diagnostic applications. Being this approach currently strengthened through synergies between environmental chemistry and the field of polymer science in the frame of SCHeMA, we will present our approach to develop sensors to monitor pollution in marine aquatic environments.

# Low-cost miniaturized algae detection module.

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We are currently developing a miniaturized low-cost device for detecting algae species based on their pigmentation. In contrast to existing technology, our device is modular and can integrate up to 8 different excitation wavelengths and 4 different emission channels. The device is operated in a flow-through mode similar to a flow-cytometer, however, using only low-cost equipment such as photodiodes and LEDs. With a sampling frequency of ~500 Hz we are able to detect single particles or cells passing the illumination chamber. Our goal is to achieve single cell sensitivity similar to laser driven flow-cytometers. First results showed that we are able to obtain signals down to concentrations of about 2 cells per 10 microliters, i.e. the illuminated volume. Using multivariate data analysis we try to develop algorithms for classifying algae passing through the device. Although the device will certainly not be able to compete with submersible imaging devices, we believe that it will be a valuable addition to existing technology considering its price of less than 200 EUR. The flexibility in choosing excitation and emission wavelengths and the high sampling rate will even enable laboratory applications, such as measuring induction kinetics. Most importantly, the ability of the device to detect and classify algae will improve with the amount of data collected. The more know samples we can analyse, the better we can train the algorithm for classification.

As the first application of the device, it will act as fully integrated early warning system for harmful algae blooms in the submersible probe for the FP7 project «SCHeMA».

# Saxitoxin detection: A simple alternative to post column oxidation and bio assays.

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Saxitoxin (STX) is one of the most toxic non-protein substances known and is responsible for the paralytic shellfish poisoning. It is naturally produced by a variety of algae species such as cyanobacteria or dinoflagellates which are consumed by shellfish. STX is a sodium channel blocker with a lethal dose for humans of 0.2 mg. The toxin was usually determined via mouse bio-assay, but due to ethical reasons alternatives such as HPLC-MS were developed, using pre- or postcolumn modifications of the toxin. However, this method suffers from several disadvantages concerning the implementation in standardized protocols due to the time consuming and costly procedure. In recent years, an optical method for the detection of STX was developed, but was not continued. This method was based on the complexion of STX to fluorescent dyes, which causes fluorescence enhancement by a reduced PET effect. During our further work on this topic, another promising way of detection of STX was discovered. This method is based on the UV assisted photo-oxidation of STX to fluorescent products without extensive sample preparation. Here, we present the direct detection of saxitoxin. Despite this approach is not yet fully developed, this novel method would not only simplify STX quantification, but also reduce the sample preparation time and can potentially be miniaturized.

# Towards in-situ Nutrient Detection in Desalinated Seawater.

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The large amount of NaCl present in seawater normally masks the determination of other, more dilute compounds. In this regard, the analysis of the nutrients nitrate, nitrite, and phosphate in seawater is an important challenge for environmental analysis as powerful techniques for anion determination are not yet available. For instance, in ion chromatography the high level of chloride saturates the anion-exchange column and the determination of anions that elute after this ion are not reliable. While a dilution steps allows for the appropriate determination of chloride, other anions may become too dilute for accurate assessment.

We report here on an online electrochemical concept to reduce the chloride concentration in seawater down to the milimolar level. A planar microfluidic cell was designed to confine the sample to a thin layer. The cell is composed of a stack consisting of a silver/silver chloride counter/reference electrode, a microfluidic channel for the reference solution, a cation exchanger membrane, a microfluidic channel for the sample solution and a silver working electrode. Chloride is plated from the sample on the silver electrode as AgCl by an appropriate controlled potential protocol while the sodium counterions are transported across the membrane to the reference solution to close the electrochemical circuit. The process can be reversed by electrochemical control.

With the proposed procedure, NaCl amount is shown to be reduced to milimolar levels in artificial and real seawater samples. The desalinated seawater samples were analyzed with ion chromatography, confirming the reduction of chloride concentration while keeping the concentration of the nutrients nitrite, nitrate and sulphate constant after desalination. The next step will be nutrient analysis by online electrochemical detection coupled to this thin layer desalination unit.

# Development of a nautic drone to sample water in marine and estuarine areas.

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The monitoring of coastal and estuarine waters is based on the use of nautical facilities which present the disadvantages: (1) not to be always available to sample water during particular events (phytoplanktonic blooms, accidental pollutions, ...), (2) to be unable to sample on less accessible environments as shallow zones (lagoons, coral reefs), (3) to involve long navigation to reach sampling zones distant from any harbour, (4) to be rather expensive. It results a need to have a simple and robust automated system to sample water in sub-surface along the coastline.

A nautical drone was designed to answer the basic needs of the Water Framework Directive (WFD):

- to go from the coast to the sampling area situated up to 500 m off the coast in less than 5 minutes, - to perform in situ measurements (temperature, salinity, turbidity),
- to collect water samples for later analysis in the laboratory (phytoplankton identification, chlorophyll, nutriments, ...).

The deployment of the drone is very simple because it has for vocation to be used by operators having no particular skills in electronic or mechanic. The drone can be launched by one operator several times in the same day on different sites. The drone does not cause chemical or physical pollution during the on-site sampling (ex: oil, excessive eddies). This machine contributes to the improvement of the sampling practice operations by enhancing the reliability of the measurement quality so as to favor the comparability of the monitoring data. The good practice of the sampling indeed determines the reliability of the measurement data and thus the interpretation that we can make. It is planned to extend the collection of water samples for the analysis of parameters requiring even higher precautions in term of contamination: trace metals, chemical contaminants, microbiology,..

# Verification and validation of an autonomous Lab-on-a- Chip biosensor for real time monitoring of sea contaminants.

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Early warning systems that can provide extreme sensitivity with appropriate selectivity are required to assess chemical contamination of estuarine and coastal areas. An EU project SEA- on-a-CHIP (2013-2017) aims to develop a miniaturized, autonomous, remote and flexible immuno-sensor based platform in a lab-on-a-chip configuration combined with electrochemical detection for real time measurement of organic micropollutants in marine waters. This system is being developed for direct application in aquaculture facilities, for the rapid assessment of 8 selected contaminants from 5 groups of compounds that affect aquaculture production (compounds which are toxic, bioaccumulative, endocrine disruptors) and also those produced by this industry that affect the environment and human health (antibiotics and pesticides). Plymouth University involvement in the project is mainly on the verification and validation of the performance of the immunosensors through conventional analytical chemistry.

This poster presentation explains how the sensors are validated in laboratory studies, under artificial mesocosms and during field experiments in aquaculture facilities. This includes the evaluation of potential interferences and the applicability of the sensors to broader environmental assessments of contamination.

# High spatial resolution nutrient data for real-time estuarine sampling using zone fluidics.

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Real-time field based analyzers for nutrient analysis in seawater are essential to better understanding of the fine-scale variability in marine and river nutrient distribution and to validate coastal biogeochemical models. Whilst continuous temperature, salinity, chlorophyll, turbidity and oxygen sensors based on electrical and optical properties have been deployed at individual sites, in underway and in profiling configurations, continuous estuarine nutrient sensors are in their infancy. In a collaboration between CSIRO and Global FIA (Fox Island, Washington, USA), a portable two-channel nutrient analyzer called the FloPro-Tracker with short analysis time (~4 minutes) and real-time data collection was developed. An automated sampling system provides a continuous fresh filtered stream of sample to the analyzer. The chemistry of measurement for $PO_4$ and $NO_2/NO_x$ uses standard nutrient protocols. The FloPro-Tracker uses Zone Fluidics (ZF) to precisely control the fluid manipulation steps required to sample and measure the nutrient on an in-situ basis. Data from a separate online system for salinity, temperature and bottom depth is stored with the nutrient data as well as the GPS location in real time. In addition to the compact size, single power entry source and high visibility screen for ease of use in the field, the use of ZF rather than continuous flow analysis (CFA) allows for discrete sampling and a simplified platform for troubleshooting. All data was collected in real time aboard a 7.5 meter boat averaging 5 knots for high spatial resolution. The survey covered approximately 200 kilometres in the Derwent River Estuary, the Huon Estuary and the D'Entrecasteaux Channel handling variation in sample temperature, salinity and CDOM content. Our observations capture fine-scale spatial variability in marine and river nutrient concentrations and characterize plumes of nutrient enrichment associated with point source discharge against a background estuarine gradient in surface water nutrient concentration.

# Temporal and diel cycling of trace elements nutrients in a barrier-lagoon complex subject to hypoxic events.

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The cycling of trace elements (Fe, Mn, Mo, V, Cu, Ni, Co) and nutrients (silicate, nitrate, ammonium and phosphate) in a quasi-pristine barrier-lagoon complex (Louro Lagoon, NW Iberian Peninsula) was studied both in a diel and temporal timescale covering different seasonal conditions. Hydrographical and meteorological conditions exert a major control on the trace elements and nutrient cycling in the lagoon. From late autumn to early spring the lagoon is characterized by oxic conditions due to significant freshwater inputs and sporadic communication with the sea. In summer, elevated primary production coupled with water stagnancy leads to bottom waters hypoxia and marked diel variation of pH, oxygen, redox potentials and redox- sensitive trace elements. Diel variation of nutrients was only evident when mixing of surface and bottom waters during the night was observed.

# Tin and organo-tin species along the Gironde fluvial-estuarine continuum: spatial distribution and speciation during two contrasting hydrological conditions.

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Organotin compounds, especially tributyltin (TBT), are used for various industrial purposes such as disinfection of circulating industrial cooling waters and antifouling agents. Tributyltin compounds are classified as priority substances under the EU Directive (2008/105/EC) due to their high toxicity. This study aims at determining the spatial distribution of dissolved and particulate inorganic tin ($Sn_D$ and $Sn_P$) and of organo-tin species (monobutyltin-MBT, dibutyltin-DBT, tributyltin-TBT) in order to evaluate the degree of contamination of the Gironde Estuary, years after the total ban of these compounds. Two oceanographic campaigns (MGTSI and MGTSII) were carried out during contrasting hydrological situations (March 2014, 1203 $m^3/s$; March 2015, 3450 $m^3/s$). The inorganic $Sn_P$ ranges were similar during both campaigns (5-15 mg/kg) and anomalies from upstream and downstream the Gironde Estuary occurred when referred to the regional geochemical background (Sn/Th=0.55). Residual organotin in water, suspended matters and sediment suggests industrial and urban sources along the Gironde Estuary and may represent a potential ecotoxicological risk for aquaculture development in the estuary mouth.

The TBT and its degradation products in the Gironde Estuary (MGTSI campaign) showed high spatio-temporal variability, e.g. <LQ–0.50 ng/l for dissolved TBT and 0.03-0.39 ng/g for particulate TBT. Samples collected in the downstream estuary frequently exceeded environmental quality standards for TBT (NQE=0.2 ng/l). The poster addresses organotin behaviour along the salinity and turbidity gradients in terms of intra-estuarine reactivity and environmental safety levels.

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