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Carbon dioxide stored and acidified low oxygen bottom waters in coastal seas, Japan

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ABSTRACT

Recently carbon dioxide fluxes between sea water and air have been measured in many coastal seas to clarify whether the coastal seas are source or sink of CO_2. In this study behavior of CO_2 within the water column was studied in a semi-enclosed coastal sea: the Seto Inland Sea, Japan. It was found that seasonal formation of hypoxic water mass is highly related to CO_2 dynamics in coastal seas. Bacterial remineralization of organic matter consumes dissolved oxygen (DO) and releases dissolved CO_2 in the bottom water when summertime thermal stratification develops. The CO_2 accumulates within the low DO bottom water (hypoxic water) and causes increasing of carbonic acid content which results in low pH. Concentrations of dissolved CO_2 and pH are highly correlated with DO concentration. The summertime low DO and acidification (low pH) occur in the lower layer every year. The accumulated CO_2 during the summer season is dispersed to the atmosphere at the beginning of mixing season.

1. Introduction

It is well known that the ocean is the biggest reservoir of carbon dioxide (CO_2) in the global CO_2 dynamics. Recently the importance of estuaries and enclosed seas for the global carbon cycle is often emphasized (Kattner and Pohl, 2007).

Estuaries act as sources of CO_2 to the atmosphere (Abril and Borges, 2004; Abril et al., 2004, 2003; Bouillon et al., 2003; Cai et al., 2003; Frankignoulle et al., 1998; Mukhopadhyay et al., 2002; Raymond et al., 2000; Sarma et al., 2001). Estuaries play a significant role in the global CO_2 cycle, as they could emit around 0.43 $Pg\,C\,yr^{-1}$, roughly balancing the amount of CO_2 absorbed ($-0.32\ Pg\,C\,yr^{-1}$) by all the other coastal ecosystems combined (Borges, 2005).

On the other, Kempe and Pegler (1991) found that the North Sea is a net sink for atmospheric CO_2 in summer. The Canadian Beaufort Sea in late summer 2000 and 2002 acted as a moderate sink for atmospheric CO_2. The air-to-sea net CO_2 flux in an extended area of the shelf of western Arctic Ocean (411,000 km^2) during the ice-free season (=100 days) was calculated as $10.2 \pm 7.7\ m\,mol\,m^{-2}\,d^{-1}$, equivalent to a regional CO_2 sink of $5.0 \pm 3.8\ Pg\,C\,yr^{-1}$ (Murata et al., 2008). Recent studies suggest that the East China Sea (ECS) is indeed a net sink for atmospheric CO_2. All year round, the shelf area in the ECS is a net sink for atmospheric CO_2, absorbing 13–30 $Pg\,C\,yr^{-1}$ (Wang et al., 2000). As recently summarized based on an literature survey, a conclusive understanding however has yet to be achieved on the role of shelf and marginal seas as sinks or sources for atmospheric CO_2 and of the underlying mechanisms (Borges, 2005; Borges et al., 2005; Thomas et al., 2009).

Moreover, future changes in ocean chemistry due to higher atmospheric carbon dioxide may cause ocean acidification and concomitant weakening of coral skeletons and reduction of the accretion of reefs, especially at higher latitudes (Hughes et al., 2003; Orr et al., 2005). Under conditions expected in the 21st century, global warming and ocean acidification will compromise carbonate accretion, with corals becoming increasingly rare on reef systems (Guldberg et al., 2007).

The data related to CO_2 dynamics in coastal seas are, however, quite scarce. To reveal CO_2 dynamics in shallow coastal seas, we have been conducting field observations in the Seto Inland Sea and developing methods to measure CO_2 related properties (Fig. 1). We would surveyed the biogeochemical process in the low oxygen bottom waters by observing pH, total alkalinity (TA), dissolved oxygen (DO), AOU (Apparent Oxygen Utilization), salinity (S) and temperature (T).

In coastal seas, nutrients and CO_2 are converted to organic matter by primary production. The phytoplankton grows in the euphotic zone, dies and sinks down toward the bottom layer, where consuming a lot of oxygen, microbes decompose the organic matter into the nutrients and dissolved inorganic carbon (DIC).

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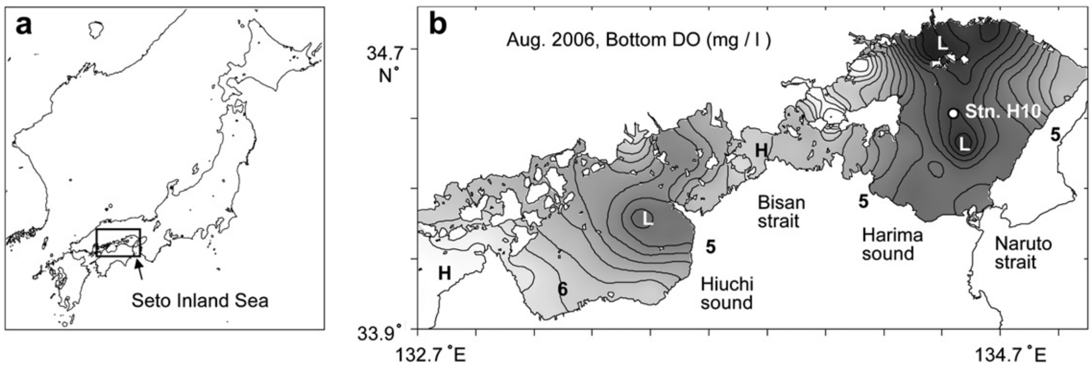

Fig. 1. (a) Map of Japan and location of the Seto Inland sea. (b) Location of station in the Seto Inland Sea and bottom DO (mg l^{-1}) in August 2006. Darker area indicates lower DO area; Contour interval is 0.2 mg l^{-1}.

In this paper, we display the vertical profile of DO, pH, TA and DIC, and clarify the seasonal variations of these parameters in the bottom layer in the Seto Inland Sea: the largest enclosed coastal sea in Japan. Then, we indicate that generation and disappearance of hypoxic water is highly related to CO_2 dynamics in coastal seas.

2. Materials and methods

In this study, values of CO_2 related properties were calculated from measured TA and pH using CO2sys software provided by CDIAC (Carbon Dioxide Information Analysis Center, http://cdiac.ornl.gov/) (Lewis and Wallace, 1998). TA was measured with the acid titration method (ISO 9963-1:1994). pH was measured with glass electrode which is calibrated with phthalate pH standard solution at pH = 4.008 at 25 °C and with phosphate pH standard solution at pH = 6.865 at 25 °C (IEC 60746-2:1982).

To analyze historical oceanographic data which contain temperature, salinity and pH without TA, empirical equation which gives TA from salinity was obtained by simultaneous measurement of salinity and TA from low salinity river mouth area to high salinity open sea area in the eastern Seto Inland Sea.

The study site was located in Harima sound in the Seto Inland Sea (Fig. 1). Harima sound is located in the eastern part of the Seto Inland Sea and has ~2,500 km^2 areas and 10 – 40 m depths. No large river flows into the Harima sound. The sea water is exchangeable with adjoining waters through three straits. Thermal stratification develops from April to September in the sound, while water column is well-mixed throughout the year in the straits, where tidal stirring is vigorous.

A vertical profile measurement was conducted at station H10, where long-term monthly measurements of T, S, DO and pH have been conducted for more than 30 years. Besides these observations, simultaneous measurements of S and TA have been conducted in an area covering the eastern Seto Inland Sea, to obtain an equation which converts S to TA.

2.1. Vertical profile measurement of TA, DIC, pH and DO

T, S, pH and DO were measured in situ at station H10 on 24 July 2007, using a portable CTD (Chlorotech AAQ 1183-H, Alec Electronics Co., Ltd.). TA and pH (at 25 °C) were measured in the laboratory within 24 h after bottle sampling. The pH was

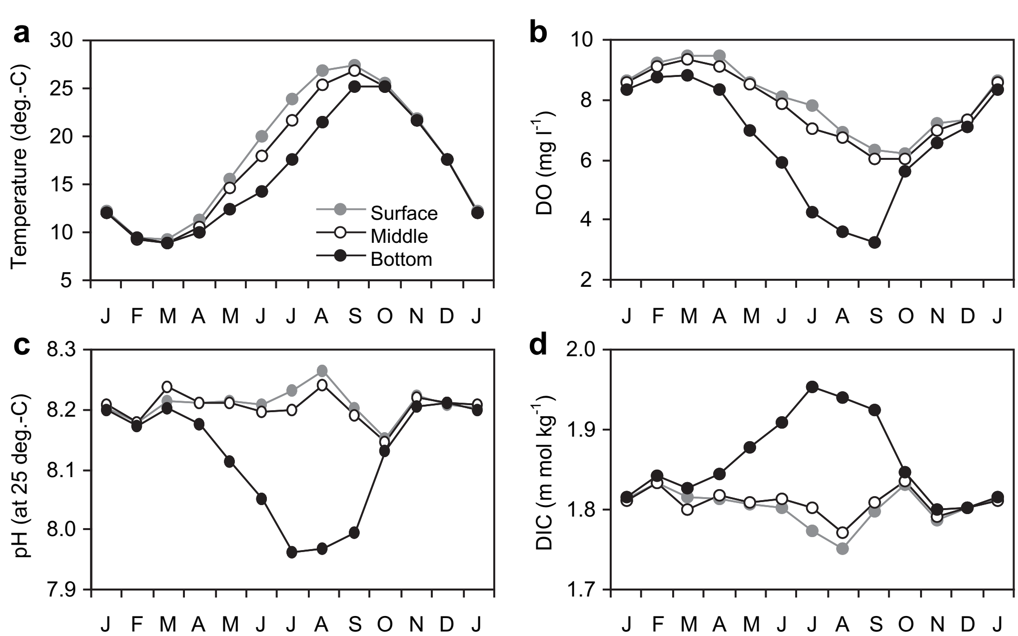

Fig. 2. Seasonal changes in (a) temperature, (b) DO, (c) pH and (d) DIC at three depths at the center of Harima sound (Stn. H10) averaged over 1998–2006.

determined using a HORIBA F-53 pH meter (HORIBA Co., Ltd.) with precision of ±0.001 pH units. Separately salinity of the sampling water was determined using a desktop salinometer (DIGI-AUTO MODEL 5 Tsurumi-seiki Co., Ltd.) calibrated with the standard sea water. TA measurements were made with HCl titration method. pH 4.5 was adapted as the endpoint pH (ISO 9963-1:1994; Theodorakos, 2002). Analyses of replicate samples yielded a mean precision of ±5 μmol kg^{-1}. DIC and partial pressures of CO_2 (pCO_2) were calculated from T, S, pressure (depth), pH, nutrients and total alkalinity, using the CO2sys software (Lewis and Wallace, 1998).

2.2. Time series study

At station H10, T, S, DO, pH and nutrients have been measured monthly at three depths (0 m, 10 m and ∼40 m (1 m above the bottom)) by Hyogo Prefectural Fisheries Research Institute from 1972 to present. Various biological data are also available at this point. In this study, data from 1998 to 2006, which were measured with similar methods described in the previous section, were used.

Since TA data were not available, value of TA was calculated from S with an equation $TA = 44.55\ S + 759$ (TA: Total alkalinity in μmol kg^{-1}) with standard error of 35 μmol kg^{-1} (Taguchi et al., 2009).

3. Results

3.1. Horizontal distribution of DO

Fig. 1 shows the horizontal distributions of DO (mg l^{-1}) in August 2006 in the bottom water in Harima sound and neighboring seas. Contour interval is 0.2 mg l^{-1}. Darker areas in this figure represent lower DO. A low DO area was observed in the northern and central parts of Harima sound. Station H10 is located near the center of the low DO area.

3.2. Seasonal variations in T, DO, pH and DIC in the surface, middle and bottom layers

Seasonal changes in temperature (°C), DO (mg l^{-1}), pH at 25 °C and DIC (m mol kg^{-1}) at the surface (0 m), middle (10 m) and bottom (∼40 m depth) layers at the center of Harima sound (Stn. H10) are illustrated in Fig. 2. These data were obtained from the data from 1998 to 2006.

Thermal stratification begins in May and develops to August. In September, the stratification weakens and then eventually disappears in October. Salinity stratification is relatively weak throughout the year in Harima sound.

DO values in the surface and middle layers are near saturated and gradually decrease from April to September following temperature rise. In contrast, the bottom DO rapidly decreases to the minimum in September and then suddenly rise at the beginning of mixing period. Bottom DIC increases from April to July concomitantly with the rapid increase of the bottom AOU. This DIC increase causes acidification (pH decrease) in the bottom layer. The pH values at the three layers are almost constant from November to the next March.

A correlation coefficient between the bottom pH and DIC exceeded 0.98. Similar high correlation has been widely seem in vertical profile and time series data in the Seto Inland Sea. It seems to be somewhat peculiar that pH, which is a logarithmic expression of the hydrogen ion concentration, relates linearly with DIC. However, theoretical analysis indicates that pH-DIC curve has a point of inflection at $pH = 7.4$, and pH linearly relates with DIC around this point.

3.3. Seasonal and inter-annual variations of TA, DIC, DO and pH

Fig. 3 show that the seasonal and inter-annual variations of TA, DIC, DO concentrations and pH in bottom water at Station H10 in Harima sound from April 1998 to June 2006. Periodical seasonal variations of DO, pH, DIC are found, and strong relationships among

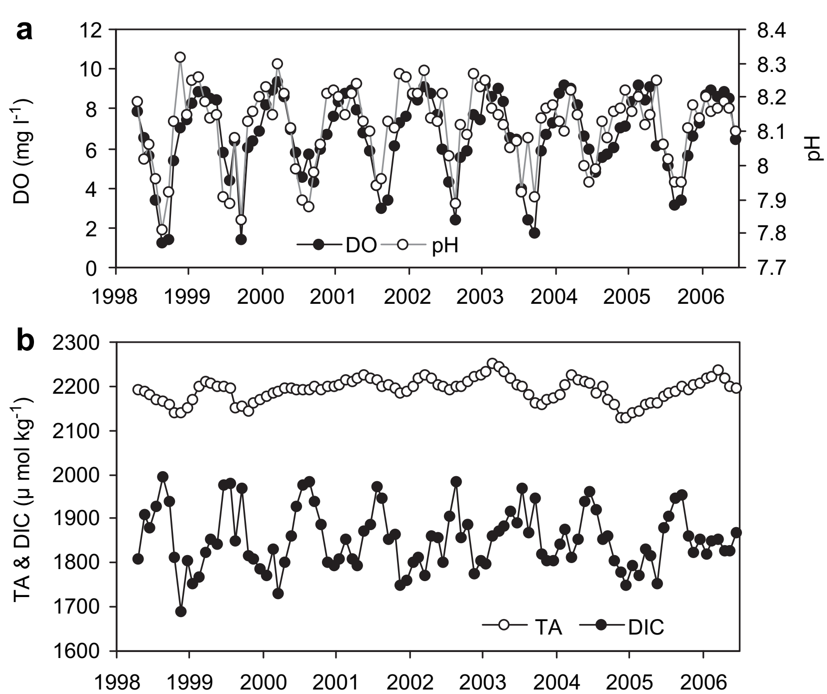

Fig. 3. Records of (a) bottom DO (mg l^{-1}) and pH (at 25 °C) and (b) Total alkalinity and DIC (μmol kg^{-1}) at the center of Harima sound (Stn. H10) from April 1998 to June 2006.

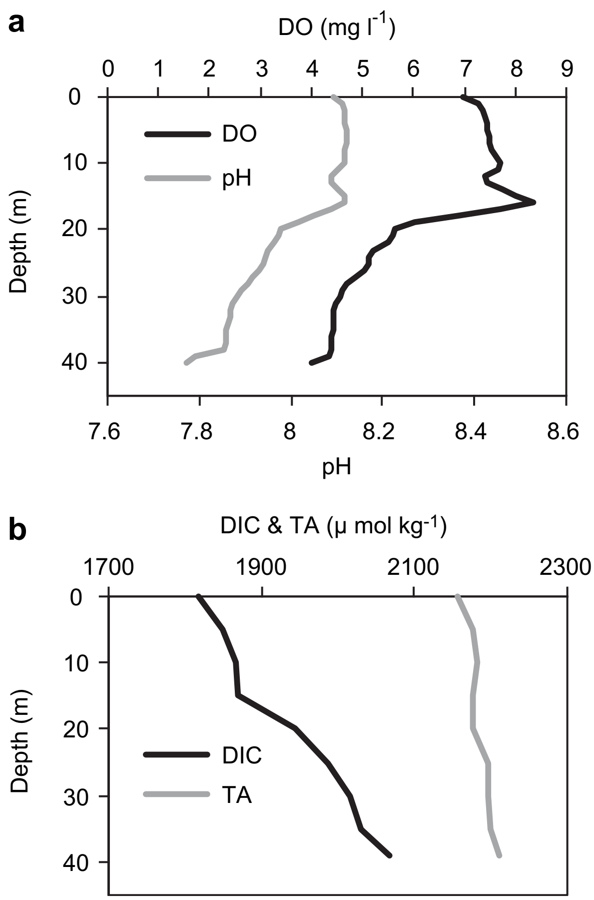

Fig. 4. Vertical profiles of (a) DO (mg l^{-1}) and pH (25 °C) and (b) total alkalinity and DIC (μmol kg^{-1}) at the center of Harima sound (Stn. H10).

DO, pH and DIC are also found. The TA exceeded DIC concentration during whole period and did not vary so much like as DIC. The DIC concentration shows summer maximums accompanying with DO and pH minimums. Briefly, the DIC co-varied with DO and pH apparently.

3.4. Vertical profiles of DO, pH, DIC and TA

Fig. 4 shows the vertical profiles of DO, pH, DIC and TA at the station H10 on 24 July 2007 when strong thermal stratification was observed. In the bottom water (39 m depth), lowest DO, lowest pH values, highest TA and highest DIC concentrations were observed. Below the 15 m depths, DO and pH value decreased and DIC concentration increased with increase in depth. TA and salinity steadily increased with depth.

4. Discussion

4.1. Horizontal distribution of DO

The condition of hypoxia results from an imbalance between biological oxygen consumption and production, and physical transport of DO, in any generic near shore environment (Rowe, 2001). Hypoxia (oxygen concentration less than 2 mg l^{-1}) occurs on the Louisiana continental shelf during summer when the oxygen consumption in sediment and water column exceeds the oxygen resupply by photosynthesis and mixing (Rowe, 2001).

Low DO (mg l^{-1}) in the northern part of Harima sound is considered to be affected by terrestrial influences. Phytoplankton blooms are stimulated by nutrients flowing into Harima sound from the northern industrial and high population area and presumably causes low DO in the bottom layer. During stratified season, mixing and circulation in the bottom water are week in the central part of Harima sound enough to cause the DO depletion in the bottom layer.

4.2. Relationship between DO and pH

In Fig. 3a, it is seen that pH varies in parallel with DO. Strong relationship between DO and pH suggests that bacterial remineralization of POC and DOC consumes DO and releases dissolved CO_2. Later is increasing of carbonic acid content (H_2CO_3) which results low pH. Especially in the bottom layer, the effects of photosynthesis and air–sea O_2 exchange are negligible, thus relationship between DO and pH is clearly observed.

4.3. Seasonal variations in pH in surface, middle and bottom layers

Rapid decrease of bottom water pH from April to July reflects the accelerated decomposition of organic matter by temperature rise. From September to October, bottom water pH increases by the breaking down of the stratification. All pH values in the three layers were almost constant from November to the next March due to convective mixing and air–sea equilibrium.

4.4. Seasonal and inter-annual variations in TA, DIC, DO and pH

Value of alkalinity in the open ocean is primarily a conservative function of salinity, and salinity is regulated by physical factors (e.g. water mass movements, mixing, evaporation and precipitation) (Broecker and Peng, 1982). Non-conservative processes, such as the precipitation or dissolution of calcium carbonate, and nitrate uptake or mineralization, can also change value of alkalinity (Brewer and Goldman, 1976; Bates et al., 1996). However, TA was governed by salinity only in the Seto Inland Sea (Taguchi et al., 2009).

It is known that DIC concentrations in estuaries are controlled by various processes: such as mixing between marine and fresh waters, atmospheric efflux, photosynthetic and remineralization processes, carbonate and atmospheric CO_2 dissolution, and sediment re-suspension of organic matter and its subsequent turnover (Wang and Veizer, 2000; Abril et al., 2003, 2004).

In this study, periodical seasonal variations in DO, pH and DIC in bottom water were found. Strong relationships among DO, pH and DIC suggests that respiratory DO consumption and CO_2 release dominate the process.

4.5. Vertical profiles of DO, pH, DIC and TA

In general, change in TA relative to change in DIC can indicate the relative amounts of photosynthesis, respiration, and calcification occurring in a system (Fagan and Mackenzie, 2007). To minimize effects of salinity change, DIC values are normalized to a constant salinity of 35. This salinity-normalized DIC (NDIC) shows a general trend of increasing with depth, as expected from the carbon enrichment by the biological pump, while the salinity-normalized TA (NTA) is near constant with depth (Penge et al., 1999). In Harima sound, DIC has an increasing trend with the depth in summer and the vertical distribution of TA shows a near constant value with depth (Fig. 4). This feature agrees with the general trend.

The estuary circulation transports the nutrients from the river mouth area to the offshore area, where phytoplankton actively produces organic matters. The organic matters sink down to the bottom and are decomposed. Then, CO_2 accumulates in the bottom water and leads to the ocean acidification there. In the Seto Inland Sea, hypoxia is intimately related with CO_2 storage in the bottom layer.

5. Conclusions

Conclusions in this study are that (1) CO_2 is stored in the bottom hypoxic water masses in the stratified season. (2) Thus hypoxic water is acidified. (3) Frequent measuring pH and TA of the coastal water is useful to analyze the carbon dynamics in coastal seas.

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