MORNING SESSION

The material presented during the morning can be found at the end of this report, so these notes summarise the discussion only.

1. Review Terms of Reference (David)

- The ToR describe our commitment to SCOR, based on the Working Group proposal. Progress towards fulfilment is reviewed in #10 below.

2. WG Timeline (Simon)

- Discussion points have been moved to the relevant detail sections.

3. Pitzer model overview (David)

- Questions: can the model include precipitation reactions and sea-ice systems? David and Simon explained that these are potential extensions to be considered in the future (the solver used is readily applicable to precipitation reactions), and the output from the current model can readily be used to assess the saturation state of specific solid phases. It was pointed out that calculations of the model below 5°C are hampered by lack of data: they can be done, but accuracy is reduced relative to temperatures closer to 25˚C.
- The lack of adequate data on the interactions of TRIS and $TRISH^+$ with the components of artificial seawater provided the starting point for new measurements discussed in sections 4 and 5.
- Wei-Jun took up the problem of modelling very low salinity waters, in particular the transition between total scale pH measurements in saline waters and NBS scale measurements in fresh waters. The total pH measurements do not extrapolate to the measured NBS pH in freshwaters. The discussion concluded that this is because the NBS scale, unlike the total pH scale, is not concentration-based (rather, it is a measure of H^+ *activity*), indicating an incompatibility between pH measurements in saline and fresh waters. This would be a good topic for discussion in the upcoming IAPSO Study Group (#10 below).

4. Solubility Experiments (Pablo)

- Analysing and modelling the results of the extensive measurements of solubilities in the TRIS/NaCl system have proved problematic: inclusion of the unusual TRIS-TRIS-Na interaction provoked discussion. This is the result of a data fitting exercise and does not provide any evidence of a physical interaction: this would require other methods such as spectroscopy, but is not needed for our purposes.
- Andrew asked about TRIS-Na complexation as an alternative approach. Simon replied that the TRIS-Na interaction is relatively weak and best treated with Pitzer coefficients, while Ca and Mg interactions are much stronger (with negative coefficients), which are generally indicative of complexation. Indeed, complexation of Mg^{2+} by TRIS has been measured in the past.

- David reported that Flo Gregson at Bristol University has recently measured the osmotic coefficient of TRIS in water at a range of concentrations well into supersaturation. In the range 1 – 10 mol/kg, these data are well fitted with interaction coefficients for TRIS-TRIS and TRIS-TRIS-TRIS. Preliminary results from the inclusion of these coefficients in our data analysis indicates a much improved quality of fit at TRIS concentrations up to 6 mol/kg, but large residuals at higher concentration. If confirmed, these data would indicate that TRIS self-interactions at higher concentrations are not readily explained by the current Pitzer formulation. However, this problem encountered at high concentrations is not relevant to modelling of TRIS buffers in artificial seawater. Furthermore, the Bristol measurements have large uncertainties, and not consistent with a small set of isopiestic measurements of the osmotic coefficient.
- Arthur asked whether TRIS would interact with organic acids in coastal systems. Almost certainly, but here we are only aiming to model TRIS in organic-free artificial seawater.

5. Collaboration with National Metrology Institutes. (Simon)

- Daniela described the JPI intercomparison that was noted on the second LNE slide. This was for pH, and she spoke of 3 "nodes": primary standard; calibration laboratories; and end users making observations. At the "calibration" level the solutions were measured by IFREMER, IOW and NIVA. LNE calculated the uncertainty budget for pH measured potentiometrically. NIVA encountered technical problems. Data are still being processed.
- Frank discussed a traceability chain for pH(T), and referred to the work on low salinity buffers with IOW.
- Regina reported that purified m-cresol (99.95% purity) has been bottled, but not yet priced. NIST are carrying out experiments in which the ratio of TRIS to $TRISH^+$ is varied giving pH values in the range 7.3 to 8.2. The temperature range is 5 - 45°C.

6. Best practices paper on chemical speciation modelling (David)

- There was general support for the revised paper outline, with the preferred journal still being Frontiers in Marine Science and their Best Practice topic. Eric noted that the publication charge for this topic has been reduced. SCOR funds only one publication charge per Working Group, so since this would be our second paper we need to look elsewhere for funds.
- The paper should include illustrate the argument with real-life examples. Estuarine systems, where CO2SYS can struggle, would be a good starting point. It was emphasised that such concrete examples in the paper, with step by step instructions for repeating the calculations, are essential.
- A key advantage that should be illustrated is the ability to model the CO_2 system and trace metal speciation in an integrated fashion. Regular CO2SYS users – those who work almost exclusively with seawater of standard

composition - are expected to be one of the harder groups to convince of the merits of our approach.
- The discussion of uncertainties should be placed in context of user needs – what levels of uncertainty are acceptable for specific applications.
- The potential for using the software as a management tool / decision support tool when interpreting environmental monitoring data should be highlighted (e.g., pH used as an indicator variable of "good environmental status").
- Stoichiometric and thermodynamic approaches and not necessarily mutually exclusive; e.g. stoichiometric constants may need to be incorporated where data are scarce, and the thermodynamic approach can be used to adjust measured stoichiometric constants for changes in the composition of the ionic medium, i.e., to that of the natural water of interest. The demonstration programs we have placed on the web are an example of this
- Documentation of all the constants and coefficients used in the model is essential in order that speciation calculations can be repeated, and that complementary calculations can be made using exactly the same model.

7. Software tools and codes (Simon)
- Andrew asked whether it would be possible to include uncertainties in the input composition in the overall uncertainty budget. Simon agreed that this is important to include, and will be added to the model
- Andrew also asked whether the concentrations of HCO_3^- or CO_3^{2-} could be used as composition inputs for inorganic carbon. Simon replied that this would be possible if needed. It was noted that this option is to be included in CO2SYS.
- The presenters should collect comments and suggestions from the "software testers" at the SCOR booth.

8. IAPWS/SCOR/IAPSO Joint Committee on Seawater (Andrew)
- The new IAPSO Study Group may contribute to our compilation of knowledge gaps and research needs

9. NICA-Donnan modelling of marine OM (Martha)
- David asked about interactions with Ca and Mg – initial measurements suggest that these are too weak to measure
- Peter asked about the preconcentration method – the column used takes up primarily hydrophobic material, about 40% of the total DOC. Discussion of the possibility of also targeting hydrophilic material.
- There was some discussion to dispel the misapprehension that this type of model could be applied to TRIS thermodynamic behaviour.

10. Progress on ToR (David)
- No specific discussion: actions arising are documented in #11 below.

AFTERNOON SESSION

11. Completing the ToR

A realistic timescale for fulfilling the remaining elements of ToR is the time period of the NERC/NSF project, which provides the major framework and funding source for this work. Following extension, the project is now planned to run until February 2022. Although our SCOR money has all been used, we see that continuation of our status as a SCOR Working Group until early 2022 would be a win-win arrangement:

- SCOR would benefit from the 2022 software release being clearly labelled as a SCOR product
- The SCOR association would enhance the status of the software release, substantially improving the prospects for adoption by the marine science community

The case will need to be out to SCOR in our annual report, which will be due in April/May. The SCOR meeting is in October, after which we will get a response to our proposal. Important points that should be made in addition to the win-win argument:

- We have attracted external funding central to our ToR (NERC/NSF project)
- We have attracted collaboration from partners who provide substantial additional support from their own resources (NMIs, GEOMAR)
- We have been very productive, and are on course to fulfil our ToR within the coming 2 years
- We should state what additional achievements, over and above the current ToR, there will be if we are granted an extension. Example: the improvements to the models made using the data provided by our NMI and GEOMAR partners.
- We have established effective collaboration with JCS; we have a strong presence in a recently approved IAPSO Study Group on seawater pH measurements; we have been invited to participate in a planned GESAMP Working Group on the effects of climate change on contaminants in seawater
- Collaboration within the WG and our partners has generated a community of marine speciation scientists who are keen to continue collaboration in the longer term
- The unusually long WG lifetime that we are proposing is in large part due to the time taken to generate the necessary external funding in the form of the NERC/NSF grant, and to accommodate the timetables of our partners The need for external funding, and the risk that it would result in delays to the WG work, was highlighted in the WG proposal.

The work remaining to fulfil our ToR commitments to SCOR can be organized under four headings (see # 10 in the morning material):

a) <u>Extend the model to trace metals (the GEOTRACES core metals) and key organic ligands</u>.
Inorganic complexation of trace metals is included in the Pierrot & Millero model, but the data sources and coefficient values should be confirmed as has

been done for the TRIS/artificial seawater and seawater electrolyte systems as described in #3 of the morning material. The key (CLE/CSV) ligands are more challenging since earlier searches by David and Peter have noted that the thermodynamic data are sparse and /or scattered. Martha's project (morning material #9) will provide some information on complexation by natural organic matter. Peter also noted that WG139 has assembled a good deal of data on trace metal complexation by marine organic matter.
Lead responsibility: David and Peter

b) Document major knowledge gaps
Much of this has already been done, but not documented in a complete form. The organic ligands discussed above will probably contribute. Paper(s) describing the software, and the uncertainty treatment, may provide routes to publication.
Lead responsibility: Simon

c) Complete the Best Practice paper
The outline in the morning material #6, together with the discussion earlier in this report, give the guidelines for this work. The work will be carried out by two groups:
Writing Group: David, Simon, Matthew, Andrew and Eric
Internal review group: Peter, Wei-Jun, Arthur, Regina and Maite
Lead responsibility: David

d) General release of the software in early 2022
This will not be in any way a final version, but will provide much of the planned capabilities. We discussed options for a high-profile launch of the software. One obvious option is the next OSM (February 2022), but this will be in Honolulu. Difficult for us with no remaining SCOR funding; it is also generally a less attractive location due to cost and long travel times. We therefore concluded that Webinars would provide a better option. Here we need to target two communities: operational oceanographers and research oceanographers. Operational oceanographers can be targeted by contributing to the GOOS Webinar series. For research oceanographers we can use our existing contact fora (SCOR, OCB, GEOTRACES etc.). Heather has access to software for Webinar generation. Peter raised the question of raising awareness outside Europe and North America. Unfortunately our South American members were unable to come to San Diego. David suggested that we talk to Elena Masferrer Dodas at the GEOTRACES IPO who organized excellent advance publicity for the launch of the first GEOTRACES data product as an OSM Town Hall.
Lead responsibility (software): Simon
Lead responsibility (Webinar and PR): Heather

We also discussed upcoming meetings where it would be good to have a presence:

- High-CO_2 World Meeting Sept 7-10 (Lima) – abstracts due in March. Andrew and Matthew may attend. This meeting clashes with the next JCS meeting in Turin: Simon will probably go to the Turin meeting
- GOA-ON meetings just before the High CO_2 World Meeting (also in Lima). Andrew may attend
- ICOS meeting, Utrecht, September. Matthew may attend if not going to Lima
- CERF meeting in Fall 2021, Richmond, VA. Regina will attend.

12. Plans and timelines for ongoing activities

- The NERC/NSF project.
  - Finish the core science (uncertainties)
  - Coding for the 2022 software release
  - Paper on uncertainties
  - Contribute to writing up existing data from NMIJ and GEOMAR (Pablo)
  - Following Ellen's resignation, work on the Harned cells at SIO has progressed very slowly, although some testing is being done to resolve the difficulties recently encountered (and likely attributable to the Cl- electrode). There are ongoing discussions as to how we should proceed.
  - There are no solid plan to address the bisulphate constant, which is however important. Simon noted that the uncertainty can make a difference of 0.01 in calculated pH.
- National Metrology Institutes
  - The intercalibration of Harned cell measurements needs to be completed
  - NMIJ have already contributed their planned Harned cell measurements
  - LNE cannot provide new measurements without external funding
  - PTB: in other conversations Frank said they still haven't got to the bottom of the offsets they are encountering in measured emfs, which are just outside the acceptable range. This will probably delay the WG 145 experiments, due to a backlog of other work, but PTB are committed to contributing the planned WG145 work
  - NIST have Harned cells ready, with electrodes working well. Highest priority is the measurements under way (see #6 above), which must be finished by June. After that there is scope for additional Harned cell work in support of WG145.
- GEOMAR
  - Pablo: priority is to write up the solubility data together with David and Simon. Additional work (e.g. TRIS-Mg and TRIS-Ca interactions) would need new money
  - Martha: more testing of Ca and Mg interactions; will have data to look at organic contributions to total alkalinity but this is not a priority. Work will focus on variability in the preconcentration and characterization of pre-concentrated DOM; improving methods for

metal-pH titrations; and applying this knowledge to test environments (e.g. the Amazon estuaries)

- The IAPSO Study Group led by Andrew will meet in in conjunction with the next IAPSO conference in Korea, July 2021, following the preliminary meeting in San Diego this week.
- The Joint Committee on Seawater will continue to focus on SI-traceability of seawater pH measurements. Here Daniela took up the question of the use of Pitzer equations vs. the Bates-Guggenheim hypothesis to define chloride activity coefficients needed to obtain pH from measured acidity functions of pH buffers. A discussion is ongoing, but it may be possible to determine in which ionic strength range the two approaches provide closely similar values. A difficulty, however, is that it is unlikely that there are Pitzer parameters for solutions of the substances used, even for common pH buffers.

13. New initiatives

- Sylvia reported on a proposed GESAMP Working Group on effect of climate change on contaminants in marine system, to include Ocean Acidification and knock-on effects on speciation and solubility, including radionuclides. The proposal has been well received and is expected to be approved at the upcoming GESAMP annual meeting in Monaco in September. The proposal will be highlighted in a side event at the GESAMP meeting. WG145 is welcome to participate in the side event and in the new WG if approved. David, Peter and Eric expressed interest. Sylvia will pass on further information to the SCOR WG.

14. Future collaborations

- Most of those present expressed in remaining in contact even after we lose SCOR affiliation. Since we have no funding for this, we will focus on virtual meetings and opportunistic in person contacts at conferences. Future JPI calls may provide a mechanism within Europe, and there may be opportunities for joint funding of software development and applications.
- Options for virtual meetings:
    - SCOR GoToMeeting licence, which we can continue to use while we have SCOR affiliation
    - Zoom is free for meetings of up to 40 minutes. The University of Gothenburg has a licence for Zoom, which should provide better options. David will look into this.
    - WHOI has a licence for Webex. Heather will look into this.
    - The NERC/NSF project will continue biweekly telephone meetings.
    - We should convene virtual meetings of the whole group or subgroups as necessary with relevant subgroups addressing specific issues
- Simon will continue to maintain the SCOR WG website marchemspec.org. It would be good if this could be used to provide updates to the group at regular intervals (e.g. quarterly).
- We have number of different Dropboxes: David will look at rationalizing this.

- David will put together a summary of this meeting based on his notes and those of Heather and Simon
- This report will go first to the meeting participants with an invitation to suggest corrections, and to indicate interest in future collaboration
- The report will then go to the remaining WG members, and to guests at previous meetings, for information and with an opportunity to indicate interest in future collaboration.

PARTICIPANTS

WG members
David Turner
Simon Clegg
Sylvia Sander (via video link)
Heather Benway
Arthur Chen
Andrew Dickson
Eric Achterberg
Martha Gledhill
Peter Croot (not whole meeting)
Regina Easley
Frank Bastkowski
Daniela Stoica (via video link)

Guests
Matthew Humphreys (NIOZ/UEA)
Wei-Jun Cai (U Delaware, not whole meeting)
Pablo Lodeiro (GEOMAR)
Kechen Zhu (GEOMAR)

SCOR
Ed Urban (parts of meeting)
Patricia Miloslavich (parts of meeting)

WG145 February 2020

Morning agenda

Guide time	No.	Subject	Presenter
08:30		Presentation of participants	
08:40	1	Review the Terms of Reference, which is our commitment to SCOR	David
08:50	2	Summary timeline of the WG, from the beginning, indicating where/when/how the items below contribute to the WG	Simon
09:10	3	Pitzer models for seawater and TRIS/artificial seawater buffers based on work from Frank Millero's group	David
09:20	4	New TRIS interaction parameters	Pablo
09:40	5	Collaboration with national standards labs	Simon
10:00		Break	
10:30	6	"Best Practice" paper	David
10:50	7	Development of software tools and codes	Simon
11:10	8	Collaboration with IAPWS/SCOR/IAPSO Joint Committee on Seawater	Andrew
11:30	9	NICA-Donnan modelling of marine organic matter	Martha
11:50	10	Review progress towards the Terms of Reference	David
12:00		Lunch	

WG145 February 2020

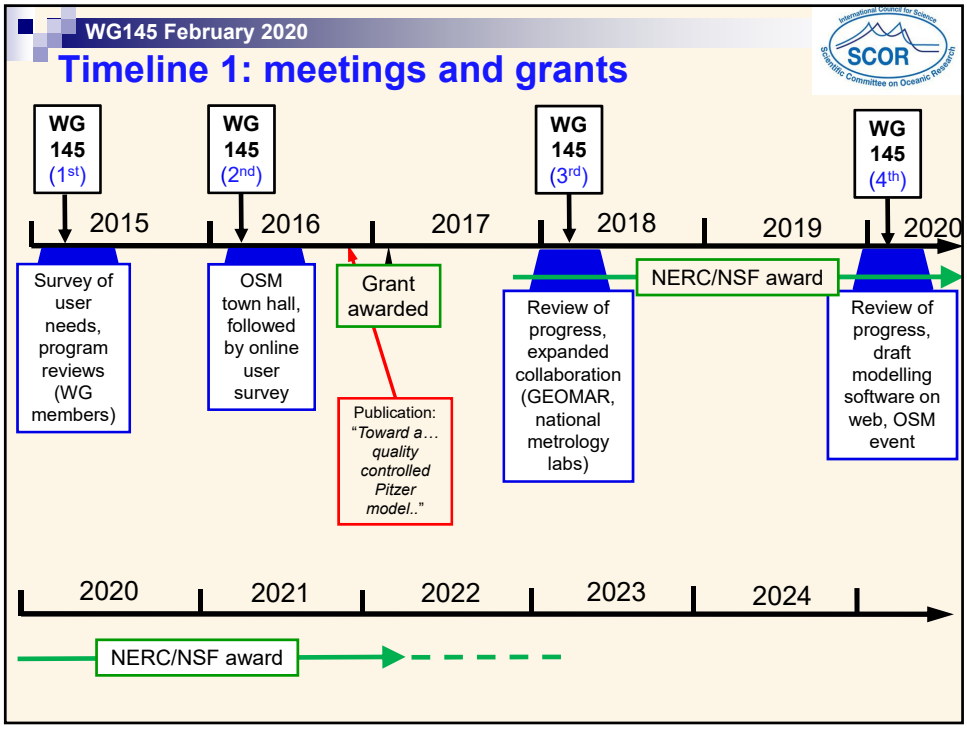
1. Terms of Reference (David)

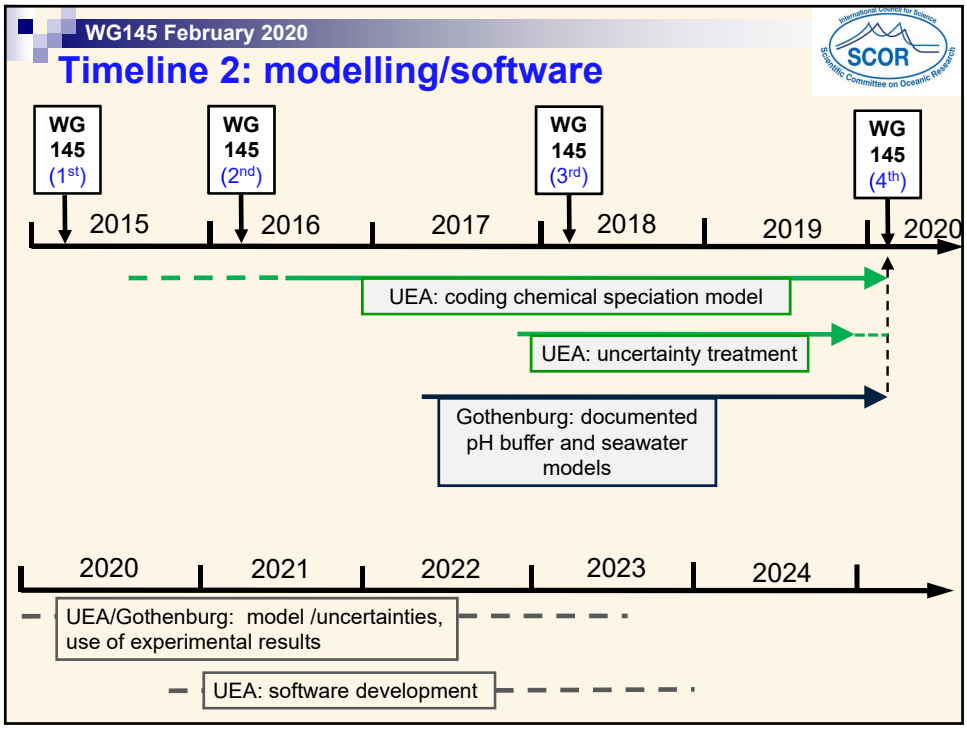
WG145 February 2020

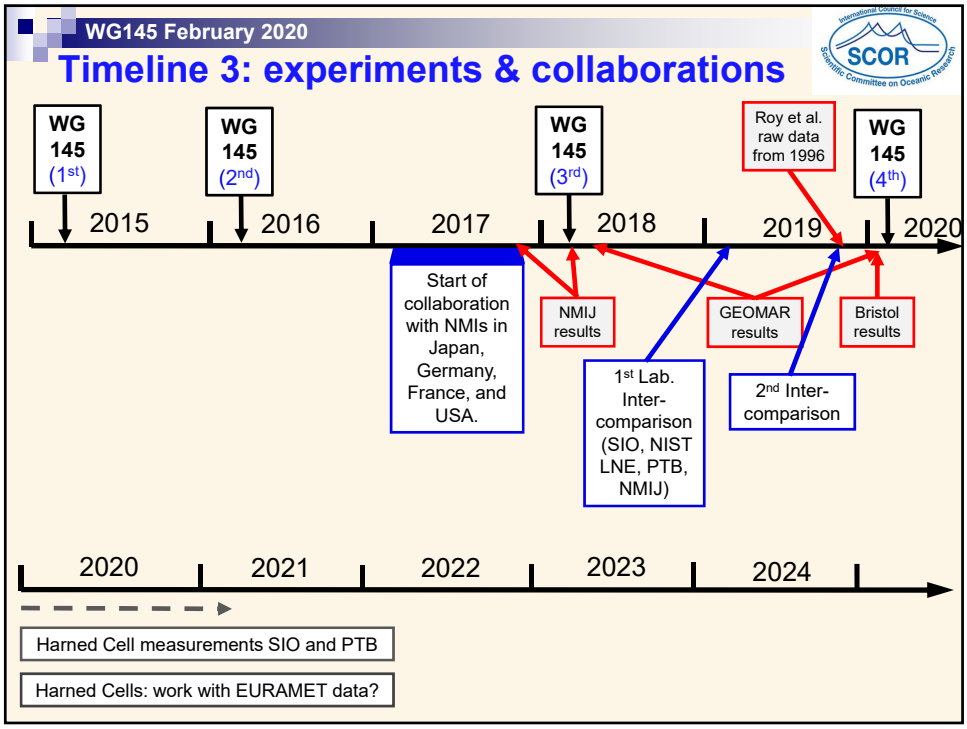
Terms of Reference	
1.	To document the current status, and basis in laboratory measurements, of Pitzer models of seawater and estuarine water focusing on the chemistry of ocean acidification and micronutrient trace metals (including, but not limited to, Fe, Cu, Cd, Co, Mn, and Zn). Current capabilities 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.
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.
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
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.

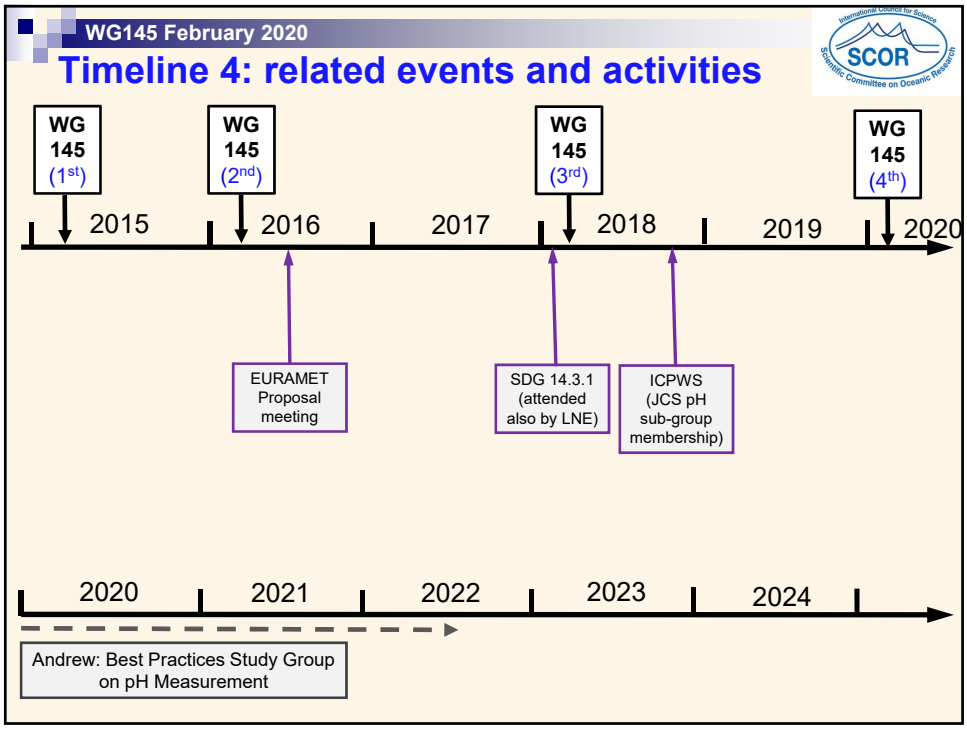
WG145 February 2020

2. Summary timeline of the Working Group (Simon)


WG145 February 2020
Timeline 1: meetings and grants
WG 145 (1st)
WG 145 (2nd)
WG 145 (3rd)
WG 145 (4th)
2015
2016
2017
2018
2019
2020
Survey of user needs, program reviews (WG members)
OSM town hall, followed by online user survey
Grant awarded
Publication: "Toward a… quality controlled Pitzer model.."
Review of progress, expanded collaboration (GEOMAR, national metrology labs)
NERC/NSF award
Review of progress, draft modelling software on web, OSM event
2020
2021
2022
2023
2024
NERC/NSF award


WG145 February 2020
Timeline 2: modelling/software
WG 145 (1st)
WG 145 (2nd)
WG 145 (3rd)
WG 145 (4th)
2015
2016
2017
2018
2019
2020
UEA: coding chemical speciation model
UEA: uncertainty treatment
Gothenburg: documented pH buffer and seawater models
2020
2021
2022
2023
2024
UEA/Gothenburg: model /uncertainties, use of experimental results
UEA: software development


WG145 February 2020
Timeline 3: experiments & collaborations
WG 145 (1st)
WG 145 (2nd)
WG 145 (3rd)
WG 145 (4th)
Roy et al. raw data from 1996
2015
2016
2017
2018
2019
2020
Start of collaboration with NMIs in Japan, Germany, France, and USA.
NMIJ results
GEOMAR results
Bristol results
1st Lab. Inter-comparison (SIO, NIST LNE, PTB, NMIJ)
2nd Inter-comparison
2020
2021
2022
2023
2024
Harned Cell measurements SIO and PTB
Harned Cells: work with EURAMET data?


WG145 February 2020
Timeline 4: related events and activities
WG 145 (1st)
WG 145 (2nd)
WG 145 (3rd)
WG 145 (4th)
2015
2016
2017
2018
2019
2020
EURAMET Proposal meeting
SDG 14.3.1 (attended also by LNE)
ICPWS (JCS pH sub-group membership)
2020
2021
2022
2023
2024
Andrew: Best Practices Study Group on pH Measurement

3. Pitzer models for seawater and TRIS/artificial seawater buffers based on work from Frank Millero's group (David)

WG145 February 2020

Seawater electrolyte model

- This model is based on the publication by Pierrot & Millero (2017), who provided an Excel file that calculates the speciation of full seawater at a fixed pH.
- We have so far focused on the components of the seawater electrolyte: H, Na, Mg, Ca, K, Sr, Cl, SO_4, CO_3, $B(OH)_3$, F, Br.
- The Pitzer coefficients used can be found in the Visual Basic code included in the Excel file: sources are also given for many interactions.
- We have checked the coefficient equations and values in all the cited sources and corrected where necessary.
- In some cases the cited sources do not exist (papers "in preparation" that were never published). Here we have in most cases substituted with coefficients from the authors' earlier publications. We have also obtained raw data on which some unpublished coefficients are based (Roy et al. 1996)
- Coefficients without citations in the Visual Basic code have been identified in the authors' earlier publications, and checked against the cited sources.
- The original sources of several equilibrium constants are hard to track down.

TRIS/artificial seawater buffers

- Waters & Millero (2013) provide full descriptions of their Pitzer coefficients for artificial seawater (H, Na, Mg, Ca, K, Cl, SO_4).
- They do not specify the equilibrium constants that they used: these have been assumed to be the same as those used in the full seawater model of Pierrot & Millero (2017).
- The values and equations for Pitzer coefficients have been checked against the cited literature and corrected where necessary.
- Values for the temperature-dependent equilibrium constant for the TRIS/$TRISH^+$ reaction have been taken from Bates & Hetzer (1961).
- Pitzer coefficients for TRIS interactions have been taken from the critical assessment of Gallego & Turner (2017). The available data are for 25°C only and far from adequate.

WG145 February 2020

Quality assurance

- Calculating equilibrium speciation using Pitzer equations involves a significant amount of coding. Errors are not impossible!
- Two independent codes have been used with exactly the same input concentrations, equilibrium constants, and Pitzer coefficients.
- The two codes use entirely different algorithms: (i) free energy minimisation (Simon); (ii) optimisation of the free concentrations of a set of independent chemical components (David).
- Comparisons on a full seawater electrolyte system show agreement to better than 1 part in 10^6.

4. New TRIS interaction parameters (Pablo)

WG145 February 2020

Solubility measurements to determine the values of the interaction parameters for the Pitzer speciation model of the TRIS/TRISH$^+$ buffer

Pablo Lodeiro*, *David R. Turner and Simon L. Clegg

GEOMAR
Helmholtz-Zentrum für Ozeanforschung Kiel

Water Column Biogeochemistry
Eric P. Achterberg

How this work contributes to SCOR WG145?

- Need of new laboratory measurements to characterise the thermodynamic properties and speciation in the aqueous Tris/TrisH$^+$ buffers used to calibrate instruments for measuring pH.

WG145 February 2020

Why is this contribution important?

- Measurements of pH in seawater rely on the accuracy of pH values assigned for the TRIS-seawater buffers currently used for calibration.
- TRIS buffers allow calibration of acid-base indicators such as meta-cresol purple for use in measuring pH in seawater.
- Our capability for accurate pH measurements in brackish and estuarine waters is severely limited by lack of well characterised buffer solutions.
- The speciation models are not yet fully characterised for all the interactions of Tris and TrisH+ that influence the pH of the buffer.
- These solubility measurements have enabled us to determine the values of the interaction (Pitzer) parameters. This is an important step towards a complete speciation model of the buffer.

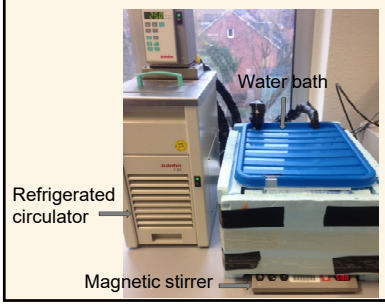
WG145 February 2020

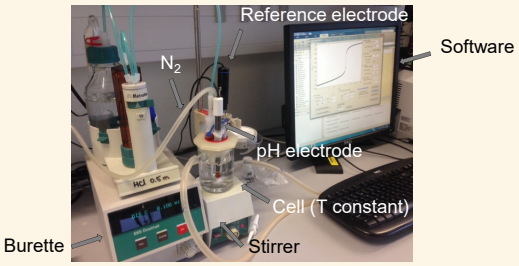
What we did?

- Quantify the interactions of TRIS with some of the major ions present in the TRIS buffer: Na^+, $TRISH^+$, Cl^- and SO_4^{2-}.

How we did it?

- Measuring the solubility of neutral TRIS in NaCl, TRISHCl and $(TRISH)_2SO_4$ salt solutions, and of NaCl in aqueous solutions of TRIS, covering a wide range of concentrations and temperatures.





WG145 February 2020

Experiments carried out

More than 1000 potentiometric titrations to quantify the concentration of TRIS or chloride.

- TRIS solubility in NaCl: temperature: 5, 10, 15, 20, 25, 30, 35, 40 and 45ºC; m_{NaCl}: 0, 1, 2, 3, 4 and 5 mol·kg^{-1}.

- NaCl solubility in TRIS: temperature: 5, 10, 15 and 20ºC; m_{TRIS}: 0, 0.5, 1, 1.5, 2 and 2.5 mol·kg^{-1}/ temp.: 25, 30, 35, 40 and 45ºC; m_{TRIS}: 0, 0.5, 1, 2, 3.5 and 4.5 mol·kg^{-1}.

- TRIS solubility in TRISHCl: temperature: 15, 25 and 35ºC; $m_{TRISHCl}$: 0, 0.5, 1, 2, 3 and 4 mol·kg^{-1}.

- TRIS solubility in $(TRISH)_2SO_4$: temperature: 15, 25 and 35ºC; $m_{(TRISH)2SO4}$: 0, 0.25, 1, 1.5 and 2 mol·kg^{-1}.

WG145 February 2020

Analysis of the obtained results

- The Pitzer model consists of a set of semi-empirical equations to describe activity coefficients in aqueous electrolytes. The Pitzer equations contain sets of parameters describing pairwise and triplet interactions, which are functions of T and P.

TRIS solubility in NaCl and NaCl solubility in TRIS

- From these solubility measurements and the respective solubility products *K*, we can obtain the contribution to the respective activity coefficients from the TRIS-NaCl interactions:

TRIS: $\Delta \ln\gamma = \ln K_{TRIS} - \ln m_{TRIS} = 2\,\lambda_{TRIS,Na}\, m_{NaCl} + \xi_{TRIS,Na,Cl}\, m^2_{NaCl} + 6\,\mu_{TRIS,TRIS,Na}\, m_{TRIS} m_{NaCl}$

NaCl: $\Delta \ln\gamma = \ln K_{NaCl} - 2 \ln m_{NaCl} - 2 \ln\gamma_{NaCl} = 2\,\lambda_{TRIS,Na}\, m_{TRIS} + 2\,\xi_{TRIS,Na,Cl}\, m_{TRIS} m_{NaCl} + 3\,\mu_{TRIS,TRIS,Na}\, m^2_{TRIS}$

TRIS solubility in TRISHCl

- These experiments enable the mixture parameters $\lambda_{Tris,TrisH}$ to be determined:

$\ln\gamma = \ln K_{TRIS} - \ln m_{TRIS} = 2\,\lambda_{TRIS,TRISH}\, m_{TRISH}$

TRIS solubility in $(TRISH)_2SO_4$

- These experiments allow the parameter $\lambda_{Tris,SO4}$ to be determined:

$\ln\gamma = \ln K_{TRIS} - \ln m_{TRIS} = 2\,\lambda_{TRIS,TRISH}\, m_{TRISH} + 2\,\lambda_{TRIS,SO4}\, m_{SO4}$

Preliminary results

We are still working to identify the optimal models

TRIS solubility in NaCl and NaCl solubility in TRIS

- Pitzer interaction parameters:

Coefficient	Value	Std.error	t
$\lambda_{TRIS\text{-}Na}$	0.0459	0.00240	19.1
$\xi_{TRIS\text{-}Na\text{-}Cl}$	-0.00468	0.00036	-13.2
$\mu_{TRIS\text{-}TRIS\text{-}Na}$	-0.00100	0.00011	-8.9

TRIS solubility in TRISHCl

- Value for $\lambda_{Tris,TrisH}$ of -0.0192 ± 0.0006

TRIS solubility in $(TRISH)_2SO_4$

- Value for $\lambda_{Tris,SO4}$ of 0.0692 ± 0.002

Our measurements do not provide any indication of temperature dependence

5. Collaboration with national metrology institutes (Simon et. al.)

WG145 February 2020

National Metrology Institute Participants

We are very glad to have the participation of four national metrology institutions, which is an addition to WG 145:

PTB Frank Bastowski (present)

LNE Daniela Stoica (online)

NMIJ Igor Maksimov

NIST Regina Easley (present), and Jason Waters

In general, the NMIs have an interest in pH standards, and the materials used in pH measurements (e.g., m-cresol purple, NIST).

WG145 February 2020

Role of the NMIs in the Project

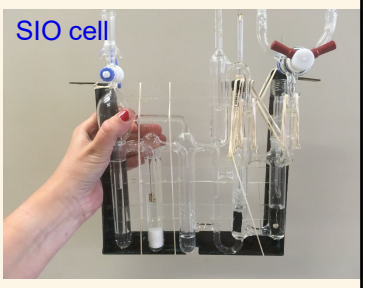
The NMIs are some of the few organisations that maintain Harned Cells, for the purposes of characterizing standard buffer solutions (**including for seawater pH**), and for research.

Harned Cell measurements in solutions containing H^+ and Cl^- yield values of the product:

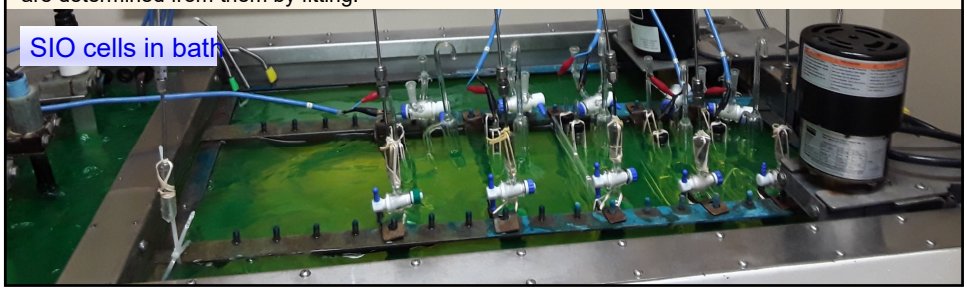
$$\gamma_H \, mH^+ \bullet \gamma_{Cl} \, mCl^-$$

The values of the activity coefficients γ are controlled by the various solutes present, and Pitzer interaction parameters are determined from them by fitting.

SIO cell



SIO cells in bath



WG145 February 2020

Role of the NMIs in the Project

Systems to be measured using Harned Cells:

Chemical system	Institution
Tris/TrisH$^+$ buffer in $NaCl_{(aq)}$	PTB
H^+ - $TrisH^+$ - Cl^- - H_2O	NMIJ (done)
H^+ - Na^+ - $TrisH^+$ - Cl^- - H_2O	NMIJ (done)
several systems inc. SO_4^{2-}	SIO

GEOMAR contribution essential for analysing these results

NIST and U Delaware are collaborating on the project "Establishing the traceability of pH measurements for long-term carbon system monitoring from coastal waters to open ocean"

Existing data, either unused or unpublished:

Chemical system	Authors/institution
$HCl/MgSO_{4(aq)}$, $HCl/K_2SO_{4(aq)}$	Roy, Pierrot, Millero (done)
Tris/TrisH$^+$ buffer in NaCl(aq) + various seawater salts	LNE and others (past EU project) (done)

WG145 February 2020

Dissemination from Inorganic Standards Section under JCSS

- NMIJ supply Japanese Calibration Service System with the six aqueous primary buffer solutions (expanded uncertainties typically <0.003)
- They have 6 Harned cells for research purposes to determine the pH for other media including artificial seawater EMRP ENV05, part of the *European Metrology Research Programme*, and our WG 145 project).
- NMIJ have contributed data for three aqueous systems:
  H^+-$TrisH^+$-Cl^--H_2O,
  H^+-Na^+-$TrisH^+$-Cl^--H_2O,
  Tris buffer-Na^+- Cl^--H_2O.

Japanese Calibration Service System

WG145 February 2020

LNE's interests

- **Establish comparability for both pH and pH^T values**
  - Primary level
    - Traceability scheme based on Harned cell measurements
    - Equivalence at primary level within BIPM/CCQM
      - **Needs for Pitzer calculation to convert acidity functions in pH**
      - **Traceability to SI for pH^T : validate and support some hypothesis made for primary pH^T method (possibly with Pitzer model?)**
  - Field level
    - Role of indicator dye in pH^T traceability scheme
    - Uncertainty calculations
    - Role of standards for robust QA/QC system
- **Establish equivalence between pHT measurements results obtained with different techniques**
  - Potentiometric pH^T vs spectrophotometric pH^T

WG145 February 2020

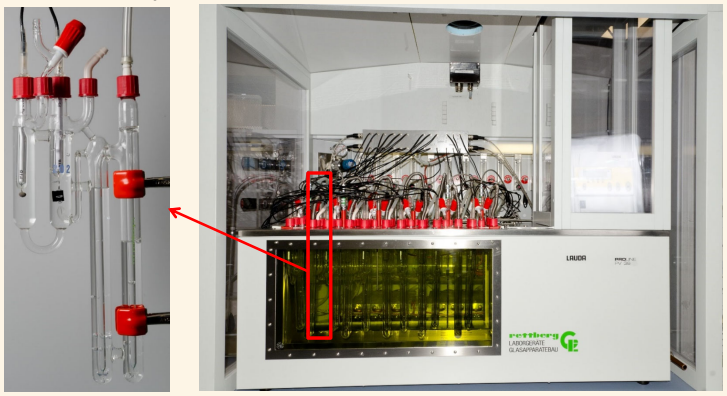
Recent LNE's activities in seawater acidity

- **Establish comparability for the potentiometric assignment of both pH and pH^T values in the routine analysis of seawater samples**
  - Multi-point calibration approach for potentiometric pH^T measurements and uncertainty evaluation of potentiometrically pH^T measurements results
  - Use TRIS buffers characterized with Harned cell
- **Participation and organization of an interlaboratory comparison within JPI Ocean "European Marine Sensor Calibration Network"**
  - Provide TRIS buffers characterized in pH^T with Harned cell
  - Participation with potentiometric pH^T method

WG145 February 2020

PTB´s research interests related to WG 145

Traceability of pH and pH_T of natural waters to the International System of Units (*SI*) by determination of Pitzer ion activity coefficients from measurement data ⇨ PTB provides **Harned cell** measurement data for **0.04 m equimolal Tris/TrisH⁺ in various $NaCl_{aq}$**

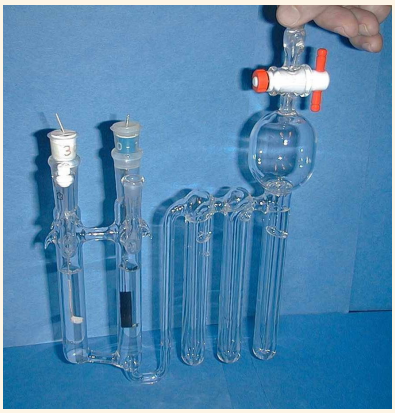


Physikalisch-Technische Bundesanstalt ■ Braunschweig and Berlin — National Metrology Institute

WG145 February 2020

NIST Capabilities and Interests

- NIST supplies seven (primary and secondary) solid buffer reagents for pH measurements with typical expanded measurement uncertainties of $0.002 < u_c < 0.003$ (at 25 °C).
- 12 Harned cells available for simultaneous measurements of pH in simple buffer systems and artificial seawater.
- A NOAA OAP funded project in collaboration with the University of Delaware is examining
  - Tris:Tris HCl artificial seawater buffers at varying mole ratios between a salinity of 5 – 45. The visible absorbance of these buffer systems will be measured to certify a new reference material (RM 8083 – Meta-cresol Purple for Seawater) and an uncertainty budget will be established.
  - Electrode calibrations for estuaries using spectrophotometric multipoint calibration and calibration with pH electrodes will be examined (summer 2020). Additional data on the ionic composition of these two estuarine systems will be analyzed.



28 / 34

6. "Best practice" paper (David)

WG145 February 2020

- At our 2018 meeting in Portland we decided to finalise a manuscript on best practices in chemical speciation modelling, and to submit the manuscript to the *Frontiers in Marine Science* Best Practice topic.
- The draft manuscript went through an internal review during the second half of 2018 – thanks to all who contributed to this process
- When discussing the internal reviews, it became clear to the lead authors that much of the manuscript read like an advertisement for WG145 rather than addressing the Best Practice theme directly.
- This initiative has been on the back burner for a while, but the 2020 meeting provides a good opportunity to get further input from WG members on the proposed content of a revised manuscript

WG145 February 2020

Proposed structure for the manuscript

- Document the current situation, its advantages, disadvantages and limitations
- Present the proposed Best Practice, identifying the potential benefits
- Discuss the challenges involved, and the work that needs to be done to implement the proposed Best Practice
- Discuss the community's progress thus far

This structure gives a clear focus on Best Practice, while giving scope to describe the work of WG145 and at the same time placing our work in a wider context.

WG145 February 2020

The current situation

- Widespread use of stoichiometric constants for speciation calculations
- No estimates of uncertainty (the new CO2SYS release is an exception)
- The software options generally available are CO2SYS, the Pierrot & Millero code for fixed pH calculations, and homemade spreadsheets
- Advantages
  - Relatively simple calculations
- Disadvantages
  - Stoichiometric constants generally available only for standard seawater
  - CO_2 system calculations are not easily combined with other species
  - Not easy to document and reproduce calculations
  - Major challenges for the non-specialist

Proposed Best Practice

- The use of thermodynamic equilibrium constants, together with calculated activity coefficients, to calculate chemical speciation
- Estimation of the uncertainty in the calculated speciation
- Readily available user-friendly software to carry out these calculations
- Advantages
  - Applicable to a wider range of natural waters
  - User-friendly software will make it easier for non-specialists to carry out speciation calculations
  - Potential to integrate CO_2-system calculations in a broader model framework
  - More standardised speciation calculations
- Disadvantages
  - Extensive development work required
  - Acceptance by the marine science community may be hard-won

Challenges

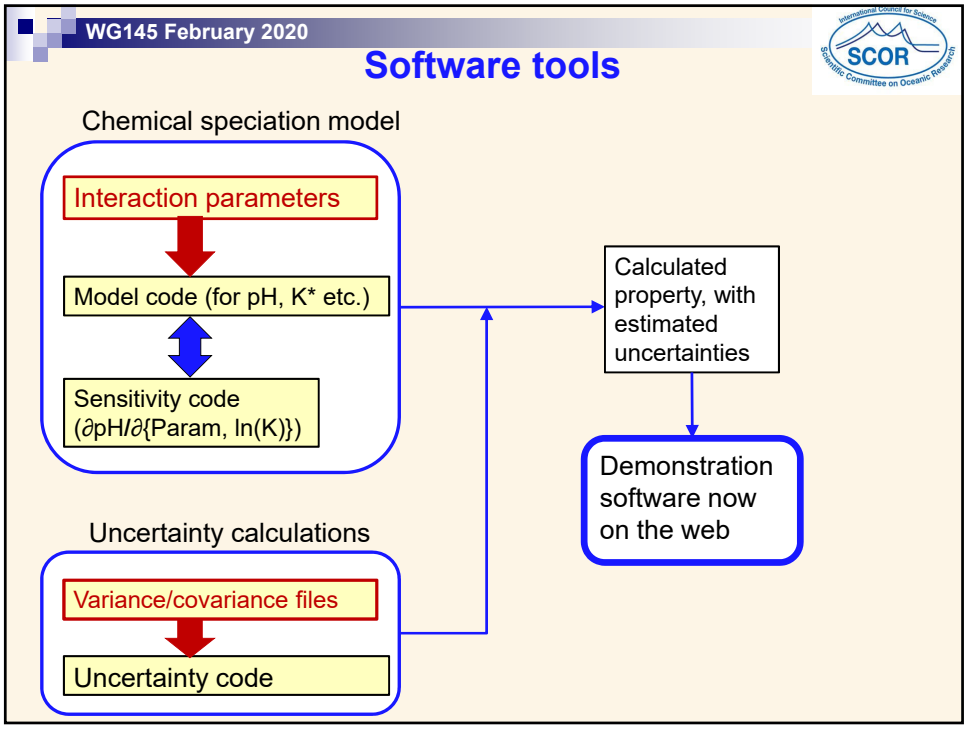
- Establishing and maintaining a state of the art Pitzer model
  - Ensuring that the model represents the CO_2 system as accurately as CO2SYS so that CO_2 system calculations can be integrated with other calculations
- Lack of thermodynamic data for key interactions in the seawater electrolyte
- For many trace metals and ligands, the scarcity of thermodynamic data may require integration of stoichiometric constants into the model structure
- Generating a user-friendly front end and linking this to an efficient calculation engine

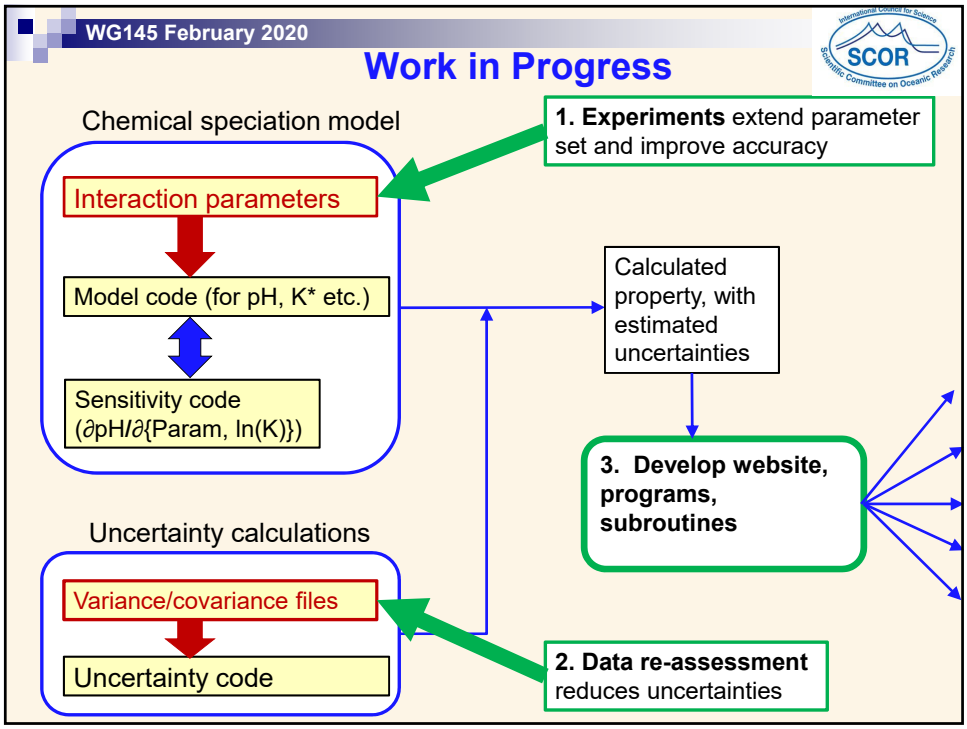
Progress so far

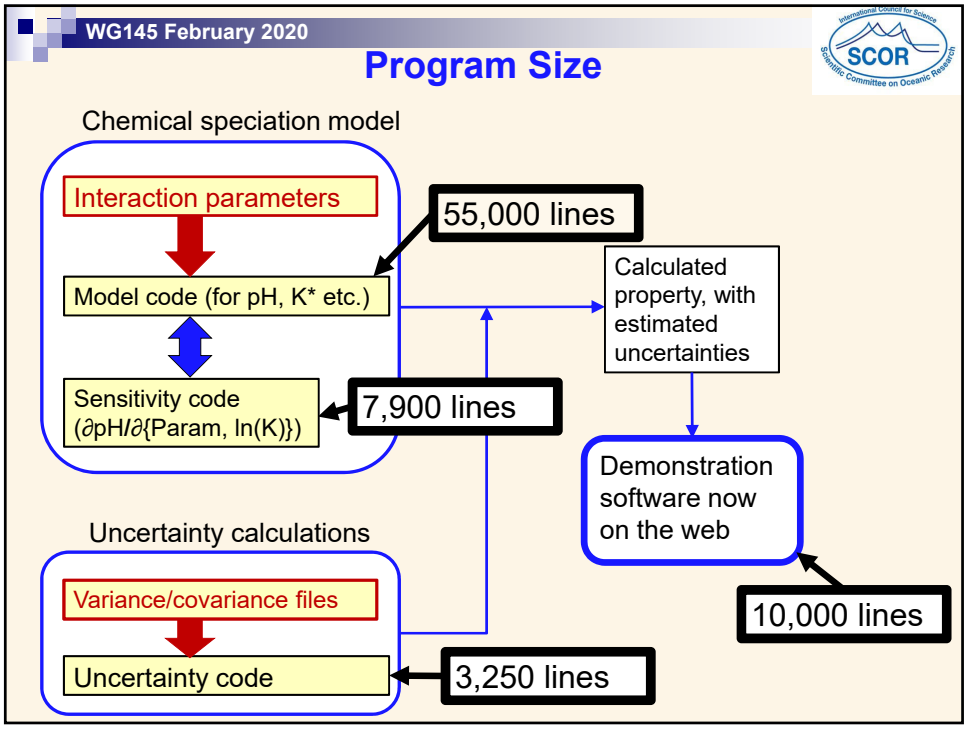
- Millero and colleagues have devoted much effort to the development of Pitzer models for seawater, but take-up has been very limited.
- Pierrot & Millero (2017) published a Pitzer-based model in Excel format
  - works only at fixed pH and cannot be updated without editing the Excel Visual Basic code
- Uncertainty estimation incorporated into the latest CO2SYS version
- Key requirements for software front end have been established through user surveys
- An early prototype Best Practice software has been developed for the seawater electrolyte and for TRIS/artificial seawater buffers

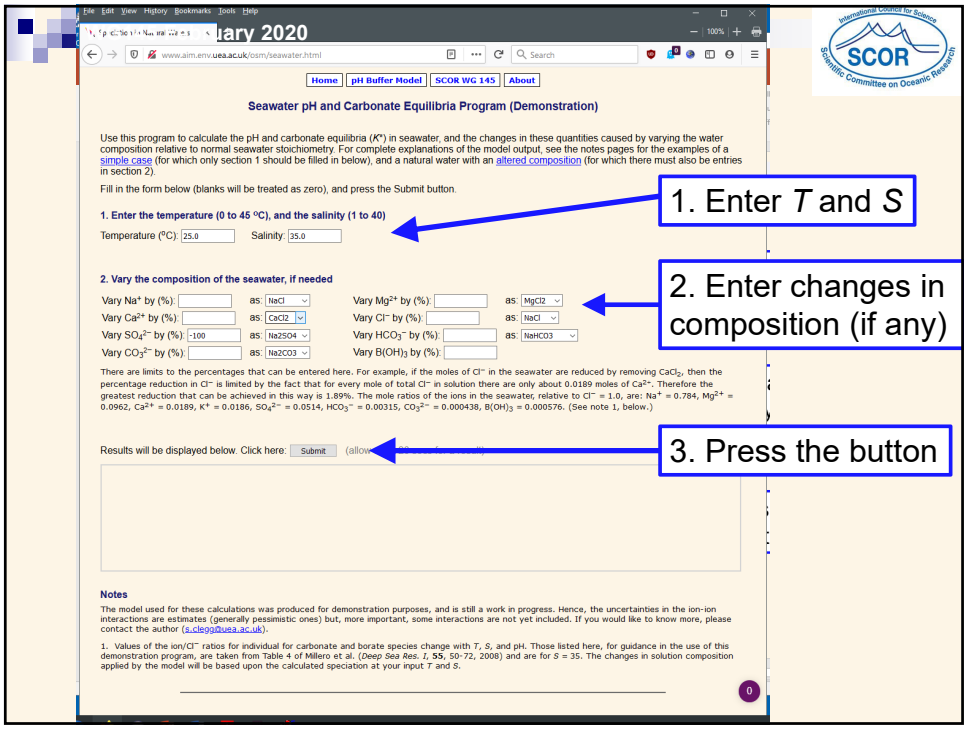
WG145 February 2020

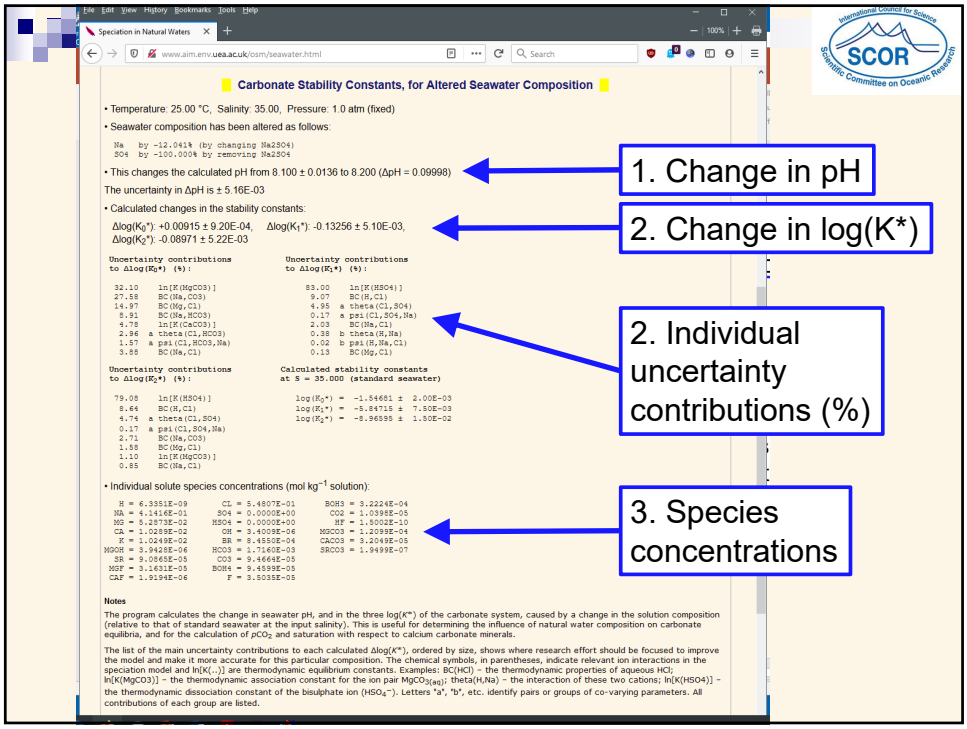
7. Development of software tools and codes (Simon)


WG145 February 2020
Software tools
Chemical speciation model
Interaction parameters
Model code (for pH, K* etc.)
Sensitivity code (∂pH/∂{Param, ln(K)})
Calculated property, with estimated uncertainties
Demonstration software now on the web
Uncertainty calculations
Variance/covariance files
Uncertainty code


WG145 February 2020
Work in Progress
Chemical speciation model
1. Experiments extend parameter set and improve accuracy
Interaction parameters
Model code (for pH, K* etc.)
Sensitivity code (∂pH/∂{Param, ln(K)})
Calculated property, with estimated uncertainties
3. Develop website, programs, subroutines
Uncertainty calculations
Variance/covariance files
Uncertainty code
2. Data re-assessment reduces uncertainties


WG145 February 2020
Program Size
Chemical speciation model
Interaction parameters
Model code (for pH, K* etc.)
Sensitivity code (∂pH/∂{Param, ln(K)})
55,000 lines
7,900 lines
Calculated property, with estimated uncertainties
Demonstration software now on the web
10,000 lines
Uncertainty calculations
Variance/covariance files
Uncertainty code
3,250 lines


Home
pH Buffer Model
SCOR WG 145
About
Seawater pH and Carbonate Equilibria Program (Demonstration)
1. Enter T and S
2. Enter changes in composition (if any)
3. Press the button
Notes



8. Collaboration with IAPWS/SCOR/IAPSO Joint Committee on Seawater (Andrew)

WG145 February 2020

IAPWS/SCOR/IAPSO Joint Committee on Seawater

The Joint Committee on Seawater of the International Association for the Properties of Water and Steam (IAPWS), SCOR, and the International Association for the Physical Sciences of the Ocean (IAPSO) was formed following the completed work of SCOR/IAPSO WG 127 on Thermodynamics and Equation of State of Seawater, which created the Themodynamic Equation of State-2010 (TEOS-10). It was recognized at that time that progress needed to continue on the development of relationships between temperature and salinity of seawater outside the range of previously available equations.

The work of the Committee is mostly conducted at annual IAPWS meetings. The Committee has subdivided its work into three task groups: (1) salinity/density, (2) pH, and (3) moist air. The Committee also has expertise in thermodynamics, numerical modeling and applications, and software. The Committee includes representation from industry.

WG145 February 2020

IAPWS/SCOR/IAPSO Joint Committee on Seawater

Membership

Chair: Rich Pawlowicz (Canada)

Vice Chairs: Rainer Feistel (Germany), Steffen Seitz (Germany)

Other Members: Paul Barker (Australia), Frank Bastkowski* (Germany), Stephanie Bell (UK), Maria Filomena Camoes* (Portugal), Simon Clegg (UK), Andrew Dickson* (USA), Olaf Hellmuth (Germany), Yohei Kayukawa (Japan), Barbara Laky (Austria), Jeremy Lovell-Smith (New Zealand), Trevor McDougall (Australia), Frank Millero (USA), Youngchao Pang (China-Beijing), Daniela Stoica* (France), Hiroshi Uchida (Japan), Stefan Weinreben (Germany), Richard Williams (UK), and Ryan Woosley* (USA)

* Members of the Task Group on pH

WG145 February 2020

IOP Publishing | Bureau International des Poids et Mesures — Metrologia
Metrologia 53 (2016) R26–R39 — doi:10.1088/0026-1394/53/1/R26

Review

Metrological challenges for measurements of key climatological observables. Part 3: Seawater pH

A G Dickson[1], M F Camões[2], P Spitzer[3], P Fisicaro[4], D Stoica[4], R Pawlowicz[5] and R Feistel[6]

A key aim of the Task Group on pH is to clarify the information required to ensure that seawater "pH" measurements are traceable to the SI. A principle feature of this requires a full understanding of the uncertainties involved in each stage of "pH" definition, measurement, and use.

Initially we have embarked on acquiring data for a detailed Pitzer model of Harned cell measurements on Tris buffers in synthetic seawater media, with the goal of enabling the uncertainty in assumptions about activity coefficients to be quantified.

Much more work will ultimately be required to characterize fully the overall uncertainties involved in making and using seawater "pH" measurements.

WG145 February 2020

IAPSO Best Practice Study Group on seawater "pH" measurement

Goals

1. Clarify the current state-of-the-art for seawater pH determination by agreeing on a detailed written assessment of the strengths and weaknesses of each of the various concepts and methodologies that presently confound the process of making seawater pH measurements.
2. Articulate appropriate best practices for seawater pH measurement.
3. Identify the research that is still needed both to improve our understanding of the uncertainty of seawater pH measurements, as well as that required to make the methodology simpler and more reliable for a wider range of likely users.

IAPSO Best Practice Study Group on seawater "pH" measurement

Membership:

F. Bastkowski, Physikalisch-Technische Bundesanstalt (*PTB*), Germany

R. H. Byrne, University of South Florida, USA

M. F. Camões*, University of Lisbon, Portugal

S. L. Clegg, University of East Anglia, United Kingdom

K. Currie, National Institute for Water & Atmospheric Research, New Zealand

A. G. Dickson*, University of California, San Diego, USA

I. Leito, University of Tartu, Estonia

D. Stoica, Laboratoire national de métrologie et d'essais (LNE), France

B. Tilbrook, CSIRO, Hobart, Australia

**Study Group Leaders*

An impromptu meeting of many of these individuals is planned for Friday, Feb 21 to make a start on planning this activity.

WG145 February 2020

9. NICA-Donnan modelling of marine organic matter (Martha)

WG145 February 2020

NICA-Donnan modelling of marine organic matter

Kechen Zhu, Pablo Lodeiro, Eric P. Achterberg and Martha Gledhill

How this work contributes to SCOR WG145?

- Investigating the complexation of trace metals, including bioavailability and metal-organic interactions.
- Consider the complexation of trace metals (by a variety of ligands) in Pitzer activity coefficient model reactions in seawater.

Why this contribution is important?

- Dissolved organic matter (DOM) present in seawater has major relevance for biogeochemical and climate systems.
- Complete modeling of the CO_2 system in organic-rich waters requires investigation of the acid-base chemistry of DOM.
- The binding of trace metals to marine DOM is controlled by the acid-base properties of DOM.

WG145 February 2020

What we did?

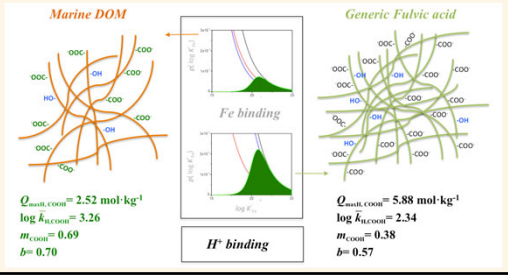
- Determine the acid-base properties of key organic ligands (dissolved organic matter) in seawater.
- Demonstrate the relevance of the acid-base properties for the modelling of iron binding to marine DOM.

How we did it?

- Measuring the proton binding properties of extracted marine DOM and assessing the major classes of active chemical groups.
- Using a combination of the non-ideal competitive adsorption (NICA) isotherm that accounts for the specific -chemical- ion binding, and the Donnan model for electrostatic effects.

Obtained results

Paper submitted to Science of the Total Environment.



WG145 February 2020

Prediction of iron binding to organic matter

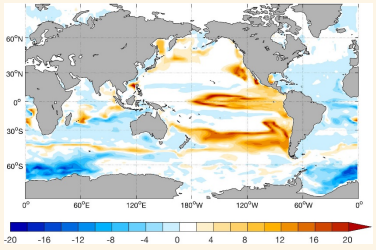
Why we use NICA-Donnan model?

- The determination of organic complexation using traditional titration method is to calculate binding constants and total ligand concentration, which are conditional for pH/DOC/metal concentration.
- The NICA-Donnan model is independent of pH/metal concentration. We assume ligand concentrations scale proportionally with DOC concentration.

Why we predict the Fe binding capacity of organic matter?

- Improve understanding of Fe distributions and Fe bioavailability
- More sophisticated representation of Fe biogeochemisty in Global Biogeochemical Models (paper in revision, Ye, Völker and Gledhill, GBC)

Predicted change in DFe (µmol m^{-3}) in acidified (NorESM1-ME) Ocean

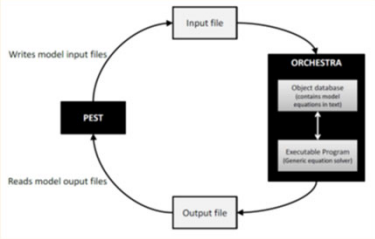


WG145 February 2020

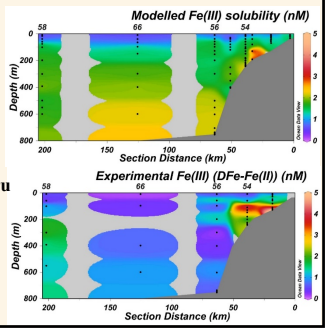
How we apply our approach

- Calculate pFe´and maximum binding capacity (= „solubility“) at ambient pH and DOC using speciation programs (e.g. visual MINTEQ).
- Specifically derive NICA constants for water masses using with two dimensional pH/Fe titrations in combination with PEST-ORCHESTRA.

Framework of PEST-ORCHETSRA



Predicted maximum binding capacity of organic matter off Peru shelf @ ~12° S



10. Progress towards the Terms of Reference (David)

WG145 February 2020

Completed | Under way | Not started

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, Cd, Co, Mn, 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.
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.
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
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.

WG145 February 2020

Research Publications Outreach and communication

Terms of reference	Progress
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, Cd, Co, Mn, 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 complete for TRIS/artificial seawater and for the seawater electrolyte. • Current status and future modelling developments have been documented in the Frontiers paper • NERC/NSF project funded 2017 – early 2022 • Collaboration with National Metrology Institutes on TRIS buffers in artificial seawater • GEOMAR: New measurements of TRIS interactions • Contact established with pH monitoring programmes (GOA-ON, IOC) • Collaboration with IAPWS/SCOR/IAPSO Joint Committee on Seawater • IAPSO Best Practice Study Group

Work remaining to fulfil the Terms of Reference:
- Extension of the model to trace metals and key organic ligands
- Document major gaps in current knowledge

WG145 February 2020

Research Publications Outreach and communication

Terms of reference	Progress
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.	• Town Hall presentation at OSM2016. • Paper published in Frontiers in Marine Science (Turner et al., 2016). • Handout for wide distribution at OSM 2018. • Lunchtime presentation at OSM 2020 • Software demonstration at the SCOR booth, OSM 2020 • "Best Practice" paper in preparation

Work remaining to fulfil the Terms of Reference:
- Complete the "Best Practice" paper

WG145 February 2020

Research Publications Outreach and communication

Terms of reference	Progress
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	• Two "Survey Monkeys" completed. • To be included in a "Best Practice" paper
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	• A demonstrator version of the web-based tool is presented at the SCOR booth at OSM2020 • Software for general release is still some distance away

Work remaining to fulfil the Terms of Reference:
- Publish the "Best Practice" paper
- General release of the calculation tool

WG145 February 2020

Afternoon agenda

Guide time	No.	Subject
13:30	1	What remains to be done to meet our commitments to SCOR (Terms of Reference) ?
13:50	2	Plans and timelines for ongoing projects
15:00		Break
15:30	3	Proposals for new initiatives
16:00	4	Timeline, actions, responsibilities
16:30	5	Potential for future collaboration after the end of WG145
17:00		Close

WG145 February 2020

1. What remains to be done to meet our commitments to SCOR (Terms of Reference) ?

- Extension of the model to trace metals and key organic ligands
- Document major gaps in current knowledge
- Complete the “Best Practice” paper
- General release of the calculation tool

It is planned to request that WG145 retain its SCOR affiliation for another 2 years, i.e. until early 2022. This coincides with the end of the NERC/NSF project that provides the major framework for completing the Terms of Reference. This would mean that the software product released in early 2022 would be identified as a product of a SCOR activity.

2. Plans and timelines for ongoing activities

- NERC/NSF project (Simon, Andrew and Heather)
- NMI measurements Frank and Daniela)
- ”NICA” project (Martha)
- TRIS measurements at GEOMAR (Pablo)
- NIST/Delaware project (Regina and Wei-Jun)
- IAPSO Study Group (Andrew)
- Collaboration with JCS (Andrew and Simon)

WG145 February 2020

3. Proposals for new initiatives

WG145 February 2020

4. Timeline, actions, responsibilities

WG145 February 2020

5. Potential for future collaboration after the end of WG145

- Aims ?
- Participants ?
- Funding ?
- Communication ?