

Reports to SCOR (2020)

1. Name of group

WG145: Chemical Speciation Modelling in Seawater to meet 21st Century Needs

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

WG meeting

- The Working Group met in San Diego on 16 February 2020. The meeting report is available at <http://marchemspec.org/wp-content/uploads/2020/03/SCOR-WG145-Report-4th-Meeting-2020.pdf>

NSFGEO-NERC project *A Thermodynamic Chemical Speciation Model for the Oceans, Seas, and Estuaries*

This project (PI's Clegg, Dickson and Benway) was initiated to support the WG aims, and provides funding for thermodynamic measurements, and speciation model and software development. The first prototype software for chemical speciation modelling, including uncertainty estimates, has been completed and was presented at a lunchtime session and at the SCOR exhibition booth at the 2020 Ocean Sciences meeting in San Diego.

Experimental measurements

- Collaboration between Dickson's laboratory at Scripps and the national standards laboratories in France, Germany, Japan and USA has continued, with a focus on intercalibration of Harned cell measurements.
- Pablo Lodeiro, working in Achterberg's laboratory at GEOMAR has extended the Tris solubility measurements to include the solubilities of Tris in TrisHCl and (Tris)₂SO₄ at different concentrations and temperatures.
- Martha Gledhill has characterised the acid-base properties of natural organic matter concentrated from seawater, and has developed a preliminary chemical speciation model for this material using the NICA-Donnan approach.

Collaborations

- SCOR/IAPSO/ICPWS Joint Committee on the Properties of Seawater: WG members Frank Bastkowski, Simon Clegg, Andrew Dickson, Frank Millero and Daniela Stoica are members of this committee, which has a particular interest in establishing SI-traceability for seawater pH: the modelling developments of WG145 will contribute to this goal.
- Andrew Dickson leads a newly established IAPSO Best Practice Study Group on seawater "pH" measurement, which will complement the work of WG145 on modelling seawater pH buffers.
- Collaborators at the University of Bristol, UK, have made measurements of the osmotic coefficients of Tris in water, complementing the solubility measurements made by Pablo Lodeiro (above).

Conference presentations

- Matthew Humphreys, Andrew Dickson, David Turner and Simon Clegg: Modelling Chemical Speciation in Seawater pH Buffers, Standard Seawater and Other Natural Waters: Applications and Uncertainties. eLightning presentation at Ocean Sciences 2020.

- Pablo Lodeiro, David Turner, Simon Clegg, Lucia González and Eric Achterberg: Determining the Pitzer interaction coefficients of TRIS in aqueous solutions of NaCl, TrisHCl and (TrisH)₂SO₄ by solubility measurements. A new experimental contribution towards the development of a traceable chemical speciation model of pH buffers used for applications involving seawater and other natural waters. Poster at Ocean Sciences 2020.

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

The prototype chemical speciation modelling software demonstrated at the 2020 Ocean Sciences Meeting has been published at the web address www.aim.env.uea.ac.uk/osm/main_page.html

4. Progress toward achieving group's terms of reference. List each term of reference separately and describe progress on each one. Limit 1000 words

1) To document the current status, and basis in laboratory measurements, of Pitzer models of seawater and estuarine water focusing on the chemistry of ocean acidification and micronutrient trace metals (including, but not limited to, Fe, Cu, Mn, Cd, and Zn). Current capabilities and limitations for oceanographic and biogeochemical calculations will be defined, and future needs established. Important gaps in knowledge, which should have high priority for new measurements, will be identified. The components to be covered will include the seawater electrolytes, the selected trace metals, and buffer solutions and key organic ligands such as those used in CLE-CSV titrations.

Documentation is complete for Tris buffers in artificial seawater, and for the seawater electrolyte.

2) To publish the results of the first term of reference in the refereed scientific literature, and to introduce the conclusions and recommendations to the oceanographic community at a "town hall" event or special session at an international ocean sciences meeting.

The WG hosted a Town Hall at the 2016 Ocean Sciences meeting, and a lunch session at the 2020 Ocean Sciences meeting presenting the prototype chemical speciation modelling software. The prototype software was made available at the SCOR exhibition booth at the 2020 meeting. The WG's progress is reported as updates to the website <http://marchemspec.org>

3) To specify the functions and capability for a web-based modelling tool that will make chemical speciation calculations easily accessible for a wide range of applications in oceanography research and teaching, and thus improve understanding and spread best practice in modelling.

The results of the web survey of potential users is guiding the software development, and will be described in a paper planned for the Research Topic "Best Practices in Ocean Observing" in the journal *Frontiers in Marine Science*.

4) To implement the web-based tool for chemical speciation calculations, based upon the specification developed in the third term of reference which will also be used to obtain external funding to develop the programs, documentation, and site.

Prototype software, including the estimation of uncertainties, was presented at the 2020 Ocean Sciences meeting.

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

We have identified four activities that will be required in order to fulfil our Terms of Reference:

- Extend the modelling to the trace metals identified in the ToR, together with key organic ligands: *trace metals to be completed in the coming year; key organic ligands in 2021/22*
- Document key knowledge gaps: *most to be completed in the coming year; key organic ligands in 2021/22*
- Complete the “Best Practice” paper: *to be done in the coming year*
- General release of the chemical speciation modelling software, supported by webinars and other forms of community engagement such as the working group website (marchemspec.org) and communications to relevant international networks (e.g., OCB, SCOR, GEOTRACES, etc.) - *early 2022*

Additional activities, beyond the Terms of Reference, for the coming year:

- Publish the Tris solubility work
- Publish the work on estimation of uncertainties
- Continue with our collaborators to make Harned cell measurements relevant to artificial seawater buffers and begin writing up this work
- Further work on modelling the chemistry of natural organic matter, and integration of the NICA-Donnan approach with a Pitzer model.
- WG145 has been invited to contribute to a proposed GESAMP Working Group on the effect of climate change on contaminants in marine systems, although this initiative is expected to be delayed due to the Coronavirus pandemic

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

The WG proposal noted that completion of the Terms of Reference would require significant additional funding, and that obtaining this funding could result in a delay. A large grant from the prestigious NERC/NSF joint programme was awarded in 2017, which provided necessary core funding for analyses and speciation model development. As noted above, we have also developed extensive collaborations with other institutions and national metrology laboratories that have made substantial in-kind contributions to our experimental programme. The NERC/NSF project will end in early 2022. We plan to complete the Terms of Reference with a software release at that time. As such, we respectfully request an extension of WG145 to April 2022, which we anticipate will be mutually beneficial, since the new chemical speciation software would be clearly seen as a product of a SCOR activity, which would in turn enhance the status and visibility of the software and encourage its use in the broader oceanographic community.

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

This WG has been effective in building a research community focused on chemical speciation in marine waters. Participants in the WG meeting in 2020 expressed interest in continued collaboration

beyond the life of the WG, which will continue to enrich the experiments and model development that is underway. Furthermore, speciation model survey respondents and participants of the 2016 and 2020 Ocean Sciences events have requested regular communication via an email list (currently ~100 members) to remain informed of new developments on the project.

Coronavirus pandemic: The WG members working on the remaining tasks in the Terms of Reference are currently working from home due to government restrictions. While future developments are hard to predict, we do not currently expect the pandemic to significantly affect the timetable for ToR completion. Planned experimental work outside the ToR that is supporting further model development will, however, be delayed