Integrated Marine Biogeochemistry and
Ecosystem Research

IMBER Update

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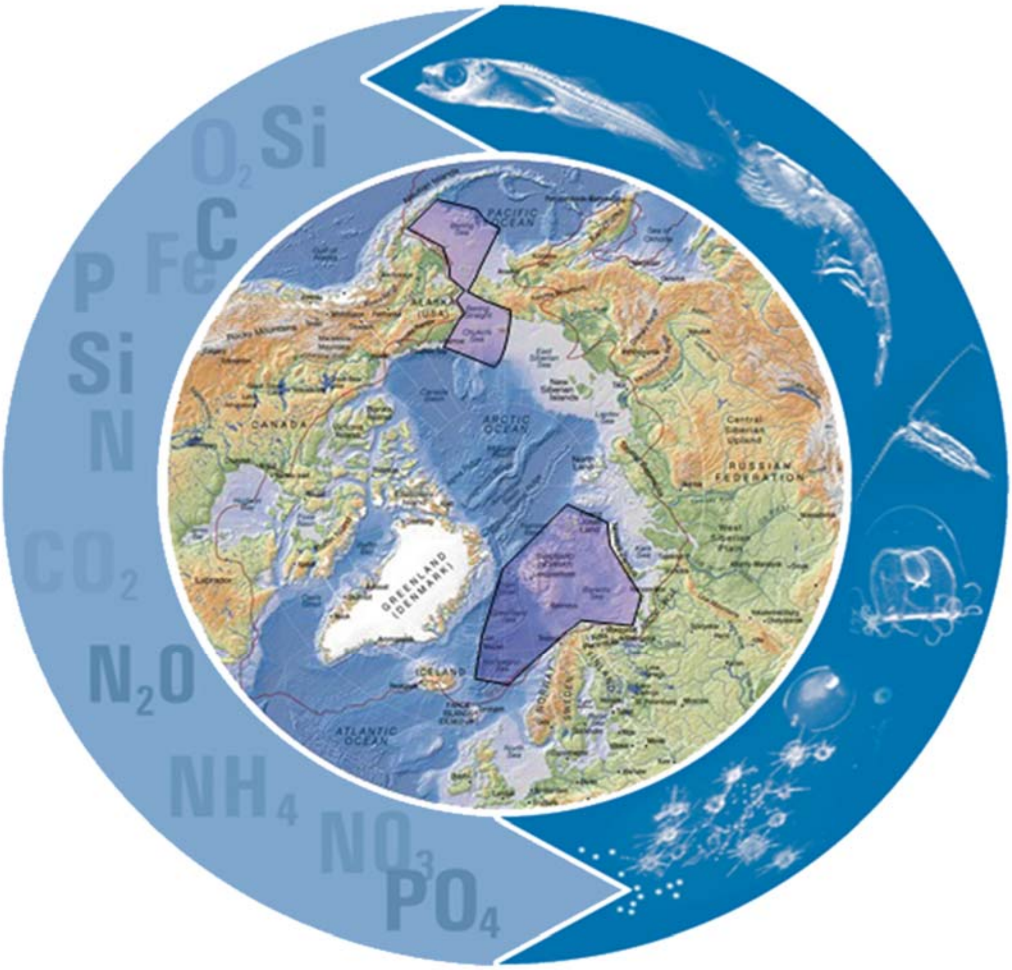

IMBER is an international project that aims to *investigate the sensitivity of marine biogeochemical cycles and ecosystems to global change, on time scales ranging from years to decades*. IMBER aims to provide a comprehensive understanding of, and accurate predictive capacity for ocean responses to accelerating global change and the consequent effects on the Earth System and human society.

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reference to eggs of the mackerel *Scomber scombrus*. *Mar. Biol*. 63: 101–106.

Coombs S, Fosh C, Keen M. 1985. The buoyancy and vertical distribution of eggs of sprat (*Sprattus sprattus*) and pilchard (*Sardina pilchardus*). *J. Mar. Biol. Assoc. UK*. 65: 461–474.

Riis-Vestergaard J. 2002. Energy density of marine pelagic fish eggs. *J. Fish. Biol*. 60: 1511–1528.

Smith H.W. 1930. The absorption and excretion of water and salts by marine teleosts. *Am. J. Physiol*. 93: 480-505.

Sundby S. 1983. A one-dimensional model for the vertical distribution of pelagic fish eggs in the mixed layer. *Deep-Sea Res*. Part A. 30: 645–661.

Sundby S. 1991. Factors affecting the vertical distribution of eggs. *ICES Mar. Sci. Symp*. 192:33–38.

Sundby S., Boyd A., Hutchings L., O'Toole M., Thorisson K., Thorsen A. 2001. Interaction between Cape hake spawning and the circulation in the Northern Benguela upwelling ecosystem. *S. Afr. J. Mar. Sci*. 23: 317-336.

Sundby S. and Kristiansen T. 2015. The principles of buoyancy in marine fish eggs and their vertical distributions across the world oceans. Submitted.

2.2 Observing changes in the surface ocean carbon inventory, autonomously

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The ocean exerts significant influence on global climate through carbon cycle feedback mechanisms that affect the air-sea exchange of carbon dioxide (CO_2) gas (Passow and Carlson, 2012; Ciais et al., 2013). Many of these feedback mechanisms are influenced by biological processes for which preindustrial baseline information does not exist. Thus, in a climate now transitioning away from preindustrial equilibrium, biogeochemical feedbacks may be even more challenging to discern and quantify.

In recognition of this issue, an immense effort has gone into the quantitative characterization of marine carbon cycling and biological carbon export from the surface ocean over the past few decades (e.g., Emerson, 2014). In particular, numerous investigators have worked to advance the technology available for autonomous carbon cycle studies (Johnson et al., 2009; Schuster et al., 2009) to learn more about the interplay of thermodynamic and biogeochemical controls on the observed global air-sea CO_2 exchange. The marine inorganic carbon system is often described by four primary parameters: dissolved inorganic carbon (DIC), total alkalinity (TA), CO_2, and pH. DIC is the sum of dissolved molecular species derived from CO_2. TA is a measure of the seawater charge balance. Measurement of any two of these four parameters, in addition to salinity and temperature, can be used to calculate all of the other carbonate system parameters (Millero, 2007) and to quantitatively evaluate the drivers of marine carbon cycling. In the past 10 years, autonomous CO_2 and pH sensors have become commercially available for moorings enabling the collection of high-frequency (<daily) time series observations of the carbonate system (Sutton et al., 2014).

Unfortunately, CO_2 and pH are the least ideal pair to constrain the carbonate system due to their strong covariance. Uncoupling of the CO_2 and pH uncertainties leads to large errors in the calculations of DIC and TA (>100 μmol kg^{-1}) *(*Dickson and Riley*, 1978;* Cullison Gray et al., 2011). Recognizing the challenges associated with further improving autonomous CO_2 and pH sensor measurement accuracies (~1 μatm and ~0.003, respectively), we set out to develop an autonomous surface ocean DIC sensor for moored application.

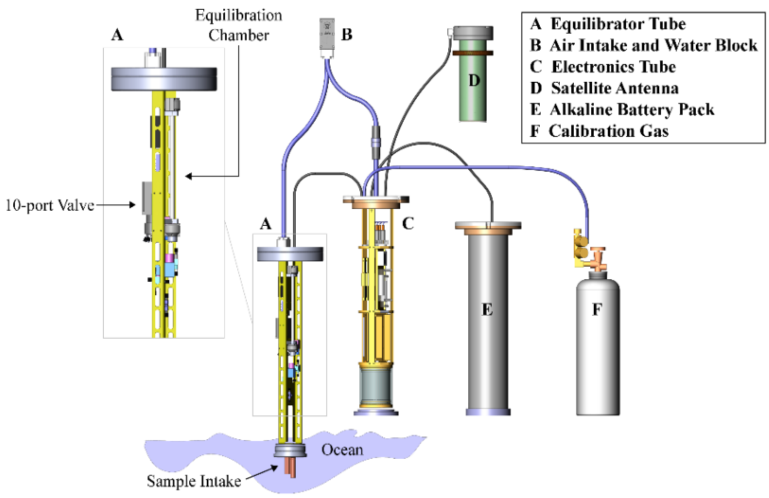

Figure 8. Diagram of the MADIC system. The equilibrator and electronics tubes house the primary instrument components and are shown here without their deployment housings. Three additional tubes house the battery pack, calibration gas, and satellite antenna. Details of the equilibrator tube are shown in the upper left. Figure reproduced from Fassbender et al., 2015.

The Moored Autonomous DIC (MADIC) sensor was modified from the Pacific Marine Environmental Laboratory $MAPCO_2$ system design (Fig. 8, Sutton et al., 2014). A 10-port valve with fixed-volume tubing loops is used to collect calibrated volumes of seawater (~1 mL) from ~1m depth, and of acid (~200 μL) from an acid reservoir within the equilibrator tube. The acid and seawater mix inside an equilibration chamber as initially CO_2-free air is bubbled through the acidic sample in a closed loop until equilibrium is reached. Most of the DIC in the acidic solution is transferred to the gas phase, and at equilibrium, CO_2 in the gas phase is measured with an infrared detector. The DIC concentration of the seawater is determined from the CO_2 content, pressure and temperature of the gas phase at equilibrium, measurements of sea water salinity and temperature from an external CTD at the time of sample injection, the Ideal Gas Law, and Henry's Law (Fassbender et al., 2015). Each measurement takes ~12 minutes to complete, including satellite transmission of the data after every two samples. The laboratory determined accuracy was found to be ±5 μmol kg^{-1}.

After rigorous testing in the laboratory and at the Seattle Aquarium, the MADIC sensor was deployed near Honolulu, Hawaii for a fully autonomous field test from November 2013 to May 2014. The sensor was mounted on a moored buoy with a Seabird Electronics CTD and $SAMI^2$ pH sensor affixed to the bridle and was positioned ~400m from shore and ~25m from another buoy carrying a $MAPCO_2$ sensor. Fifty two discrete samples were collected throughout the deployment and analyzed for DIC via coulometry at the University of Hawaii SOEST Laboratory. Results indicate that the MADIC sensor measurements were ~90% more accurate than DIC values calculated from in situ measurements of pH and CO_2, based on the 52 high-quality discrete DIC samples that were collected (Fig. 9, Fassbender et al., 2015).

The MADIC system is a first step toward autonomous and continuous monitoring of the surface ocean carbon inventory. Near real-time data transmission and remote control of the sensor through two-way satellite communication makes it possible to increase the sample frequency (up to 4 samples per hour) during interesting or intermittent environmental events. In addition, the sample injection volume can be altered so that a wider range of DIC concentrations than those observed in the surface ocean can be measured. The utility of the MADIC analyzer for long-term observing is particularly apparent in nearshore and high-latitude regions where fresh water input can lead to environmental conditions outside of the charge balance assumptions used to define ocean pH and TA (Dickson, 1981, 1984). In these environments, the direct measurement of DIC may be essential for robust constraint of the carbonate system until charge balance definitions are expanded.

The next phase in advancing autonomous marine carbon cycle observing capabilities will be the combination of two carbonate system sensors in one package, such that one platform can house multiple sensors and over constrain the carbonate system. The development of dual carbonate system sensors is well underway (Wang et al., 2015) and sensors for a variety of monitoring platforms and applications have proliferated over the past 5 years (for example: Martz et al., 2010; Easley et al., 2013; Li et al., 2013; Liu et al., 2013; Spaulding et al., 2014). Commercialization of these sensors coupled with continued technology advancement in the coming years will provide a wealth of new research opportunities for the broader carbon research community.

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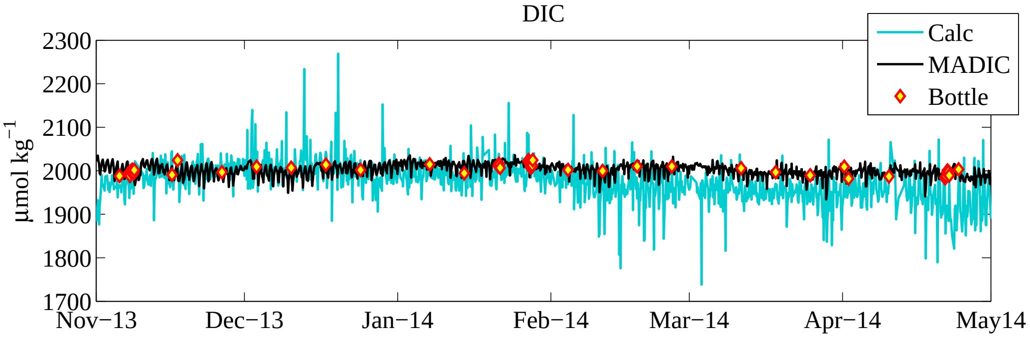

Figure 9. DIC concentrations measured by the DIC sensor (MADIC), calculated from in situ measurements of $x\mathrm{CO}_2$ and pH (Calc), and determined via coulometry (Bottle).

References

Ciais, P. et al. 2013. Carbon and Other Biogeochemical Cycles, in *Climate Change 2013: The Physical Science Basis*, edited by V. B. and P. M. M. (eds. . Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Cullison Gray, S. E., M. D. DeGrandpre, T. S. Moore, T. R. Martz, G. Friederich, and K. S. Johnson. 2011. Applications of in situ pH measurements for inorganic carbon calculations, *Mar. Chem.*, 125, 82–90, doi:10.1016/j.marchem.2011.02.005.

Dickson, a. G. 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, *Deep Sea Res. Part A. Oceanogr. Res. Pap.*, 28(6), 609–623, doi:10.1016/0198-0149(81)90121-7.

Dickson, A. G. 1984. pH scales and proton-transfer reactions in saline media such as sea water, *Geochim. Cosmochim. Acta*, 48(11), 2299–2308, doi:10.1016/0016-7037(84)90225-4.

Dickson, A. G., and J. Riley. 1978. The effect of analytical error on the evaluation of the components of the aquatic carbon-dioxide system, *Mar. Chem.*, 6, 77–85, doi:10.1016/0304-4203(78)90008-7.

Easley, R. a, M. C. Patsavas, R. H. R. H. Byrne, X. Liu, R. R. A. R. a Feely, and J. T. Mathis. 2013. Spectrophotometric measurement of calcium carbonate saturation states in seawater., *Environ. Sci. Technol.*, 47(3), 1468–77, doi:10.1021/es303631g.

Emerson, S. R. 2014. Annual net community production and the biological carbon flux in the ocean, *Global Biogeochem. Cycles*, 14–28, doi:10.1002/2013GB004680.Received.

Fassbender, A. J., C. L. Sabine, N. Lawrence-Slavas, E. H. De Carlo, C. Meinig, and S. Maenner Jones. 2015. Robust Sensor for Extended Autonomous Measurements of Surface Ocean Dissolved Inorganic Carbon, *Environ. Sci. Technol.*, doi:10.1021/es5047183.

Johnson, K. S., W. M. Berelson, E. S. Boss, Z. Chase, H. Claustre, S. R. Emerson, N. Gruber, A. Kortzinger, M. J. Perry, and S. C. Riser. 2009. Observing biogeochemical cycles at global scales with profiling floats and gliders: Prospects for a global array, *Oceanography*, 22, 216–225.

Li, Q., F. Wang, Z. A. Wang, D. Yuan, M. Dai, J. Chen, J. Dai, and K. A. Hoering. 2013. Automated spectrophotometric analyzer for rapid single-point titration of seawater total alkalinity., *Environ. Sci. Technol.*, 47(19), 11139–46, doi:10.1021/es402421a.

Liu, X., R. H. Byrne, L. Adornato, K. K. Yates, E. Kaltenbacher, X. Ding, and B. Yang. 2013. In situ spectrophotometric measurement of dissolved inorganic carbon in seawater., *Environ. Sci. Technol.*, 47, 11106–11114, doi:10.1021/es4014807.

Martz, T. R., J. G. Connery, and K. S. Johnson. 2010. Testing the Honeywell Durafet for seawater pH applications, *Limnol. Oceanogr. Methods*, 8, 172–184, doi:10.4319/lom.2010.8.172.

Millero, F. J. 2007. The marine inorganic carbon cycle., *Chem. Rev.*, 107, 308–341, doi:10.1021/cr0503557.

Passow, U., and C. A. Carlson. 2012. The biological pump in a high CO_2 world, *Mar. Ecol. Prog. Ser.*, 470(2), 249–271, doi:10.3354/meps09985.

Schuster, U., A. Hannides, L. Mintrop, and A. Körtzinger. 2009. Sensors and instruments for oceanic dissolved carbon measurements, *Ocean Sci. Discuss.*, 5(1), 491–524, doi:10.5194/osd-6-491-2009.

Spaulding, R. S., M. D. DeGrandpre, J. C. Beck, R. D. Hart, B. Peterson, E. H. De Carlo, P. S. Drupp, and T. R. Hammar. 2014. Autonomous in situ measurements of seawater alkalinity., *Environ. Sci. Technol.*, 48(16), 9573–81, doi:10.1021/es501615x.

Sutton, A. J. et al. 2014. A high-frequency atmospheric and seawater pCO_2 data set from 14 open ocean sites using a moored autonomous system, *Earth Syst. Sci. Data Discuss.*, 7, 385–418, doi:10.5194/essdd-7-385-2014.

Wang, Z. A., F. N. Sonnichsen, A. M. Bradley, K. a. Hoering, T. M. Lanagan, S. N. Chu, T. R. Hammar, and R. Camilli. 2015. An In-situ Sensor Technology for Simultaneous Spectrophotometric Measurements of Seawater Total Dissolved Inorganic Carbon and pH, *Environ. Sci. Technol.*, 150226220706007, doi:10.1021/es504893n.