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A significant net sink for CO₂ in Tokyo Bay

Atsushi Kubo, Yosaku Maeda & Jota Kanda

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Most estuaries and inland waters are significant source for atmospheric CO₂ because of input of terrestrial inorganic carbon and mineralization of terrestrially supplied organic carbon. In contrast to most coastal waters, some estuaries with small freshwater discharge are weak source or sometimes sink for CO₂. Extensive surveys of pCO₂ in Tokyo Bay showed that the overall bay acts as a strong net sink for atmospheric CO₂. Although small area was a consistent source for CO₂, active photosynthesis driven by nutrient loading from the land overwhelmed the CO₂ budget in the bay. Here we show a comprehensive scheme with a border where air-sea CO₂ flux was ± 0 between nearshore waters emitting CO₂ and offshore waters absorbing CO₂. The border in Tokyo Bay was extremely shifted toward the land-side. The shift is characteristic of highly urbanized coastal waters with an extensive sewage treatment system in the catchment area. Because highly urbanized coastal areas worldwide are expected to quadruple by 2050, coastal waters such as Tokyo Bay are expected to increase as well. Through extrapolation of Tokyo Bay data, CO₂ emission from global estuaries would be expected to decrease roughly from the current 0.074 PgC year⁻¹ to 0.014 PgC year⁻¹ in 2050.

Despite their relatively small areal coverage, coastal waters significantly contribute to the global account of CO₂ exchange due to their dense biological activities^{1–3}. Coastal waters have been regarded as CO₂ sources to the atmosphere because of their input of terrestrial organic carbon and subsequent mineralization^{2,3}. However, current estimates of the coastal CO₂ budget are based on observations in only limited types of marine systems, irrespective of the large heterogeneity in such biogeochemical settings. In fact, Kuwae *et al.*⁴ have recently discussed the possibility of net carbon fixation in certain types of coastal systems including those affected by intense anthropogenic activities. Furthermore, the available observational data from a particular system are generally insufficient to cover the large spatial and temporal variability of the coastal carbon cycle, thus resulting in an uncertain estimate of the carbon budget. More data from various systems with sufficient areal and temporal coverage are thus needed.

We conducted extensive observations of the partial pressure of carbon dioxide (pCO₂) in Tokyo Bay from March 2007 to December 2010 during 49 observational cruises. Tokyo Bay is a semi-enclosed embayment with an area of approximately 1320 km² and a mean water depth of 19 m. The bay is bounded by highly urbanized areas. The bay has suffered from severe cultural eutrophication since the late 1950s, along with rapid development in catchment areas including the Tokyo metropolis. Sewer systems with secondary or tertiary treatment cover most of the urban regions, and yet phytoplankton blooms persist throughout the year and anoxic bottom waters consistently appear during the summer. In some estuary, carbonate dissolution contribute to coastal CO₂ concentration about 20%⁵. As regard to Tokyo Bay, shellfish at the bottom water are the major calcifier and calcifying plankton rarely dominates⁶. In addition, surface waters at the bay are oversaturated with respect to calcium carbonate saturation throughout the year⁷. Therefore, we suppose that carbonate dissolution do not contribute to coastal CO₂ in the bay.

Results and Discussion

All of the pCO₂ data points (n = 21,076) from our observations are plotted against salinity in Fig. 1, and each point in the figure represents the value of pCO₂ at an interval of one minute during the observation. R/V Seiyō-maru observed most of the area during 40 cruises from March 2007 to December 2010 on a monthly basis. R/V Hiyodori observed the innermost head of the bay during nine cruises during the period from May 2009 to October 2010. The pCO₂ values of surface bay ranged from 10 to 7218 μatm. The pCO₂ values for 21,076 data

Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo, 108-8477, Japan. Correspondence and requests for materials should be addressed to A.K. (email: kuboatsushi0412@gmail.com)

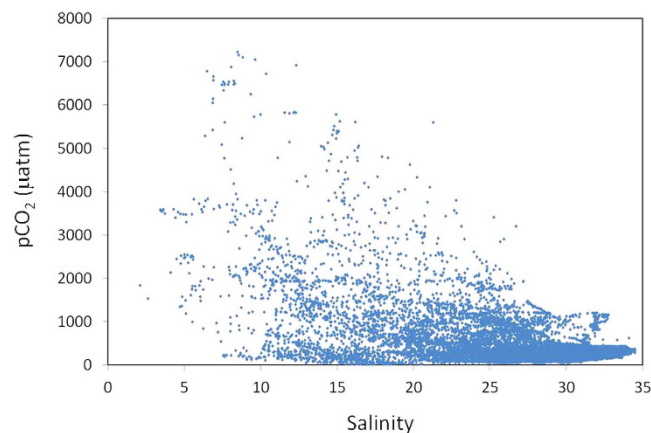


Figure 1. All $p\text{CO}_2$ (μatm) data points ($n = 21,706$) plotted against salinity.

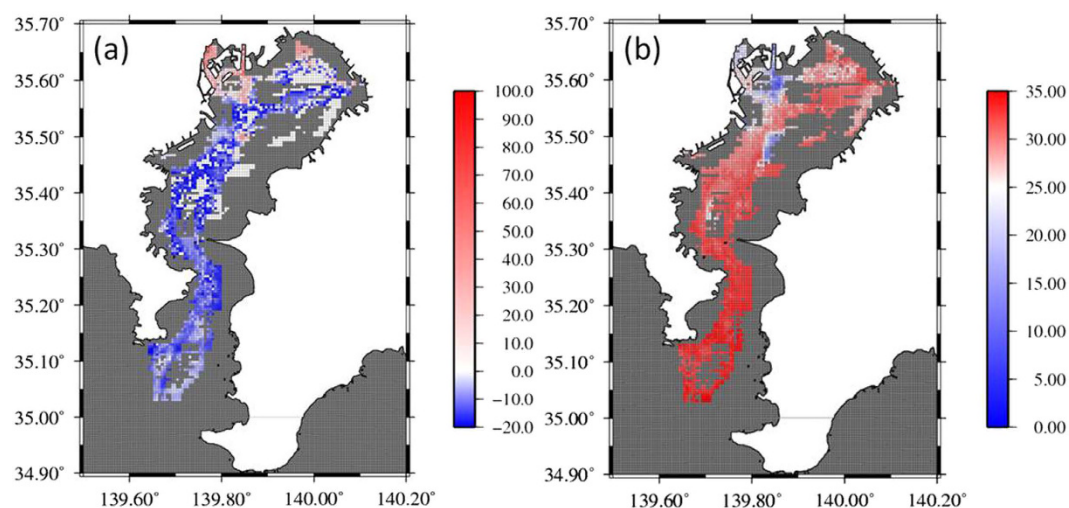


Figure 2. Map of (a) sea-air flux ($\text{mmol C m}^{-2} \text{day}^{-1}$) and (b) salinity, binned into a $500 \text{ m} \times 500 \text{ m}$ horizontal resolution grid. Positive flux values (red) represent outgassing of CO_2 to the atmosphere, and negative values (blue) represent uptake. Maps were created using Generic Mapping Tools software (GMT v4.5.12; <http://gmt.soest.hawaii.edu/>)³⁷.

indicated that a total of 16,345 points were under-saturated with respect to the atmospheric equilibrium; oversaturation was found only in 4,731 data points.

The air-sea CO_2 fluxes were calculated from all of the $p\text{CO}_2$ data (see Methods). The results obtained from different times were binned into a $500 \text{ m} \times 500 \text{ m}$ horizontal resolution grid and then averaged together (Fig. 2a). The northwestern head of the bay was the only area with consistent positive CO_2 flux to the atmosphere, whereas the central bay and bay mouth were a sink for atmospheric CO_2 . The location where CO_2 flux was ± 0 roughly coincided with the location where the average annual surface salinity was 25 (Fig. 2b). The areas where salinity was above and below 25 were estimated according to methodology described in Ninomiya *et al.*⁸. The average CO_2 flux (positive values indicate efflux into the air) for areas where salinity was less than 25 (81 km^2) was $15.2 \text{ mmol C m}^{-2} \text{day}^{-1}$. In contrast, the average CO_2 flux for areas where salinity was greater than 25 (1239 km^2) was $-10.6 \text{ mmol C m}^{-2} \text{day}^{-1}$. The area weighted annual CO_2 flux in Tokyo Bay had a rate of $-8.8 \text{ mmol C m}^{-2} \text{day}^{-1}$; the bay as a whole was a strong net sink for atmospheric CO_2 . The annual CO_2 flux in Tokyo Bay was calculated to be $-5.2 \times 10^{10} \text{ gC year}^{-1}$.

The seasonal variations of $p\text{CO}_2$ and related parameters at three representative stations in the bay are presented in Fig. 3. The parameters include the observed $p\text{CO}_2$, $p\text{CO}_2$ normalized to average temperature (19°C), temperature, salinity and chlorophyll *a* (Chl *a*) concentration. In the northwestern head of the bay (St. TPE), where salinity was lowest among the three stations, $p\text{CO}_2$ values generally exceeded the atmospheric equilibrium. There was no distinct pattern observed for the seasonal variation of $p\text{CO}_2$ ($93\text{--}1920 \mu\text{atm}$), and the variation of $p\text{CO}_2$ was not correlated with Chl *a* ($R^2 = 0.03$, $P > 0.1$, $n = 39$). At the central bay (St.F6) and the bay mouth (St.06), low values of $p\text{CO}_2$ were observed during spring and summer ($70\text{--}336 \mu\text{atm}$), whereas $p\text{CO}_2$ values were close to atmospheric equilibrium values during autumn and winter ($264\text{--}449 \mu\text{atm}$). In terms of the seasonal

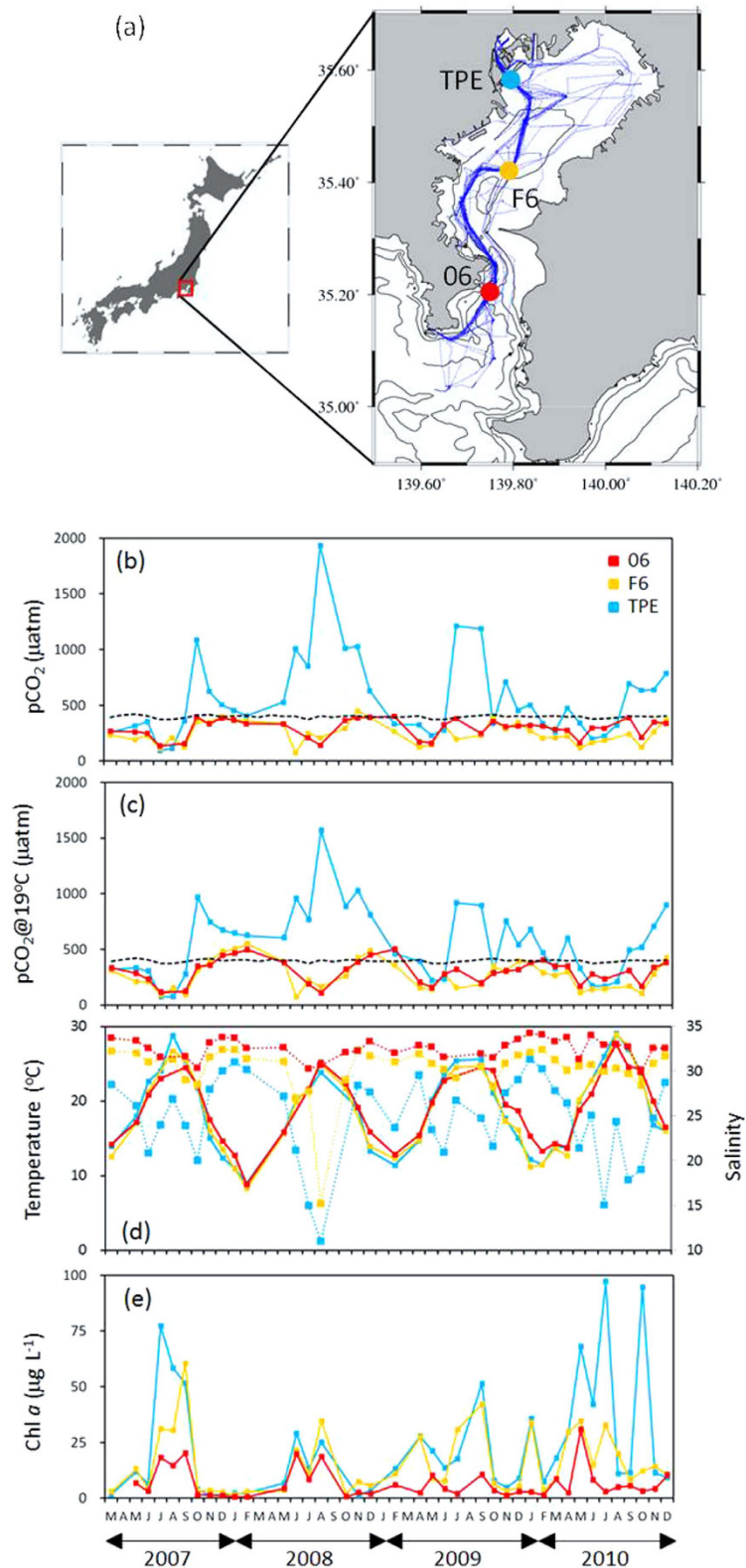


Figure 3. (a) Map of the study site. The ship routes of all cruises are shown as blue lines. Data were measured with a sampling frequency of one minute ($n = 21076$). Circles indicate the three representative stations (O6, F6, and TPE). TPE stands for Tokyo Port Entrance. Isobaths of 20-, 50- and 200-m are also shown. (b) Seasonal variations of pCO₂ (µatm) and atmospheric pCO₂ (the dotted line). (c) pCO₂ normalized to average temperature (19°C). (d) Temperature (°C) and salinity and (e) Chl *a* (µg L⁻¹) at the three representative stations during the observation period (March 2007 – December 2010). Map (a) was created using Generic Mapping Tools software (GMT v4.5.12; <http://gmt.soest.hawaii.edu/>)³⁷.

variation of $p\text{CO}_2$ in the central bay and bay mouth, a negative correlation was found between $p\text{CO}_2$ and Chl *a* ($R^2 = 0.64$, $P < 0.001$, $n = 77$). The correlation suggests that active photosynthesis reduced $p\text{CO}_2$ during spring and summer, hence suggesting that $p\text{CO}_2$ in surface waters is mainly controlled by biological activity. The stratified water column prevents the CO_2 supply from the deeper waters with high CO_2 levels. In autumn and winter, the low photosynthetic rate along with the well-mixed water column resulted in $p\text{CO}_2$ values close to the atmospheric equilibrium. Temperature did not significantly contribute to the seasonal variation of $p\text{CO}_2$. The $p\text{CO}_2$ values normalized to annual average temperature (19°C), which accounted for the temperature dependence of equilibrium constants and the solubility coefficient⁹, did not affect the seasonal variation of $p\text{CO}_2$.

In June 2010, $p\text{CO}_2$ decreased to a low of $10\ \mu\text{atm}$, and Chl *a* concentration was $>300\ \mu\text{g L}^{-1}$, which we found to be the lowest reported value in a marine environment. Based on the low observed CO_2 concentrations, the exhaustion of gaseous CO_2 in seawater resulted in the limitation of the CO_2 supply to algal cells, which may limit the cells growth. In such CO_2 limiting conditions, phytoplankton would need to take up bicarbonate using the proton pump mechanism and the carbonic anhydrase¹⁰.

The CO_2 absorption of $5.2 \times 10^{10}\ \text{gC year}^{-1}$ in Tokyo Bay was in accordance with the overall carbon budget of the bay. A mass balance model estimated the total organic carbon (TOC) influx from the rivers to Tokyo Bay to be $8.1 \times 10^{10}\ \text{gC year}^{-1}$ and the TOC efflux from the bay to the open ocean to be $9.4 \times 10^{10}\ \text{gC year}^{-1}$ ¹¹. On the basis of actual observations, the amount of organic carbon burial was estimated to be $4.2 \times 10^{10}\ \text{gC year}^{-1}$ ¹². A different box model estimated the dissolved inorganic carbon (DIC) influx to Tokyo Bay to be $11.2 \times 10^{10}\ \text{gC year}^{-1}$ and the DIC efflux from the bay to be $13.4 \times 10^{10}\ \text{gC year}^{-1}$ ¹³. By combining these budget estimates, an additional carbon input of $7.7 \times 10^{10}\ \text{gC year}^{-1}$ will be required, a value roughly equal to our estimate of net CO_2 uptake. In addition, the above analysis also suggests that the eventual sink of the fixed carbon from CO_2 absorption in Tokyo Bay would be both from its burial in bay sediments and export to outer oceanic areas.

Because our observations were conducted on monthly basis, our estimates of CO_2 flux may have failed to report on events on a daily and/or weekly time-scale. We acknowledge that our results regarding the net CO_2 uptake in the bay might be compromised if these short-term temporal events contributed to significant CO_2 emission or outgassing from surface waters. We postulated two types of outgassing events in Tokyo Bay and found that such outgassing events should be insignificant to our carbon budget. First, we postulated a sudden vertical mixing event in early autumn when stratification was weakened. The observed $p\text{CO}_2$ values of the bottom waters during the stratification season from June to September were $400\text{--}940\ \mu\text{atm}$ ⁷, with a typical water-column average of approximately $600\ \mu\text{atm}$. Even if the outgassing from seawater at this level of CO_2 occurred in the entire area of the bay for 30 days, the amount of CO_2 efflux under typical wind speed would be $0.6 \times 10^{10}\ \text{gC}$, which would account for 12% of the air-sea CO_2 exchange in the bay ($5.2 \times 10^{10}\ \text{gC}$). Second, we postulated coastal upwelling events, which are generally observed in the northeastern part of the bay in late summer. These upwelling events cause conspicuous milky turquoise waters¹⁴ due to the oxidation of hydrogen sulfide in anoxic bottom waters. We observed these bottom waters on 16 and 23 September, 2010, in which $p\text{CO}_2$ values ranged from 765 to $1,161\ \mu\text{atm}$ with an average of $967\ \mu\text{atm}$ and the average CO_2 flux was estimated to be $54.0\ \text{mmolC m}^{-2}\text{day}^{-1}$. Because of the conspicuous water color, the area and duration of the upwelling events are well described in the bay; the events were observed for an average of 11.4 days a year from 2007 to 2010, with a maximum area of $80\ \text{km}^2$ ¹⁵. On the basis of this average duration and area, the observed CO_2 flux would yield an annual flux of $5.9 \times 10^8\ \text{gC year}^{-1}$. This value accounts for only 1.2% of the air-sea CO_2 exchange in the entire bay.

This study clearly demonstrated that Tokyo Bay as a whole is a net sink for atmospheric CO_2 ; however, this finding may contradict those of many studies on coastal waters. Most inland waters and estuaries have been reported to be significant sources of CO_2 to the atmosphere due to respiration of terrestrial organic carbon^{2,3,16} and terrestrial input of freshwater CO_2 ¹⁷. In contrast, continental shelf areas, which are laid offshore of coastal areas, have generally been reported to be sinks for atmospheric CO_2 due to nutrient input through coastal waters and from pelagic deep waters^{2,3,18,19}. Oceanic basins that are further offshore are either weak sinks or weak sources of atmospheric CO_2 , depending on the biogeochemical settings of the basin²⁰. Although it is confined to a very small inner part of the bay, Tokyo Bay certainly has an area of CO_2 emission, and the CO_2 emission mechanism in this area is common to that of other coastal areas. The net CO_2 absorption in the main body of the bay is driven either by a mechanism similar to that of continental shelf regions or by biological CO_2 fixation with a terrestrial supply of nutrients. On the basis of these considerations, we propose a generalized scheme for the CO_2 budget in a continuing water system composed of nearshore water emitting CO_2 , an outer water absorbing CO_2 , and pelagic water with a neutral CO_2 budget (Fig. 4).

In this scheme, there would be a border where the air-sea CO_2 flux is ± 0 between the nearshore waters emitting CO_2 and an outer waters absorbing CO_2 . On the land-side of this border, CO_2 emission due to biological degradation of terrestrial organic matter would exceed CO_2 uptake due to photosynthesis. The CO_2 emission would decrease toward the offshore side, and photosynthetic CO_2 uptake would exceed emissions on the offshore side of this border. The location of this border may shift either offshore or inshore. In fact, several studies have observed that some waters in estuaries with small freshwater discharge are weak sources or sometimes weak sinks of CO_2 ^{21–23}. In addition, some continental shelves with large freshwater discharge have been reported to be sources of CO_2 to the atmosphere¹⁹. We interpret that these rather atypical observations are associated with the shift of the aforementioned border. The shift is likely caused by the different terrestrial organic carbon load accompanied by freshwater discharge²⁴. Other factors that may affect the border shift and intensity of CO_2 flux include hydrographic and geomorphological characteristics such as a stratified estuarine system²², a microtidal estuarine system²⁵, an open/enclosed nature of the coast^{23,26}, and a submerged aquatic vegetation in shallow coastal waters²⁷.

In the case of Tokyo Bay, the border is extremely shifted inshore. The shift reflects the relatively low organic carbon supply from land and the active organic matter production driven by the massive nutrient supply from land. The seasonal stratification and semi-enclosed nature of the embayment should further facilitate the net uptake of CO_2 in Tokyo Bay. The low organic matter supply and large nutrient supply from land may seem

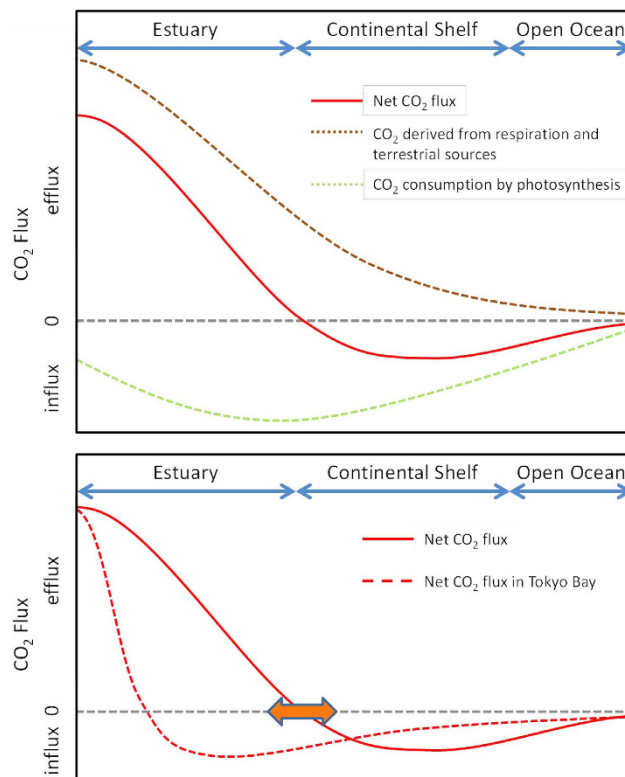


Figure 4. Conceptual scheme of net CO₂ flux in coastal waters and open ocean. The upper panel shows net CO₂ flux (red line), which is estimated from the “CO₂ derived from respiration and terrestrial sources (dotted brown line)” plus the “CO₂ consumption by photosynthesis (dotted green line)” The lower panel shows net CO₂ flux in Tokyo Bay (dotted red line). The dotted gray line denotes the atmospheric CO₂ equilibrium (air-sea CO₂ flux is ±0). The orange arrow indicates the border shift where air-sea CO₂ flux is ±0 between the nearshore waters emitting CO₂ and outer waters absorbing CO₂. In the case of Tokyo Bay, the border is extremely shifted inshore because of the low organic carbon supply and expansive coverage of secondary sewage treatment plants (STPs) in the catchment area.

contradictory. We believe that this imbalance between organic matter and nutrient supply is largely derived from the secondary sewage treatment in the catchment area of Tokyo Bay⁴. Currently, secondary-treated effluent flowing into Tokyo Bay accounts for 50% of the total freshwater discharge²⁸. Sewage treatment plants along Tokyo Bay remove organic carbon from freshwater at a rate of 7.7×10^{10} gC year⁻¹²⁸. This value is comparable to the uptake of CO₂ observed in this study (5.2×10^{10} gC year⁻¹). As the quantity of dissolved organic carbon (DOC) flowing into the bay has decreased by 60% in the last 40 years, the quality of DOC has become more recalcitrant due to improved sewage treatment²⁹. The decrease in turbidity due to the decrease in organic carbon inflow has also enhanced phytoplankton activity from the improvement of light availability³⁰. The effect of sewage treatment has also been reported in other estuary systems; Amann *et al.*³¹ have recently reported that pCO₂ decreased from 7000 to 2500 μatm at the oxygen minimum zone in 1986 and 2007 due to the installation of sewage treatment plants in the Elbe estuary.

Urbanized coastal waters that have a relatively large coverage of secondary sewage treatment tend to act as a strong net sink for atmospheric CO₂. The progress made in the urbanization of coastal areas with improved sewage treatment is common in many parts of the world³². This development will have an impact on the future budget of marine CO₂. Moreover, approximately 40% of the world's population is currently settled in coastal zones, and developed urban areas with completed sewer systems are expected to expand rapidly³². According to a UNEP report³², highly developed coastal areas occupied only 15% of the world coastal zones in 2002, but this figure is expected to rise to 60% in 2050. Therefore, the CO₂ budget characteristic of Tokyo Bay is expected to be observed in more marine coastal areas in the future. Although it may be difficult to predict future trends, we assume that highly urbanized coastal waters currently occupy 15% of the world coastal zones and are expected to occupy 60% by 2050. When the CO₂ fluxes in highly urbanized coastal waters and ordinal coastal waters are the same values as that of Tokyo Bay (-3.2 molC m⁻² year⁻¹) and previously published data³ (7.7 molC m⁻² year⁻¹), respectively, the CO₂ emissions from global coastal waters will be estimated to be approximately 0.074 PgC year⁻¹ at present and 0.014 PgC year⁻¹ in 2050. The emission of CO₂ to the atmosphere from estuaries is calculated to be 21% and 85% lower than previous estimates. As a result, the CO₂ budget of the global coastal waters would be expected to be a sink rather than a source.

Methods

The ship routes of all cruises were presented in Fig. 3 (a). Each point in this figure represents a pCO₂ value measured at a one-minute interval. Observations of pCO₂, salinity, and temperature were conducted during 40 cruises of the R/V Seiyō-maru and 9 cruises of the R/V Hiyodori. Measurements of pCO₂, salinity, and temperature were taken with a sampling frequency of one minute. Surface seawater was pumped up from the ship's bottom at ca. 2-m depth. Our pCO₂ measuring system consisted of a NDIR analyzer (LI-820, Li-Cor) and a membrane equilibrator. The membrane equilibrator was composed of multi-layered composite hollow-fiber membrane modules³³ (MHF module, Mitsubishi Rayon Co., Ltd.). The equilibrator was made of 6 MHF modules to create more surface area and a more rapid response. The response time and the standard error of this system were approximately 100 seconds, and smaller than 0.4 μatm, respectively. Atmospheric pCO₂ (pCO₂^{air}) was measured every three hours. *In situ* surface water salinity and temperature were measured using a thermosalinograph (Tsurumi Seiki Co., Ltd. at Seiyō-maru and YSI 6920 at Hiyodori). The net flux of CO₂ across the air-sea interface was calculated as the product of the solubility of CO₂ in seawater³⁴, the gas transfer piston velocity of CO₂, and the difference between pCO₂^{sea} and pCO₂^{air}. The gas transfer piston velocity was calculated using the equation given by Wanninkhof³⁵. Wind speed data were obtained from the Japan Coast Guard (<http://www6.kaiho.mlit.go.jp/tokyowan/>) from stations (Tsurugisaki, Kannonzaki, Honmoku, and Tokyo 13 gouchi) close to the observation areas. The samples for chlorophyll *a* (Chl *a*) measurement were collected at each stations using bucket and filtered through precombusted (450 °C, 3 h) GF/F filters. After filtration, chlorophyllous pigments were extracted using N, N-dimethylformamide, and the concentrations of Chl *a* were determined by the fluorometric method³⁶ (fluorometer used TD-700, Turner Desings).

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Author Contributions

A.K. designed the experimental setup, carried out part of the experiments, and wrote the manuscript; Y.M. carried out a portion of the experiments; and J.K. contributed to the design of the experiments and discussion of results. All authors discussed the results and contributed to the manuscript.

Additional Information

Competing Interests: The authors declare no competing financial interests.

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