COST Action 735/801 Workshop on

"Trace Metal speciation: Current state of the art

and towards the construction of a database "

IFM-GEOMAR, Kiel, Germany, 16-17 August 2010

Workshop Summary and Report

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Meeting Support provided by Dr M Heller and O Baars.

The meeting was attended by 35 people from 14 countries, with 20 of those attending being supported directly by either COST Action 735 or 801. The aim of the meeting was to discuss the current state of the field with respect to measurements of trace metal speciation, identify the current groups working in this field and the current and potential users of this data. The main goal of the meeting was to bring workers in this field together and to develop a common criterion for data analysis and quality control for use in submitting data to a common database. For this purpose we also invited experts in data management to help facilitate this interchange of information. The topic is crucial to our understanding of the role of iron and other trace metals in ocean productivity, not only for the High Nutrient Low Chlorophyll (HNLC) regions which are strongly iron limited, but also in the Tropical oligotrophic gyres where productivity is limited by the availability of fixed nitrogen, and the direct fixation of atmospheric nitrogen by marine organisms may be influenced by metal supply and bioavailability. Furthering our understanding of the speciation of bioactive-elements in the present data ocean is also central to the testing and validating of paleoclimate proxies (e.g. Cadmium).

The organization of this meeting was undertaken as part of the activities of Working Group I (Short-lived trace gas production and biological feedbacks) in Cost Action 735 (Tools for Assessing Global Air–Sea Fluxes of Climate and Air Pollution Relevant Gases) and Working Groups 2 (Intercalibration) and 3 (Data Management) in Cost Action 801 (The Ocean

Chemistry of Bioactive Trace Elements and Paleoclimate Proxies). This meeting would not have been possible without the support of the COST office in Brussels and from the chairs of Action 735 (Prof Peter Liss, UEA) and 801 (Prof Gideon Henderson, Oxford) who helped support this proposal. Gideon Henderson also was helpful for gaining support for this meeting through his role as co-chair of GEOTRACES as was his counterpart at SOLAS (Prof. Douglas Wallace, IFM-GEOMAR). Special thanks goes to Kath Mortimer (COST 735: UEA) and to Sara Tennakoon (COST 801: Oxford) who handled the paperwork connected to this meeting. The meeting could not have taken place without the help of Maeve Lohan (University of Plymouth) and Emilie Breviere (SOLAS IPO, Kiel).

The participants at the meeting were chosen so as to include researchers actively working on trace element speciation and to represent a wide range of different disciplines and approaches to this topic. Unfortunately some invited participants, from Australia, Turkey and Poland, could not attend at the last minute due to family commitments but were keen to participate in the follow up discussions via email to this meeting (see section on outputs later in this report). A number of early career scientists were also able to attend the meeting and took an active part in both the formal and informal discussions. A press release in both German and English was made on the 16th of August, and included a group photo of the participants, and was available on the homepage of IFM-GEOMAR later that day. The press release was subsequently used by 11 media organizations the next morning (see appendixes below).

The meeting agenda (see appendix) was constructed around 3 invited talks that outlined the current state of the art and then a series of sessions devoted to key aspects related to constructing a database. All the sessions were designed to enable plenty of debate and to facilitate exchange of information between the participants. Overall there were a number of key issues pertinent to the goals of this meeting and that of a construction of a centralised database that were directly addressed:

(1) What is the current state of knowledge on trace metal speciation in seawater?
(2) What techniques are currently employed?
(3) What historical data is available?
(4) How should the database be constructed? What are the critical parameters?How should the data quality be assessed?
(5) What meta data is critical to include (e.g. detection window, competing ligand etc...)
(6) Prospects for Intercalibration samples/standards (Includes preservation issues).

August 16

Dr Croot (IFM-GEOMAR) gave a short introduction and welcome to the participants of the meeting. Dr Croot stressed the need for the community of trace metal speciation scientists to work together and develop their own criteria for data quality and to ensure that it is easily recoverable, and interpretable, from databases. He then introduced the 3 invited speakers who would make presentations on the current state of the field.

The first invited speaker was Dr Kristen Buck from the Bermuda Institute of Ocean Sciences (BIOS) who gave a presentation entitled "State of the art: Dissolved Fe and Cu speciation in the open ocean". The main points of her talk are listed below:

- 99% of Fe and Cu in seawater is organically complexed.
- Complexed Fe is apparently to some extent bioavailable, and has a long residence time,
- Complexed Cu less bioavailable, presumably to limit toxicity, though recent research shows that Cu is also important for phytoplankton.
- Method used historically and in the recent GEOTRACES intercalibration:
    - CLE-ACSV with NN, TAC and SA for iron ligands and SA for copper ligands,
- Hardware improvements:
    - Signal to noise ratio
    - Autosampler
    - TM rosette
- Improvements in sensitivity can be driven by:
    - Bigger Hg drops
    - Buffer
- GEOTRACES sections planned
- High resolution studies and process studies (Incubations),
    - Fe ligand conc. went up under Fe limitation during incubation,
    - Cu ligand did show significant difference,
    - Low Fe ligand → high Cu ligands,
- Ligand sources and sinks
    - Atmospheric deposition and *in situ* production
    - Active bio production vs. passive production via degradation of cells

Following her talk there were a number of questions raised in discussion:

- What is the role of colloidal iron? Is this the major source of ligands in the dissolved phase?
- What is the effect of iron limitation on ligand concentrations?
- What is the lifetime of the Fe and Cu complexing ligands and how do they influence deepwater residence times for the elements?

Dr Mak Saito of the Woods Hole Oceanographic Institution (WHOI) gave a very interesting overview of the speciation of Cobalt and Nickel in seawater with his talk entitled "Cobalt and Nickel speciation in the marine environment". The main point of his talk are summarized below:

- Overview of the current methods employed for Co and Ni:
  - HMDE, CSV, CLE-ACSV,
- Nickel: A fraction is complexed by strong organic ligands.
- Cobalt:
  - labile Co is increasing with depth at the Costa Rica dome (Co depleted surface, probably due to the high concentrations of Cyanobacteria present there).
  - higher labile fraction in the Ross Sea,
- N_2O and Co show linear relationship, possibly due to similar remineralization processes.
- Co(II) much better soluble than Co(III), and almost all Co is Co(II) since Co(III) is much more particle reactive than Fe(III),
- All known NiL complexes have a higher K than CoL
- However Ni does not apparently replace Co from CoL in titrations.
- Cobalt in vitamin B12, excreted by bacteria (lyses) but they cannot take it up. B12 can be decomposed by irradiation.
- Co-limitation of phytoplankton: B12-Fe, B12-Co, N-Co, N-Fe

There were a number of comments and questions following the talk:

- The equilibration time is crucial to the interpretation of Co(II)/Ni(II) replacement titrations. The slow kinetics of Ni exchange may require days for this replacement to occur.
- Observed cobalt tongue between Africa and South America may be due to release from sediments in the Namibian OMZ.
- What forms of Co is taken up by phytoplankton and bacteria?

The last of the element overview talks was given by Dr Jay Cullen, from Victoria University in Canada, with his presentation entitled "Overview of Cd and Zn speciation in Open Ocean seawater". The main points of his talk are shown below:

- Total dissolved Zn conc. is much higher in the deep Pacific than in the Atlantic Ocean, both depleted in the surface water.
- The same for Cd, but generally lower concentrations.
- Analytical Methods employed presently:
    - RDE, CLE-ACSV (Zn with APDC), ASV Pseudopolarography
- Limited number of studies reported:
    - Zn (95%) and Cd (70%) are organically complexed,
    - Ligands are in excess in the surface, at depth metal becomes in excesss leading to large change in the calculated free metal concentrations.
    - Ligand source in the surface

Following his talk there was once again a lively exchange of comments and questions, including the following:

- Possible ligand sources for Cd and Zn include molecules with protein like structures.
- Intracellular transport mechanisms for these metals involve chaperones, can these leak out and also fill the same role in the ocean?
- Inorganic speciation is also important here, do we really know this as well as we think we do?

The next phase of the meeting was devoted to the interpretation of speciation data and the discussion was lead by Dr Croot. The main points from this discussion are listed below:

- We should report data in Volumetric units (nmol L^{-1})
- Report both Thermodynamic and Kinetic measurements
- Types of Speciation data:
    - Organic complexation:
        - First order: specific compounds (e.g. Vitamin B_{12})
        - Second order: K, L from titrations.
    - Redox species:
        - Type 1: rate measurements
        - Type 2: concentrations
- We need to adopt a quality flag system for reporting the data. Examples already exist for WOCE nutrient data.
- Critical data to report:
    - Depth or pressure (Must state which)
    - Competitive ligand, T, Equilibration time, Buffer (EPPS, Ammonia/Boric Acid), pH and pH scale, Voltammetric, Side reaction coefficient, Model for K and L.
    - Dissolved or soluble metal concentration.
    - O_2 and H_2O_2, also DOC and CDOM where possible.
    - Fitting Methods for Titration Data:
        - Currently employed methods include: Scatchard, van den Berg/Ruzic/Lee Linearization, Gerringa (non-linear fit), and Moffet (non-linear fit).
        - Possible to include iterative method to parameterize the sensitivity as a function of the concentration.
    - Do we archive the raw titration data or just the final calculated values of L and K?

After the break for lunch and the taking of a group photo, Dr Maeve Lohan from the University of Plymouth, continued the formal part of the meeting with her presentation entitled "Preservation, storage and intercalibration issues". Dr Lohan mostly discussed results from the recent US GEOTRACES intercalibration cruises where the speciation of Cu and Fe was also included and frozen samples were made available to other international groups:

- Methodology used in the US GEOTRACES intercalibration work at the SAFe station in the Pacific:
  - 0.45 µm filtered seawater (Osmonics – behaves as 0.2 µm)
  - Comparison of fresh samples vs frozen for titrations
  - Tested microwaving samples for 3 x 15 s
  - frozen at -20°C and -80°C (in average lower FeL at -80°C),
- 1000 m sample:
  - strong variability in samples that were stored in Teflon bottles and then melted during transportation. Customs and logistics issues.
  - Problems with CO_2 from dry ice lowering the sample pH in transport.
- 3000 m sample:
  - Large variability observed between all laboratories.
  - Sensitivity issues with deep samples?
- Filtration issues appear to be under control
  - Good results found with Acropack capsule (0.2 µm), Sartobran capsule (0.2µm), Osmonics (risk of contamination).

Discussion after Maeve's talk covered a broad spectrum of issues:

- Problems with 0.4 µm filtration as Archaea are in this size range between 0.2 and 0.4 µm. Most systems used currently have 0.2 µm final filtration.
- Important to recognize limits of fitting methods when the ligands are fully saturated in the samples. No meaningful value of K is obtainable.
- Acid washed bottles must be filled with MQ for at least a week to avoid problems with low pH in samples from residual acid in bottle. May be related to volume of water used for rinsing the sample bottles?
- Proposal for a summer school on Intercalibration and Training exercises for speciation measurements in seawater.
- Possible suggestions for voltammetric speciation standards that did not require freezing or other stability issues:
  i. UV seawater with known ligand such as DFO-B.
  ii. KCl with EDTA. (Use of KCl in some labs may be limited due to safety issues).
  iii. $CaCl_2$ with EDTA (Ca more important cation for side reactions with ligands)

The next presentation was by Dr Alessandro Tagliabule (LSCE, Paris, France), with help from Dr Christoph Völker (AWI, Bremerhaven, Germany) whio gave their case for the value of an Fe speciation database.

- The numbers of Ligand measurements have increased, and will increase substantially under GEOTRACES, making validation of models for this parameter far easier for modelers.
- Using DOC as a proxy for L enables testing of models for a number of scenarios.
- Ligand concentrations are needed for concentration fields and are thus relatively more important than the value of K.
- The colloidal cycle is important and this data is very scarce at present.

Despite this being the second last discussion session during a long day of talks, this session provoked a good exchange between the modelers and the experimentalists. The key topics of discussion were as follows:

- Is the relationship between DOC and iron binding ligands robust?
- Can you use humic substances as a model for iron binding ligands in GCMs? Possibly not as humic fluorescence is anti-correlated to ligand distributions in surface waters, may be better as a component for deep water ligand concentrations.
- Redox data important as models currently do not replicate O_2 distributions adequately.
- Model – database feedback important for proposing new study regions or processes and for checking oceanographic consistency of the data.

The final presentation of the day was by Dr Ed Mawji (BODC, United Kingdom) who gave a nice overview of the current and future plans for the GEOTRACES database and how it might apply to the goal of this meeting:

- The GEOTRACES database now includes 14 IPY and 4 section cruises in the database.
- There are over 40.000 parameters in the BODC databases. Have to be aware of legacy issues with regards to the naming of parameters.
- Issue of having to submit to national databases first as requirement of funding. No funding for historical datasets, this has to be done by the community itself.
- If you want an open access database for ligand data:
    - Where the database will be kept?
    - Distribution
    - Funding
    - Quality control
- Possible Databases for this purpose include:
    - GCMD (used for SOLAS metadata)
    - PANGAEA (issues with doi when data is changed)
    - SEADANET (good option)

The final discussion session of the day was focused on database issues and was a good opportunity for the scientists present to learn first hand from the experiences of the database managers:

- Authorships rights can be tricky. However there are precedence's for publications of data collections where all those who contributed were included as a co-author.
- Metadata is necessary ("It's all about preservation!")
- Documentation must be clear: Reporting how the data and metadata were obtained.
- We need to learn from the business world – they have been archiving material for decades.
- Helps to have similar data in the same format. Develop a standard template within this community for use with scientific databases. This can be done through the new Wiki (see below).

August 17

Identifying the tasks ahead

The participants were given a short presentation by Dirk Fleischer and Pina Springer from the IFM-GEOMAR on different databases and the establishment of a Wiki for Trace Metal Speciation in Seawater. The main German database, PANGAEA, was introduced by Dirk and he showed us some examples of data already existing in that database. It was also stressed that the inclusion of specific keywords would also help in data mining for speciation related work. He also stressed the importance of data quality flags and quality control as this was best assessed by the data providers and not the data managers or end users. Pina Springer then introduced the participants to the newly created Trace Metal Speciation in Seawater Wiki page that had been set up that morning. The development of this Wiki will help facilitate further discussion of the issues raised at this meeting and with a wider audience of scientists.

The final session of the meeting was a group discussion chaired by Dr Croot which covered all the topics raised during the meeting. This session lead to the creation of a list of final products and outcomes of the meeting:

Products and outcomes

- An article summarizing the results of the meeting for submission to EOS.
- Establishment of a Wiki for the exchange of information on trace metal speciation theory and techniques. This Wiki is already functioning (https://portal.ifm-geomar.de/web/tmsis/wiki) and is being constanly updated. People interested in participating in this wiki should contact Dr Peter Croot for more information (pecr@pml.ac.uk).
- That the Wiki should also form as the initial repository for historical speciation data currently not available in online databases.
- Templates for the format of speciation data to be submitted to national and international databases will be made available on the Wiki for comment before a final recommendation is made within the next year.

- The Wiki will also include database links and bibliographies of published works on trace metal speciation in seawater.
- Student exchanges between laboratories via COST Action 801 STSM should be encouraged. For exchanges where COST funds cannot be used, alternative funding sources should be explored.
- Explore and develop a proposal for a research school for trace metal speciation. These efforts would complement existing plans within GEOTRACES for shipboard intercalibrations for trace metal speciation.
- Examine the possibility of an ESF meeting/workshop to be held in 2 years time on the subject of trace metal speciation and bioavailability.

Appendix I – Participant List:

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Appendix II: ***Workshop Agenda***

Monday Aug 16

08:30 *Welcome and general introduction* **P Croot**

08:45 *Discussion* - ***What is the current state of knowledge on trace metal speciation in seawater?***

08:45-09:15 *Fe and Cu speciation in the open ocean.* **K Buck (Invited)**

09:15-09:45 *Co and Ni speciation in the open ocean.* **M Saito (Invited)**

09:45-10:15 *Zn and Cd speciation in the open ocean.* **J Cullen (Invited)**

10:30 Coffee Break – Informal Discussions

11:00 *Discussion* – ***Interpretation of Speciation Data***

11:00-12:30 – *Model fitting as meta-data and other issues* *Open*

12:30 Lunch – Informal Discussions (12:15-12:30 Group Photo Foyer)

13:30 *Discussion* – ***Quality control of speciation data***

13:30 – 13.45 – *Preservation, Storage and Intercalibration issues* **M Lohan**

15:00 Coffee Break – Informal Discussions

15:30 *Discussion* – ***What do modellers want from a database?*** **A Tagliabue & C Volker**

16:00 *Discussion* – ***How do you construct a database?***

16:00 – 16.15 – *The GEOTRACES database* **E Mawji**

19:30 Group Dinner – Louf (Kielinie)

Tuesday Aug 17

08:30 *Open Discussion* – ***Identifying the tasks ahead***

09:00-09.15 – *Other Databases and the TSMIS Wiki* **D Fleischer & P Springer**

10:00 Coffee Break – Informal Discussions

11:00 ***Final Synthesis and Recommendations for Future work***

Appendix III: Press Release August 16, 2010

Participants at the COST 735/801 Meeting in Kiel, Aug 16-17, 2010 (Photo: A Villwock).