Moderate dissolved inorganic carbon ($DI^{13}C$) isotope enrichment (MoDIE) for improved evaluation of DIC photochemical production in seawater

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A fundamental question in marine chemistry has been whether photochemistry plays a globally significant role in the removal of dissolved organic carbon (DOC) via the production of dissolved inorganic carbon (DIC) in the ocean. This question remains unanswered due to the analytical challenge involved in accurately measuring very low production rates (likely sub-μM h^{-1} for blue ocean waters) relative to high background DIC concentrations (~ 2 mM). Almost all previous attempts to overcome this analytical limitation in marine systems have relied on removing the background DIC prior to irradiation, with unknown consequences for the integrity of the DOC pool and its photoreactivity, and none have resulted in a satisfactory determination of photoproduced DIC in open ocean waters. Here, we use small additions of $NaH^{13}CO_3$ (< 10% of background DIC concentrations) to achieve moderate $DI^{13}C$ isotope enrichment (MoDIE) of samples. We then quantify the $\delta^{13}C$ shift of DIC in irradiated samples via liquid chromatography - isotope ratio mass spectrometry (LC-IRMS) and use these shifts to calculate photoproduced DIC. The MoDIE method was evaluated by determining initial DIC photoproduction rates, along with associated photochemical efficiency data (i.e. apparent quantum yield spectra), in riverine to offshore waters, and has produced the earliest time point and most precise measurement of DIC photoproduction in unmodified, low-CDOM, blue water ($a_g(325)$ = 0.30 m^{-1}) reported to date. With its ability to measure small DIC changes from photochemistry, MoDIE allows for improved photochemical models that redefine the global photochemical sink for oceanic DOC.