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Discussions

Interactive comment on “On CO_2 pertubation experiments: over-determination of carbonate chemistry reveals inconsistencies” *by* C. J. M. Hoppe et al.

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Hoppe et al. report very large discrepancies between measured pCO2 and pCO2 calculated from other carbonate system parameters, in natural seawater treated to adjust pCO2. In particular, pCO2 calculated from the DIC (dissolved inorganic carbon) and TA (total alkalinity) pair is approximately 300 μatm lower than measured pCO2 and pCO2 calculated from other pairs, in the high pCO2 manipulations.

We suspect that these important discrepancies can probably be largely resolved by considering DOM (dissolved organic matter)-related alkalinity (TA-DOM), which was suggested to be important in a recent paper (Kim & Lee, 2009). Kim and Lee found large impacts on TA in phytoplankton culture experiments in which large amounts of DOM were generated, including a ratio of ∼1:1 between amount of DOC (dissolved organic carbon) produced and increase in TA-DOM (their figure 3).

This could be highly relevant to explaining Hoppe et al's results, if the source water for Hoppe et al.'s experiments (collected from the North Sea) was preconditioned by biological activity leading to high levels of TA-DOM. High levels of DOC occur in the North Sea, with levels in the central North Sea observed to vary seasonally between an average of about 100 μM C in autumn and an average of about 200 μM C in spring (figure 4 of Suratman et al., 2009).

We recalculated Table 1 of Hoppe et al using the program SWCO2 (we also used other programs, with similar results), but with all TA values adjusted downwards by 50 μmol kg-1, to examine the implications of an assumed 50 μmol kg-1 contribution of TA-DOM (the figure of 50 μmol kg-1 is chosen to give the best numerical results).

The table below shows that this removes the worst discrepancies for pCO2 calculated from TA & DIC. At the same time, the changes to TA make a much smaller difference to pCO2 calculated from TA & pH. This is because, at the high pCO2 values, pCO2 calculated from TA & DIC is at least an order of magnitude more sensitive to variations in TA than is pCO2 calculated from TA & pH. It can also be seen that whereas decreasing TA by 50 μmol kg-1 raises calculated pCO2 (from TA&DIC) by 260-410 μatm in the high pCO2 experiments, it raises it by only 30-40 μatm in the low pCO2 experiments.

We suggest that the puzzling lack of agreement in the over-constrained carbonate chemistry may be due to DOM-related alkalinity, as in fact specifically predicted by Kim & Lee: "... if the contribution of DOM remains unrecognized and is not taken into consideration, the prediction of surface pCO2 from pairs of carbon system parameters involving AT will be in error. . .”. Hoppe et al’s results and the calculations above suggest that the associated errors are particularly significant for pCO2 derived from DIC and TA, less so for pCO2 derived from pH and TA.

It would be helpful if more information about time and place of seawater collection could be provided in the final MS, to allow a better evaluation of this potential explanation. .

Kim, H.-C., and K. Lee (2009) Significant contribution of dissolved organic matter to seawater alkalinity, Geophys. Res. Lett., 36, L20603, doi:10.1029/2009GL040271.

Suratman, S., K. Weston. T. Jickells and L. Fernand (2009) Spatial and seasonal changes of dissolved and particulate organic C in the North Sea. Hydrobiologia, 628: 13-25.

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		Calculated $p\text{CO}_2$ (µatm)			
	TA (µmol kg^{-1})	(MIMS)	(TA; DIC)	(TA; pH)	(DIC; pH)
low pCO2 (via DIC)	2338	205	181	237	231
	2335	203	184	195	194
	2333	219	185	203	201
high $p\text{CO}_2$ (via DIC)	2346	1042	956	943	945
	2336	1000	1023		
	2338	1117	1024	996	1000
low pCO2 (via TA)	2593	259	241	221	224
	2592	268	248	218	221
	2590	238	253	218	222
high $p\text{CO}_2$ (via TA)	2226	1202	1332	1202	1210
	2228	1247	1251	1221	1224
	2226	1257	1332	1199	1208

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