Decomposing monthly declines of subsurface-water pH and aragonite saturation state from spring to autumn in the North Yellow Sea

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Introduction

Since the beginning of the industrial period, ocean water chemistry has responded the increasing atmospheric CO_2 by decreasing sea surface pH and $CaCO_3$ saturation states. This is a process known as ocean acidification [*Orr et al.*, 2005]. However, coastal oceans respond to this CO_2 problem differently to that of open oceans [*Borges and Gypens*, 2010]. Marine pH and Ω_{arag} reduction will result in more difficult for calcium carbonate skeleton and shell formation for many marine organisms [*Sabine et al.*, 2004]. Surrounding the North Yellow Sea (NYS), the Liaoning and Shandong provinces of China are teeming with fast-developing and highly populating marine aquaculture activities. Previous studies have suggested that seasonal declines of subsurface pH and Ω_{arag} from spring to autumn may have hurt those acidification-sensitive bivalve mollusks and thereby the adjacent marine aquaculture (Zhai et al., 2014). To quantify controlling processes of the seasonal declines of subsurface pH and Ω_{arag} in the NYS, we attempted to decompose them into fundamental biogeochemical processes, using the traditional Redfield ratio (Redfield et al., 1963) and a modified methodology from Murata and Shu (2012) and Kuchinke et al. (2014). We studied the relationship between regional net community calcification and seawater aragonite saturation state. This is the first try to do so in China Seas. We explored possible future changes in pH and Ω_{arag} by combining both effects of the increasing anthropogenic CO_2 in the ocean and the seasonal variations due to biogeochemical processes in this important ocean margin. Our result suggested that the very low Ω_{arag} values of <1.5 may exist all year round in the NYS cold water mass in the 2050s, bringing much stress on local benthic fauna community.

Data

The repeat observation results of bottom waters salinity (S), total dissolved inorganic carbon (DIC), total alkalinity (TAlk), Ω_{arag} and pH in the NYS in spring, summer and autumn in 2011, and summer and autumn in 2013 were obtained from Zhai et al. (2014, 2015).
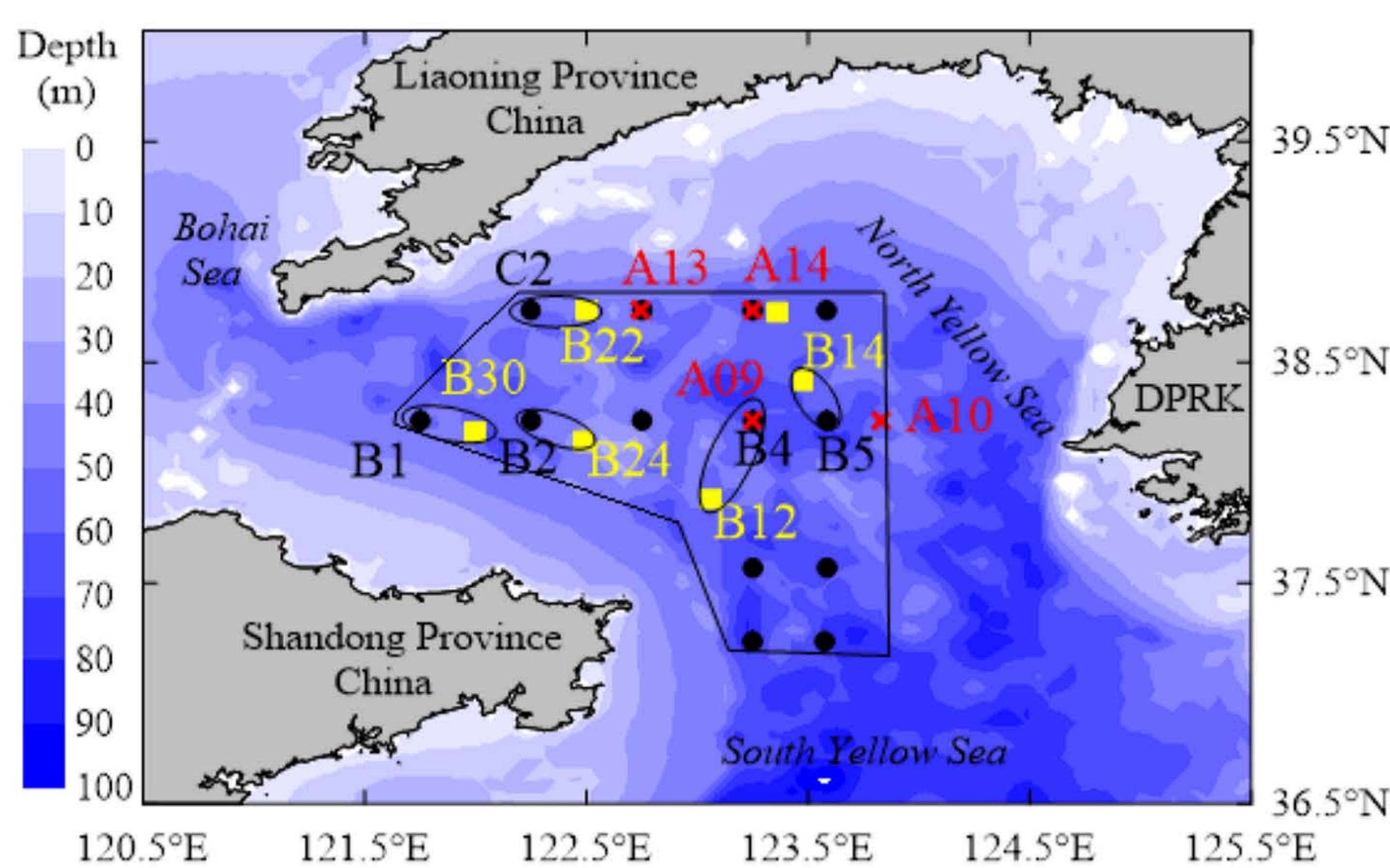

Fig. 1. Study area and sampling sites. DPRK = Democratic People's Republic of Korea. According to Zhai et al. (2014a), closed circles show deep stations that were sampled in May, July, and October 2011, while Yellow rectangles sketch deep stations that were sampled in June and August 2011. Red crosses show deep stations that were sampled in August and September 2013 (Zhai et al., 2015).

Table. 1. Summary of bottom-water carbonate parameters (mean ± S.D.) in the central area of the North Yellow Sea and/or the NYSCWM during our 15 cruises.

Cruises	Salinity	Water temperature (℃)	DIC (μmol kg⁻¹)	TAlk (μmol kg⁻¹)	Ω_{arag}	pH$_T$	fCO$_2$ (μatm)	Station numbers	Ref.
May-11	32.12 ± 0.12	5.18 ± 1.25	2146 ± 20	2307 ± 12	1.81 ± 0.10	8.10 ± 0.02	350 ± 18	13	Zhai et al., 2014a
Jun-11	32.06 ± 0.10	5.57 ± 1.56	2155 ± 25	2299 ± 3	1.67 ± 0.21	8.05 ± 0.04	398 ± 36	6	Zhai et al., 2014a
Jul-11	31.99 ± 0.09	6.90 ± 1.90	2160 ± 26	2295 ± 7	1.60 ± 0.20	8.01 ± 0.04	444 ± 45	10	Zhai et al., 2014a
Aug-11	31.85 ± 0.12	9.24 ± 3.01	2162 ± 30	2286 ± 16	1.52 ± 0.17	7.95 ± 0.02	522 ± 20	5	Zhai et al., 2014a
Oct-11	31.90 ± 0.22	8.94 ± 1.78	2193 ± 18	2284 ± 7	1.25 ± 0.12	7.86 ± 0.04	660 ± 71	8	Zhai et al., 2014a
Nov-11	31.93 ± 0.25	9.72 ± 1.72	2165 ± 19	2268 ± 16	1.34 ± 0.13	7.88 ± 0.05	618 ± 89	10	Zhai et al., 2014a
Jan-12	31.88 ± 0.18	6.07 ± 0.63	2132 ± 12	2243 ± 9	1.37 ± 0.08	7.96 ± 0.04	487 ± 45	5	Zhai et al., 2014a
May-12	32.09 ± 0.30	5.77 ± 1.30	2129 ± 20	2287 ± 8	1.80 ± 0.16	8.09 ± 0.05	359 ± 41	10	Zhai et al., 2014a
Nov-12	32.08 ± 0.53	10.14 ± 1.68	2157 ± 33	2260 ± 10	1.35 ± 0.22	7.87 ± 0.06	630 ± 92	9	Zhai, 2018
May-13	31.78 ± 0.17	5.19 ± 1.42	2132 ± 24	2270 ± 13	1.61 ± 0.15	8.05 ± 0.05	397 ± 56	10	Fig. S2k
Aug-13	31.73 ± 0.12	9.82 ± 1.17	2112 ± 17	2270 ± 7	1.82 ± 0.12	8.03 ± 0.02	418 ± 18	4	Zhai et al., 2015
Sep-13	31.69 ± 0.07	10.58 ± 1.23	2143 ± 21	2262 ± 8	1.48 ± 0.12	7.92 ± 0.02	559 ± 28	3	Zhai et al., 2015
Nov-13	31.70 ± 0.22	9.77 ± 1.19	2169 ± 12	2270 ± 8	1.33 ± 0.11	7.88 ± 0.05	623 ± 76	8	Fig. S2n
Aug-15	32.13 ± 0.13	8.77 ± 1.74	2183 ± 24	2296 ± 10	1.43 ± 0.14	7.92 ± 0.03	562 ± 45	15	Zhai, 2018
Jan-16	32.28 ± 0.08	6.14 ± 0.84	2152 ± 14	2306 ± 12	1.76 ± 0.13	8.07 ± 0.04	384 ± 41	19	Zhai, 2018

Methods

To further quantify contributions of above-mentioned biogeochemical processes on the temporal changes in seawater Ω_{arag} ($\Delta\Omega_{arag}$) and pH (ΔpH), we used a systematic procedure as described by Murata and Shu (2012) and Kuchinke et al. (2014) to decompose $\Delta\Omega_{arag}$ into contributions of individual water chemistry parameter changes in DIC (ΔDIC), TAlk (ΔTAlk), temperature (ΔT) and salinity (ΔSal), i.e..We applied Murata's (2012) procedure to decompose $\Delta\Omega_{arag}$ as follows:

$$\Delta\Omega_{arag} = (\partial\Omega_{arag}/\partial DIC)\Delta DIC + (\partial\Omega_{arag}/\partial TAlk)\Delta TAlk + (\partial\Omega_{arag}/\partial T)\Delta T + (\partial\Omega_{arag}/\partial S)\Delta S + residual$$

We used $\Delta\Omega^{\Delta DIC}=(\partial\Omega_{arag}/\partial DIC)\Delta DIC$, $\Delta\Omega^{\Delta TAlk}=(\partial\Omega_{arag}/\partial TAlk)\Delta TAlk$, $\Delta\Omega^{\Delta T}=(\partial\Omega_{arag}/\partial T)\Delta T$, and $\Delta\Omega^{\Delta Sal}=(\partial\Omega_{arag}/\partial Sal)\Delta Sal$ for short.
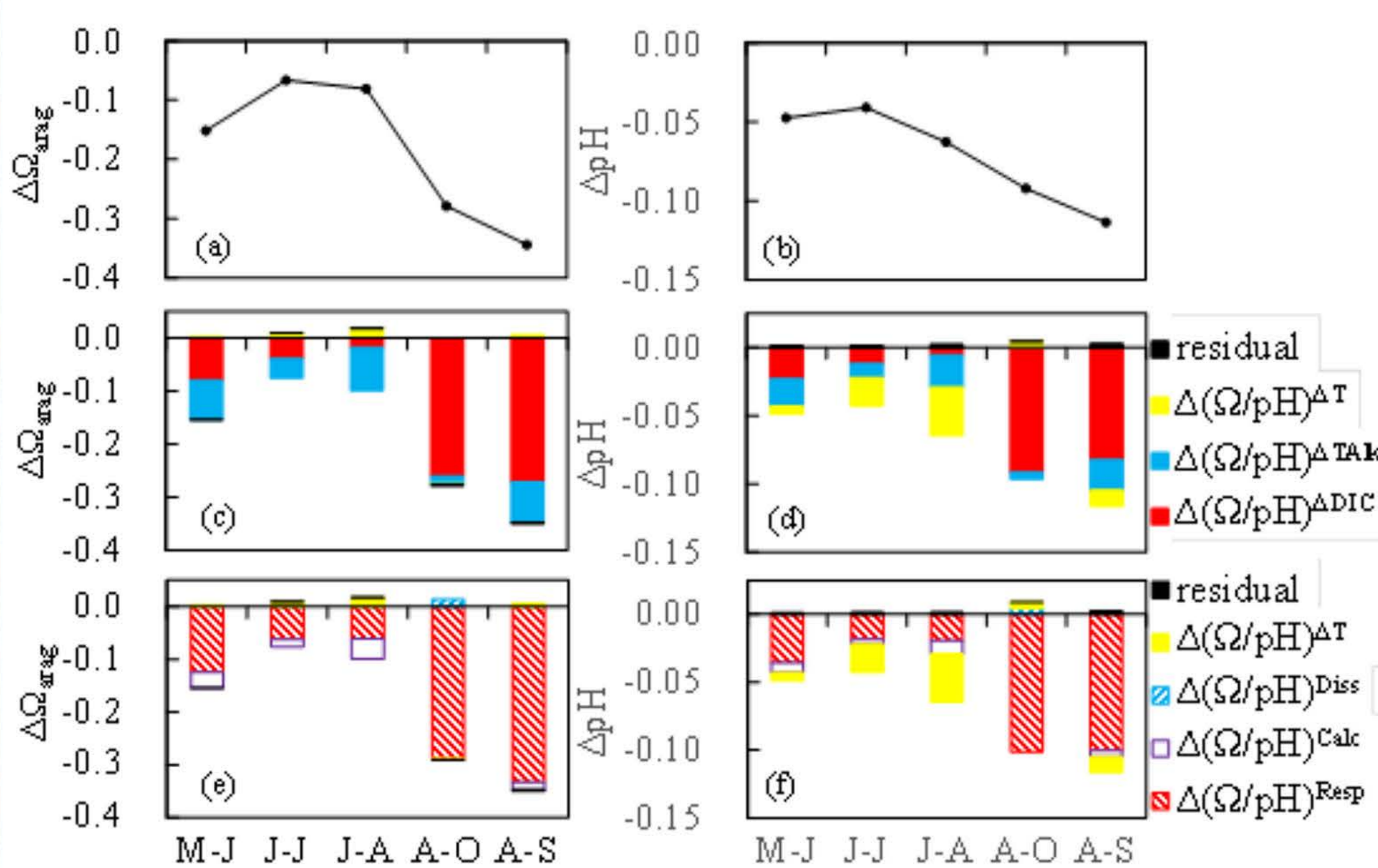
Results and discussion

Figure 2. Monthly/bimonthly changes in aragonite saturation state (Ω_{arag}) (a) and pH$_T$ (b), and partial changes in Ω_{arag} (c) and pH$_T$ (d) due to individual parameters of DIC, TAlk and water temperature, and partial changes in Ω_{arag} (e) and pH$_T$ (f) due to individual processes of community respiration (Resp), calcification (Calc), CaCO$_3$ dissolution (Diss), and temperature changes (ΔT), from May to June 2011 (M-J), from June to July 2011 (J-J), from July to August 2011 (J-A), from October to August 2011 (A-O), and from August to September 2013 (A-S).
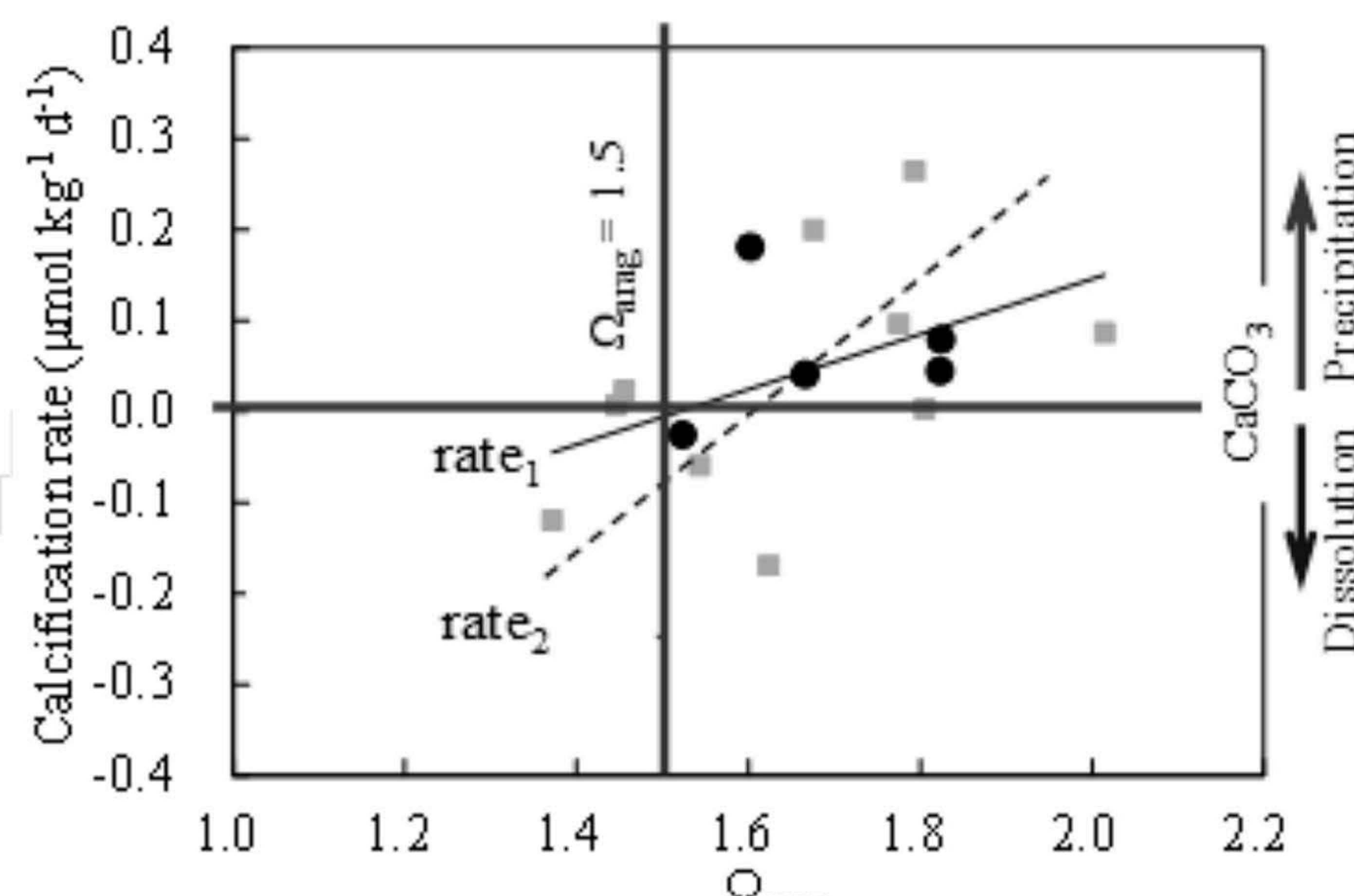

Figure 3. Calcification rates versus bottom-water Ω_{arag}. Closed circles represent the calcification rates calculated from monthly/bimonthly mean changes, while squares represent the calcification rates calculated from monthly/bimonthly changes at those nearby stations (Fig. 1). All data (Table 5) were regressed with solid (statistical analysis, y_1=0.3042x-0.46) and dashed (trend analysis, y_2=0.7273x-1.16) lines.

Table 2. The seasonal variations in the NYSCWM pH$_T$ and Ω_{arag} corresponding to various basin-averaged net community respiration and calcification rates at the present-day (with the atmospheric xCO$_2$ of 395 ppm) and in a future scenario (with the atmospheric xCO$_2$ of 500 ppm in the 2050s). Ppm = parts of CO$_2$ per million dry air. Rate$^{calc}_1$ and rate$^{calc}_2$ refer to Fig. 3.

Spring (May) values				Fundamental biogeochemical processes		Autumn (October) values				Seasonal changes	
xCO$_2$ (ppm)	fCO$_2$ (μatm)	DO (μmol kg⁻¹)	pH$_T$	Ω_{arag}	Calcification rate (μmol kg⁻¹ d⁻¹)	Basin-averaged net community respiration rate (μmol-O$_2$ kg⁻¹)	fCO$_2$ (μatm)	DO (μmol kg⁻¹)	pH$_T$	Ω_{arag}	ΔpH$_T$ (158d)	ΔΩ_{arag} (158d)
395	350	300	8.10	1.82	rate$^{calc}_1$	0.60	701	227	7.83	1.19	-0.27	-0.63
395	350	300	8.10	1.82	rate$^{calc}_2$	0.60	717	227	7.82	1.17	-0.28	-0.64
500	456	300	8.00	1.48	0	0.60	932	227	7.72	0.94	-0.28	-0.54
500	456	300	8.00	1.48	0	0.80	1134	203	7.64	0.79	-0.36	-0.69
500	456	300	8.00	1.48	0	1.00	1385	179	7.56	0.66	-0.44	-0.82
500	456	300	8.00	1.48	0	1.20	1684	154	7.47	0.55	-0.52	-0.93

Conclusion

We decomposed monthly/bimonthly variations of the NYS cold water mass (sustained from spring to autumn) Ω_{arag} and pH into fundamental biogeochemical processes, including net community respiration and CaCO$_3$ precipitation/dissolution. Results showed that the contributions of respiration, water temperature change, and calcification to the monthly Ω_{arag} variations were 84 ± 9%, -13 ± 10%, and 30 ± 16% from spring to summer, while the contributions of respiration, water temperature change, and CaCO$_3$ dissolution to the bimonthly Ω_{arag} variation were 103%, 1% and -5% from late summer to autumn. Correspondingly, the contributions of respiration, water temperature change, and calcification to the monthly pH variations were 50 ± 23%, 39 ± 23%, and 13 ± 4% from spring to summer, while the contributions of respiration, water temperature change, and CaCO$_3$ dissolution to the bimonthly pH$_T$ variation were 110%, -5% and -5% from late summer to autumn.

For the first time we studied the relationship between regional net community calcification and the aragonite saturation state in China Seas. The results suggested that the NYS cold water mass net calcification rate declined to nearly zero when the seawater Ω_{arag} reached a critical level of 1.5-1.6. This is much different from a recently published coral reef case observed by Bradley et al. (2018), which suggest that the Ω_{arag} threshold of net calcification rate reaching zero should be 2.9-3.0 in coral reef systems. Thus the relationships between biogenic CaCO$_3$ dissolution rate and Ω_{arag} may vary in different systems and that much remains to be investigated in order to quantitatively evaluate the effect of ocean acidification on marine CaCO$_3$ cycles. Due to the combined effect of constant/accelerating community respiration and the increasing anthropogenic CO$_2$ in the ocean, the seriously acidified waters with very low Ω_{arag} of < 1.5 may exist in the NYS subsurface waters all year round in the 2050s.

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