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Biogeosciences Discussions

Interactive comment on "TECHNICAL NOTE: Coupling infrared gas analysis and cavity ring down spectroscopy for autonomous, high temporal resolution measurements of DIC and δ^{13}C-DIC" *by* Mitchell Call et al.

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General comments:

This article describes the analytical procedure and performance of two commercial instruments coupled to provide near-simultaneous, high quality data on DIC concentrations and DIC 12C/13C isotope ratios (delta 13C). Similar automated and high-frequency data have previously been obtained using custom designed instruments in both the laboratory and the field (as referenced). The merit of the approach described

here is that the interfacing of the two instruments, each optimised for their respective analysis, provides combined data with improved precision and accuracy compared to the previously described methods.

The authors convincingly demonstrate that the technique works well in the laboratory and comment that it may also be field deployable with adequate power and shelter. However, the practicalities of field deployment would not be easy as the several components (CRDS, AIRICA, LICOR, PC, monitor, air tank, power etc) must weigh 50-60 kg. Also, the authors describe their system as 'simple' which might be slightly 'optimistic', especially in a field setting. Further testing would be needed to demonstrate performance in the field (e.g. sensitivity to temperature changes).

I find this a high quality technical note that reads very well and the procedures are mostly clearly described, it is also great that the supplement includes computer coding to aid other researchers setting up this technique.

I'm curious as to why 'zero air' (CO2 free air) was not used as carrier – instead, air with a reduced CO2 content was used requiring a mass balance calculation to derive the sample isotope results. I would think this potentially degrades performance.

Regarding the previous comment (ref #1) on the use of the Keeling plot for the linear sections of Fig. 4 (discussion P 8 re respiration and photosynthetic fixation during the algae bloom experiment), I agree that this treatment seem valid for the dark sections (respiration) – here the two mixing components would be (1) the existing DIC pool and (2) the added DIC (respired CO2 – although this could be a constant mixture of CO2 coming from more than one source). For the light sections (photosynthesis), the 'mixing' line is in effect an 'un-mixing' line (CO2 - and preferentially 12CO2 – being removed from the DIC pool). How such a line should be interpreted seems highly uncertain given the associated (and uncertain/variable) isotopic fractionation effects. I suggest modifying this section of the discussion but an exhaustive explanation should not be necessary in this technical note.

Specific comments: 1. P3 line 12-14: need more specifics for the 'Dickson CRM', justify why CO2 free air was not used 2. P3 line 17: 'CO2 only operating mode' is confusing here – is it because this instrument also can measure CH4? 3. P5: May point out that blooming algae would have been present in the sampled seawater – is there any information on the type/species? 4. P7 line 21: Similar systematic changes in DIC and d13C was previously described for coral by the Bass et al 2012 study 5. P8: For the algae bloom experiment, additional details are required on how the uncertainty of the intercept d13C values in the Keeling plots were derived (Fig. S2) – the uncertainties should be added to the figures. 6. P8 line 3: It should be emphasised that uncertainty of the intercept d13C value is very dependent on the range of [DIC] in each plot – and much higher than the uncertainty of the individual d13C DIC data points. Could this uncertainty be improved by manipulating carrier flow and sample size etc to increase the [DIC] range? Would using CO2 free air as carrier increase the range? 7. P8 line 10: Suggest expanding this explanation a bit: initial source is terrestrial OM present in the sampled coastal seawater, then marine OM from the Ulva sp introduced later in the experiment 8. Figure 3 shows a very good correlation between AIRICA-CRDS and IRMS results for samples, yet supplement Table S1 seems to show an offset of 0.3-0.5 ‰ between the two techniques 9. Supplement Fig. S1: Seems surprising that rinse, DIC and d13C cycles produce same concentration (peak value) - is the concentration limited by settings of the AIRICA?

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