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CRDS-Based Underway Monitoring of Surface Water $\delta^{13}C(CO_2)$ During Two Atlantic Transects: Intercomparison and Gas Matrix Effects

Gernot Friedrichs (1), Nils Andersen (2), Meike Becker (1), and Arne Körtzinger (3)

(1) Christian-Albrechts-University Kiel, Institute of Physical Chemistry, Kiel, Germany (friedrichs@phc.uni-kiel.de, becker@phc.uni-kiel.de), (2) Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research, Kiel, Germany (nandersen@leibniz.uni-kiel.de), (3) Leibniz Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany (akoertzinger@ifm-geomar.de)

Measurement of dissolved inorganic carbon (DIC) and its isotopic composition can be used to understand carbon dynamics in the surface ocean and to quantify its function as a source and sink for atmospheric CO_2. Diverse processes such as photosynthesis, mixing, and the oceanic Suess effect influence the surface layer carbon budget. A reliable estimate of the relative contributions of these processes has to be based on time-series data with sufficient spatial and temporal resolution. So far, corresponding studies are scarce due to the difficulties of establishing the required isotopic measurements. Modern optical analyzers based on cavity-ringdown spectroscopy hold the potential to fill the gap of affordable high-precision instrumentation that can be installed aboard ships.

A commercial CRDS $^{13}CO_2/^{12}CO_2$ isotopic gas analyzer has been operated in combination with a water-air equilibration setup during two R/V Polarstern cruises (ANT XXVI/ 1 and XXVI/4) in continuous underway mode. For the first time, ten weeks of continuous data of oceanic $\delta^{13}C(CO_2)$ *and* pCO_2 of carbon dioxide dissolved in seawater have been collected. These data were converted to oceanic $\delta^{13}C(DIC)$ and DIC values by taking into account temperature and pH dependent fractionation and speciation within the carbonate system. Especially in biologically active waters, distinct variability and strong correlations between $\delta^{13}C(DIC)$ and DIC were observed. However, prior to a further analysis in terms of carbon dynamics, it has to be ascertained that the dataset is free of potential natural interferences and technical flaws. Therefore, in this presentation, a focus is set on a detailed intercomparison of the CRDS/equilibrator method with conventional reference measurements including isotope ratio mass spectrometric $\delta^{13}C(DIC)$ analysis of discrete water samples and pCO_2 measurements using non-dispersive infrared (NDIR) carbon dioxide sensors. In order to meet the high accuracy demands, the raw CRDS data had to be corrected for gas matrix effects originating from subtle pressure broadening linewidth effects of the measured CO_2 absorption lines [1]. These effects can be quantitatively taken into account by a spectroscopically based correction procedure. With the oxygen mole fraction in the analyzed gas sample stream as the sole input parameter, the procedure was verified to yield reliable results. The required O_2 content has been measured separately with an optode, but alternatively could also be directly extracted from the measured spectral CRDS data at somewhat lower precision. Overall, our results demonstrate that the CRDS/equilibrator setup is capable of precise and accurate online monitoring of surface ocean CO_2 parameters without the need for frequent recalibration.

[1] G. Friedrichs, J. Bock, F. Temps, P. Fietzek, A. Körtzinger, D. W. R. Wallace, *Limnol. Oceanogr.: Methods* **8** (2010) 539-551.