Template for Annual SCOR Working Group Reports to SCOR

1. Name of group

SCOR WG 139: Organic Ligands – A Key Control on Trace Metal Biogeochemistry in the Ocean

2. Activities since previous report to SCOR (e.g., virtual or in-person meetings, email discussions, special sessions). Limit 1000 words

SCOR WG 139 is in finalizing its work this year and this will be the last report for WG 139. We had no official meeting in the last reporting year, but continued to work on the completion of our goals as outlined in the terms of references. Outstanding activities are:

1. Samples for the intercomparison of ligand titrations have been taken and the distribution of samples will follow in due course to selected laboratories.
2. The compilation of databases for metal-binding ligand measurements by members of the working group for Co, Cu, Fe and Zn are ongoing.

3. Documents published since previous report to SCOR (e.g., peer-reviewed journal articles, reports, Web pages) and should be limited to publications that resulted directly from WG activities and which acknowledge SCOR support

In 2017, a series of 21 peer-reviewed articles were published in a second special issue in *Frontiers - Marine Science/Chemistry* related to activities of this SCOR WG. An editorial for this special issue was written by WG chairs and acknowledged SCOR support for this effort.

Some of the papers published since the last report are listed here (selection only):

- Hassler C.S., van den Berg C., Boyd P.W. Using a regional classification to provide a more inclusive examination of the ocean biogeochemistry of iron-binding ligands. *Frontiers in Marine Sciences*. DOI: 10.3389/fmars.2017.00019. 2017.
- Cabanes, D.J.E., Norman, L., Santos-Echeandia, J., Iversen, M.H., Trimborn, S., Laglera, L.M., Hassler, C.S. First evaluation on the role of salp fecal pellets on iron biogeochemistry. *Frontiers in Marine Science*. DOI:10.3389/fmars.2016.00289. 2017.
- Trimborn, S., Brenneis T., Hoppe C.J.M., Laglera, L. Norman L., Santos-Echeandia J., Völkner C., Wolf-Gladrow D., Hassler C.S. Iron sources alter the response of Southern Ocean phytoplankton to ocean acidification. *Marine Ecology Progress Series*, 578: 35-50. 2017.
- H. Waska, H. J. Brumsack, G. Massmann, A. Koschinsky, B. Schnetger, H. Simon, T. Dittmar (2018): Inorganic and organic iron and copper species of the subterranean estuary: Origins and fate. *Geochimica et Cosmochimica Acta* (in review).

- K.N. Buck, P.N Sedwick, B. Sohst, C.A. Carlson. (2017): Organic complexation of iron in the eastern tropical South Pacific: Results from US GEOTRACES Eastern Pacific Zonal Transect (GEOTRACES cruise GP16). *Marine Chemistry* 201:229-241.
- A. Tagliabue, A.R. Bowie, P.W. Boyd, K.N. Buck, K.S. Johnson, M.A. Saito. (2017): The integral role of iron in ocean biogeochemistry *Nature* 543(7643):51-59.
- E.P. Achterberg, S. Steigenberger, C.M Marsay, F.A.C. LeMoigne, S.C. Painter, A.R. Baker, D.P. Connelly, C.M. Moore, A. Tagliabue, T. Tanhua. (2018): Iron biogeochemistry in the high latitude North Atlantic Ocean. *Scientific Reports* 8 (1), 1283
- H. Whitby, A.M. Posacka, M.T. Maldonado, C.M.G. van den Berg. (In press): Copper-binding ligands in the NE Pacific. *Marine Chemistry* https://doi.org/10.1016/j.marchem.2018.05.008
- A.M. Posacka, D.M. Semeniuk, H. Whitby, C.M.G van den Berg, J.T. Cullen, K. Orians, M.T. Maldonado. (2017): Dissolved copper (dCu) biogeochemical cycling in the subarctic Northeast Pacific and a call for improving methodologies. *Marine Chemistry* 196:47-61.

4. Progress toward achieving group's terms of reference. List each term of reference separately and describe progress on each one.

1. To inform the Ocean Sciences community of this WG and related objectives via a widely distributed publication in EOS or analogous journal.

The initiation of this SCOR Working Group, including the terms of reference and overall objectives of this working group, was announced in two publications in 2012:

- S.G. Sander, K.N. Buck, and M.C. Lohan. 26 June 2012. Improving understanding of organic metal-binding ligands in the ocean. *EOS*, 93(26): 244.
- K.N. Buck, M.C. Lohan, and S.G. Sander. July 2012. Metal-binding organic ligands. *IUPAC Chemistry International*, 34(4): 23.

2. To summarize published results on all aspects of metal-binding ligands in the oceans (*e.g.,* distributions, chemical structure, sources, sinks, stability constants), and to contribute to the organic ligand database for use in biogeochemical models and for those working in the field (including results from ongoing GEOTRACES, SOLAS and CLIVAR efforts). The summary will be included in a review paper published after year 2, as well as in the database on the proposed website.

Databases for metal-binding ligand measurements have been compiled by members of the working group for Co (Mak Saito), Cu (Jim Moffett), Fe (Alessandro Tagliabue) and Zn (Maeve Lohan). The iron-binding ligand database is the most developed and an additional database for the raw titration data (Micha Rijkenberg) used to calculate iron-binding ligands has also

been initiated. A compilation review of iron-binding ligands based on these databases was published in the *Frontiers in Marine Science* special issue for this working group (http://journal.frontiersin.org/article/10.3389/fmars.2016.00221/full).

3. To expand upon the ligand intercalibration programme, initiated by GEOTRACES, to evaluate key analytical issues with currently employed methodologies and determine how to best link ongoing efforts in trace metal and organic geochemistry to assess natural metal-binding ligands.

A large intercalibration of the interpretation techniques routinely used for determining ligand concentrations and conditional stability constants from titration data was conducted, and results were published (Pizeta et al. 2015) in the first WG139 special issue. Powerful new interpretation tools developed by participants in this working group were also presented in the special issue and evaluated in the intercalibration, all of which are now freely available to download from the SCOR WG139 website http://www.marine.usf.edu/scor139/.

For field-based intercalibration efforts, large volumes of filtered seawater were collected for this purpose from the Gulf of Mexico and from the Southern Ocean. Initial analyses of these samples for dissolved metals have been done in the host lab and samples for ligand analyses and intercomparison samples will be sent to selected laboratories with known expertise in the analysis of Cu and Fe-ligands analysis by the end of 2018. The results of this intercomparison will be written up in a peer-reviewed article. This article will include a recommendation on best practices for measurements. The best practices need to be seen as a living document that will be updated and disseminated including on the SCOR WG 139 website.

4. To identify how best to incorporate published and future data into biogeochemical models.

The working group discussed several aspects of incorporating ligands into models, including how analysts can provide ligand concentrations, their sources and sinks and complexation kinetics such as the variability in conditional stability constants of iron, how to distinguish between different iron-binding ligand classes, and if trace metals compete for the same class of ligands. A paper published by Volker and Tagliabue (2015) in the first special issue examined how organic iron-binding ligands could be represented in a biogeochemical ocean models. This effort is ongoing and will be part of a new SCOR Working Group, WG151: Iron Model Intercomparison Project.

5. To debate the nature of sampling strategies and experimental approaches employed in laboratory and field efforts from different communities in workshops and meeting discussions to foster cross-fertilization of ideas across groups, capitalize on joint expertise between specialties and ultimately enhance our understanding of the links between the provenance, fate, distribution, and chemistry and biological functions of these organic metal-binding ligands in the oceans.

This working group has met annually from 2012-2014 coinciding with the February Ocean/Aquatic Sciences Meetings. Notes from each of these meetings are posted on our website. The co-chairs of this Working Group have also chaired a special session related to the working group at each of the conferences in 2012, 2014, and 2016. A Town Hall Meeting during the 2014 Ocean Sciences meeting was attended by 47 people and served to highlight accomplishments of the working group to date and engage broader community participation in working group activities. These meetings have fostered discussions on the need for improved modeling of trace metal speciation in seawater and have led to a new SCOR Working Group, WG145: Modeling Chemical Speciation in Seawater to Meet 21st Century Needs. Several members of SCOR WG139 are also members of WG145 and the new model will incorporate trace metal-organic ligand interactions across marine environments.

6. To recommend future approaches to ligand biogeochemistry in a designated symposium, including ongoing GEOTRACES field efforts (i.e., regional surveys and process studies), integration of CLE-ACSV and organic geochemistry techniques, and the need for rapid incorporation of this research in biogeochemical models. Such future recommendations will also be included in the aforementioned downloadable manual. It will also include a series of recommended downloadable digital products on multiple platforms for interpreting ACSV data.

A final two-day symposium was held for SCOR WG139 in Sibenik, Croatia. This symposium was open to the broader scientific community and was used as a platform to recommend future approaches to ligand measurements and highlight results from intercalibration and field activities. A total of 51 people attended the symposium, including 24 students and postdocs, who were each allotted time to present their research results in the field of ligand biogeochemistry. Twenty of the 51 symposium attendees also participated in a training workshop held the day before the symposium. This workshop was held at the Martinska Marine Station in Sibenik, and consisted of hands-on training in analyzing samples for metal-binding ligands and in using the state-of-the-art interpretation techniques developed in part through the activities of the working group.

7. To establish a webpage for this SCOR working group, to promote a forum for discussion of ideas and results in form of a blog, soliciting input from the trace metal biogeochemistry, organic geochemistry and modelling communities and provide a platform to propose special sessions on trace metal-binding ligands at international meetings such as Ocean Sciences, AGU and/or EGU.

A webpage was created for this SCOR working group hosted by the University of Otago. However, since co-chair Sander relocated to the Marine Environment Laboratories of the IAEA in Monaco the webpage was moved to co-chair Buck's institution, the University of South Florida http://www.marine.usf.edu/scor139/ . An email list for the WG members and another for those interested in following the working group's activities is hosted at the University of South Florida (scorwg139members@marine.usf.edu and scorwg139all@marine.usf.edu). The 'all' email list for this SCOR WG currently has 188

followers and will remain active for continued use in discussing accomplishments and activities of the working group.

8. To produce conclusions resulting from the outcome of the above objectives in the form of a Website, a journal special issue or book, and a report to SCOR.

Information regarding the webpage, see above. The first special issue resulting from this WG's activities was published in July 2015 in *Marine Chemistry*, and included 28 research articles plus an editorial (http://www.sciencedirect.com/science/journal/03044203/173). The second special issue was published in *Frontiers Marine Biogeochemistry* in June 2017 with a total of 21 research articles and an additional editorial (http://journal.frontiersin.org/researchtopic/3981/organic-ligands---a-key-control-on-trace-metal-biogeochemistry-in-the-ocean#articles). This second special has now been published as an open access e-book in summer 2017 and has been made available from the SCOR WG 139 website.

5. WG activities planned for the coming year. Limit 500 words

The official WG139 activities will finish this year, but thanks to the framework of this SCOR WG 139 the network between researchers involved has become very tight and work will continue beyond the lifespan of the SCOR WG. These include continued progress on the best practices manual for ligand measurements, and completion of speciation analyses on the intercalibration samples collected from the Gulf of Mexico and Southern Ocean.

6. Is the group having difficulties expected in achieving terms of reference or meeting original time schedule? If so, why, and what is being done to address the difficulties Limit 200 words

WG139 has met the majority of their goals under each of the original Terms of Reference and will (although outside the framework of the SCOR WG 139) continue to make progress on remaining goals moving forward. For example, samples collected and characterized for the intercalibration exercise will be send to participating laboratories in due course for the analysis of Fe and Cu ligands.

7. Any special comments or requests to SCOR. Limit 100 words.

The chairs and all full and associated members of this SCOR WG 139 would like to express our sincere thanks to SCOR, who gave us support beyond our initial application. Ed Urban went many times the extra mile to accommodate our logistical needs. Thank you for your support it was a great honor to chair this WG!