SCOR WG 139:
Organic Ligands- A Key Control on Trace metal Biogeochemistry in the Ocean

Meeting 2, 16th February 2013
New Orleans Convention Centre,
New Orleans, LA, USA

Present: Maeve Lohan, Kristen Buck, Sylvia Sander, Kathy Barbeau, Ron Benner, Martha Gledhill, Katsumi Hirose, Ivanka Pizeta, Alessandro Tagliabue, Rujun Yang, Thorsten Dittmar, Christel Hassler, Micha Rijkenberg, Mak Saito.

Agenda

8:30 am Coffee, mingle
8:50 am Introductions
9:00 am Review action items from Salt Lake meeting (Buck)
9:30 am Updates on website, database (Sander, Lohan)
10:00 am Coffee break
10:30 am Results from data interpretation intercalibration (Pizeta, Sander)
11:15 am Additional intercalibration opportunities (Lohan, Sander, others?)
12:00 pm Lunch
12:45 pm Invited Talks on New Developments
- 12:45 pm Reverse titration CLE-CSV for high Fe environments (Gledhill)
- 1:15 pm Recent results from HPLC-ICP-MS and ESI-MS (Rene Boiteau)
- 1:45 pm What modellers need from analysts (Tagliabue)
- 2:15 pm Metal-binding ligands and DOM: what we know, future directions (Benner)

3:00 pm Cookie break
3:30 pm Synthesis: A mass balance model for metal-binding ligands within DOM- where do we stand, and what do we need to achieve this? (All)
4:30 pm Wrap up discussions; agree on tasks and timelines following this meeting. Plan for publications and other outputs. Determine next meeting details, symposium
5:30 pm The End, stroll to bar

A review of last year's action items

Ron Benner: Sent reference list of DOM studies from BATS region. Target year for BATS could be any year where measurements made (see reference list).

Phil Boyd: Sent summary table of metal-binding ligands, ecological/biogeochemical roles and associated references. Database discussion took place at this meeting (see below).

On-going: Identify 'omics' data resources for BATS/Line P, with J. Moffett.

Ken Bruland:

Added: Summary page of SAFe metal profiles and references, with M. Lohan.

Added: Collate BATS metals data and references, with M. Lohan.

Kristen Buck: BATS database information sent to R. Benner & Phil Boyd. Ken Bruland has offered to provide UVSW, but participants should cover the cost of bottles and shipping.

Added: Circulate completed one pagers to Members for editing using Dropbox or similar document sharing.

Jay Cullen: Sent summary page of metal-biology relationships and references.

Ongoing: Identify target year/season for Line P data compilation, with R. Keil.

Thorsten Dittmar:

Ongoing: Provide a summary page with references on organic techniques, target DOM classes for ligands, and related terminology.

Rick Keil:

Ongoing: Identify target year/season for Line P data compilation, with J. Cullen.

Ongoing: Collate DOM data and references from targeted Line P studies.

Maeve Lohan: Provided white paper on operational definitions.

Ongoing: Summary page of SAFe metal profiles and references, with K. Bruland

Ongoing: Collate BATS metals data and references, with K. Bruland.

Jim Moffett: Sent the summary page for best practices for ACSV measurements.

Ongoing: Identify 'omics' data resources for BATS/Line P, with P. Boyd.

Ivanka Pizeta: Provided simulated titration data for S. Sander for the intercalibration exercise, which was completed with 15 contributors (see discussion notes below).

Mak Saito:

Ongoing: Provide a summary of ASV and ACSV interpretation approaches in use, with references and noting labs currently employing them.

Sylvia Sander: Provided simulated titration data for the intercalibration exercise, which was completed with I. Pizeta (more on this below).

Ongoing: Summary page(s) with references on electrochemistry techniques employed for ligands, information provided by these techniques.

Added: Upload completed one pagers (post group edit) to WG website.

Ed Urban: No longer hiring a database manager (see discussion below).

ACTION : **All Members** to review one pagers when circulated and provide edits/comments using Track Changes or similar notation.

Website

Sylvia Sander provided an update on the website, which went live in February 2013 (http://neon.otago.ac.nz/research/scor/index.html). She asked for suggestion of

external links. Links to SOLAS, GEOTRACES, Wiki, were agreed. Also link to COST "Voltammetry and GEOTRACES" meeting held in Croatia.

ACTION: **All Members** to provide information to Sylvia on other links for site.

Database Discussion

In discussing the database for field ligand data, it was noted that this data already exists in several databases, from those of the modellers currently using published data in their models, to the GEOTRACES and national databases for recent studies. Thus, in an effort not to reinvent the wheel, it was concluded that we would attempt to merge existing databases for ligands with those of DOM, and to provide some insight on the parameters needed for future data submissions.

Alessandro Tagliabue has a ligand database for Fe, which he is happy to share. Mak Saito and Maeve Lohan will begin to collate Co and Zn ligand data, respectively.

Database discussion was based around the parameters required for modellers and analysts to be able to evaluate trends in ligand parameters. These parameters will be forwarded to Ed Mawji, the GEOTRACES data manager, to provide guidance for future data submissions. The key point was that we should start doing this now in light of all the new data being generated on the GEOTRACES programme.

The following parameters were agreed upon: latitude, longitude, year, month, bottom depth, depth, metal concentration, filter size (e.g., 0.45 µm, 0.2 µm, 0.02 µm), ligand concentration and stability constants (in the case of Fe, L_1 Log K > 12, L_2 log K 11-12, L_3 log K<11; taken from Gledhill & Buck 2012), method applied (e.g., AdCSV, ASV), concentration of added ligand, interpretation method used (e.g., van den Berg/ Ruzic, Scatchard, non-linear Gerringa), DOC (note in metadata if measured on the same sample).

With the continual development of new interpretation techniques for raw speciation data, the importance of raw titration data being included in the database was discussed, as this could potentially facilitate additional intercomparison opportunities between new and established interpretation techniques. At present this is not included but Kristen Buck will investigate how BCO-DMO might store this and if this is something we could be adding.

Thorsten commented that a database for organic material was not yet available, but that at present he was involved with Microsoft on developing a program that can process DOC results from raw data. This sounded like a promising avenue for raw metal speciation data in the future, and Thorsten will update the group on this experience at the next meeting.

The addition of a CDOM database would also be helpful as this is a global measurement that relates to ligands. Kristen will contact Norm Nelson about whether such a database exists already.

ACTIONS:

Maeve Lohan to communicate with Ed Mawji about the proposed parameters for GEOTRACES ligand data submission. Collate data for Zn ligand database.

Kristen Buck to investigate if/how BCO-DMO would store raw titration data. Contact Norm Nelson about any existing CDOM databases.

Mak Saito to collate Co speciation data for the database.

Jim Moffett to collate Cu speciation data for the database.

Alessandro Tagliabue to provide iron binding ligand database compiled so far.
Update: Elliot Sherman (Keith Moore's student) has also submitted his database of published Fe speciation data.

Thorsten Dittmar to update the group at the next WG meeting on the Microsoft program for processing organic data.

Sylvia Sander to begin assembling databases provided by members on password-protected side of WG website. These databases will become publicly available only once merged between DOC/DOM and ligand data.

Results from data interpretation intercalibration (Pizeta, Sander)

Sylvia and Ivanka presented the initial results from the intercalibration exercise of estimating metal ligand parameters from a simulated titration dataset. In total, 15 people contributed to this and this resulted in 23 different datasets as some analysts provide multiple interpretation outcomes. From this intercalibration exercise, the results showed that once the system contained more than one ligand, results were more variable and in some cases did not reflect the simulated parameters well. It was confirmed that the strongest ligand is easier to determine with a reasonable accuracy compared to the weaker ligand(s). As expected, data that had realistic noise added was more difficult to analyse than the same dataset with no noise.

From the discussion, main points to be addressed for this study include:

- Where is the biggest error in the calculation- is it the linear or non-linear fitting method, or the computer program used, or the sensitivity determination, or is it operator error?
- How do the errors impact the calculation of the free metal ion or inorganic metal concentration (i.e., impact on estimated bioavailability)?
- SGS and IP will calculate the concentration of the free metal ion, so that this can also be compared to the simulated data provided.

- The EF used in the results discussion needs some more consideration as if you only fit 2 ligands rather than 3 you are only dividing by 2 so therefore will have a lower error.
- As there is no reference material for speciation analysis, should we use a simulated data set as a quality check for our data analysis method?
- Are there errors in analysts' spreadsheets that have been carried forward over time?
- As a general advice Ivanka pointed out, that every analysit can verify themselves if the right model (e.g. right number of ligands) has been chosen, by simulating a titration curve using the results of their own data analysis (i.e. ligand parameters: L_1, K_{ML1}^{cond} , L_2, K_{ML2}^{cond} etc., and given parameters such as sensitivity (S), α_{inorg}, α_{MALx}, [M]) and compare the measured titration curve with the simulated. Further, it is advised to compare those two sets of data after different transformations (log-log, van den Berg-Ruzic, Scatchard, Gerringa) because each of the transformation emphasizes different segments of the titration curve. Dario Omanovic (from RBI) has updated his MCC softward to simulate titration curves in an easy manner. Please contact Dario (omanovic@irb.hr) to receive a copy.

ACTIONS:

Sylvia Sander to contact each analyst and let them know which letter they are in the intercalibration exercise so they can see how they compare to others. Direct participants and members to the password-protected part of the website where results posted to allow further discussion. A draft of the results summary will be posted by May 2013.

Sylvia Sander and Ivanka Pizeta promised to supply the participants of the intercomparison with a program that calculates titration curve from the fitted parameters as well as free metal concentration.

Sylvia Sander to investigate the use of a simulated data set to be used as a quality check for analyses. This may need to be different for situations with 1 or 2 ligands, with ACSV or ASV analyses, and for different trace metals.

Mak Saito to send around an Excel spreadsheet with correct calculations and equations for people to look at and compare their spreadsheets with.

Sample-based intercalibration

Maeve Lohan has offered to collect samples from a cruise to the Celtic Sea (UK) during 2014. This would be for Fe and Cu speciation analysis. This will be from 2 depths, the chlorophyll *a* maximum and at depth ~1500 m. These would be collected in 1L FLPE bottles. All interested parties will provide a FedEx number for shipping of

frozen (-20 ºC) samples back to their laboratory. Thorsten would also like 4 L samples which can be acidified. Ron Benner would like 50 mL frozen in HDPE (not fluorinated) for DOC analysis.

ACTIONS:

Maeve Lohan to send an e-mail asking for participants from our mailing list.

Kristen Buck to investigate possible use of SCOR funds to mediate collection costs.

Invited Talks

All presentations from this meeting agenda have been posted in PDF form on the password-protected side of the group website.

DOM-Metal ligand discussion

To start with we need to put together metal ligand data from HOT and BATS to complement Ron's assemblage of DOM and DOM component data from these locations. However, there is no metal ligand data at HOT, so it was suggested we ask Jay Cullen about DOM and metal ligand data from Line P.

For Fe fertilisation studies important to consider changes in total ligand concentration vs. changes in excess ligand concentrations when discussing changes in ligand concentrations in response to Fe fertilisation events.

Several recommendations were noted for future studies, including size fractionation and targeted DOM analyses.

ACTIONS:

Kathy Barbeau to assemble size-fractionated ligand data from BATS and surrounding region, merge with DOM size-fractionation targets from R. Benner.

Ron Benner to provide a list of size-fractionated DOM components to target in future metal ligand studies.

Kristen Buck to put together metal ligand data and references from BATS studies. Assess changes in excess ligands vs. total ligands in Fe fertilisation studies.

Jay Cullen to compile any metal ligand data with references from Line P and note if there is any DOM/DOC data to go along with those studies.

Publications

Peter Croot emailed in advance of the meeting to highlight that he is organising a special issue in Environmental Chemistry. This came out of the COST "Voltammetry and GEOTRACES" meeting in Croatia last October. If anyone would like to contribute an article, please send an e-mail to Peter Croot; tentative due date for these articles is August 2013.

Sylvia Sander had contacted Frank Millero at Marine Chemistry, who agreed to host a special issue specific to the outcomes of this WG. Other journals, such as Biogeosciences or Deep Sea Research, were also suggested, but Marine Chemistry was regarded as the best medium. It was also suggested that we plan to have papers for this special issue ready for submission at the next WG meeting or symposium, although further discussion is needed to narrow down the timing and components.

ACTIONS:

All Members and other interested researchers to inform co-chairs of interest in writing a paper for the special issue, and proposed topic and timeline for the submission. The goal for the submissions is with the next meeting, ASLO 2014.

Sylvia Sander to organize a special issue in Marine Chemistry.

Next Meeting

A long discussion took place on what type of meeting(s) we should have as a SCOR WG in the remaining two years. Many other people outside this WG would like to participate in these discussions so it was felt that it would be good to hold a workshop/symposium that would be open to the interested scientific community. This would be based more on a Gordon Conference type symposium. Funding is a major issue in organizing a separate symposium and possible sources of funding identified for this were OCB and ESF. Christel Hassler suggested we apply for Centro Stefano Foundation (CSF) funding, who have a conference centre in Monte Verita, Switzerland and organize similar events. OCB was an additional recommendation for the symposium.

No dates were chosen for this symposium, as it is dependent upon getting funding for this.

It was agreed that we should apply for a special session once more for the Ocean Sciences Meeting in Hawaii, February 2014. In addition, the next WG meeting should take place alongside this conference.

ACTIONS:

Christel Hassler to investigate ESF/CSF about running a workshop/symposium.

Kathy Barbeau to contact OCB about running a workshop/symposium.

Maeve Lohan to submit a special session request to ASLO 2014 in Hawaii.