

Template for Annual SCOR Working Group Reports to SCOR

Summary:

WG145 is working towards the first release of freely available software for chemical speciation calculations, including uncertainty estimates, in late 2022. The systems that can be modelled include artificial seawater (Na, Mg, Ca, K, Cl, SO₄); Tris buffers in artificial seawater; and the full seawater electrolyte (Na, Mg, Ca, K, Sr, Cl, SO₄, CO₃, B(OH)₃, Br, F) together with the GEOTRACES core elements (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Si, P). “Wrappers” will be available to allow the calculations to be integrated into Fortran, MATLAB and Python.

Full documentation of the chemical speciation models is in the process of publication: papers on artificial seawater and Tris buffers are published; a paper on the seawater electrolyte has been submitted for publication and a paper on the GEOTRACES core elements is in preparation. Each of these papers includes an assessment of the model performance against published data together with priorities for future work to improve the model. For the Tris buffers this work is already under way in collaboration with the National Metrology Institutes of Germany, Japan and the United States.

WG145 will have fulfilled its terms of reference with this first software release and will then be disbanded. In order to maintain a respected international affiliation for further development of the software and the model parameters, it has been proposed that the IAPWS/SCOR/IAPSO Joint Committee on the Properties of Seawater (JCS) establish a new Taskgroup on chemical speciation. JCS, SCOR and IAPSO have approved this proposal: a decision from IAPWS is expected this autumn.

1. Name of group

WG145: Chemical Speciation Modelling in Seawater to Meet 21st Century Needs (MARCHEMSPEC)

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

- Preparation of papers describing the chemical speciation model (see sections 3 and 5).
- Software development
- Collaboration with NIST to complete the measurements required for improvement of the speciation model for Tris buffers in artificial seawater.
- Annual WG meeting, 23 February 2022, Zoom, 10 participants. The main focus of the meeting was the plan to continue the MARCHEMSPEC initiative as a Taskgroup within the IAPWS/SCOR/IAPSO Joint Committee on the Properties of Seawater

- Fortnightly meetings between the WG145 leadership and the NSFGEO-NERC project A Thermodynamic Chemical Speciation Model for the Oceans, Seas, and Estuaries (PI's Clegg, Benway and Dickson)
- Conference presentations:
 - Ocean Sciences Meeting (OSM) 2022. A talk was presented, entitled: *An Examination of Assumptions Underlying the Definition of 'Total' pH, and Implications for Measured Carbonate Dissociation Constants in Seawater.*
 - Ocean Carbon & Biogeochemistry (OCB) working group *Ocean Carbonate System Intercomparison Forum* (OCSIF): the OSM 2022 presentation was repeated, followed by contributions of WG 145 Vice Chair Simon Clegg to the discussion. He will also contribute to the OCSIF white paper that is being prepared.
 - International Bureau of Weights and Measures (BIPM). An abstract has been submitted to the Metrology for Climate Action Workshop to be held at the BIPM annual meeting in September 2022. This describes the collaboration between WG 145 and members of the national metrological institutes of the USA, France, Germany, and Japan. The abstract is entitled: *Metrological Needs for Traceable Oceanic pH Measurements*.
 - 5th International Symposium On The Ocean In A High CO₂ World. An abstract has been submitted to this meeting, to be held in September 2022, and is entitled: *A New Chemical Model to Constrain the Impacts of Ocean Acidification in Aquatic Systems: Application to pH and the Carbonate System.*

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

- Matthew P. Humphreys, Jason F. Waters, David R. Turner, Andrew G. Dickson, Simon L. Clegg. Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties: Artificial seawater from 0 to 45 °C. *Marine Chemistry*, 244, 104095 (2022). <https://doi.org/10.1016/j.marchem.2022.104095>
- Simon L. Clegg, Matthew P. Humphreys, Jason F. Waters, David R. Turner, Andrew G. Dickson. Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties. II. Tris buffers in artificial seawater at 25 °C, and an assessment of the seawater 'Total' pH scale. *Marine Chemistry*, 244, 104096 (2022). <https://doi.org/10.1016/j.marchem.2022.104096>

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. A first draft of the documentation for the GEOTRACES core elements has been completed.

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 four papers: one covering artificial seawater; one covering Tris buffers; and one covering the full seawater electrolyte. The first two papers, covering artificial seawater and Tris buffers have now been published. The third paper, covering the seawater electrolyte has been submitted to *Marine Chemistry*. Work is under way on the fourth paper, covering the GEOTRACES core elements.

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. Presentations at the 2020 and 2022 Ocean Sciences Meetings, and also at the 2021 virtual OCB summer workshop, have been used to spread information to the scientific community. The WG's progress is reported as updates to the website (<http://marchempspec.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.

This software will be released towards the end of 2022, see section 5 below.

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

- Following the two published papers on speciation modelling, a third paper describing the chemical speciation model for the full seawater electrolyte (components Na, Mg, Ca, K, Sr, B(OH)₃, Br, Cl, CO₃, F, SO₄) has been submitted to *Marine Chemistry*
- A planned fourth paper will cover the GEOTRACES core elements (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, PO₄, Si(OH)₄). A first draft of the documentation of the equilibrium constants and Pitzer coefficients for these elements has been completed, and work on the paper is under way.
- The first version of the chemical speciation software will be released towards the end of 2022, with a further release (with enhanced features) likely in mid 2023. This will include all the material described in the four completed and planned papers listed above. The software will be freely available to run stand-alone or with “wrappers” allowing it to be integrated with Fortran, MATLAB, and Python. The output from the software will include estimates of the

uncertainty in the calculated results. It is likely that the software will be available initially as downloads from the WG 145 website marchemspec.org.

- Looking forward, we have identified the Symposium for the Ocean in a High-CO₂ World and the annual OCB summer workshop as opportune venues to reach a broad community of prospective speciation model users. We will be considering other events in 2022-2023 as more information becomes available.

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

We are on track to release the first software version by the end of 2022, thus fulfilling our terms of reference. In order that this first software release can be designated as a SCOR product, we propose that WG145 is not disbanded until after the software release.

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

In order to continue the development of the software and the underlying chemical speciation model, it has been proposed to establish a chemical speciation Taskgroup within the IAPWS/SCOR/IAPSO Joint Committee on the Properties of Seawater. SCOR and IAPSO have approved this proposal: a decision from IAPWS is awaited. It is anticipated that this Taskgroup will begin its work when WG145 is disbanded following the software release.

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.