Definition of alkalinity:

Dickson, A. G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep Sea Research Part A. Oceanographic Research Papers 28, 609-623.

Dickson, A. G., 1992. The development of the alkalinity concept in marine chemistry. Marine Chemistry 40, 49-63.

$$
\begin{aligned}
A_T = {} & \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] \\
& + 2\left[PO_4^{3-}\right] + \left[SiO(OH)_3^-\right] + \left[NH_3\right] + \left[HS^-\right] \\
& - \left[H^+\right]_F - \left[HSO_4^-\right] - \left[HF\right] - \left[H_3PO_4\right] \\
& + \left[\text{minor bases} - \text{minor acids}\right]
\end{aligned}
$$

Calculations of the carbonate system assume that carbonate alkalinity is a known fraction of the measured TA. This <u>may</u> not be true in some waters relevant to the study of ocean acidification. Organic alkalinity – organic matter that reacts with the acid used in the measurement of alkalinity by titration - is not accounted for in the calculations.

- Hernandez-Ayon, J. M., et al 2007. Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters. Limnology and Oceanography: Methods 5, 225-232
- Hoppe, C. J. M., et al., 2010. On CO2 pertubation experiments: over-determination of carbonate chemistry reveals inconsistencies. Biogeosciences Discuss., 7, 1707–1726.
- 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.
- Muller, F. L. L. and Bleie, B., 2008. Estimating the organic acid contribution to coastal seawater alkalinity by potentiometric titrations in a closed cell. Analytica Chimica Acta 619, 183-191.

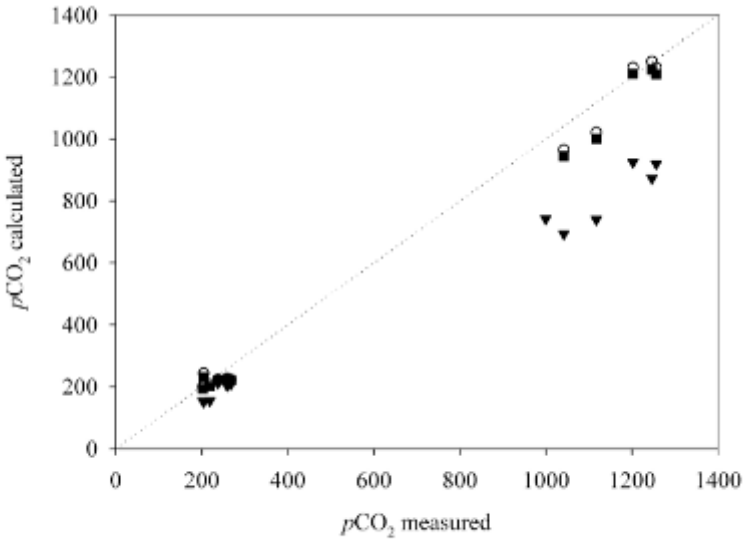


Fig. 2. Calculated pCO_2 from different input parameters (triangles: TA and DIC, circles: TA and pH, squares: DIC and pH) versus measured pCO_2 values.

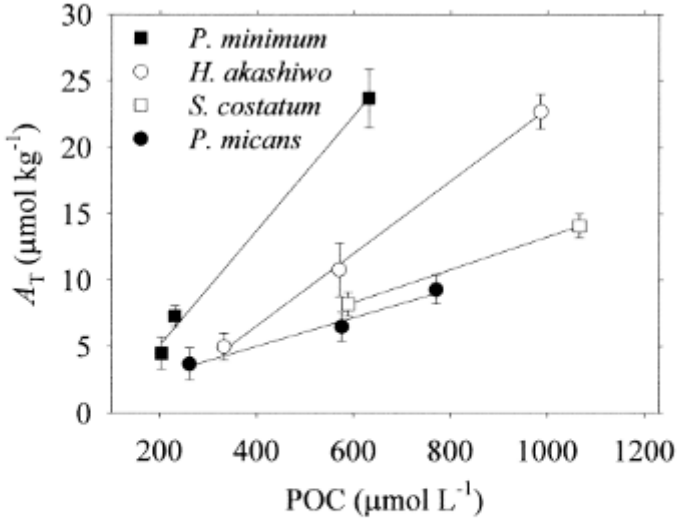
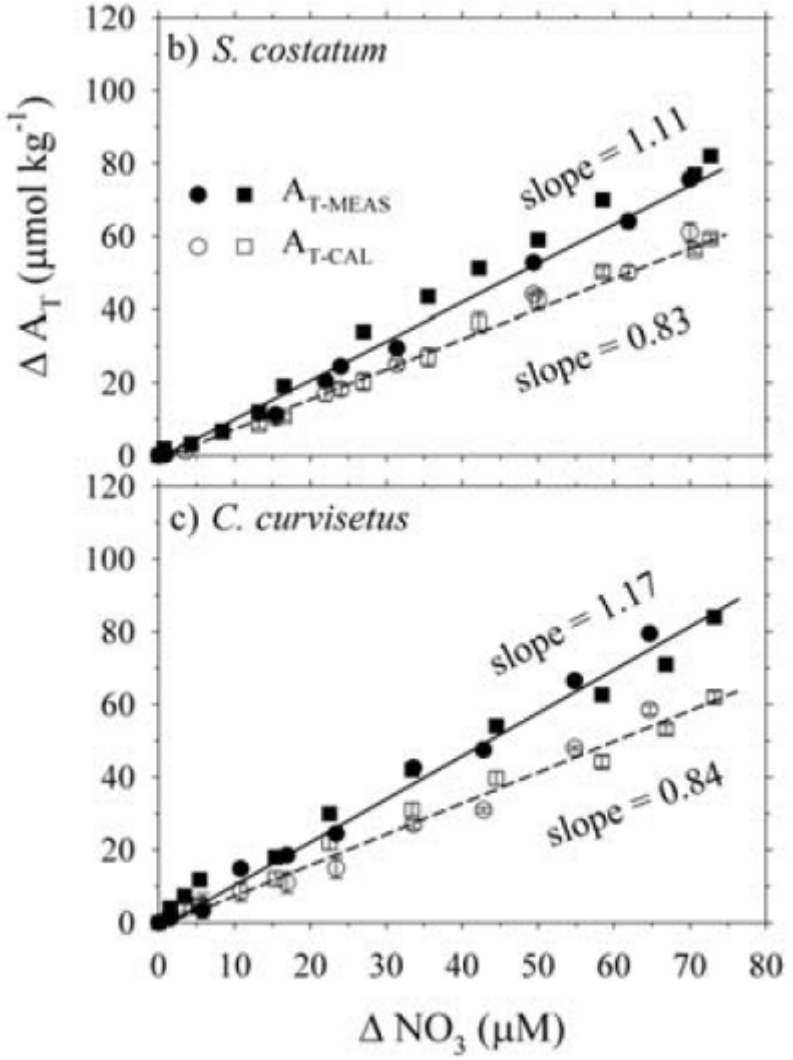


Fig. 5. Measured alkalinity differences ($\Delta A_{T-PLANKTON}$) between unfiltered seawater containing each of the four cultured phytoplankton species and the same seawater passed through a 0.7-μm filter. The solid lines show linear regression plots between $\Delta A_{T-PLANETON}$ and the POC concentration for four phytoplankton species.

Figure 2. Increase ($\Delta A_{T\text{-}MEAS}$ and $\Delta A_{T\text{-}CAL}$) in $A_{T\text{-}MEAS}$ and $A_{T\text{-}CAL}$ as a function of nitrate consumption (ΔNO_3) in phytoplankton cultures of (a) *P. minimum*, (b) *S. costatum*, and (c) *C. curvisetus*. The solid and dashed lines show linear regression plots between $\Delta A_{T\text{-}MEAS}$ and ΔNO_3 and between $\Delta A_{T\text{-}CAL}$ and ΔNO_3, respectively. Error bars for $\Delta A_{T\text{-}MEAS}$ (not shown as they are comparable in size to or smaller than the symbols) and $\Delta A_{T\text{-}CAL}$ were calculated using $(E_{t+1}^2 + E_t^2)^{0.5}$, where E_{t+1} is the error at time t + 1 and E_t is the error at time t.



Reported errors in measurements of TA and the propagated errors in calculated values of other carbonate system variables - pCO_2 and pH around pCO_2 levels of 380 and 1000 ppm

Source of error	Report	Total C uM/l	TA error uM/l	pCO_2 (DIC) 380/1000 decrease	pCO_2 (pH) increase	pH ($pC0_2$) increase
PIC	Shelf sea [1]	8	<16	26/101	3/7	0.003/0.003
Plankton	Cultures [2]	~ 200	<5	9/33	1/2	0.001/0.001
Bacteria	Coastal [2]	<30	<6	10/40	1/3	0.001/0.001
DOC	Cultures [3]	80	80	107/386	14/36	0.013/0.014
DOC	Cultures [4]		<800	338/927	136/351	0.112/0.120
DOC	Coastal [4]		<200	199/646	34/88	0.032/0.034
DOC	Mesocosm [5]		20	32/124	3/9	0.003/0.003

TA - total alkalinity; DIC - total dissolved inorganic carbon, PIC - particulate inorganic carbon; DOC - dissolved organic carbon

380/1000 calculations performed to give final pCO2 concentrations of 380 amd 1000 ppm

Errors on direct measuremnts TA ± 2, DIC ± 2, pCO2 ± 2, pH ± 0.005 and annual rate of increase in pCO_2 (+2 pH -0.002)

[1] Harlay J et al (2010) Progress in Oceanography 86, 317-336.
[2] Kim HC et al (2006) Limnol. Oceanogr., 51, 331Š338.
[3] Kim HC & K Lee , (2009) Geophys. Res. Lett., 36, L20603, doi:10.1029/2009GL040271.
[4] Hernandez-Ayon, JM et al (2007) Limnology and Oceanography: Methods 5, 225-232.
[5] Muller FLL. & B Bleie (2008) Analytica Chimica Acta 619, 183-191.

Impact on UKOARP and related studies

1. Area A - potentially little impact.
2. DEFRA-pH - potential problem
3. UKOARP cruises need to over-determine the carbonate chemistry when not in open ocean waters.
4. **UKOARP culture experiments. Measurements of TA in these systems are likely to be effected by the presence of dissolved organic matter.**
5. **Analysis Service needs to take account of likely organic alkalinity inaccuracies.**

Recommendations UKOARP

1. All work supported by UKOARP must provide an assessment of error in the data they report for the determination of pCO_2 and pH in their systems.
2. Established best practice for measurements must be followed.
3. Meta-data must be fully reported (template).
4. The UKOARP Analytical Service must measure a third parameter (pH).
5. Organic TA error must be assessed