Working Group Title: Carbonate system intercomparison forum
Acronym: CSIF

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Table of Contents

Summary

Recent literature has highlighted several ongoing challenges regarding the consistency of seawater CO_2 measurements with estimates from alternate input pairs. These gaps in our knowledge of the ocean carbonate system are probably related to carbonate constant uncertainties, frequently-unknown concentrations of organic bases in seawater, and unrecognized measurement uncertainties. CO_2 measurement intercomparability is also challenged by the large and growing variety of instruments and approaches used for measurements and the lack of a robust assessment of some methods. While measurement strategies diversify and evolve, the need remains for consistent records of key measurements over time to assess marine CO_2 cycling and its impacts: e.g. dissolved inorganic carbon (DIC) records for anthropogenic carbon storage, partial pressure of CO_2 ($p$$CO_2$) records for air-sea flux estimates, pH records for ocean acidification (OA) monitoring, and seawater alkalinity (A_T) records for assessing the impacts of OA on carbonate mineral cycling. It is therefore more critical than ever that scientists develop a strategy for identifying and addressing carbonate system intercomparability uncertainties, thus enabling existing and future data to be reconciled into internally-consistent data products with associated uncertainties. We therefore propose a forum between experts in carbonate system parameter measurements, data documentation, and interconversion to debate the nature of the problems, advocate for needed research to resolve these problems, and provide guidance for data product assembly and documentation. The forum will have the additional goal of bringing new and developing analytical marine chemistry labs into ongoing intercomparison and standardization efforts, and lowering barriers for such groups to participate.

Scientific background and rationale

In principle, any of the commonly-measured seawater carbonate parameter measurements (pH, pCO_2, DIC, A_T, and, as of recently, carbonate ion) can be calculated from any two of the others along with carbonate constants (as functions of S, T, and pressure) and knowledge of the chemical properties of all other acid-base systems in the seawater. Moreover, great progress has been made toward standardization of measurement practices through the distribution of Best Practices literature (Dickson et al. 2007; Riebesell et al. 2011) and Certified Reference Materials (Dickson et al. 2003) for key measurements. However, recent literature has highlighted that disagreements remain between direct measurements of carbonate parameters and calculations of these parameters from other measurements (e.g. Kulinski et al., 2014; Chen et al., 2015; Patsavas et al. 2016; Carter et al. 2017; Woosley et al., 2017). These disagreements are comparable in magnitude to, or larger than, the likely decadal changes from climate forcing. Furthermore, there are biases between calculations obtained from different sets of commonly-used carbonate chemistry constants (Woosley et al., 2017). Disagreements between measured and calculated carbonate parameter values and the diversity of measurement types are hampering efforts to combine data sets into unified data products (e.g. Olsen et al. 2016), to interpret existing data products and infer climate signals (e.g. Carter et al., 2017), and to fully utilize measurements from new sensors and measurement platforms to make inferences about the full carbonate system in seawater (e.g. Williams et al., 2017).

Seawater pH can provide an example of this problem and why it is urgent that it be addressed. One of the main symptoms of OA is the ocean pH decrease, however, direct detection of OA based on ocean pH measurements was not feasible prior to the development of the highly-precise spectrophotometric methods (Clayton and Byrne, 1993; see the review of Dickson, 2015). The lack of a certified pH seawater reference material is an additional ongoing challenge for pH measurements. Also, seawater pH has been measured with a variety of methods--and reported on a small collection of pH scales and at a range of temperatures and pressures--over the last several decades. The pH measurement approaches used include potentiometric measurements, sensor measurements, and spectrophotometric measurements made with several different dyes and different batches of dyes, all with differing concentrations of impurities that affect the measured pH (Yao et al., 2008; Liu et al., 2011). The recent emergence of purified m-Cresol dyes and dye coefficients raised the possibility that pH measurements would be brought in line with other carbonate system measurements (Liu et al. 2011). However, pH calculated from other measured parameters such as DIC and A_T) has been observed to still have a pH-dependent offset from spectrophotometrically measured pH, even when purified dyes are used (Patsavas et al., 2015; Williams et al., 2017; Carter et al., 2017). This problem is not thought to come from analytical or instrumental uncertainty in the pH spectrophotometric method (DeGrandpre et al., 2014) but rather from gaps in the knowledge of the information used to calculate carbonate system properties from one another (e.g. various measurements and their calibrations, K constants, and the concentrations of borate and other minor seawater acid-base pairs). As a result of these issues and the infrequency with which seawater pH was measured, discrete water column pH measurements were completely absent in the first effort synthesizing a globally consistent CO_2 data product, GLODAPv1 (Key et al., 2004). Instead, the mismatch between calculated and measured pH was made apparent with the introduction and quality assessment of water column pH data in regional data products such as CARINA (Velo et al., 2010) and the most recent version of GLODAPv2 (Olsen et al., 2016). Moreover, over these same recent years, the number of seawater pH measurements available has increased by orders of magnitude following the development of inexpensive, low-power, pressure-tolerant, occasionally reagent-free pH sensors (see: Wendy Schmidt Ocean Health XPRIZE), and their implementation on biogeochemical profiling floats and other sensor platforms. A float observing strategy is under consideration for implementation as a global array, and related strategies are being developed for other moored and autonomous platforms. Any limitations to the interchangeability of pH with other carbonate parameters will directly limit the utility of sensor measurements for observing air-sea carbon fluxes (from $p\mathrm{CO_2}$ calculations) and carbon storage (from DIC calculations). Essentially random measurement errors and offsets are mitigated by the large number of profiling floats that would compose such a global array, but consistent errors from carbonate parameter calculations would result in significant biases.

These are problems with solutions. The ideal solution to the problems for intercomparability of future measurements would be to identify the remaining factors limiting carbonate measurement comparability and address them through carefully planned and agreed upon research among independent research laboratories. Even should such efforts prove unsuccessful at resolving all the issues, an improved understanding of the biases inherent in various approaches for constraining the carbonate system should allow information from these approaches to be appropriately interpreted. In some cases, the biases may even be able to be countered with carefully considered adjustments. This Working Group proposal aims to workshop these solutions. It would assemble a team of experts to identify the remaining unknown aspects (including measurement uncertainties) of the carbonate system in seawater; the terms in the equations for carbonate parameter interconversion where these uncertainties have the greatest influence; and the research efforts most likely to reduce these uncertainties. Further, the experts would provide guidance on how best to proceed with data assembly and documentation. Finally, the working group will include members of emerging carbonate chemistry groups, and consider how best to encourage widespread adoption of the proposed improvements by both established and emerging laboratories internationally.

Terms of reference

The working group will pursue the following goals through discussion, debate, and writing peer-reviewed articles:

1. Identify and quantify the remaining unknowns for describing seawater CO_2 chemistry (e.g. uncertainties in measurements, CO_2 system calculations and constants, and organic base concentrations);
    a. estimate the magnitudes of these uncertainties, and thereby determine how important each unknown is to address;
    b. outline and advocate for research that could fill the most important gaps in our understanding;
2. review measurement reporting practices (e.g. reporting of pH scales, reference temperatures, uncertainty, and measurement methods);
    a. debate whether standardized reporting practices would be appropriate, and develop and advocate standardized reporting practices if so;

3. review the current state of reference materials for seawater CO_2 system measurements, and identify which seawater CO_2 parameters need more viable or available reference materials;
   a. make recommendations for making such materials more viable or available;
   b. make recommendations for how to best use reference materials to characterize measurement uncertainties;
4. review the barriers preventing groups from making seawater CO_2 measurements with low uncertainties (e.g. availability of calibrated titrant or purified spectrophotometric dyes);
   a. make recommendations for lowering those barriers;
5. identify barriers preventing research groups from participating in international standardization and intercomparison efforts;
   a. make recommendations aimed at lowering those barriers and increasing participation.

The metric for the success of these efforts will be publication of 1-2 peer-reviewed white papers on the Working Group's findings, and citation of such papers in research proposals and papers.

Working plan

The CSIF team will make progress on its terms of reference primarily at 2 to 3 day-long meetings associated with major international ocean science themed research conferences. Between each of these meetings, spaced by ~1 year, the Working Group will collaborate remotely to build upon and publish their findings from these meetings. The schedule for these meetings will be determined based upon the availability of full members to attend, but the meetings will begin in either Europe or the United States. The second meeting will then be on the other continent. The third meeting, if one is necessary to conclude business and if funding allows, will be held in association with a conference in Asia or Australia. Examples of potential two-meeting schedules include:

Meeting 1: EGU2019 Vienna, Austria, 7-12 April
Meeting 2: Ocean Sciences 2020, San Diego, CA, USA, 16-20 Feb
-Possibly AGU 2021 instead of OS2020

Or…

Meeting 1: OceanObs2019, Honolulu, Hawaii, USA, 16-20 September, 2019
Meeting 2: EGU2020 Vienna, Austria, 3-8 May, 2020.

Year 0-3:
Prior to the first meeting and throughout the duration of the Working Group, CSIF would aim to increase the Working Group's visibility by hosting sessions and town halls at major international research conferences. This will serve both to increase awareness of relevant research, and to generate enthusiasm and involvement from the community, with special consideration given to involving emerging CO_2 laboratories.

Year 1:
The first meeting would begin with a review of the evidence for carbonate system intercomparability problems, as well as a summary of the various uncertainties that have been

proposed to account for these problems, and a round-table discussion of what research is thought to be most likely to clarify these issues (ToR 1,1a,1b). The meeting would then commence preliminary discussions on how best to assemble consistent data products from diverse measurements (ToR 2,2a), given what was discussed earlier. The final part of the meeting would involve planning the work involved in writing a review paper designed to articulate the Working Group's current understanding of the likely uncertainties involved in computing CO_2 parameters from other measurements (see Deliverables - part b) together with specific recommendations where practical. It is intended that this paper be written and submitted with the 12 months immediately after the meeting. Collaboration will be maintained remotely through E-mail correspondence and, if deemed appropriate by CSIF members, free online collaboration software such as Slack. Once specific values have been agreed on for the various likely uncertainties, it will be practical to start (as a group) on the work required to produce the second proposed manuscript.

Year 2:
The second meeting would occur 1 to 2 years after the first, and will be held alongside another major international oceanographic meeting. The format of this meeting is expected to be similar to the first, beginning with a refresher on the major issues and including an update on research and new results that have come to light in the intervening year and the work done by Working Group members towards the papers proposed in the "Deliverables". The team would then break into two groups. The focus of the first group would again be considering what additional research is likely needed to address the remaining uncertainties (ToR 1,1a,1b). The focus of the second group would be on ideas for new efforts aimed at establishing carbonate measurement and data reporting best-practices, as well as identifying issues that may have prevented more complete adoption of past and ongoing best-practices guidelines (ToR 3,3a,3b,4,4a,5,5a). The working group would then meet in plenary to discuss authorship of documents summarizing the findings of the group's 2nd meeting. The first of these would aim to finalize the second manuscript proposed in the deliverables, and started in the first intersession. The second would be a white paper proposing explicit best-practice guidelines for CO_2 measurement and reporting, that also aims to address necessary quality control issue such as ensuring accessibility to appropriate reference materials.

Year 3:
The third CSIF meeting would occur provided there is travel funding and would focus on ensuring that the proposed publications were completed and submitted. This meeting would have a dual focus on wrapping up these efforts and on planning for future intercomparison efforts.

Deliverables

The expected deliverables from the activities of the proposed Working Group are:

(a) Reports to SCOR on the details of the meetings that were held.

(b) A series of papers (probably submitted to Frontiers in Marine Science under their topic "Best Practices in Ocean Observing"). These will comprise:

An initial methodological paper that primarily focuses on assessing the likely uncertainties of the manifold factors contributing to the overall uncertainty of computed results for the CO_2 system for a particular sample of seawater. Once these have been assessed and documented, it will be possible to use them in conjunction with publicly available computational software that propagates such uncertainties so as to estimate uncertainties in calculated values (Orr et al., in prep.)

A second review paper that re-assesses a number of published "over-determined" data sets to assess the degree to which the careful assessment of uncertainties does indeed provide an explanation for previously noted discrepancies, and to identify if additional contributions to uncertainty still remain to be found. Ideally, as more and more data are examined carefully, it may become practical to identify potential biases in one or more of the parameters, to suggest potential adjustments, and to modify the estimated uncertainty appropriately.

A third white-paper that makes explicit recommendations for CO_2 system measurement and reporting best practices that build upon the community experience to date, and that aim to address those issues that are believed to have compromised wholesale adoption of previous "best practice" guides.

Capacity building

The Working Group (CSIF) will be engaged in capacity building for many distinct aspects of seawater CO_2 chemistry science. CSIF will aim to improve capacities related to:

1. Uncertainty estimation: In order to be meaningfully interpreted, CO_2 measurements require accurate and well-estimated uncertainties. The first-order CSIF goal of estimating the uncertainties for several key gaps in our understanding of seawater CO_2 chemistry will have direct impacts on our interpretation of measured and calculated seawater CO_2 chemistry values. An improved understanding of how comparable measurements are to the true seawater chemistry and to one another will broadly improve the capacity of the oceanographic community to make correct inferences based on seawater CO_2 measurements.
2. Reference material diversity, availability, affordability, and viability: Reference materials for DIC and A_T measurements have had large positive impacts on the quality of the carbonate chemistry measurements since their introduction in the early 90s. CSIF will examine whether this impact can be extended by encouraging development of additional reference materials for other seawater carbonate measurements, or with a wider range of carbonate chemistry states than are current readily available, and that are more inexpensively available (perhaps more efficiently distributed) to laboratories globally.
3. Measurement material availability: The availability of purified or calibrated measurement materials (e.g. dyes and titrants) is one identified barrier preventing some research groups from making seawater chemistry measurements of the highest quality. CSIF will explore ways to lower this barrier and thereby potentially improve measurement capacities worldwide.
4. Data product development: CSIF plans to debate the metadata requirements for data products that combine measurements made using a range of approaches. The goal for this debate is to

create guidelines that will assist members of the community working to compile such data products, and thus resolve challenging questions that are limiting data product development capacities.

5. Intercomparison exercises: These exercises are one of the key audits for the success of efforts to improve laboratory-to-laboratory CO_2 measurement comparability globally. They also provide some of the only independent feedback for how comparable measurements from an individual laboratory are with the measurements of the global community. CSIF will work to bring more laboratories into these exercises, and thereby increase both the impact of the exercises and their value as an assessment for laboratories that already participate.

Working group composition

All full and associate members of this working group have extensive expertise with seawater carbonate chemistry measurements. Here we note additional relevant expertise that would likely prove useful for the Working Group.

Name	Gender	Place of work	Expertise
Andrew Dickson (co-chair)	M	Univ. California San Diego (UCSD), USA	Physical chemist and modeler: CO_2 system in seawater, uncertainties of CO_2 system measurements, reference materials for seawater CO_2 measurements
Marta Álvarez (co-chair)	F	Instituto Español de Oceanografía (IEO), Spain	Seawater CO_2 internal consistency, time-series, anthropogenic carbon. North Atlantic, Mediterranean Sea. CO_2 facility
Robert Byrne	M	Univ. South Florida, USA	Marine CO_2 system chemistry and ocean acidification and development of in situ methods and instrumentation
Kim Currie	F	National Institute of Water and Atmospheric Research, NIWA, New Zeeland	Surface ocean IOCCP co-chair, IP for ocean acidification multi disciplinary observatories in NZ coast and open ocean
Sue Hartman	F	National Oceanography Center (NOC), UK	Open ocean and coastal UK observatories, ferry-box continuous biogeochemical data, CO_2 facility
José Martín Hernandez-Ayon	M	Univ. Autónoma de Baja California, México	Member of the Mexican Carbon project, specialist in coastal carbon cycle and anthropogenic stressors
Siv Lauvset	F	Bjerknes Center for Climate Research, Norway	GLODAPv2, SOCAT CO_2 quality control, global pH distributions and ocean acidification mechanisms.
Claire Lo Monaco	F	Laboratoire d'Océanographie et du Climat (LOCEAN), France	GLODAPv2, air-sea CO_2 exchange, decadal changes, Indian Ocean and CO_2 French facility

Akihiko Murata	M	Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan	Japanese GO-SHIP cruises, decadal changes in biogeochemical variables, focus on pH and anthropogenic carbon
Weidong Zhai	M	Institute of Marine Science and Technology, Shandong Univ., China	Marine carbon cycle in the coastal ocean: air-sea CO_2 exchange, terrestrial inputs, stressors, ocean acidification

Associate Members

Name	Gender	Place of work	Expertise
Brendan Carter	M	University of Washington/National Oceanic and Atmospheric Administration, (UW/NOAA) USA	Estimating decadal anthropogenic carbon changes, developing algorithms for CO_2 parameter estimation
Socrates Loucaides	M	NOC, UK	Head of analytical Science team in the ocean technology group at NOC. Spectrophotometric assays and electrochemical techniques. Sensor development and optimization for carbonate chemistry methods
Triona McGrath	F	National University of Ireland (NUI), Ireland	Responsible for NUI ocean acidification program, expertise in discrete biogeochemical measurements.
Yui Takeshita	M	Monterey Bay Aquarium Research Institute (MBARI), USA	Involved in developing and applying autonomous sensing technology to observe marine biogeochemical cycles in situ, SOCCOM program.
Melissa Chierici	F	Institute of Marine Research (IMR), Tromsø, Norway	Expert in CO_2 variability in the Arctic Ocean, responsible for monitoring programs in Norway.
Louisa Giannoudi	F	Hellenic Center for Marine Research (HCMR), Greece	Expertise in biosensors and responsible for discrete CO_2 measurements in the Greek near waters.
Karol Kuliński	M	Institute of Oceanology of the Polish Academy of Sciences (IO PAN), Poland	Biogeochemistry in the Baltic Sea, ocean acidification and organic matter contribution to alkalinity
Henry Bittig	M	Laboratoire	Expert in Biogeochemical Argo

		d'Océanographie de Villefranche (LOV), France	measurements, neural networks for biogeochemistry
Carolina Cantoni	F	Consiglio Nazionale delle Ricerche, Istituto de Scienze Marine (CNR-ISMAR), Italy	Time series in the Adriatic Sea and Western Mediterranean Sea
James Orr	M	Laboratoire des Sciences du Climat et l'eEnvironnement (LSCE/CEA), France	Expertise in Global Carbon Chemical Modelling and intercomparability, global carbon cycle, CO_2 software calculations

Working Group contributions

Andrew Dickson
Expert in laboratory measurement of CO_2 parameters and modelling of chemical speciation; and also in the development of standard materials, calculation methods and documentation for the marine CO_2 system.

Marta Álvarez
Chemical oceanographer, expertise in CO_2 discrete data, CO_2 internal consistency and decadal biogeochemical changes. IEO IP for biogeochemistry in coastal North Atlantic. MEDSHIP program.

Robert H. Byrne
Expertise in marine and riverine CO_2 system chemistry and internal consistency, and in developing in-situ methods for measurements of carbon system parameters

Kim Currie
Responsible for the New Zealand Ocean Acidification Observing Network, studying long term changes in subantarctic waters (Munida transect) and New Zeeland coastal waters.

Sue Hartman
Chemical oceanographer, expertise in ferry-box sensor data processing and calibration. Responsible for biogeochemistry in PAP time series and UK ocean acidification cruises, UKOA CO_2 facility.

José Martín Hernández-Ayón
Chemical Oceanographer with experience in quality data for coastal regions and the potential contribution of organic bases to the alkalinity of seawater samples.

Siv K. Lauvset
Expert in quality control of seawater CO_2 measurements from surface CO_2 to water column and sensors. Active in Global Ocean Data Analysis Project (GLODAP), SOCAT (Surface Ocean CO2 Atlas) and ICOS (Integrated Carbon Observation System).

Claire Lo Monaco
Expertise in quality control for surface and water column CO_2 data (GLODAP and SOCAT), decadal changes in biogeochemistry and carbon cycle in the Indian Oc. IP for CO_2 French facility.

Akihiko Murata
Chemical oceanographer, expertise in producing high-quality data for carbonate system and the related properties through repeat hydrography (GO-SHIP) cruises.

Weidong Zhai
Expertise in surface and water column CO_2 and carbonate measurements and studies. Representative for ocean carbon cycle investigations in China.

Key References

Carter, B. R., R. A. Feely, N. L. Williams, A. G. Dickson, M. B. Fong, and Y. Takeshita (2017), Updated methods for global locally interpolated estimation of alkalinity, pH, and nitrate, *Limnol. Oceanogr. Methods*, doi:10.1002/lom3.10232.
Chen, B., Cai, W.-J., and Chen, L. (2015) The marine carbonate system of the Arctic Ocean: assessment of internal consistency and sampling considerations, summer 2010. *Mar. Chem. 176, 174-188.* doi: 10.1016/j.marchem.2015.09.007.
Clayton, T. D., and R. H. Byrne (1993), Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, *Deep Sea Res. Part I Oceanogr. Res. Pap.*, 40(10), 2115–2129, doi:10.1016/0967-0637(93)90048-8.
DeGrandpre, M. D., R. S. Spaulding, J. O. Newton, E. J. Jaqueth, S. E. Hamblock, A. A. Umansky, and K. E. Harris (2014), Considerations for the measurement of spectrophotometric pH for ocean acidification and other studies, *Limnol. Oceanogr. Methods,* 12(12), 830–839, doi:10.4319/lom.2014.12.830.
Dickson, A. G., J. D. Afghan, and G. C. Anderson (2003), Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity, *Mar. Chem.*, *80*(2–3), 185–197, doi:10.1016/S0304-4203(02)00133-0.
Dickson et al. (2015 – see Appendix).
Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, *18*(4), 1–23, doi:10.1029/2004GB002247.

Liu, X., M. C. Patsavas, and R. H. Byrne (2011), Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements, *Environ. Sci. Technol.*, *45*(11), 4862–4868, doi:10.1021/es200665d.

Olsen, A. et al. (2016), The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean, *Earth Syst. Sci. Data*, *8*(2), 297–323, doi:10.5194/essd-8-297-2016.

Patsavas, M. C., R. H. Byrne, R. Wanninkhof, R. A. Feely, and W.-J. Cai (2015), Internal consistency of marine carbonate system measurements and assessments of aragonite saturation state: Insights from two U.S. coastal cruises, *Mar. Chem.*, *176*, 9–20, doi:10.1016/j.marchem.2015.06.022.

Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2011 Guide to best practices for ocean acidification research and data reporting. Luxembourg, Publications Office of the European Union, 258pp. (EUR 24872 EN). doi: 10.2777/66906.

Velo, A., F. F. Pérez, X. Lin, R. M. Key, T. Tanhua, M. De La Paz, A. Olsen, S. Van Heuven, S. Jutterström, and A. F. Ríos (2010), CARINA data synthesis project: pH data scale unification and cruise adjustments, *Earth Syst. Sci. Data*, *2*, 133–155, doi:10.3334/CDIAC/otg.CARINA.SO.V1.0.

Williams, N. L. et al. (2017), Calculating surface ocean pCO_2 from biogeochemical Argo floats equipped with pH: An uncertainty analysis, *Global Biogeochem. Cycles*, *31*(3), 591–604, doi:10.1002/2016GB005541.

Woosley, R. J., F. J. Millero, and T. Takahashi (2017), Internal consistency of the inorganic carbon system in the Arctic Ocean, *Limnol. Oceanogr. Methods*, *15*(10), 887–896, doi:10.1002/lom3.10208.

Yao, W., X. Liu, and R. H. Byrne (2007), Impurities in indicators used for spectrophotometric seawater pH measurements: Assessment and remedies, *Mar. Chem.*, *107*(2), 167–172, doi:10.1016/j.marchem.2007.06.012.

Appendix –Relevant publications for each full member

Andrew G. Dickson

Bockmon, EE, **Dickson AG**. (2015). An inter-laboratory comparison assessing the quality of seawater carbon dioxide measurements. Marine Chemistry. 171:36-43. doi: 10.1016/j.marchem.2015.02.002.

Dickson, AG, M F Camões, P Spitzer, P Fisicaro, D Stoica, R Pawlowicz and R Feistel (2016). Metrological challenges for measurements of key climatological observables. Part 3: seawater pH. Metrologia 53 R26. https://doi.org/10.1088/0026-1394/53/1/R26.

Loucaides, S, Rerolle VMC, Papadimitriou S, Kennedy H, Mowlem MC, **Dickson AG**, Gledhill M, Achterberg EP. (2017). Characterization of meta-Cresol Purple for spectrophotometric pH measurements in saline and hypersaline media at sub-zero temperatures. Scientific Reports. 7, doi:10.1038/s41598-017-02624-0.

Okazaki, RR, Sutton AJ, Feely RA, **Dickson AG**, Alin SR, Sabine CL, Bunje PME, Virmani JI. (2017). Evaluation of marine pH sensors under controlled and natural conditions for the Wendy Schmidt Ocean Health XPRIZE. Limnology and Oceanography-Methods. 15:586-600. 10.1002/lom3.10189.

Williams, NL, Juranek LW, Feely RA, Johnson KS, Sarmiento JL, Talley LD, **Dickson AG**, Gray AR, Wanninkhof R, Russell JL, Riser SC, Takeshita Y. (2017). Calculating surface ocean pCO_2 from biogeochemical Argo floats equipped with pH: An uncertainty analysis. Global Biogeochemical Cycles. 31:591-604. doi: 10.1002/2016gb005541.

Marta Álvarez

Álvarez M., C. Lo Monaco, T. Tanhua, A. Yool, A. Oschlies, J. L. Bullister, C. Goyet, N. Metzl, F. Touratier, E. McDonagh, and H. L. Bryden (2009). Estimating the storage of anthropogenic carbon in the subtropical Indian Ocean: a comparison of five different approaches. *Biogeosciences* **6**: 681-703.

Álvarez M., T. Tanhua, H. Brix, C. Lo Monaco, N. Metzl (2011). Decadal biogeochemical changes in the subtropical Indian Ocean associated with subantarctic mode water. *J. Geophys. Res*., 116, C09016, doi:10.1029/2010JC006475.

Álvarez, M., H. Sanleón-Bartolomé, T. Tanhua, L. Mintrop, A. Luchetta, C. Cantoni, K. Schroeder, and G. Civitarese (2014). The CO_2 system in the Mediterranean Sea: a basin wide perspective. *Ocean Sci.*, 10, 69-92, doi:10.5194/os-10-69-2014.

Fajar N.M., M.I. García-Ibáñez, H. SanLeón-Bartolomé, **M. Álvarez**, and F.F. Pérez (2015). Spectrophotometric Measurements of the Carbonate Ion Concentration: Aragonite Saturation States in the Mediterranean Sea and Atlantic Ocean. *Environ. Sci. Technol.*, 2015, 49 (19), pp 11679–11687, doi: 10.1021/acs.est.5b03033.

Schroeder, K., T. Tanhua, H.L. Bryden, **M. Álvarez**, J. Chiggiato, and S. Aracri. (2015). Mediterranean Sea Ship-based Hydrographic Investigations Program (Med-SHIP) Oceanography 28 (3) :12–15, dx.doi.org/10.5670/oceanog.2015.71.

Robert H. Byrne

Byrne, R.H. (2014). Measuring Ocean Acidification: New Technology for a New Era of Ocean Chemistry. Environmental Science and Technology 48: 5352 -5360. doi: dx.doi.org/10.1021/es405819p.

Clayton, T.D., **R.H. Byrne**, J.A. Breland, R.A. Feely, F.J. Millero, D.M. Campbell, P.R. Murphy, and M.F. Lamb. (1995). The role of pH Measurements in modern oceanic CO2-system characterizations: Precision and thermodynamic consistency. Deep Sea Research 42: 411–429.

McElligott, S., **R.H. Byrne**, K. Lee, R. Wanninkhof, F.J. Millero, and R.A. Feely. (1998). Discrete water column measurements of CO2 fugacity and pHT in seawater: A comparison of direct measurements and thermodynamic calculations. Marine Chemistry 60: 63–73.

Patsavas, M.C., **Byrne, R.H**., Wanninkhof, R., Feely, R.A. and W-J. Cai. (2015). Internal Consistency of Marine Carbonate System Measurements and Assessments of Aragonite Saturation States: Insights from Two U.S. Coastal Cruises. Marine Chemistry 176: 9-20; http://dx.doi.org/10.1016/j.marchem.2015.06.022.

Sharp, J.S., **R.H. Byrne**, X. Liu, R.A. Feely, E.E. Cuyler, R. Wanninkhof and S. Alin. (2017). Spectrophotometric Determination of Carbonate Ion Concentrations: Elimination of Instrument-Dependent Offsets and Calculation of In Situ Saturation States. Environmental Science and Technology, 51: 9127-9136. doi: http://dx.doi.org/10.1021/acs.est.7b02266.

Kim Currie

Bostock, H.C., Tracey, D.M., **Currie, K.I**., Dunbar, G.B., Handler, M.R., Mikaloff Fletcher, S.E., Smith, A.M., Williams, M.J.M., (2015). The carbonate mineralogy and distribution of habitat forming deep-sea corals in the southwest Pacific region. Deep-Sea Research I, 100, 88-104, https://doi.org/10.1016/j.dsr.2015.02.008.

Law, C., Bell, J., Bostock, H., Cornwall, C., Cummings, V., **Currie, K**., Davy, S., Gammon, M., Hepburn, C., Hurd, C., Lamare, M., Mikaloff-Fletcher, S., Nelson, W., Parsons, D., Ragg, N., Sewell, M., Smith, A., Tracey, D., (2018). Ocean Acidification in New Zealand waters. New Zealand Journal of Marine and Freshwater Research, 52, 155-195. https://doi.org/10.1080/00288330.2017.1374983.

Law, C.S., Rickard, G.J., Mikaloff-Fletcher, S.E., Pinkerton, M.H., Gorman, R., Behrens, E., Chiswell, S.M., Bostock, H.C., Anderson, O., **Currie, K.**, (2017). Climate Change projections for the surface ocean around New Zealand New Zealand Journal of Marine and Freshwater Research. https://doi.org/10.1080/00288330.2017.1390772.

Morales, S., Meyer, M.K., **Currie, K**., Baltar, F., (2018). Are oceanic fronts ecotones? Seasonal changes along the Subtropical Front show fronts as bacterioplankton transition zones but not diversity hotspots. Environmental Microbiology Reports, 10, 184-189. https://doi.org/10.1111/1758-2229.12618.

Shadwick, E.H., Tilbrook, B., **Currie, K.I.,** (2017). Late-summer biogeochemistry in the Mertz Polynya: East Antarctica. Journal of Geophysical Research, 122, 7380-7394.

Sue Hartman

León, P.; Walsham, P., Bresnan, E.; **Hartman, SE**.; Hughes, S.; Mackenzie, K.; Webster, L. (2018). Seasonal variability of the carbonate system and coccolithophore Emiliania huxleyi at a Scottish Coastal Observatory monitoring site. Estuarine, Coastal and Shelf Science, 202. 302-314.https://doi.org/10.1016/j.ecss.2018.01.011.

Hartman, S.E.; Humphreys, M.P.; Kivimae, C.; Woodward, E.M.S.; Kitidis, V.; McGrath, T.; Hydes, D.J.; Greenwood, N.; Hull, T.; Ostle, C.; Pearce, D.J.; Sivyer, D.; Stewart, B.M.; Walsham, P.; Painter, S.C.; McGovern, E.; Harris, C.; Griffiths, A.; Smilenova, A.; Clarke, J.; Davis, C.; Sanders, R.; Nightingale, P.. (2018). Seasonality and spatial heterogeneity of the surface ocean carbonate system in the northwest European continental shelf. Progress in Oceanography. https://doi.org/10.1016/j.pocean.2018.02.005 (In Press).

Painter, S C.; **Hartman, SE**.; Kivimae, C.; Salt, L.A.; Clargo, N.; Daniels, C.J.; Bozec, Y.; Munns, L; Allen, S; Hemsley, VS.; Moschonas, G; Davidson, K. (2017) The elemental stoichiometry (C, Si, N, P) of the Hebrides Shelf and its role in carbon export. Progress in Oceanography, 159. 154-177.10.1016/j.pocean.2017.10.001.

Hátún, H.; Azetsu-Scott, K.; Somavilla, R.; Rey, F.; Johnson, C.; Mathis, M.; Mikolajewicz, U.; Coupel, P.; Tremblay, J.-É.; **Hartman, S.;** Pacariz, S.V.; Salter, I.; Ólafsson, J.. (2017). The subpolar gyre regulates silicate concentrations in the North Atlantic. Scientific Reports, 7 (1). 14576. https://doi.org/10.1038/s41598-017-14837-4.

Humphreys, M. P.; Griffiths, A. M.; Achterberg, E.P.; Holliday, N. P.; Rerolle, VM.C.; Menzel Barraqueta, JL; Couldrey, M.P.; Oliver, K. I.C.; **Hartman, S**.; Esposito, M.; Boyce, A J. (2016). Multidecadal accumulation of anthropogenic and remineralized dissolved inorganic carbon along the Extended Ellett Line in the northeast Atlantic Ocean. Global Biogeochemical Cycles, 30 (2). 293-310.10.1002/2015GB005246.

José Martín Hernández Ayón

Chapa-Balcorta, C., **Hernandez-Ayon, J.M**., Durazo, R., Beier, E., Alin, S.R. and Lopez-Perez, A., (2015). Influence of post-Tehuano oceanographic processes in the dynamics of the CO_2 system in the Gulf of Tehuantepec, Mexico. Geophys. Res. Oceans*,* 120*,* 7752–7770*, doi:*10.1002/2015JC011249.

Feely, R.A., C.L. Sabine, **J.M. Hernandez-Ayon,** D. Ianson, and B. Hales (2008): Evidence for upwelling of corrosive "acidified" water onto the Continental Shelf. *Science*, *320*(5882), doi: 10.1126/science.1155676, 1490–1492.

Hernandez-Ayon J. Martin, A. Zirino, A.G: Dickson, T. Camiro Vargas y E. Valenzuela-Espinoza (2007). Effect of microalgal products on the titration alkalinity in coastal seawater. Limnology and Oceanography: Methods. 5, 225-232.

Norzagaray-López, C. O., **Hernández-Ayon, J. M.,** Calderon Aguilera, L. E., Reyes-Bonilla, H., Chapa-Balcorta, C. and Ayala-Bocos, A. (2017). Aragonite saturation and pH variation in a fringing reef are strongly influenced by oceanic conditions. Limnol. Oceanography. doi:10.1002/lno.10571.

Ribas-Ribas,M., **J.M. Hernandez-Ayon**, V.F. Camacho-Ibar, A. Cabello-Pasini, A. Mejia-Trejo, R. Durazo, S. Galindo-Bect, A.J. Souza, J.M. Forja, A. Siqueiros-Valencia, (2011). Effects of upwelling, tides and biological processes on the inorganic carbon system of a coastal lagoon in Baja California. Estuarine, Coastal and Shelf Science. 95(4): 367-376.

Siv Kari Lauset

Lauvset, S.K., Gruber, N., 2014. Long-term trends in surface ocean pH in the North Atlantic. *Marine Chemistry*, 162, 71-76. doi:10.1016/j.marchem.2014.03.009.

Lauvset, S.K., Gruber, N., Landschützer, P., Olsen, A., Tjiputra, J., 2015. Trends and drivers in global surface ocean pH over the past 3 decades. *Biogeosciences*, 12, 1285-1298. doi:10.5194/bg-12-1285-2015.

Lauvset, S.K., Key, R.M., Olsen, A., van Heuven, S., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Perez, F.F., Suzuki, T., Watelet, S., 2016. A new global interior ocean mapped climatology: the 1° × 1° GLODAP version 2. *Earth Syst. Sci. Data*, 8, 325-340. 10.5194/essd-8-325-2016.

Olsen, A., Key, R.M., van Heuven, S., **Lauvset**, S.K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Pérez, F.F., Suzuki, T., 2016. The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean. Earth Syst. Sci. Data, 8, 297-323. doi: 10.5194/essd-8-297-2016.

Turk, D., Dowd, M., **Lauvset**, S.K., Koelling, J., Alonso-Pérez, F., Pérez, F.F., 2017. Can Empirical Algorithms Successfully Estimate Aragonite Saturation State in the Subpolar North Atlantic? Frontiers in Marine Science, 4. doi: 10.3389/fmars.2017.00385.

Claire Lo Monaco

Blain, S., et al., 2007. Effect of natural iron fertilization on carbon sequestration in the Southern Ocean, Nature, 446, doi: 10.1038/nature05700.

Lo Monaco, C., C. Goyet, N. Metzl, A. Poisson, and F. Touratier, 2005. Distribution and inventory of anthropogenic CO2 in the Southern Ocean: Comparison of three data-based methods, J. Geophys. Res., 110, C09S02, doi:10.1029/2004JC002571.

Lo Monaco, C., M. Álvarez, R. M. Key, X. Lin, T. Tanhua, B. Tilbrook, D. C. E. Bakker, S. van Heuven, M. Hoppema, N. Metzl, A. F. Ríos, C. L. Sabine, and A. Velo, 2010. Assessing the internal consistency of the CARINA database in the Indian sector of the Southern Ocean, Earth Syst. Sci. Data, 2, 51-70, doi:10.5194/essd-2-51-2010.

Racapé, V., Pierre C., N. Metzl, **C. Lo Monaco**, G. Reverdin, P. Morin, F.F. Perez, A. Olsen, A.F. Rios, M. Vazquez-Rodriguez, 2013. Anthropogenic carbon changes in the Irminger Basin (1981-2006): Coupling d13CDIC and DIC observations. Journal of Marine Systems, doi:10.1016/j.jmarsys.2012.12.005

Vázquez-Rodríguez, M., F. Touratier, **C. Lo Monaco**, D. W. Waugh, X. A. Padin, R. G. J. Bellerby, C. Goyet, N. Metzl, A. F. Ríos, and F. F. Pérez, 2009. Anthropogenic carbon distributions in the Atlantic Ocean: data-based estimates from the Arctic to the Antarctic, Biogeosciences, 6, 439-451.

Akihiko Murata

Kouketsu K., **Murata A.** (2014). Detecting decadal scale increases in anthropogenic CO_2 in the ocean. Geophysical Research Letters, 41, https://doi.org/10.1002/2014GL06516.

Kouketsu S., **Murata A.**, Doi T. (2013). Decadal changes in dissolved inorganic carbon in the Pacific Ocean. Global Biogeochemical Cycles*,* 27, https://doi.org/10.1029/2012GB004413.

Murata A., Hayashi K., Kumamoto Y., Sasaki K. (2015). Detecting the progression of ocean acidification from the saturation state of $CaCO_3$ in the subtropical South Pacific. Global Biogeochemical Cycles, 29*,* https://doi.org/10.1002/2014GB004908.

Murata A., Kumamoto Y., Sasaki K., Watanabe S., Fukasawa M. (2010). Decadal increases in anthropogenic CO_2 along 20°S in the South Indian Ocean. Journal of Geophysical Research, 115, C12055, https://doi.org/10.1029/2010JC006250.

Murata A., Saito S. (2012). Decadal changes in the $CaCO_3$ saturation state along 179°E in the Pacific Ocean. Geophysical Research Letters, 39, L12604, https://doi.org/10.1029/2012GL052297.

Weidong Zhai

Zhai, W.-D., 2018. Exploring seasonal acidification in the Yellow Sea. Science China Earth Science, in press, https://doi.org/10.1007/s11430-017-9151-4.

Zhai, W.-D., Chen, J.-F., Jin, H.-Y., Li, H.-L., Liu, J.-W., He, X.-Q., Bai, Y., 2014. Spring carbonate chemistry dynamics of surface waters in the northern East China Sea: Water mixing, biological uptake of CO_2, and chemical buffering capacity. Journal of Geophysical Research: Oceans 119, 5638-5653. https://doi.org/10.1002/2014JC009856.

Zhai, W.-D., Dai, M.-H., 2009. On the seasonal variation of air-sea CO_2 fluxes in the outer Changjiang (Yangtze River) Estuary, East China Sea. Marine Chemistry 117, 2–10. https://doi.org/10.1016/j.marchem.2009.02.008.

Zhai, W.-D., Dai, M.-H., Chen, B.-S., Guo, X.-H., Shang, S.-L., Zhang, C.-Y., Cai, W.-J., Wang, D.-X., 2013. Seasonal variations of sea–air CO_2 fluxes in the largest tropical marginal sea (South China Sea) based on multiple-year underway measurements. Biogeosciences 10, 7775–7791. https://doi.org/10.5194/bg-10-7775-2013.

Zhai, W.-D., Zheng, N., Huo, C., Xu, Y., Zhao, H.-D., Li, Y.-W., Zang, K.-P., Wang, J.-Y., Xu, X.-M., 2014. Subsurface pH and carbonate saturation state of aragonite on the Chinese side of the North Yellow Sea: seasonal variations and controls. Biogeosciences 11, 1103-1123. https://doi.org/10.5194/bg-11-1103-2014.