

**U.S. GEOTRACES North Atlantic Section, Leg 1: Dissolved Fe Speciation**

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The organic complexation of dissolved Fe was analyzed in full depth profile samples collected along the first leg of the U.S. GEOTRACES North Atlantic Section cruise from Portugal to Cape Verde in late fall 2010. Dissolved Fe speciation was determined using competitive ligand exchange- adsorptive cathodic stripping voltammetry (CLE-ACSV) with salicylaldoxime as the added competitive ligand. Strong Fe-binding ligands ( $\log K > 11$ ) were found to exceed dissolved Fe in concentration for all samples and all depths measured from the profiles. A weaker Fe-binding ligand class was detected in some of the samples, although the presence of this ligand class was unpredictable. A comparison between results obtained from fresh versus frozen samples was conducted for two of the profiles, indicating that freezing at  $-20\text{ }^{\circ}\text{C}$  did not change measured Fe-binding ligand concentrations but did, in some cases, result in a small offset in conditional stability constants measured for those ligands.

# **A new linear-nonlinear optimization mathematical tool for the evaluation of sources and transport of metal complexing ligands in water masses**

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Using Anodic Stripping Voltammetry (ASV), the complexation and chemical speciation of Zn and Cd has been determined in seawater in several open-ocean and coastal samples. Using a novel mathematical interpretative tool (Titration Data Interpreter, TDI) that allows for precise, non-biased ligand parameter optimization of the Gerringa linearization, the ligand concentration and binding strength of these ligands were calculated.

TDI was tested with modeled ligand data (and can interpret data from both ASV and CSV titrations), and results indicate very good agreement with the true ligand parameters. This method offers three main advantages over previous interpretative methods. First, using an initial estimation of parameters from an analysis of a Scatchard plot, this method determines the number of ligands present in a titration (1-, 2- or 3-ligand, in case of zero-signals), and an initial approximation to the ligand parameters. Secondly, in the posterior optimization of the initial parameters into final ones on a Gerringa plot, a very robust Levenberg-Marquardt algorithm is used. Thirdly, the very fine logK resolution of these final ligand parameters allows for interpretation of trends of ligand decay previously not reported. Additionally, no S-correction is made on the titration dataset in this program, emphasizing the need of a titration that is both complete and consists of more points than customarily obtained (e.g. 13 or more) to enhance statistical value of the ligand parameters produced.

A consortium of strong ligands complexes Zn and Cd, affecting their chemical speciation in surface, intermediate and deep waters. The results obtained with TDI indicate marginal seas and other pointed sources provide both metals and strong ligands, combining riverine, terrestrial, marine and anthropogenic matter, as recent literature suggests. The ligands are transported and decay with time along the trajectory of some water masses, implying connections to ligands produced at the water formation regions and from estuarine origin. This decay is observed in different permutations of concentration and binding strength increase/decrease, where logK decrease has a major role in changing the chemical speciation of Zn.

Future directions include the study of samples from major rivers, as well as water formation locations and further down along the trajectory of some water masses.

# PLATINUM IN OCEANIC AND ESTUARINE WATERS AND ITS DETERMINATION USING CATHODIC STRIPPING VOLTAMMETRY

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The geochemical behavior of Pt in the aquatic environment is not yet fully understood, despite of the recent scientific efforts in this matter – mainly focused on urban water systems – derived after the introduction of catalytic converters in cars (containing Pt and other platinum group elements: Pd, Rh) during the late 70's in USA and late 80's in Europe<sup>1</sup>. The few studies on the oceanic distribution of Pt were performed about 2 decades ago, reporting concentrations ranging from 0.2 to 1.6 pM<sup>2-4</sup>; in these studies, a conservative behavior in the North Atlantic<sup>2</sup>, a scavenged-type profile in the Indian Ocean<sup>3</sup>, and a recycled-type<sup>4</sup> and conservative<sup>5</sup> in the Pacific Ocean were observed. The extent to which these contrasting vertical profiles reflect a true basin-to-basin variability and not analytical artifacts remains unclear<sup>6</sup>. The analytical challenge of measuring the ultra-trace Pt concentrations in natural waters – generally at the sub-picomolar level in oceanic and uncontaminated river waters<sup>7</sup> – remains as a major drawback for its routine analysis.

Here we discuss the reliability of adsorptive cathodic stripping voltammetry for the determination of Pt in seawater. The method, based on the catalytic effect of the Pt-formazone on the development of hydrogen at the mercury electrode<sup>8</sup>, offers typical detection limits (<0.05 pM for a deposition of 10 min) sufficient for the Pt determination in seawater. Results on the Pt behavior during estuarine mixing (Lérez estuary, Pontevedra Ria, NW Iberian Peninsula) and in the Atlantic Ocean (samples from the Dutch GEOTRACES West Atlantic section) will be presented.

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# Voltammetry and GEOTRACES

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Voltammetry/polarography was first described 90 years ago by Jaroslav Heyrovský in and for his pioneering role he later became the first scientist to receive a Nobel prize (1959) “...for his discovery and development of the polarographic methods of analysis”. Polarography thus became the first chemical method of analysis to be awarded a Nobel Prize. Polarography was initially an exclusively European pursuit and led to many key developments in the field of analytical chemistry. In 1935 Heyrovský along with his colleague Dionýz Ilkovič were the first to study the equilibria of complex compounds polarographically and laid the foundations for later studies into chemical speciation. A further key milestone in the history of polarographic techniques was the introduction of ‘Die Methode des Eichzusatzes’ (the method of standard additions) by Hans Hohn in 1937.

By the 1940’s and 50’s, studies into polarography began to take off in the USA through the work of the Dutch Émigré, Izaak Kolthoff. Kolthoff and his students, most noticeably James Lingane, Herbert Latinen, and David Hume helped to develop the theoretical basis for the application of voltammetric data for speciation purposes.

Applications of polarography to seawater chemistry only truly began with the work of Marko Branica and colleagues at the Rugjer Bošković Institute in the late 60s and 70s, who used voltammeter to assess metal speciation in seawater and were the first to apply polarography to the determination of surface active substances in water. At the same time on the other side of the world in Australia, Mark Florence and Graham Batley begin to link their speciation work in seawater with trace metal (bio)availability linked to the development of the free ion association model. From the early 1980’s, new developments in electronics significantly improved electrochemical systems and they were applied at sea and to open ocean waters for speciation for the first time, through the pioneering work of Ken Bruland, Stan van den Berg and George Luther.

However the routine application of electrochemical methods to seawater analysis came apparently too late to play a role in the first major geochemical and biogeochemical investigations of the ocean (e.g. GEOSECS 1973-1976). The use of voltammetric techniques in international oceanographic programs has steadily increased since the 1980s with involvement in JGOFS, SOLAS, IMBER and GEOTRACES. While currently mass spectrometer or flow injection (spectrophotometric or chemiluminescence) techniques are the predominant analysis methods for trace metals in seawater, voltammetric methods can still play a significant role, most importantly in speciation studies. This talk will examine the history of voltammetry in the marine sciences and discuss the problems that exist and the role that it can play within GEOTRACES.

# Investigating the distribution of dissolved copper, zinc, silver and cadmium in the Pacific Ocean: Particle impact voltammetry as a tool for investigating metal speciation

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A stated goal of the GEOTRACES program is to better understand the large-scale distribution of trace metals in the marine environment [1]. A characteristic feature of the soft Lewis acid metals like copper (Cu), zinc (Zn), silver (Ag) and cadmium (Cd) is their correlation with the major algal nutrients [2]. These correlations imply that the proximate control on the distribution of these metals is microbial uptake at the ocean surface, sinking associated with particulate organic matter and subsequent remineralization in the ocean interior. Combined with sedimentary records of past metal concentrations such correlations can provide much needed information on water mass circulation and nutrient cycling in the paleo-ocean [3-5]. Today, as trace nutrients and/or toxins these metals help shape microbial community composition and influence productivity [6]. Here we present depth profiles through the low dissolved oxygen waters of the north Pacific which show decoupling of trace metal-macronutrient relationships driven by depletion anomalies of trace metal concentrations in the broad, low oxygen layer. Similar anomalies have been previously reported in permanently anoxic layers (e.g. fjords) or in waters in contact with suboxic sediments and attributed to sulfidic removal of soft trace metals [7]. The observed trace metal behavior and trace metal-macronutrient relationships in the oxygen minimum layer in the northeastern Pacific is consistent with the possibility of sulfidic scavenging of soft metals and the formation of insoluble metal sulfides in the water column. Implications of this influence on the basin scale distribution of soft metals like Cu, Zn, Ag, Cd through scavenging in the spreading low oxygen layer in the northeastern Pacific are discussed. Recent studies applying particle impact voltammetry [8,9] as a tool for measuring nanoparticles in natural waters and investigating their role in future studies of metal partitioning in seawater will be presented.

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## The place of voltammetry in today's chemical speciation studies

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In the first edition (1970) of the classical (in the environmental field) Stumm and Morgan's book "Aquatic Chemistry", the term 'chemical speciation' does not appear in the index while, in the third and last edition (1996), not only 'chemical speciation' is listed but the following sentence is found in the introduction: "The notion of chemical speciation is central in equilibrium and kinetics aspects of aquatic chemistry, as will be evident throughout the book". The contrast between both editions perfectly reflects the strides made by the concept in the environmental field over the years that separate both editions. Initial developments was accompanied by internal community misunderstandings and disagreements that made a well-known scientist to write in 1991: "Speciation is the titillating effort to speciate among the different definitions of speciation to identify the correct meaning of the term speciation" (K.J. Irgolic, In: *Metal Speciation in the Environment*, J.A.C. Broekaert et al. (Eds), Springer-Verlag 1991, p. 642) and forced IUPAC's clarification of meanings and concepts in 2000 (D.M. Templeton et al., *Pure Appl. Chem.*, 72, 1453, 2000). As explained below, a split research community might still be one of the characteristics of this field.

A characteristic of the development of chemical speciation studies in the environment has been the progressive loss of the weight of the electroanalytical techniques. Although alive (this workshop is a proof), they have experienced a lower level of development, as compared to hyphenated techniques, and are much less used. A fast look at the EVISA ("the primary source of information for speciation analysis"!) webpage ([www.speciation.net/](http://www.speciation.net/)) or the fact that not a single paper not dealing with hyphenated techniques was included in a recent issue meant to "give an overview of the state-of-the-art in this area" (*JAAS*, volume 26, 2011) are a good proof of it. On the other hand, a thriving community exists using modelling and so-called dynamic techniques where hyphenated techniques are plainly ignored (for instance, not a single mention of them appears in a recent article on "How well can we predict and measure chemical speciation in freshwaters?" (J. Hamilton-Taylor et al., *Env. Chem.*, 8, 46, 2011)). Since environmental problems are diverse, techniques to be used also need to be diverse but it seems that current use of techniques often hides deep misunderstandings of basic concepts such as lability and, probably in some cases, of chemical speciation itself. This is worrying.

These issues, as well as more general ones, such as (i) why, in the 'dynamic speciation' community, other techniques, such as DGT, are nowadays more popular than voltammetry; (ii) why voltammetric methods are generally utilised only by the groups that proposed them originally (most of them, active in the field for many years); (iii) why the same (few) elements are systematically studied, will be discussed in this communication. And, hopefully, in the workshop.

# AGNES: a voltammetric technique for determining free metal ion concentrations in natural waters

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AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) is a voltammetric technique specifically designed for the determination of free metal ion concentrations [1]. This presentation will review its principles, implementation, validation and applications.

In the implementation section, we will present: different working electrodes (HMDE, Ir-Hg microelectrode [2], thin film on a RDE [3] and SPE[4,5]); the various possibilities of blanks (synthetic, shifted and EDTA), the variants of the first stage (one pulse or two pulses [6]) and the variants for the second stage (diffusion limited current or charge from a pulse or LSV or SCP[5,7]).

In the validation, we will see agreement with theoretical codes [8], ISE, SSCP [9], Resin Titration techniques [10] and Donnan Membrane Technique [11].

As applications we will mention: humic acids studies [12-14]; speciation in river water [11,15](dealing with anomalous effects arising from low ionic strength); Cu interference on Zn due to intermetallic compounds [16]; the study of the solubilization of ZnO nanoparticles (thermodynamics and kinetics)[17] or Cd quantum dots [18] and the analysis of Zn in wines [19].

Special emphasis will be given to the determination of free Zn in sea water [20].

The section of challenges will consider new electrodes, other elements and future systems.

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# Trace metal speciation by ASV: recent analytical and modelling improvements

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The bioavailability and toxicity of metal ions to aquatic organisms is mainly related to concentrations of their free (hydrated) form. The distribution of inorganic metal species in natural waters with known composition of major anions is predictable. However, for many metals, such as Cu<sup>2+</sup> or Fe<sup>3+</sup>, the speciation is predominantly controlled by interactions with dissolved organic ligands. In most cases, complexation of trace metals with organic ligands decreases their bioavailability and toxicity, even if it was demonstrated that some organic forms can be also bioavailable and/or of different toxicity. Among several methods for determination of chemical speciation, anodic stripping voltammetry (ASV) is an attractive method which satisfies the requirements concerning sensitivity and selectivity, while offering the benefit of low contamination risk and alteration of original sample composition during analysis. Speciation of trace metals by ASV can be performed using 2 main approaches: (a) by pseudopolarography (i.e. varying the deposition potential) to evaluate the metal distribution between different forms (labile, directly reducible, inert, ...), (b) by performing a titration (i.e. adding the metal and measuring it as labile) followed by a mathematical treatment of the obtained data (e.g. Ružić-van den Berg or Scatchard linearizations, non-linear fitting) in order to characterize the interaction between organic ligands and metals (concentration/density, stability constant) and then calculate the metal speciation.

This presentation will concern recent studies aiming to improve the reliability of the obtained parameters modifying: (a) the ASV procedure to reduce the effect of surfactants <sup>(1)</sup> and adjusting the time between metal additions to reach the chemical equilibrium <sup>(2)</sup>, (b) the titration (range of concentration, distribution of additions) <sup>(3)</sup>, (c) the data modelling using appropriate fitting tools <sup>(3, 4)</sup>, (d) the studied interactions, to describe competing effects (pH, major cations, ...) influencing metal-ligands interactions <sup>(5, 6)</sup>, or (e) evaluate not only the thermodynamic of these interactions, but also their kinetic <sup>(7)</sup>.

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## The interpretation of organic Fe complexation data

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Most methods to determine the organic complexation of metals (in this talk specifically iron) use adsorptive Cathodic Stripping Voltammetry (adCSV) based on ligand exchange (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Croot and Johansson, 2000 and Van den Berg, 2006). Ligand exchange is based on the addition of a well characterised ligand that competes with the natural unknown ligands for Fe. It is an indirect method since the natural ligands are not measured, but saturated with Fe and the formation of the Fe complex of the competing ligand is measured. Therefore the calculation and interpretation of the data is not as straightforward as we would wish. The calculation of the characteristics of the natural ligands, the total ligand concentration ( $[L_t]$ ) and the conditional binding constant  $K'$  is done by using the Langmuir isotherm model (Van den Berg, 1982). Using this model assumptions have to be made, such as: a) equilibrium of the system, b) all binding sites of a ligand with Fe are equal to each other, c) no other elements than Fe are influencing the free ligand concentration, and d) binding of Fe is reversibly. The consequences of not fulfilling these assumptions on the results of data are discussed.

A second focus of the talk will be the influence of natural variations on the data interpretation, such as the effects of the saturation state of the ligands on the accuracy of the results. This will be illustrated with data from the IPY GEOTRACES cruises (Thuróczy et al, 2011a,b).

A simple method in R to model the data with the Langmuir isotherm will be shown.

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**Recent advances for using in situ voltammetry to characterize oxic-anoxic transitions in marine environments**

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# **New insights and performance enhancement of the determination of total iron in seawater by catalytic cathodic voltammetry of its complexes with dihydroxynaphthalene**

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Despite the advance of ICP-MS for the analysis of trace metals in ocean waters due to its multielement resolution, there is still need for the development of robust methods for the on-board analysis of trace metal analysis. Here, voltammetry could play a key role due to its extremely low detection limit and its low requirement of expensive reagents. Total dissolved iron is barely measured by voltammetry despite the availability of different methods with several commercial ligands. In this work we revisited the method based on the measurement of iron-dihydroxynaphthalene complexes with the catalytic aid of bromate. Several tests showed that a non reversible reaction to pH changes is overlapping the catalytic reaction described in the initial paper. Switch of the pH with the subsequent maximization of this reaction boosts the sensitivity of the method by a factor of 4 ( $\sim 40 \text{ nAnMmin}^{-1}$ ) at no cost of baseline enhancement. Then, we corrected the original method establishing the effect of prior-to-analysis acidification, we tested the method with multiple CRM at different concentrations and we present the first set of data obtained onboard for total dissolved iron in oligotrophic waters of the Southern Ocean backed up by the most used method for onboard analysis of iron (FIA-Chemiluminescence). Although the exact description of the reaction mechanism is still under evaluation, the proposed method is a powerful tool for the preconcentration-free measurement of iron in oligotrophic waters ( $\sim 0.1 \text{ nM}$ ).

# **Taking the voltammetric system out of the lab; alternative electrode materials and remote monitoring**

**“Monitoring of trace metals, toxicants and nutrients in seawater “**

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Automated monitoring at site can increase the frequency of sampling and measurements significantly, giving environmental data with a high time resolution. Such data compared to data from traditional manual sampling routines will improve the analytical routines through better validation and quality assurance. Further, high frequency sampling and measurements could bring new information about dynamic systems. Recent developments and results in the field of remote monitoring of trace metals will be presented. Some years ago an automatic trace metal system (ATMS) using different modes of voltammetry in combination with innovative solid alloy electrodes was invented in our group. The ATMS device is an integrated system specifically designed for early warning detection and continuously monitoring of natural water. By using different solid alloy electrodes like dental amalgam electrode (DAM), silver-bismuth electrodes and gold-bismuth electrodes the system can be used to measure low concentrations of several metals with long-time stability and low maintenance. In the presentation an important factors to succeed with automatic field measurements will be discussed as well as a brief review of the ATMS system.

# **Optimising voltammetric procedures: small volumes, fast analysis and reliable data?**

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Voltammetric methods based on adsorptive accumulation have experienced an unpaired growth in the field of elemental analysis in the last decades. The possibility to exploit the richness of organometallic chemistry and to reach subnanomolar detection limits without sample pretreatment definitely boosted this expansion. Fast electronics and more efficient scanning modes should also be mentioned as they created the necessary conditions for the revitalization of voltammetric techniques.

Nevertheless, voltammetric methods suffer from several issues: the major factors limiting their extensive application are sample throughput, sample volume and the reliability of the results.

Reducing analysis and operator time, retaining the detection capabilities of AdCSV methods, is a first challenging task. It should be highlighted that extensive multielemental analysis may be difficultly achieved in AdCSV: the use of mixed ligands enables the determination of a few (up to six) elements simultaneously but advancement in this direction may be difficultly foreseen. Accordingly, analysis and operator time might be reduced by lowering the pretreatment time (higher efficiency UV treatment unit, faster degassing methods), lowering the deposition times (introducing more and more efficient organic ligands) and making automated methods available.

The required amount of sample is the second fundamental issue, as the voltammetric analysis typically requires 30 mL for the triplicate determination of a single element. A one order of magnitude reduction in sample need may be achieved by carefully designing the voltammetric cell, employing a standard three electrode configuration.

The reliability of voltammetric data is mainly a matter of method validation, quality control and operator experience, although it is expected that automation may play an important role also. Round Robin exercises comparing different techniques may also contribute in increasing the awareness of the reliability of AdSV methods.

This presentation will discuss the aforementioned issues in view of the ongoing (and completed) research in our laboratory.

# Signal processing and measurement automation in electroanalysis

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In electroanalysis, the main focus of signal processing is the transformation of measured data, in order to conveniently extract the appropriate information (e.g. peak intensity). Such mathematical transformation should minimize the distortion of the original information as much as possible. The most frequently employed signal processing routines are the noise removal (digital smoothing), the baseline correction, the signal intensity determination, the overlapped peaks separation, and various ways of mathematical manipulations (e.g. differentiation, integration).

Usually, voltammetric curves are treated one at the time using the best “decision maker” method known as the “expert eye”. The produced effect depends mainly on experience of the operator and the capabilities of the software used. Once the sequence of treatment procedures is defined, an automatic processing method could be applied. Having this option available within the software, would be of great advantage for electroanalytical applications with a large number of curves. However, software packages supplied with electrochemical instrumentation usually do not provide such a functionality (or it is very limited), and researchers are referred to specialized independent data treatment software packages.

The signal-to-noise ratio and the signal-to-background relationships are the two major voltammetric curve characteristics that should be improved after signal processing. Digital filtering (smoothing) and baseline corrections are applied for this purpose. These two steps become more important as the electrochemical analysis approaches the limit of quantification of the applied method (Fig. 1). Transformation of voltammetric curves by a derivative function is an optional approach that can eliminate the need to use the baseline correction method, which is user dependent (subjective). However, it is very important for the user to identify the capabilities and limitations of the used processing routines, as an inappropriate use could result in incorrect final results.

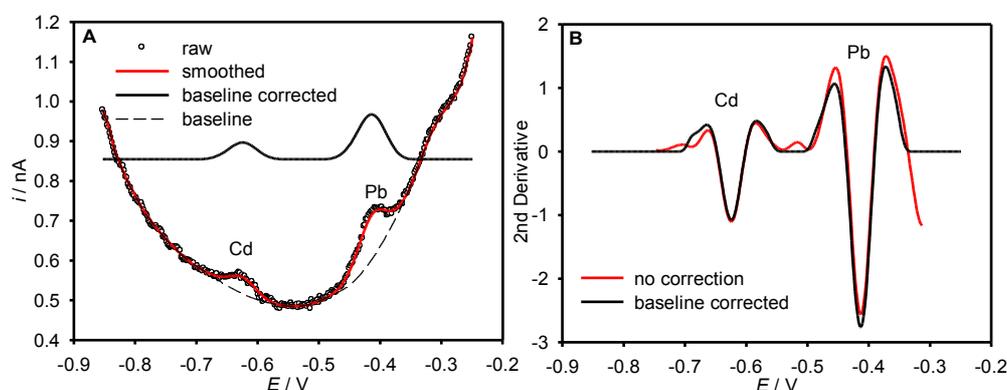


Figure 1. Digital filtering (smoothing) and baseline correction (A) and the 2<sup>nd</sup> derivative transformation of smoothed curves (B)

Various effects on the final result produced by signal processing and mathematical transformations will be demonstrated through examples of determination of unknown analyte concentration using the standard addition method. Several options for the improvement of analysis accuracy and precision, based on the internal standard method, will be presented. The consequences of improper signal processing in environmental studies will be illustrated on the example of determination of copper complexing capacity. Guidelines of signal processing and the experimental design will be provided.

A home-made automatic station for the voltammetric analyses of trace metals will be presented. It consists of the voltammetric analyser, measurement electrode stand, sample changer, peristaltic pump and burette system for addition of standards and chemical. New software which manages preparation of the measurement procedures and subsequent metal quantification was developed.

## Organic matter - metal ions interaction - some highlights

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In 1970 some investigations and measurements have suggested that the free metal ion, rather than total metal ion concentration, was a biologically important form that better correlated with the toxicity to sensitive aquatic organisms, such as bacteria and algae (Stumm and Morgan, 1981). In 70's a development of a very sensitive electroanalytical technique ASV (anodic stripping voltammetry) enabled the study of free metal ion concentrations of environmentally important metals such as copper, lead, cadmium and zinc in natural waters (Merian et al., 2004). ASV is a specific speciation technique which responds only to those metal species that are reducible at the mercury electrode at the chosen deposition potential. This operationally defined "labile" fraction contained the free metal ion and its weak complexes (Rayeshwar and Ibanez, 2002). The pioneers of this method applied to natural water studies were for e.g. the groups of M. Branica in Rudjer Bošković Institute in Croatia, T.M. Florence in the Chemical Technology Division of the Australian Energy Division, Australia and H.W. Nürnberg in the KFA Institute in Jülich, Germany. A major objective of metal speciation measurements is that they provide quantitative information on metal bioavailability. Bioavailability as a concept is commonly assumed as the ability of metals to cross a biological membrane and presumably be taken up. Most of current information on metal complexation by dissolved organic matter comes from methods that rely on the titration of water samples by addition of known increments of metal ion and measurement of the concentration of labile metal ion species after a period of equilibration by ASV. This procedure is called complexing capacity determination is similar to the concept of pH representing the "metal ion buffering capacity". Dissolved organic carbon (DOC) which makes a pool of organic ligands in seawater originates from different sources. The concentration of DOC in seawater varies between 0.3 to 3 mg C/L (Stumm and Morgan, 1981). A part of DOC exhibits the property of surface activity, i.e. the accumulation at different phase boundaries (seawater/atmosphere, seawater/particles, seawater/biological membranes) due to its hydrophilic/hydrophobic moieties and change the physico-chemical properties of these interfaces. The surfactants present in sea-surface microlayer are mostly of biological origin (primary production) and are seasonally dependant (Ćosović, B., 1985).

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## Solid gold electrodes for the speciation of metal and metalloids

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Solid electrodes are notoriously known to suffer from stability problems due to memory effects: previous analysis or recent “history” of the electrode may affect the subsequent analysis. In contrast to the mercury drop electrode which renew its surface for each analysis, this “non-stability” together with the ease of use of the mercury drop electrode have probably prevented the wider use of solid electrodes for trace element speciation where sensor stability is of paramount importance.

This talk will give an overview of the use of gold solid electrodes for the speciation of metal (Cu, Hg, Mn, Zn) and metalloids (As, Sb) that were developed in the recent years. It will highlight tips and tricks that are key to obtain good stability and reproducible behavior. The electrodes consist in a gold wire electrode (5, 10 or 25  $\mu\text{m}$ ) embedded in a melted plastic matrix and connected to a small vibrating device (1.5 V, 150 Hz frequency) that vibrates the electrode in place of the standard stirring of the solution. Under vibrated conditions, sub  $\mu\text{m}$  diffusion layer sizes are obtained and chronoamperometric current are significantly more stable than under stirred conditions. This results in low detection limits together with very good stability and reproducibility, best exemplified with the scanned stripping voltammetry (SSV) of natural levels of copper in coastal seawater.

Another advantage of the vibrated microwire electrode is its relative insensitivity to hydrogen generation which allows the use of very low cathodic deposition. This is beneficial for the determination of total inorganic arsenic and total inorganic antimony, this latter being achieved at pH 1 using a deposition potential of -1.8 V. However, the application of low deposition potentials induces unforeseen reactions with cations (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ) as seen by the detection of Sb(V) in neutral conditions of pH.

# **Incorporating the results of voltammetric measurements into chemical speciation models**

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Modelling of the chemical speciation of trace metals in seawater often focuses on inorganic complexation where the ligands are well defined and where there is a well developed state of the art (Pitzer equations). Many studies have shown that many trace metals are strongly complexed by organic matter, and that this complexation dominates the metals' speciation in many cases. However, the routine incorporation of organic complexation into trace metal speciation models is hampered by an inability to use experimental measurements to develop predictive speciation models.

The dominant method for studying the organic complexation of trace metals in seawater is CLE-CSV, which uses a competing ligand to quantify the complexation of added trace metal. The strength of the complexation thus characterised is of the same order of magnitude as that of the competing ligand. This complexation strength is usually described as the detection window. The form of data analysis employed results in values of concentration and stability constant for a small number (usually 1 or 2) "ligands". These are, however, not chemically distinct ligands, rather an operational description dependent on the nature of the binding ligands present, the detection window and the method of data analysis. This approach has several major drawbacks: it inevitably leads to difficulties in comparison between different data sets; incorporation of the results into chemical speciation models has a limited validity; and there is a tendency for these operational "ligands" to be viewed as real, discrete ligands.

In the GEOTRACES context a further fundamental problem arises. CLE-CSV titrations are generally carried out at 20-25°C, and at a fixed pH that may differ from that of the original seawater sample. The measurement conditions are thus not representative of the ocean sections sampled by GEOTRACES, and we have little or no information as to how the metal-organic binding will be affected by the master variables temperature, pressure, pH and salinity.

What is the way forward? Firstly, we should follow the freshwater chemists in using metal-organic binding models that recognise the polydisperse nature of the organic matter. This will require developments both in modelling and in analysis of titration data. Secondly, it would be valuable to begin to assess the effects of master variables on the metal-organic binding: pH and temperature are expected to be the most important variables in this respect.

# **Advances in chemical speciation of iron using catalytic cathodic stripping voltammetry**

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Problems with existing methods will be discussed and a new method will be described. The new method is very sensitive, and the selected oxidant has no iron contamination. The optimisation and calibration are presented and the new method is applied to the determination of iron complexation in seawater.

This abstract is deliberately kept short because the method has not yet been written up. The new material will be presented at the meeting.

# Stripping chronopotentiometry and several applications in marine systems

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In stripping chronopotentiometry (SCP), the preconcentration step is the same as in stripping voltammetry (SV), whereas the scanning for the stripping step is performed by measuring the variation of potential (E) through the application of a low constant current or by chemical reaction (e.g. by oxidation with O<sub>2</sub>, naturally present in the sample). In this technique, the aim is to obtain the time needed to strip the metal from the working electrode. The basically correct strategy to effectively eliminate the capacitive charging current is to determine stripping times from the area under peaks in dt/dE versus E plots. Due to the requirement of a high frequency for E measurements (~10-100 kHz), SCP for trace species quantification in seawater was only possible with few specific apparatus and thus studies that compares performances between voltammetry and SCP are still scarce. It was shown however that SCP is less susceptible than SV to interference from adsorption of organic species (Town and van Leeuwen 2002, J. Electroanal. Chem. 523, 1).

In this presentation, I will briefly present few SCP procedures developed in our team. These procedures involve different types of electrodes (i.e. solid disks, films and vibrating gold microwire) and allow the determination of several trace species in seawater (e.g. inorganic As species, free sulfide). I will also comment some applications in various marine systems such as: the strong decoupling between Cd and P in the Angola Basin (South East Atlantic) or the high-resolution examination of the colloidal fraction of trace metals in a macrotidal estuary (Penzé, NW France).

# Speciation And Distribution Of Trace Metals In The Krka River Estuary (Croatia)

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Water column of the Krka River estuary is permanently stratified with high salinity gradient increasing from <5 to >30 in the range of up to 1 m, at depth around 2 meters (freshwater-seawater interface, FSI). In order to determine the distribution of trace metals and to identify anthropogenic sources, water samples were taken at three depths (freshwater layer, FSI and seawater layer) along the whole Krka River estuary transect (25 km) during summer and winter season. Anodic (Zn, Cd, Pb and Cu) and cathodic (Ni and Co) stripping voltammetry on HMDE were applied as analytical techniques. Metals were quantified using method of standard addition. Two regions with elevated metal contents were identified: nautical marina in upper part of the estuary and a bay in front of Šibenik town. In general, high nautical traffic accompanied by the release of the metals from the antifouling paints caused significant increase of trace metal concentrations (e.g. 3-5 times for copper) during summer season along the estuary.

A more detailed speciation study was conducted at two distinctive sites: a “clean” site (RBI Marine station Martinska), and a “polluted” one (in a nautical marina). Trace metal speciation has been studied by using *diffusive gradients in thin films* (DGT) and stripping voltammetry. Vertical profiles of dissolved trace metals showed the same trend as DGT-labile concentrations, however the percentage of DGT-labile metal varied due to the different affinity of metals to dissolved organic matter (DOC): >90% for Cd, ~50% for Pb, >20% for Cu, ~60% for Ni. Vertical profile of ASV-labile copper determined at natural pH showed a good agreement with DGT-labile copper, indicating similarities in the accumulation processes of two complementary speciation techniques.

# Investigation of FeS nanoparticles electrochemical behavior with use of voltammetric and amperometric measurements

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In recent years, nanoparticles (particles in the size range of 1 nm to 100 nm) have received considerable attention from both science and industry because of their unique properties and potential societal benefits. Naturally-occurring nanomaterials such as volcanic ash, ocean spray, magnetotactic bacteria, mineral composites and others are ubiquitously present in the environment but still there is lack of published data and knowledge about their abundance, environmental transformations, toxicity and chemical and/or physical properties<sup>1</sup>. Absence of data is consequence of lack of analytical techniques needed for their detection at low environmental level.

In anoxic environments FeS nanoparticles play an important role in many biogeochemical processes such as control of bioavailability of many trace metals and pyrite formation. We already demonstrated possibility of using voltammetric measurements for chalcogenide, particularly FeS nanoparticles detection in anoxic waters<sup>2-5</sup>. However, combination of voltammetric and amperometric measurements seems to be promising for concentration and size determination of FeS nanoparticles in natural waters.

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# **Autonomous Voltammetric Sensor For Monitoring Sulfide Variability In Deep Sea Chemosynthetic Habitats**

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Because of the unstable behavior of deep sea sulfidic environments, such as hydrothermal vents, where concentration and chemical speciation can change within seconds, in situ measurements become necessary to understand its complex dynamics. The use of electrochemical instruments for this purpose has several advantageous features like small size, low-energy consumption, and low cost, which are attractive for these applications. Voltammetric sensors were adapted for continuous in situ measurement of sulfide at great depth, and tested for autonomous monitoring over periods exceeding the usual duration of a few hours during submersible dive. We used an 800  $\mu\text{m}$  diameter silver bare disc as working electrode which has allowed registering a broad concentration range and fast fluctuation. It has been deployed at 850m and 2500m depth along ~8-10 days in hydrothermal habitats of Mid Atlantic Ridge and East Pacific Rise, respectively. Besides a need for technical and operational optimizations, the relevance of voltammetric systems with silver bare electrode, for the assessment of temporal changes of sulfide levels in deep sea chemosynthetic habitats is demonstrated from these first results.

## **The interest of analyzing trace metals at a number of accumulation potentials**

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Voltammetric analysis using a range of accumulation potentials allows some further information to be gained about the natural speciation of the trace metals present in the sample. Operational parameters such as lability and ligand metal thermodynamic stability constants are complicated to interpret in unaltered natural samples; however comparisons can be made within a single environment, which could indicate a change in species complexation. With optimization, monitoring using a number of accumulation potentials could help to indicate changes in a system, which could potentially relate to species bioavailability.

Pseudopolarography of natural samples has been performed in seawater and freshwater at mercury based electrodes, and even in-situ in porewaters. However, its low throughput could make such a technique unsuitable for monitoring. After an initial full 'pseudopolarographic' calibration of a system, monitoring using fewer accumulation potentials could prove to be an efficient use of time.

The vibrating gold microwire electrode (VGME) provides a complimentary technique to mercury electrodes and non-electrochemical techniques (e.g. DGT), by which such monitoring could be performed with high sensitivity and reproducibility. To measure at varied accumulation potentials using the VGME requires a conditioning potential to be applied between scans as well as the implementation of a desorption potential.

# Adhesion based detection of organic microparticles in aquatic systems

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The organic microparticles in aquatic systems (organic droplets, vesicles and cells with fluid membrane) can be characterized through appearance of the well-defined amperometric signals at the mercury electrode (1-3). Mercury electrode serves as adhesion based sensor where interfacial properties could be controlled by changing of applied potential. Adhesion and spreading of a soft organic particle at a charged mercury/water interface causes double-layer charge displacement from the inner Helmholtz plane, and the transient flow of compensating current can be recorded as an amperometric signal.

We have interpreted amperometric signal of individual particle on kinetical and mechanical level using two independent models, where extracted complementary information are important for better understanding of adhesion mechanism (4). Further, adhesion based detection is sensitive to polar head groups in phospholipids vesicles. We have identified a narrow potential window around the point of zero charge of electrode where the interaction of polar head groups of lipid vesicles with the substrate is manifested in the form of specific bidirectional signals (5).

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# Reagentless and silicate interference free electrochemical method for phosphate detection: Application to the Oxygen Minimum Zone

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Oxygen Minimum Zones (OMZ), mainly localized in the EBUS, are known to play a crucial role on climate evolution via greenhouse gases budgets and on marine ecosystems (respiratory barrier, modifications of the nitrogen cycle). Deoxygenation will have widespread consequences due to the role O<sub>2</sub> plays in the biogeochemical cycling of carbon, nitrogen, phosphorus and other important elements such as Fe, S.

Developing new sensors for improving our understanding of the coupled biogeochemical cycles (P-O-C-N) in these regions constitutes an immense challenge. Electrochemistry provides promising liquid reagentless methods by going further in miniaturization, decreasing the response time and energy requirements and thus increasing our observing capacities in the ocean.

We present an electrochemical method for phosphate determination in seawater based on the anodic oxidation of molybdenum in seawater in order to create molybdophosphate complexes electrochemically detected on a gold electrode by means of amperometry [1] or differential pulse voltammetry [2]. We propose a solution to address the silicate interference issue based on an appropriate ratio of proton/molybdate within an electrochemical cell using specialized membrane technology. The detection limit can be as low as 0.11 μM (amperometry) or 0.19 μM (differential pulse voltammetry). An application of this method is presented in the OMZ offshore Peru. The results show excellent agreement when compared to colorimetry with an average deviation of 5.1%. This work will lead to the development of the first autonomous *in situ* sensor for electrochemical detection of phosphate in seawater.

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# **Geo-Bio interactions in shallow water hydrothermal vents and their impact on trace metals**

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Life at shallow- and deep-sea hydrothermal vents is exposed to high concentrations of different metals in the venting fluids. Some are biologically essential, while others react toxic at even low quantities (e.g. Copper), whereas the chemical speciation determines the metal toxicity rather than the total concentration of an element.

There is evidence that not only organic molecules constitute ligands that are able to form strong complexes with Cu to reduce its toxicity, but also, that these ligands are produced by bacteria in response to increasing Cu concentrations (Klevenz et al., 2012). Hydrothermal vents at the sea floor release large volumes of these metal rich fluids into the ocean. Therefore, due to the binding of organic compounds to metals, the trace metal flux into the ocean is expected to be higher than assumed until recently (Sander and Koschinsky, 2011).

In this study, we want to examine the total dissolved copper concentrations and responding ligand concentrations at shallow water hydrothermal vent fields by a voltammetric ligand titration, using adsorptive stripping voltammetry. Samples were taken during a sampling campaign on Milos, Greece in May 2012.

Copper-complexing ligand concentrations are determined using an indirect method of competing ligand equilibration, whereas a well-characterized ligand (Salicylaldoxime) is added to the sample. Salicylaldoxime was chosen as the competing ligand because its complexation parameters with Cu in seawater are well studied, and its sensitivity allows the detection of even the lowest ligand and copper concentrations (Campos and van den Berg, 1994). Despite of a buffer, increasing concentrations of a copper standard and Salicylaldoxime are given to the sample in different, increasing amounts, depending on the expected ligand concentration in the titration window, respectively. This study will give insight into the geo-bio interactions at shallow hydrothermal vents which are influenced by photosynthetic and chemosynthetic processes, in contrast to deep-sea hydrothermal systems which are only chemosynthetic affected.

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## Electrochemical and STM studies of FeS nanoparticles in NaCl model solutions

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The scientific interest in nanoparticles (NPs) or nanomaterials (NMs) mostly derives from the dramatic change in physical and chemical characteristics that substances experience at reduced length scales (1–100 nm), but because of their dimensions they present potential risk in the terms of ecotoxicity<sup>1</sup>. Our understanding is also limited by lack of efficient methods to characterize natural and synthetic NPs. The NPs interactions in the environment require a greater understanding of structure of the nanoparticles in their in-situ state.

In order to get more insight in the FeS NPs electrochemical behavior, in-situ Electrochemical Scanning Tunnelling Microscopy (EC-STM)<sup>2</sup> has been used for characterization and determination of FeS NPs at the Au(111) electrode in NaCl solutions. In parallel, voltammetric measurements at different electrode systems (Hg and Au) were conducted because the electrochemical methods are shown to be a good choice for characterization and determination of chalcogenide nanoparticles in model solution and natural waters<sup>3-5</sup>. EC-STM has been used for the first time for characterization and determination of FeS NPs in NaCl electrolyte solution with an idea of getting more information related to attachment, adsorption, deposition and interaction between FeS NPs and functionalized electrode surfaces. Particle deposition was studied in relation to variations of applied and scanning electrode potentials in the range from 0.01 to -1.5 V vs. Ag/AgCl. EC-STM images, obtained on the Au(111) electrode, revealed the presence of FeS NPs which was accompanied with a drastic transformation of electrode surface topography during scanning potential from 0.1 V to -1.2 V. Majority of FeS NPs (diameter 2-5 nm) were detected around -0.3 V. EC-STM clearly revealed presence of FeS NPs on the Au(111) electrode surface which previously were detected by voltammetric measurements at the Hg electrode<sup>6</sup>. Combination of in-situ EC-STM and cyclic voltammetry as two different but complementary techniques appears to be a powerful tool for simple, selective, qualitative and quantitative chalcogenide NPs characterization of complex electrochemical systems such as NPs in the aqueous solutions.

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# Development of a New Electrochemical Cell for Remote Sensing of Low Levels of Heavy Metals

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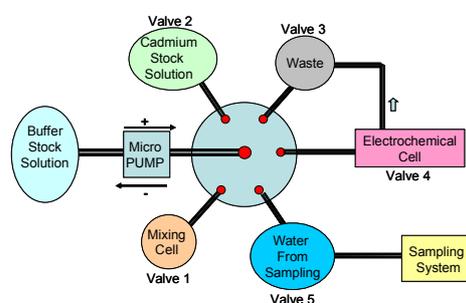
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Remote sensing is the ability to acquire information and collect data in far or inaccessible areas. The rising public concern for the quality of the drinking water as well as the rivers, lagoons and coastal water has increased the quest for new, improved and remote sensing methods. The Hydronet project aimed on developing a remote platform to monitor different environment parameters, especially heavy metals in natural aquatic environments. Heavy metals pose a potential environmental hazard and health hazard even in small quantities due to their ability to bioaccumulate. Most heavy metals are electroactive and therefore can be detected electrochemically.

Recently we published a detailed study<sup>[1]</sup> whereby a gold electrode modified by different self-assembled monolayers (SAMs) based on short  $\omega$ -functionalized alkanethiols,  $X-(CH_2)_n-SH$  ( $n=2$  or  $3$ ) and  $X=NH_2$ ,  $SO_3H$  and  $CO_2H$ , is used for the determination of low levels of Cd by under potential deposition (UPD). The LoD of Cd was as low as 10 ppt using subtractive square wave anodic stripping voltammetry (SASV) and the precision was better than 1%. The application of the short SAMs improved the signal and prevented fouling of the electrode surface. The different parameters that affect the electrochemical signal were studied and optimized. The electrode showed a wide linear range and highly reproducibility over a period of more than a week.

Here we present the next level in the automation of our system, which is the development of a state-of-the-art, fully-automated flow system for measuring the concentration of cadmium ions in natural coastal rivers and lagoons. The system is capable of self-calibration followed by repeated measurements. The heart of the system is our newly developed flow cell, which enables obtaining good sensitivity and at the same time reducing the volume of the sample.



**Figure 1** Schematics of the flow system.

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## Usefulness of voltammetric measurements to assess trace metals transfer at the continental/coastal zone interface: case of Marseille agglomeration (FRANCE)

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Coastal ecosystems in the Mediterranean Sea are known to be strongly influenced by continental inputs from large rivers but also small coastal ones. Inputs of urban areas, such as Marseille city (~ 1.7M Ha), should be investigated. The objectives of the GIRAC-PACA and MARSECO projects are (a) to quantify the contaminants brought to the sea by the Marseille city, (b) to study their impact on the coastal zone and (c) to characterize the relationships between pollution levels, contaminant distribution between dissolved and particulate fractions and type of particles, in order to evaluate contaminant net fluxes to the marine environment. In such environments, voltammetric techniques are useful either to quantify metal content or qualify metal speciation despite trace levels and matrix complexity <sup>(1)</sup>. Various sampling campaigns were carried out during dry and wet periods in the main tributaries upstream and downstream of the Marseille sewage treatment plant and in the freshwater/seawater mixing zone (depth profile and transect). Dissolved metals (after acidification/UV irradiation, by DPASV: Cd, Cu, Pb, Zn; by DPCSV: As, Co and Ni) and organic carbon (DOC) contents were determined after samples filtration (on-field and at the laboratory). Moreover, interactions between Cu and dissolved organic ligands were characterized by sample titration (logarithmic scale, DPASV-labile Cu measurements and non-linear fitting using PROSECE software <sup>(2)</sup>) on two set of samples (collected during wet and dry season respectively). The obtained results attest the usefulness of voltammetric measurements to evaluate trace metals dynamic and transfer in the environment, and especially in coastal zones submitted to numerous anthropogenic inputs.

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## Developing an *in-situ* electrochemical method for PAH detection

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The aquatic environment is exposed to an increasing amount of pollution from various sources which make close monitoring and early detection of potentially dangerous substances crucial. Most common pollutants found in the aquatic environments are biomembrane active hydrophobic substances such as polycyclic aromatic hydrocarbons (PAH). Such pollutants interact with phospholipid monolayers on a mercury electrode surface by causing disruption of the monolayer's structure and fluidity. This interaction is monitored electrochemically by using rapid cyclic voltammetry (rcv) in a semi-automated flow cell system which incorporates a *chip-based* Hg microelectrode<sup>1</sup>. A mixed monolayer of palmitoyl-2-oleoyl-sn-glicero-3-phosphocholine (POPC) and triolein, an oleic acid triglyceride (TG), in 3:1 molar ratio, proved to be very sensitive to the presence of phenantrene and pyrene with the lowest detection limit around 2 µg L<sup>-1</sup>. Optimising the monolayers to make them susceptible to different pollutants could lead to a subsequent incorporation of the flow cell into a robust system for use *in-situ*.

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# Chromium speciation in the oceanic water column

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Within this study, which is part of the international GEOTRACES program, the distribution of redox species of chromium will be investigated in the Atlantic and Pacific Ocean.

Chromium (Cr) in the aquatic environment has natural and anthropogenic sources. As Cr is enriched in ultramafic rocks, weathering of rocks and riverine input as well as atmospheric input represent natural sources for Cr in seawater (Ellis et al., 2002). Anthropogenic Cr is supplied by discharge of liquid, gaseous and solid waste through the usage of Cr in various industrial processes like metallurgy and electroplating (Kostas & Stasicka, 2000). Total chromium concentrations in seawater range between 2-5 nmol/kg (Geisler & Schmidt, 1992). Although Cr may have different oxidation states it mostly occurs in seawater as trivalent and hexavalent species,  $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})^{2+}$  and  $\text{CrO}_4^{2-}$ , respectively (Gardner & Ravenscroft, 1996). The oxidation state influences its toxicological behavior and its bioavailability. Trivalent Cr serves as a micronutrient and shows high affinity to particles at neutral pH (Mertz, 1993). In contrast, Cr(VI) functions as a microtoxin, crossing cell membranes and acting as a oxidizing agent. The bioavailability of Cr(VI) is higher compared to Cr(III) by its lower tendency to sorb on particulate surfaces. Obviously, redox conditions of the environment influence directly the species distribution and effect the toxicity and bioavailability to marine organisms. Consequently, more knowledge about the biogeochemical cycle of Cr in the oceanic water column is required in order to assess its toxicity in seawater.

Thermodynamic calculations for oxygenated seawater predict that Cr(VI) is the main component, resulting in a ratio of Cr(VI) to Cr(III) of 1021 (Elderfield, 1970). However, Cr(III) has been detected in analytical significant ranges leading to a ratio of Cr(VI) to Cr(III) of 1.6-3.1 (Hirata et al., 2000). In plumes above hydrothermal vents and surface waters in non-hydrothermal areas also significant amounts of Cr(III) were observed (Sander et al., 2003). A recent study agrees with previous results displaying significant concentrations of trivalent Cr throughout the water column in the Tropical Atlantic Ocean and a slight increase in total chromium in surface waters (Moos, 2011). An explanation for the significant presence of Cr(III) may result from slow interconversion of Cr(VI) to the less thermodynamically stable Cr(III). Furthermore, Li et al., 2009 confirmed for the first time the direct influence of marine phytoplankton on the photochemical reduction of Cr(VI) leading a ratios of Cr(VI) to Cr(III) in the range of 1.45 to 2.16.

Within this study samples taken on a GEOTRACES cruise in the Pacific Ocean in 2011 will be analyzed for chromium speciation in three water column profiles, each resolved by 18-21 samples. Through application of a trace metal clean CTD for seawater sampling, these samples fulfill the requirements for trace metal analysis and are stored frozen in the home-laboratory at Jacobs University Bremen.

Cathodic adsorptive stripping voltammetry is used for the determination of Cr(VI), reactive Cr and total Cr in 0.2  $\mu\text{m}$  filtered seawater samples following the method described in (Sander & Koschinsky, 2000). Prior to analysis for total Cr the sample is UV-digested after addition of hydrochloric acid and hydrogen peroxide. During this step stable chromium compounds such as complexes with natural ligands or stable inorganic compounds will be decomposed and all Cr present will be oxidized to Cr(VI). The voltammetric measurement will then be performed with the UV-digested and deaerated sample containing final concentrations of 1 M  $\text{NaNO}_3$  as supporting electrolyte, 0.01 M acetate buffer (pH 5.2) and 0.015 M DTPA as

complexing agent. Hexavalent chromium is reduced to Cr(III) at potentials below -50 mV followed by in-situ formation of the DTPA-Cr(III) complex at the electrode surface. The differential pulse voltammetric scan (DPV) is recorded from -1000 to -1400 mV. Hence, at -1200 mV appears a peak which corresponds to the reduction of Cr(III) to Cr(II) in the complex. Due to the chemical reoxidation of Cr(II) to Cr(III) this peak may be enhanced in the presence of nitrate which works as a oxidative catalyst.

In seawater Cr(VI) is present as chromate,  $\text{CrO}_4^{2-}$ , which is chemically inactive and therefore forms no complexes with organic ligands. As DTPA is used as a complexing agent forming electrochemically inactive Cr(III)-complex, Cr(VI) can be selectively determined in not-UV-digested seawater by voltammetry after complex formation is completed (30 min). Directly after addition of DTPA and deaeration of the sample reactive Cr, which consists of reactive Cr(III) and Cr(VI), is determined in the sample without prior UV-digestion. The Cr(VI) concentration can be deducted from the reactive Cr concentration in order to receive reactive Cr(III) concentrations. The total Cr(III) concentrations can be calculated by comparison of total Cr with Cr(VI) concentrations. Finally, the reactive Cr(III) can be compared to total Cr(III) to achieve knowledge about the electrochemically unreactive Cr(III) part, which may be associated with colloidal or organic matter.

It is intended to compare the results of this study with the water column profiles of the Tropical Atlantic Ocean (Moos, 2011) to receive an interoceanic comparison with main focus on the oxygen minimum zone gaining insights in the species distribution of chromium under variable environmental conditions.

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# Trace Metals And Natural Reduced Sulphur Species (NRSS) Detection With A Voltammetric Automatic Monitoring System: Calibration And Correction Issues

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An On-line Automatic Monitoring System has been assembled based on voltammetry with the hanging mercury drop electrode (HMDE) and used in some natural river systems in order to detect trace metals and natural reduced sulphur species (NRSS). Cycles of measurements at natural pH and acidic pH have been done for several days and during all seasons of the year. Variations of peak height have been recorded for trace metals and NRSS. But problems to link peak intensities with concentrations appeared due to several parameters:

- Temperature variations change diffusion coefficient and mercury drop volume.
- The calibration of the trace metal peaks after UV irradiation of the solution permit to obtain a linear curve but does not take into account parameters influencing the sensitivity of the method such as the interaction between natural organic matter and the electrode surface and the electroactive organic-metal complexes that can represent a significant fraction of the detected signal;
- The calibration through a titration curve (by adding known concentrations of metals in the raw solution) could be a promising alternative to take in account, at least partially, the influence of organic matter. However, as the speciation of the metals in the river may change continuously, the slope of the titration curve may also change and it appears impossible to calibrate each sample with such a method;
- The presence of metals (Cu, Zn, Pb, Cd...) in the solution attenuates the NRSS peak (competition with Hg in the mechanism).

When possible, evaluation of the induced errors and their corrections have been done but they should be considered as semi-quantitative ones. Additionally, to our best knowledge, no standard solutions including speciation certified values are yet proposed to validate our results.

## **Competition between copper and iron for ligands and possible effects on bioavailability of iron**

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Previous work has shown that iron is complexed with organic matter in seawater. The composition of the ligands is still being studied, and candidates for the ligands are for instances siderophores and humic substances. Humic substances occur in coastal as well as ocean waters, and these could be a good model for the iron-binding ligands in the marine system. Recent work in our laboratory has shown that copper competes with iron for humic complexation. This means that variations in the concentration of copper could cause the speciation of iron to vary as well. This in turn could cause the availability of iron to marine microorganisms to vary. This hypothesis will be investigated in experimental work.