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Carbonation and Acidification of the Backyard Waters of Taiwan under Rising Atmospheric CO_2

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While there have been fluctuations in the concentration of atmospheric CO_2 through out geologic time, its rate of increase since the advent of the industrial revolution in about 1750 has been much accelerated. Thus, in the pre-industrial time between 1000 and 1750, the concentration of atmospheric CO_2 varied only within a narrow range of 275 to 285 ppm, and without a definitive systematic increasing trend. In the next 200 years, it increased steadily by some 50 ppm, or at a rate of about 0.25 ppm/year. In the recent years, between 1995 and 2005, that rate of increase has accelerated dramatically to 1.9 ppm/year, or about eight fold of that in those previous 200 years (Forster et al., 2007). The present concentration of 380 ppm is unprecedented in at least the last 650,000 years (Jansen et al., 2007). Concomitantly, the average global atmospheric temperature also increases at an ever quickened pace, at ~0.007 ^{o}C/year over the last 100 years and at twice that rate, or 0.013 ^{o}C/year, in the last 50 years (Trenberth et al., 2007). It is now generally accepted that this recent rise in the concentration of atmospheric CO_2 is linked to the ever accelerating emission of anthropogenic CO_2 to the atmosphere through the use of fossil fuel, cement production, and changes in land use practice. Furthermore, it is likely that the increase in the concentration of atmospheric CO_2 has contributed to the rising average global temperature which can in turn lead to changes in global climate (IPCC, 2007).

Although the observed elevation in the concentration of atmospheric CO_2 is obviously significant, it could have been even more drastic as recent estimates (Sabine et al., 2004) indicate that only 39-48% of the anthropogenic CO_2 that has been released to the environment during the anthropocene can be found in the atmosphere. A substantially similar amount, about 28-34%, has been sequestered in the ocean so that the partition of the anthropogenic CO_2 is a major determinant of the concentration of atmospheric CO_2. Hence, the ocean is a critical player in regulating the concentration of atmospheric CO_2, and, by extension, global climate. Furthermore, Sabine et al. (2004) also reported that the strength of this oceanic sink might be temporally variable and it has apparently shrunk in recent years as it can only account for a smaller fraction, about 26%, of the anthropogenic input between 1980 and 1999. Thus, a thorough understanding of the marine carbon cycle, its temporal variability and its coupling to the atmospheric processes is essential for predicting the future level of atmospheric CO_2 and climate change.

In view of this need, the international oceanographic community initiated the Joint Global Ocean Flux Study (JGOFS) under the auspices of the Scientific Committee on Oceanic Research (SCOR) and the International Geosphere and Biosphere Program (IGBP) (SCOR, 1992; McCarthy, 2000; Buesseler, 2001) in the eighties. Through this study, two time-series stations: BATS (the

Bermuda Atlantic Time-series Study) and HOT (Hawaii Ocean Time-series), have been established in the North Atlantic and the North Pacific in order to directly document the temporal variations in and the response of the marine carbon cycle under a rising concentration of atmospheric CO_2 (USGOFS, 1986; Wiebe et al., 1987). These time-series stations are maintained to this date. Taiwan joined this international effort and established a time-series stations of its own at 18.3°N and 115.5°E in the northern South China Sea (Fig. 1): SEATS (the SouthEast Asian Time-series Study) in 1999 (Wong et al., 2007a). SEATS is a formally recognized component of JGOFS. Its initial findings have been published in a recent dedicated special issue (Wong et al., 2007b) and some of them are reported here. Carbon dioxide is a soluble reactive gas. When it comes into contact with water, it enters the aqueous phase through the following chemical equilibria:

$$CO_2(g) \leftrightarrow CO_2(l)$$
$$CO_2(l) + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2}$$

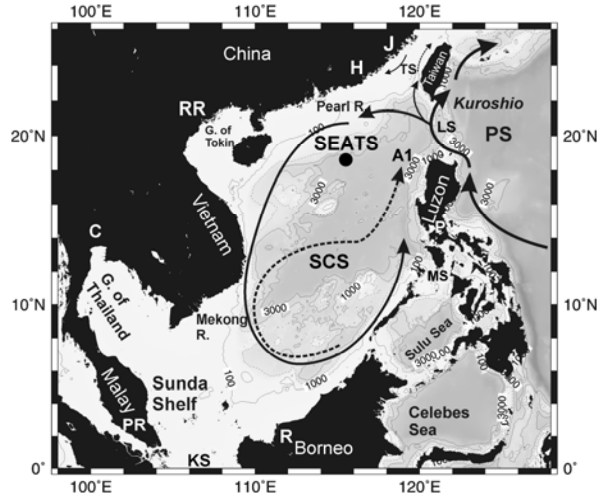

Figure 1:
The study site of the SouthEast Asian Time-series Study (SEATS) at 18.3°N and 115.5°E in the tropical northern South China Sea (From Wong et al., 2007a). The solid line in the South China Sea, SCS, represents the basin wide cyclonic gyre in the winter. The dashed line indicates the eastward jet off the coast of Vietnam and the anticylonic gyre over the southern half of the Sea during the summer. The Kuroshio and its intrusions into the northern South China Sea are also shown schematically around the Luzon Strait. KS – Karimata Strait; LS – Luzon Strait; MS – Mindoro Strait; PS – Philippine Sea; TS – Taiwan Strait. The locations where the major rivers reach the SCS are also shown: C – Chao Phraya; H – Hanjiang; J – Jiulongjiang; P – Pasig River; PR – Pahang River; R – Rajang River; RR – Red River.

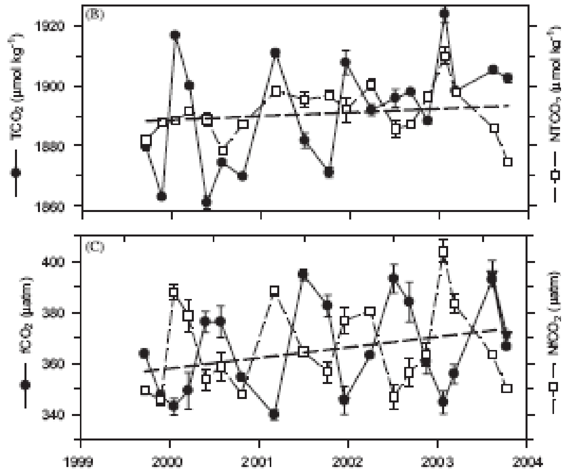

Figure 2:
Variations in the average total dissolved CO_2 (TCO_2), TCO_2 corrected to a constant salinity ($NTCO_2$), fugacity of CO_2 (fCO_2) and fCO_2 corrected to a constant temperature ($NfCO_2$) in the mixed layer at the SEATS station between September 1999 and October 2003. Thick dashed lines indicate the best fit lines for $NTCO_2$ and fCO_2 by a linear regression analysis. (From Tseng et al., 2007)

Thus, an increase in the concentration of atmospheric CO_2 will tend to push the reactions to the right. As a result, for the ocean as a whole, there will be an increase in the concentrations of $CO_2(l)$, which is expressed as the fugacity CO_2 in the aqueous phase or fCO_2, total dissolved CO_2, which is the sum of all the inorganic carbon species or TCO_2, and in H^+. Hence, in general, the ocean will be carbonated and acidified under a rising concentration of atmospheric CO_2. However, regionally, the changes can be much more variable spatially and temporally as fCO_2 can vary widely in response to changes in the local environmental conditions. On the one hand, cooling and freshening of the water, and the photosynthetic uptake of CO_2 can lower fCO_2 and enhance the invasion of atmospheric CO_2 to the ocean. On the other hand, warming and increasing the salinity of the water, and the respiratory production of CO_2 can raise fCO_2 and lead even to the evasion of CO_2 from the ocean to the atmosphere. Thus, both physical processes, such as summer surface warming, winter surface cooling, precipitation, evaporation and sea ice formation, and biological processes, such as photosynthesis and respiration, can affect the regional air-sea exchange of CO_2. Furthermore, calcareous organisms are plentiful in the ocean. The formation of calcium carbonate:

$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$$

removes TCO_2 and alkalinity from the water. The resulting water becomes more acidic. This leads to an increase in fCO_2 and the invasion of atmospheric CO_2 will be impeded. The dissolution of calcium carbonate would have the opposite effect. Thus, regional air-sea exchange of atmospheric CO_2 is affected not only by biological activities in general, but all the specific types of organism that may be involved.

Variations in the average TCO_2, TCO_2 corrected to a constant salinity or $NTCO_2$, fCO_2 and fCO_2 corrected to a constant temperature or $NfCO_2$ in the mixed layer at the SEATS station between September 1999 and October 2003 are shown in Fig. 2 (Tseng et al., 2007). These initial results indicate that, intra-annually, during the winter, fCO_2 reached a minimum, CO_2 invaded into the Sea from the atmosphere, while TCO_2 and $NTCO_2$ reached a maximum. These phenomena were consistent with the effect of surface cooling and the accompanying enhanced vertical mixing, which could bring the saline and TCO_2-rich subsurface water to the mixed layer. In contrast, during the summer, fCO_2 reached a maximum, CO_2 evaded from the Sea to the atmosphere, while TCO_2, $NTCO_2$ and $NfCO_2$ reached a minimum. These could have resulted from the combined effects of surface heating and photosynthetic activities. Nevertheless, when the invasion and evasion of CO_2 are summed together, the annual net exchange of CO_2 at the SEATS station over the year was negligible, indicating that the northern South China Sea is neither a significant net sink nor net source of atmospheric CO_2. Superimposed on these intra-annual changes were subtle trends of inter-annual increase in $NTCO_2$ and fCO_2. These trends are consistent with the expected response of the ocean to a steadily rising concentration of atmospheric CO_2. Similar trends have also been found at BATS and HOT. Together, they suggest that the effect of rising atmospheric CO_2 can now be felt by the oceans globally. In fact, it has reached the backyard waters of Taiwan.

While the time-series records at SEATS are still too short for making definitive quantitative conclusions, the results from 1999 to 2003 indicate that $NTCO_2$ and fCO_2 were rising at rates of 1.5μmol/kg/yr and 4.2 μatm/yr respectively. If these rates can be confirmed, they indicate that the total dissolved carbon content in the northern South China Sea is increasing in the absence of a significant local invasion of atmospheric CO_2. Furthermore, the fCO_2 is increasing at more than twice the rate of the corresponding increase in the concentration of atmospheric CO_2. These apparently paradoxical phenomena need to be confirmed and accounted for in future studies.

The corresponding pH at 10 m in the mixed layer at the SEATS station suggests that pH might have decreased by 0.003 pH unit per year between 1999 and 2003. Again, if this trend can be confirmed, it indicates that the northern South China Sea is being progressively acidified as expected as a result of the rising atmospheric CO_2. The waters around Taiwan are rich in coral reef ecosystems, which are globally significant benthic calcareous ecosystems. The lowering of the pH will reduce the saturation state and enhance the dissolution of calcium carbonate through the reaction (Feely et al., 2005):

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^-$$

The crystalline form aragonite, in which the corals form their skeleton, is especially susceptible to this acidic attack. The observations at the SEATS station suggest that the aragonite saturation state in the northern South China Sea has been reduced by 15 to 20% since the pre-industrial time (Chou et al., 2007). The present saturation state is at the low end of the range that is considered adequate for coral calcification but it is projected to become inadequate by 2040 (Kleypas et al., 2006). Thus, the stress that stems from the continued acidification of the ocean by the rising atmospheric CO_2, together with that from the rising seawater temperature as a result of global warming and from possible local pollution, may potentially become devastating to the survival of these precious ecological assets of Taiwan within the foreseeable future.

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