Computation of fCO_2 and the concentration of carbonate ions and the potential role of DOM accumulation in ocean acidification experiments

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The internal consistency of measurements and computations of components of the CO_2-system, namely total alkalinity (A_T), total dissolved carbon dioxide (C_T), CO_2 fugacity (fCO_2), and pH, has been confirmed repeatedly in open ocean studies when the CO_2 system had been over determined. Differences between measured and computed properties, e.g. ΔfCO_2 ($=fCO_{2meas} - fCO_{2(AT + CT)}$)/ fCO_{2meas}*100), there are usually below 5%. Recently, Hoppe et al. (2010, Biogeosciences Discussions) provided evidence of significantly larger ΔfCO_2 (about 25% on average). These observations are currently not well understood. Here we provide additional examples from phytoplankton culture and mesocosm experiments of ΔfCO_2 of up to 40%. In one set of experiments a clear correlation with the accumulation of dissolved organic carbon (DOC) is evident. Most importantly, in these and other experiments ΔfCO_2 varied systematically during the course of the experiments. Culture and mesocosm experiments are usually carried out under very high initial nutrient concentrations, yielding high biomass concentrations that in turn often lead to a substantial build-up DOC. DOC can reach concentrations much higher than typically observed in the open ocean. To the extent that DOC includes organic acids and bases, it will contribute to the alkalinity of the sea water contained in the experimental device. Our analysis suggests that whenever substantial amounts of DOC are produced during the experiment, standard computer programs used to compute CO_2 fugacity can underestimate true fCO_2 significantly. Alternative explanations for large ΔfCO_2, e.g. uncertainties of pKs, are explore as well, but are found to be of minor importance.