

COST Action ES0801 Workshop on

“Voltammetry and GEOTRACES“

Rudjer Boskovic Institute, Sibenik, Croatia, 6-9 October 2012

Workshop Summary and Report

Report Authors: dr. Irena Ciglencečki, dr. Antonio Cobelo-García, dr. Peter Croot, dr. Cédric Garnier, dr. Dario Omanović, dr. Ivanka Pižeta

Contact: dr. Irena Ciglencečki

Meeting Rapporteurs: dr. Antonio Cobelo-García, dr. Cédric Garnier

The meeting was attended by 37 people from 14 countries, with 23 of those attending being supported directly by COST Action ES0801. The application of voltammetry on oceanographic studies has led to a better understanding of the distribution, speciation and biogeochemical cycling of trace elements in the oceans. The aim of the meeting was to critically discuss the role of voltammetric techniques on today's chemical oceanography and especially in the current international GEOTRACES program. Special attention was paid to new advances in voltammetry (e.g. new types of sensors, improvements on analytical and modeling trace metal speciation by voltammetry, etc.) valuable for the scientific community working under the GEOTRACES program.

Participants at the meeting were chosen on that way to gather researchers actively working on the application of voltammetric techniques for the determination and speciation of trace elements in the marine environment. A number of early career scientists (13 PhD students and post-docs) also participated at the meeting, by giving short presentations and take a part in the discussions.

The meeting agenda (see appendix) was designed around a series of thematic sessions, each focusing on a different aspect of voltammetry and GEOTRACES; briefly it will be discussed below:

1. Voltammetry and GEOTRACES: Past, Present and Future

Peter Croot gave an historical overview of electrochemistry and voltammetry/polarography, since their start in 1922 by Jaroslav Heyrovský until today. Applications of voltammetry to seawater chemistry only truly began with the work of Marko Branica and colleagues at the Rudjer Bošković Insitutute in the late 60s and 70s, to assess metal speciation in seawater. At the same time, in Australia M. Florence and G. Batley began to link their speciation work in seawater with trace metal bioavailability developing the free ion association model. From the early 80s, the new developments in electronics improved significantly the electrochemical systems and they were applied at sea and to open ocean waters for speciation for the first time (K. Bruland,

S. van den Berg and G. Luther). The routine application of these methods to seawater analysis came too late to play a role in the first major geochemical and biogeochemical investigations of the oceans (e.g. GEOSECS 1973-76). The use of voltammetric techniques in international oceanographic programs has steadily increased since the 80s with involvement in JGOFS, SOLAS, IMBER and GEOTRACES. While other techniques (e.g. flow injection, mass spectrometry) are the predominant in trace metal analysis in seawater, voltammetric methods can still play a significant role, most importantly in speciation studies.

Jay Cullen presented depth profiles distribution of Cu, Zn, Ag, and Cd through the low dissolved oxygen waters of the North Pacific Ocean from samples collected during GEOTRACES section cruises. Results showed a decoupling of trace metal-macronutrients relationships driven by depletion anomalies of trace metal concentrations in the broad, low oxygen layer. This behavior is consistent with the sulfidic scavenging of soft metals and the formation of insoluble metal sulfides in low oxygen waters. The application of particle impact voltammetry, which is under development (Stuart et al. 2012a,b), appears as a promising tool to characterize metal-sulfide particles.

Loes Gerringa makes a critical evaluation of the common methods used to determine the organic complexation of metals by means of CLE-ACSV. The calculation of the stability constants and ligand concentrations using the Langmuir isotherm model (van den Berg 1982) requires several assumptions to be made (e.g. equilibrium of the system, all binding sites of a ligand with the metal are equal to each other, binding of the metal is reversible, etc.). These are not always fulfilled and the consequences on the results of data are discussed. Using data from the IPY GEOTRACES cruises (Thuroczy et al. 2011), the effects of natural variations such as the saturation state of the ligands on the accuracy of the speciation results is evaluated.

Kristen Buck reported the organic complexation of Fe by means of CLE-ACSV titration (with 25 μ M SA) in depth profile samples collected along the first leg of the US GEOTRACES North Atlantic Section cruise from Portugal to Cape Verde (2010). Good agreement was found between the concentrations of the strong Fe-ligand (L1) in fresh (onboard) vs. frozen samples. In some cases, however, freezing at -20 C resulted in a small offset in conditional stability constants. Dr K. Buck raises the question on whether the discrepancy of K1 values reported in the literature (e.g. Gledhill and Buck, 2012) reflects a natural variability or arises from different data fitting procedures.

Antonio Cobelo-García discusses the determination of Pt in oceanic and estuarine waters by means of catalytic adsorptive cathodic stripping voltammetry (van den Berg and Jacinto, 1988). The geochemical behavior of this trace element – currently facing a global contamination – in the oceans is not yet fully understood, and the reliability of its oceanic distribution available so far is questionable. Here, voltammetry offers several advantages for the analysis of Pt over other techniques (FIA, mass spectrometry) due to its capability of sub-picomolar detection limits and low sample pretreatment needed. Results of Pt from samples collected in the Atlantic Ocean during the Dutch GEOTRACES cruise along the American coast (S-N) show a slight but significant increase of Pt in surface water in the northern hemisphere, raising the question on

whether this may be connected to higher anthropogenic inputs at high latitudes. The depth profile of Pt is similar to that previously reported two decades ago, although the results presented suggests that Pt may be subject to (bio) geochemical cycling to a certain extent.

2. Voltammetry and Speciation

Gonzalo Carrasco spoke about development of a new technique for non linear fitting, based on initialization by Scatchard, followed by Levenberg-Marquardt iterative technique.

Luis Laglera showed a revised method for the determination of total iron in seawater by catalytic cathodic voltammetry of its complexes with dihydroxynaphthalene with the catalytic aid of bromate, which is a powerful tool for the preconcentration-free measurement of iron in oligotrophic waters (~0.1 nM), comparable with the most used method for onboard analysis of iron (FIA – Chemiluminescence).

Montserrat Filella stressed in her talk how place of voltammetry in today's chemical speciation studies is different than 40 years ago, voltammetric studies are less present. Since then, however, the term “chemical speciation” has become central in equilibrium and kinetics aspects. She pointed to the challenge of building a humic-metal binding constants database for more than few elements, due to their use in new technologies and further release in the environment. She is a task group leader, searching for collaboration. Also, Filella warned that we are “bad sellers” of our technique which should have higher impact among techniques used for diverse environmental problems. She called for discussion why, in the ‘dynamic speciation’ community, other techniques, such as DGT, are nowadays more popular than voltammetry; why voltammetric methods are generally utilized only by the groups that proposed them originally (most of them, active in the field for many years); and why the same (few) elements are systematically studied.

David Turner spoke about incorporating the results of voltammetric measurements into chemical speciation models. The main problem is that the data entering into the model should be corrected for temperature, pressure, pH and salinity. 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. It has several drawbacks coming from simplification of the natural ligands by operationally dividing them into 1 or 2 groups, which are affected by concentration and strength of a competing ligand, leading to difficulties in comparison between different data sets. The way forward would be to follow the freshwater chemists in using metal-organic binding models that recognize the polydisperse nature of the organic matter. This will require developments both in modeling and in analysis of titration data. Also, 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.

Stan van den Berg showed on a particular case advances in the chemical speciation of iron using catalytic cathodic stripping voltammetry. Starting from the method published by Rue and Bruland (1995), he explained problems of loss of sensitivity during the measurement protocol and he proposed solutions and

further optimization of the parameters of the measuring protocol. He also spoke about competition of metals: clear decrease of the Fe peak by additions of other elements (Zn, Cu, Co, Al), which is an important feature of voltammetric measurements that should be addressed when dealing with environmental samples.

Cédric Garnier spoke about recent analytical and modelling improvements of trace metal speciation by ASV. The bioavailability and toxicity of metal ions to aquatic organisms is mainly related to concentrations of their free (hydrated) form, and while the distribution of inorganic metal species in natural waters with known composition of major anions is predictable, complexation of trace metals with organic ligands is predominant; it decreases their bioavailability and toxicity but is more difficult to predict. 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 followed by a mathematical treatment of the obtained data in order to characterize the interaction between organic ligands and metals (concentration/density, stability constant) and then calculate the metal speciation. C. Garnier spoke about improvements in measurements procedures aiming to improve the reliability of the measured signals and the treatment of signals, strategy of distribution and timing of analyte additions, use and validation of appropriate fitting tools, as well as modeling programs that should be able to take into consideration competing effects in interactions of metals with ligands and evaluate not only thermodynamic but also kinetic of these interactions.

Josep Galceran presented AGNES (Absence of Gradients and Nernstian Equilibrium Stripping), a voltammetric technique for determining free metal ion concentrations in natural waters. This method could serve in situations where ion selective electrodes are not enough sensitive, knowing that information of free metal concentration is valuable regarding its bioavailability. Principles, implementation, validation and applications of the technique were given.

Marta Plavšić in her contribution *Organic matter - metal ions interaction - some highlights* gave an overview of “how it was” concerning the beginnings of metal speciation and organic matter characterization assessed by voltammetric techniques.

Hannah Whitby, a PhD student of Stan van den Berg, told about her first steps in research about competition between copper and iron for ligands and possible effects on bioavailability of iron that she will apply to marine systems.

Ana-Marija Blatarić, a PhD student of Dario Omanović exposed her work on speciation and distribution of trace metals in the Krka River estuary (Croatia). She showed the results, total and dissolved concentration of trace metals along the salinity profile of the estuary in various seasons, assessed by voltammetry and DGT.

Sandra Pohle, a PhD student of Andrea Koschinsky presented results obtained on a GEOTRACES cruise in the Pacific Ocean, concerning chromium speciation. They found high sorption of Cr(III) on particles, so low solubility and bioavailability, to the contrary for Cr(VI). They measured by CSV, using DTPA.

Charlotte Kleint, a PhD student of Andrea Koschinsky spoke about Geo-Bio interactions in shallow water hydrothermal vents and their impact on trace metals concentration and speciation. They examined 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. This study gave 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.

Benjamin Oursel, a PhD student of Cédric Garnier presented his results about usefulness of voltammetric measurements to assess trace metals transfer at the continental/coastal zone interface: example of Marseille agglomeration (SE, France). The objectives of the projects were to quantify the contaminants brought to the sea by the Marseille city, to study their impact on the coastal zone and 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 both, to quantify metal content and to qualify metal speciation despite trace levels and matrix complexity. Dissolved metals (after acidification/UV irradiation, by DPASV: Cd, Cu, Pb, Zn; by DPCSV: As, Co and Ni) and organic carbon (DOC) concentrations were determined after samples filtration (on-field and in the laboratory). 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 (Louis et al., 2009) on two set of samples (collected during wet and dry season respectively).

3. Application of Electrochemical Techniques for the Study of Nanoparticles in Seawater

Elvira Bura-Nakić, spoke about investigation of FeS nanoparticles electrochemical behaviour with use of voltammetric and amperometric measurements and showed that 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. They already demonstrated possibility of using voltammetric measurements for chalcogenide, particularly FeS nanoparticles detection in anoxic waters (Ciglenečki et al., 2005, Bura-Nakić et al., 2007, Bura-Nakić et al., 2011, Helz et al., 2011). However, combination of voltammetric and amperometric measurements seems to be promising for concentration and size determination of FeS nanoparticles in natural waters.

Marija Marguš, a PhD student of Irena Ciglenečki spoke about electrochemical and STM studies of FeS nanoparticles in NaCl model solutions. In order to get more insight in the FeS NPs electrochemical behaviour, in-situ Electrochemical Scanning Tunnelling Microscopy (EC-STM) (Magnussen et al., 1993) has been used for characterization and determination of FeS NPs at the Au(111) electrode in NaCl solutions. 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.

Nadica Ivošević DeNardis plastically demonstrated the adhesion based detection of organic microparticles in aquatic environment through appearance of the well-defined amperometric signals at the mercury electrode (Žutić et al., 1993, Svetličić et al., 2000, Ivošević DeNardis et al., 2007). 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. They 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 (Ivošević DeNardis et al., 2012a). Further, adhesion based detection is sensitive to polar head groups in phospholipids vesicles, so they 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 (Ivošević DeNardis et al., 2012b).

4. New types of sensors

Pascal Salaün gave an overview of use of solid gold electrodes for the speciation of metal and metalloids that were developed in the recent years. The electrodes consist in a gold wire electrode (5, 10 or 25 μm) 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 μm diffusion layer sizes are obtained and chronoamperometric current are significantly more stable than under stirred conditions. These 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. Na^+ , K^+ , Mg^{2+}) as seen by the detection of Sb(V) in neutral conditions of pH.

5. Automation in Voltammetry

Øyvind Mikkelsen informed us about an automatic trace metal system (ATMS) using different modes of voltammetry in combination with innovative solid alloy electrodes that was invented in their group and has been applied in field for many years. 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 (e.g. Mikkelsen et al., 2003, Mikkelsen et al. 2004, Skogvold et al., 2005). Special electrode material could be envisaged for special application. Use of Ag as electrode can also play the role of “antifouling” due to its toxicity for biota.

Adaptation for monitoring of trace metals, toxicants and nutrients in seawater is easily achieved by combination of procedures and electrode materials and sensitivities.

Tomer Noyhouzer, a PhD student of Daniel Mandler talked about development of a new electrochemical cell for remote sensing of low levels of heavy metals (Noyhouzer and Mandler, 2011). They introduced a gold electrode modified by different self-assembled monolayers (SAMs) which were used for the determination of low levels of Cd by under potential deposition (UPD). The next level was automation of the system, 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 newly developed flow cell, which enables obtaining good sensitivity and at the same time reducing the volume of the sample.

Abra Penezić, a PhD student of Blaženka Gašparović spoke about their work on developing an in-situ electrochemical method for polycyclic aromatic hydrocarbons (PAH) detection (Coldrick et al., 2011). Such pollutants interact with phospholipids' 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.

Justyna Jońca (PhD of Veronique Garcon) presented reagentless and silicate interference free electrochemical method for phosphate detection and its application to the Oxygen Minimum Zone (OMZ). She presented 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 (Jońca et al., 2011) or differential pulse voltammetry (Jońca et al., 2012). 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.

Pierre-Jean Superville, a PhD student of Gabriel Billon presented on going work on trace metals and natural reduced sulphur species (NRSS) detection with a voltammetric automatic monitoring system. An On-line Automatic Monitoring System has been assembled based on voltammetry with the hanging mercury drop electrode (HMDE) (Superville et al., 2011) and used in some natural river systems in order to detect trace metals and natural reduced sulphur species (NRSS). Calibration and correction issues have been discussed. On conclusion, when possible, evaluation of the induced errors and their corrections has been done but they should be considered as semi-quantitative ones. Standard solutions including speciation certified values to validate the results are not yet proposed. Suggestions for corrections are welcome.

Brian Glazer talked about recent advances for using in situ voltammetry to characterize oxic-anoxic transitions in marine environments. They use a 100 μ m polished Au working electrode covered with Hg. O₂ measurements are used to check the reactivity of the electrode. Different applications of the sensor are developed: for water column, bacterial mud, coastal waters/sediments, hydrothermal events where chemical

speciation is driven by biology and chemistry. A lot of measurements by voltammetry at ocean bottom, closed to hydrothermal were performed (proof of the usability of such technique for deep oceans (e.g. Glazer and Rouxel 2009)).

6. Tips and Tricks in Voltammetry

Damiano Monticelli posed the question if we could optimize voltammetric procedures by smaller volumes, faster analysis and more reliable data. He analyzed sample treatment steps showing where and how one can save time and presence of an operator. Careful design of UV digester could shorten the necessary time of exposure, purging can be made more effective, determination time can be reduced by increased sensitivity and full optimization of instrumental parameters. Rational design of new ligands could lead to multielement analysis. 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.

Kristoff B. Gibbon-Walsh explained the interest of analyzing trace metals at a number of accumulation potentials. 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. 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.

Mathieu Waeles gave a short overview of stripping chronopotentiometry (SCP) comparing it with stripping voltammetry (SV), and pointing out that SCP is less susceptible than SV to interference from adsorption of organic species He also gave applications in marine systems, one in strong decoupling between Cd and P in the Angola Basin (South East Atlantic) and the other about the high-resolution examination of the colloidal fraction of trace metals in a macrotidal estuary (Penzé, NW France).

Dario Omanović showed how proper signal processing and measurement automation in electroanalysis could help in obtaining reliable data. The consequences of improper signal processing in environmental

studies were illustrated on the example of determination of copper complexing capacity (Omanović et al., 2010). Guidelines of signal processing and the experimental design were provided. A home-made automatic station for the voltammetric analyses of trace metals consisting of voltammetric analyzer, measurement electrode stand, sample changer, peristaltic pump and burette system for addition of standards and chemical was presented. New software which manages preparation of the measurement procedures and subsequent metal quantification was developed.

7. Round Table Discussion

8th October held by Peter Croot:

We discussed:

- 1) different opportunities for publishing workshop results: (GEOSECS – cruises JGOFS BATS & HOTS; IMBER, SOLAS, EVISA, EOS / IUPAC, Special issue Env. Chem.)
- 2) opportunities for next meeting and further funding

9th October held by Cedric Garnier:

After visiting the Marine station Martinska, a final round table discussion in a form of questions, suggestions, ideas and conclusions was organised. Several questions are posted around:

- a) What are directions that will be taken in the future?
- b) If there is a need for publishing workshop results for example in a special issue of journals?
- c) Regarding data treatment: are we able to agree for the best choice of data treatment in order to improve accuracy and repeatability, reproducibility?
 - It would be useful to generate an exercise of data treatment for “quality control”
 - It would be useful to validate the “fitting” techniques to really verify their abilities; cross checking technique (same electrode-different techniques, same technique-different electrode) in a systematic manner, to “check” new approaches and compare it to the previous ones
 - Suggestions: keep the data to be able to treat them again (more precisely, with up-to-date techniques), especially in programs such as GEOTRACES!
 - Think about discussion list (mail) to gather the ideas-respond to problems, giving information (list of supplier, how is it working, ...): either using already existing technology (wiki) or new one. **But really use it!**
 - Recommendation to GEOTRACES: to gather the raw data
 - Ideas from IUPAC: produce in the published papers the important information (pH, I, exact measured data), supplementary information
 - In the database: not limit to the final parameters, but maybe also the raw data (i.e. voltammograms)
- d) Monitoring: what could be done to enhance sensitivity?

e) Is there need to have more intercalibration studies on the same field samples

f) Future meetings and funding for them: there is possibility to apply for new COST action in the framework of GEOTRACES, which can be focused on outputs of this workshop: deadline is in January 2013 (starting date if approved would be in 2014)

Main workshop conclusions:

1. The workshop was support to SCOR WG 139. Some of the members of the WG139 were present at the workshop. They discussed about the first results of intercalibration study with synthetic data sent to community by Sylvia Sander, one of the chairs of WG139. A main idea was to check different software packages which are frequently used for calculation and determination of complexing capacity and stability constants. The need of mutual tuning, i.e. agreement about the procedures of sampling, sample preservation, treatment, measurement and finally data treatment including software, in order to be able to make comparison between different GEOTRACES cruises should be of the utmost importance.

2. Position of voltammetry in GEOTRACES community must be more emphasized and strength.

Dr. Montserrat Filella pointed that there are skills in some groups that use their own constructed systems for years, but for some reason this knowledge do not transfer to other groups. What can we do to change it? We should put our knowledge together and act together.

3. In voltammetric community different groups of people exist who develop methodologies, sensors, collect samples during cruises and interpret data obtained after measurements. A better linkage between those groups would be beneficiary to all. This meeting could be a good start to make connections and propose new common projects, where researchers from all mentioned groups would benefit of working together.

4. There is a need for intercalibration studies on the same field samples.

5. The need for the next meeting in two years period is discussed and agreed.

6. Application for new COST action which can gather all interested researchers to work on using voltammetry and speciation of GEOTRACES important elements would be considered seriously in the future.

6. Publishing workshop contributions in a special issue journal dedicated to the meeting is considered but not jet agreed.

Appendix I – Participant List:

Organizing committee

1	Irena Ciglencečki	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	irena@irb.hr
2	Antonio Cobelo-García	IIM-CSIC, Vigo, Spain	acobelo@iim.csic.es
3	Peter Croot	Earth and Ocean Sciences, National Univ. Of Ireland, Galway, Ireland	peter.croot@nuigalway.ie
4	Cédric Garnier	Laboratoire PROTEE, Université du Sud Toulon, La Garde, France	cgarnier@univ-tln.fr
5	Dario Omanović	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	omanovic@irb.hr
6	Ivanka Pižeta	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	pizeta@irb.hr

COST invited

7	Kristen Buck	Bermuda Institute of Ocean Sciences, Bermuda, USA	Kristen.Buck@bios.edu
8	Gonzalo Carrasco	Earth, Atmos. and Planet. Sciences Dept., MIT, Cambridge, MA, USA	gonzalo.g.carrasco@gmail.com
9	Jay Cullen	School of Earth and Ocean Sciences, University of Victoria, Canada	jcullen@uvic.ca
10	Montserrat Filella	Univ Geneva, Inst FA Forel, Versoix, Switzerland	montserrat.filella@unige.ch
11	Josep Galceran	Universitat de Lleida, Lleida, Spain	galceran@quimica.udl.es
12	Loes Gerringa	Royal Netherlands Inst Sea Res, Den Burg, The Netherlands	loes@nioz.nl
13	Luis Laglera	Universidad de las Islas Baleares, Spain	luis.laglera@uib.es
14	Øyvind Mikkelsen	Department of chemistry, NTNU Trondheim, Norway	oyvind.mikkelsen@chem.ntnu.no
15	Damiano Monticelli	Univ Insubria Sede Como, Dipartimento Sci Chim & Ambientali, Como, Italy	damiano.monticelli@uninsubria.it
16	Marta Plavšić	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	plavsic@irb.hr
17	Pascal Salaün	Univ Liverpool, Sch Environm Sci, Liverpool, United Kingdom	pascal.salaun@liv.ac.uk
18	David Turner	Department of Analytical and Marine Chemistry, University of Göteborg, S-412 96, Sweden	davidt@chem.gu.se
19	Matthieu Waeles	Univ Bretagne Occidentale, UMR, IUEM, CNRS, Lab Chim Marine, Plouzane, France	matthieu.waeles@univ-brest.fr

Other participants

20	Blaženka Gašparović	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	Blazenka.Gasparovic@irb.hr
21	Brian Glazer	Department of Oceanography, University of Hawaii, Honolulu, HI 96822, USA	glazer@hawaii.edu
22	Nadica Ivošević	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	Nadica.Ivosevic.DeNardis@irb.hr
23	Palma Orlović Leko	Faculty of Mining, Geology and Petrology Engineering, University of Zagreb, Croatia	paorleko@rgn.hr
24	Stan van den Berg	Univ Liverpool, Sch Environm Sci, Liverpool, UK	vandenbergliverpool.ac.uk
25	Vesna Žic	Central Water Management Laboratory, Hrvatske vode, Šibenik, Croatia	vesna.zic@voda.hr

POST-DOCS and PhD STUDENTS

26	Ana-Marija Blatarić	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	Ana-Marija.Blataric@irb.hr
27	Elvira Bura-Nakić	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	ebnacic@irb.hr
28	Kristopher Gibbon-Walsh	Laboratoire PROTEE, Université du Sud Toulon, La Garde, France	kristopher.gibbon-walsh@univ-tln.fr
29	Justyna Jońca	Laboratoire d'Etudes en Géophysique et Oceanographie Spatiales, Toulouse, France	justyna.jonca@legos.obs-mip.fr
30	Charlotte Kleint	Jacobs University in Bremen, Germany	c.kleint@jacobs-university.de
31	Marija Marguš	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	Marija.Margus@irb.hr
32	Tomer Noyhouzer	Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel	Tomer79@gmail.com
33	Benjamin Oursel	Laboratoire PROTEE, Université du Sud Toulon, La Garde, France	oursel@univ-tln.fr
34	Abra Penezić	Division for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia	Abra.Penezic@irb.hr
35	Sandra Pöhle	Jacobs University in Bremen, Germany	s.poehle@jacobs-university.de
36	Pierre-Jean Superville	Laboratoire Géosystèmes, USTL1, Villeneuve d'Ascq, France	pierre-jean.superville@wanadoo.fr
37	Hannah Whitby	University of Liverpool, Liverpool, United Kingdom	es0u81c3@student.liverpool.ac.uk

Appendix II: Workshop Agenda

Saturday October 6 **Participants arrive to Šibenik**

20:00 Welcome drink and dinner in hotel Jadran

Sunday October 7

09:00 – 09:15 – *Welcome and general introduction* **Irena Ciglenečki**

09:15 – 09:20 – *Welcome from the Mayor of Šibenik* **Ante Županović**

09:20 – 09:55 – *Introduction – Voltammetry and GEOTRACES* (p.7)..... **Peter Croot**

09:55 – 12:35 Voltammetry and GEOTRACES Present - Discussion

09:55 – 10:30 – *Investigating the distribution of dissolved copper, zinc, silver and cadmium in the Pacific Ocean:*

Particle impact voltammetry as a tool for investigating metal speciation (p.8)..... **Jay Cullen**

10:30 – 11:05 – *Pt in oceanic and estuarine waters and its determination using voltammetry (data from the GEOTRACES Dutch cruise, West Atlantic)* (p.6)..... **Antonio Cobelo-García**

11:05 – 11:25 Coffee Break – Informal Discussions

11:25 – 12:00 – *The interpretation of organic Fe complexation data* (p.12)..... **Loes Gerringa**

12:00 – 12:35 – *U.S. GEOTRACES North Atlantic Section, Leg 1: Dissolved Fe Speciation* (p.4)..... **Kristen Buck**

12:35 – 13:05 Post-doc and student presentations:

12:35 – 12:45 – *A new linear-nonlinear optimization mathematical tool for the evaluation of sources and transport of metal complexing ligands in water masses* (p.5)..... **Gonzalo Carrasco**

12:45 – 12:55 – *Investigation of FeS nanoparticles electrochemical behavior with use of voltammetric and amperometric measurements* (p.24) **Elvira Bura-Nakić**

12:55 – 13:05 – *Electrochemical and STM studies of FeS nanoparticles in NaCl model solutions* (p.30) **Marija Marguš**

13:05 – 15:30 Lunch – Informal Discussions

15:30 – 17:45 New Types of Sensors - Discussion

15:30 – 16:05 – *Taking the voltammetric system out of the lab; alternative electrode materials and remote monitoring* (p.15).....
..... **Øyvind Mikkelsen**

16:05 – 16:40 – *Solid gold electrodes for the speciation of metal and metalloids* (p.19)..... **Pascal Salaün**

16:40 – 17:00 Coffee Break – Informal Discussions

17:00 – 17:35 – *New insights and performance enhancement of the determination of total iron in seawater by catalytic cathodic voltammetry of its complexes with dihydroxynaphthalene* (p.14)..... **Luis Laglera**

17:35 - 17:45 – *Adhesion based detection of organic microparticles in aquatic systems* (p.27)..... **Nadica Ivošević**

17:45 – 18:35 - Student presentations:

17:45 – 17:55 – *Autonomous Voltammetric Sensor For Monitoring Sulfide Variability In Deep Sea Chemosynthetic Habitats* (p.25)
..... **Leonardo Contreira Pereira**

17:55 – 18:05 – *Development of a New Electrochemical Cell for Remote Sensing of Low Levels of Heavy Metals* (p.31). **Tomer Noyhouzer**

18:05 – 18:15 – *Developing an in-situ electrochemical method for PAH detection* (p.33) **Abra Penezić**

18:15 – 18:25 – *Reagentless and silicate interference free electrochemical method for phosphate detection: Application to the Oxygen Minimum Zone* (p.28)..... **Justyna Jońca**

18:25 – 18:35 – *Trace metals and natural reduced sulphur species (nrss) detection with a voltammetric automatic monitoring system: calibration and correction issues* (p.36)..... **Pierre-Jean Superville**

19:30 Dinner

Monday October 8

09:00 – 18:05 Intercalibration, Speciation and Operating Procedures - Discussion

09:00 – 09:35 – *The place of voltammetry in today's chemical speciation studies* (p.9)..... **Montserrat Filella**

09:35 – 10:10 – *Optimising voltammetric procedures: small volumes, fast analysis and reliable data?* (p.16) ..**Damiano Monticelli**

10:10 – 10:45 – *Incorporating the results of voltammetric measurements into chemical speciation models* (p.20).....**David Turner**

10:45 – 11:05 Coffee Break – Informal Discussions

11:05 – 11:40 – *Advances in the chemical speciation of iron using catalytic cathodic stripping voltammetry* (p.21) **Stan van den Berg**

11:40 – 12:15 – *Trace metal speciation by ASV: recent analytical and modelling improvements* (p.11) **Cédric Garnier**

12:15 – 12:50 – *Recent advances for using in situ voltammetry to characterize oxic-anoxic transitions in marine environments* (p.13)

..... **Brian Glazer**

12:50 – 13:00 Post-doc presentation:

12:50 – 13:00 – *The interest of analyzing trace metals at a number of accumulation potentials* (p.26).....**Kristopher Gibbon-Walsh**

13:00 – 15:30 Lunch – Informal Discussions

15:30 – 16:05 – *AGNES as a technique for determining free metal ion concentrations in natural waters* (p.10) **Josep Galceran**

16:05 – 16:40 – *Organic matter-metal ions interaction-some highlights* (p.18).....**Marta Plavšić**

16:40 – 17:00 Coffee Break – Informal Discussions

17:00-17:35 – *Stripping chronopotentiometry and several applications in marine systems* (p.22)..... **Matthieu Waeles**

17:35 – 18:05 – *Signal processing and measurement automation in electroanalysis* (p.17)..... **Dario Omanović**

18:05 – 18:55 Student Presentations:

18:05 – 18:15 – *Competition between copper and iron for ligands and possible effects on bioavailability of iron* (p.37) .**Hannah Whitby**

18:15 – 18:25 – *Speciation and distributions of metals in Krka River estuary* (p.23)**Ana Marija Blatarić**

18:25 – 18:35 – *Chromium speciation in the oceanic water column* (p.34)**Sandra Pöhle**

18:35 – 18:45 – *Geo-Bio interactions in shallow water hydrothermal vents and their impact on trace metals* (p.29) ... **Charlotte Kleint**

18:45 – 18:55 – *Usefulness of voltammetric measurements to assess trace metals transfer at the continental/coastal zone interface: example of Marseille agglomeration (SE, France)* (p.32) **Benjamin Oursel**

19:30 Workshop Dinner

Tuesday October 9

08:30 – 12:00 **Open Discussion - Final Synthesis and Recommendations for Future work**
(Short trip by boat to RBI Marine station Martinska)

12:30 Lunch - Departure of participants

Appendix III: Reference List

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Appendix IV: Mutual cooperation of participants

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1 MET EACH OTHER 2 WORKED TOGETHER 3 PUBLISHED TOGETHER	Irena Ciglenečki	Antonio Cobelo-García	Peter Croot	Cédric Garnier	Dario Omanović	Ivanka Pižeta	Kristen Buck	Gonzalo Carrasco	Jay Cullen	Montserrat Filella	Josep Galceran	Loes Gerringa	Luis Laglera	Øyvind Mikkelsen	Damiano Monticelli	Marta Plavšić	Pascal Salaün	David Turner	Matthieu Waeles	Blaženka Gašparović	Brian Glazer	Nadica Ivošević	Palma Orlović Leko	Stan van den Berg	Vesna Žic	Ana-Marija Blatarić	Elvira Bura-Nakić	Kristopher Gibbon-Walsh	Justyna Jońca	Charlotte Kleint	Marija Marguš	Tomer Noyhouzer	Benjamin Oursel	Abra Penezić	Sandra Pöhle	Pierre-Jean Superville	Hannah Whitby				
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1 Irena Ciglenečki		1		1	2	2				1						3	1	1		2		1	2	1	3		1	3			3			2					17	19	
2 Antonio Cobelo-García	1							1					1																											4	32
3 Peter Croot							1	1	1			2	1																											8	28
4 Cédric Garnier	1				3	3				1				3		1	2		3	1				1	3		2	1	2		1		2			2				17	19
5 Dario Omanović	2			3		3								1	1	3	2		1	2		2	2	2	2	2	2	2	2		1		2	2		3			20	16	
6 Ivanka Pižeta	2			3	3		2		1	1	1			3		2	2		1	2		2	2	3	2		2	2	2		1		2	2		3			23	13	
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7 Kristen Buck			1			2		2	3			2	1								1				3														8	28	
8 Gonzalo Carrasco		2	1	1			2		1	1		1																											8	28	
9 Jay Cullen	2	2			1		3	2				2	2											3															7	29	
10 Montserrat Filella				1	1						1	1	1				1	1	1					1															9	27	
11 Josep Galceran						1					1		1				1	1	1	1				1															7	29	
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13 Luis Laglera	1	1					1		1	1	1	1			3		2						3		3													11	25		
14 Øyvind Mikkelsen				3	1	3												1						3														7	29		
15 Damiano Monticelli					1									3										3														4	32		
16 Marta Plavšić	3			1	3	2					2									3		1	3	2			1	3	1		1			1				16	20		
17 Pascal Salaün	1			2	2	1				1	1	1	1		1	1			2		3		3	3	2		2	1	3						2	2		18	18		
18 David Turner											1	1	1	1										3														4	32		
19 Matthieu Waeles				3	1	1					1						3							3			2	3				1						9	27		
OTHER PARTICIPANTS																																									
20 Blaženka Gašparović	2			1	2	2					1					3						1	1	1	1		1	2			1	1	3					15	21		
21 Brian Glazer							1		1																														3	33	
22 Nadica Ivošević	1				2	2										1				1			1	1	1		1	1											12	24	
23 Palma Orlović Leko	2				2	2										3					1	1		2			1	3										11	25		
24 Stan van den Berg	1		1	3	1	3	1		1	1	1	2	2	3	3	3	3	3	3	1							1		3								2	21	15		
25 Vesna Žic	3			3	2	2										1	1			1		1	1	1			1	1	1								1	17	19		
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26 Ana-Marija Blatarić	1			2	2	2						1	1	1	1	2		2		1		1	2	2	1		1	2			1	2	1	2			1	21	15		
27 Elvira Bura-Nakić	3			1	2	2										2	1			2		1	3	1	2		1		1									1	17	19	
28 Kristopher Gibbon-Walsh	1			2	2	2							1	1					2					3			1										1	1	13	23	
29 Justyna Jońca			1																		1			1														3	33		
30 Charlotte Kleint																																							1	35	
31 Marija Marguš	3			1	1	1										1				1		1	1	1			1	3	1								1	15	21		
32 Tomer Noyhouzer																																							0	36	
33 Benjamin Oursel	1			3	3	2							1			1		1		1			1	1			2	1	2							1	15	21			
34 Abra Penezić	1			1	2	2														3		1	1					1	1									1	11	25	
35 Sandra Pöhle																														1								1	35		
36 Pierre-Jean Superville				2	3	3							2				2										2	1	2									10	26		
37 Hannah Whitby												1					2							2														4	32		