Template for Annual SCOR Working Group Reports to SCOR

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 held an online meeting on 21 June 2021 attended by 13 WG members and four guests. The meeting reviewed progress towards the WG's terms of reference and concluded that the WG is on track to complete its terms of reference in 2022. Reports from collaborative projects were also presented. The meeting discussed the need for further work on model development following completion of the SCOR terms of reference next year. It was agreed to hold the next online meeting in March 2022.

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

- This project (PIs 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.
- The project organises fortnightly video meetings, which are also attended by the WG145 leadership to facilitate joint review and planning for both the project and WG145.

Experimental measurements

- Collaboration between Dickson's laboratory at Scripps and the national standards laboratories in France, Germany, Japan and USA has continued: the programme of measurements relevant to Tris buffers is expected to be completed within the next 6 months.

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 an IAPSO Best Practice Study Group on seawater "pH" measurement, which will complement the work of WG145 on modelling seawater pH buffers.
- WG145 has been asked to contribute to the newly established GESAMP Working Group 45 "Climate Change and Related Impacts on Contaminants in the Ocean"
- We have begun discussions on collaboration on modelling and new measurements with researchers at UC Santa Cruz (Hain) and University of Hawaii (Zeebe)

- Our initial modelling results for Tris pH buffer solutions provide valuable assistance to the new EU project "SApHTIES: Metrology for standardised seawater pHT measurements in support of international and European climate strategies"

Conference presentations

- Poster presentation at the Ocean Carbon and Biogeochemistry online meeting in June 2021. M.P. Humphreys, J.F. Waters, D.R. Turner, H. Benway, A.G. Dickson, and S.L. Clegg. Chemical Speciation Models Including the Propagation of Uncertainties: Application to the Marine 'Total' pH Scale

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

Lodeiro P., Turner D.R., Achterberg E.P., Gregson, F.K.A, Reid J.P, and Clegg S.L. (2021). Solid–Liquid Equilibria in Aqueous Solutions of Tris, Tris-NaCl, Tris-TrisHCl, and Tris-$(TrisH)_2SO_4$ at Temperatures from 5 to 45 °C. Journal of Chemical & Engineering Data, 66(1): 437-455. https://doi.org/10.1021/acs.jced.0c00744

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 documentation noted in #1 above will be published in three papers: one covering artificial seawater; one covering Tris buffers; and one covering the full seawater electrolyte. The first of these papers is now complete "Chemical Speciation Models Based Upon the Pitzer Activity Coefficient Equations, Including the Propagation of Uncertainties: Artificial Seawater from 0 to 45 °C" (M.P. Humphreys, J.F. Waters, D.R. Turner, A.G. Dickson and S.L. Clegg). This manuscript is in internal review at the US National Institute of Standards and Technology (necessary since one co-author is a NIST employee) before submission to *Marine Chemistry*. The other two papers are in preparation and will be submitted during 2021

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. Work has started on "packaging" the code to be accessible from different programming environments including Python, Matlab and Excel as well as Fortran

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, and which we plan to complete before the 2022 SCOR meeting:

- Complete and submit the papers on Tris buffers and the seawater electrolyte; extend the modelling to the trace metals identified in the ToR, together with key organic ligands
- Document key knowledge gaps for trace metals and key organic ligands
- Complete and submit the "Best Practice" paper
- 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.)

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

- 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.
- Contribute to the work of GESAMP Working Group 45 "Climate Change and Related Impacts on Contaminants in the 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

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. An important set of measurements (of Tris buffer in aqueous NaCl) was completed by PTB late in 2020.
The NERC/NSF project currently ends in early 2022. It is likely that the PI's will apply for an extension given that the transfer of the experimental programme to NIST has taken a year to arrange, and measurements are expected to begin only in the 3rd quarter of 2021.
We plan to complete the Terms of Reference with a software release in mid 2022. As such, we respectfully request an extension of WG145 to the 2022 SCOR meeting, 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 and the online meeting in 2021 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.

Additional information can be submitted and will be included in the background book for the SCOR meeting at the discretion of the SCOR Executive Committee Reporter for the WG and the SCOR Secretariat.