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ORIGINAL ARTICLE

Calcium carbonate saturation and ocean acidification in Tokyo Bay, Japan

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Abstract From April 2011 to January 2012, seasonal variation of the aragonite saturation state (Ωar) was observed for the first time in Tokyo Bay, in order to understand the current state of ocean acidification in a highly eutrophicated bay in Japan. Ωar in the bay ranged between 1.55 and 5.12, much greater than observed in offshore waters. At the surface, Ωar was high during summer as a result of photosynthesis with some conflicting effect of freshwater input. At the bottom, Ωar was low during summer due to remineralization of organic matter. Based on an assumption that our observations represent current conditions in Tokyo Bay, it is estimated that the emission of anthropogenic CO_2 has already decreased Ωar by 0.6 since the preindustrial period and will further decrease by 1.0–1.6 by the end of this century if emission of CO_2 is continued at a high level [representative concentration pathway (RCP) 8.5 scenario]. With other conditions remaining the same, bottom waters of the bay will reach seasonal aragonite undersaturation by 2060–2070. However, because coastal regions have a large interannual variability, we need further observations to evaluate our estimations and future predictions presented here. Nevertheless, it should be safe to say that the larger seasonal variation in Ω causes the Tokyo Bay to reach aragonite undersaturation earlier than offshore regions and such conditions have negative consequences on the variety of calcifying organisms living in Tokyo Bay. Ocean acidification could thus give an additional stress to the ecosystem of the bay, which is now suffering from eutrophication and hypoxia.

Keywords Ocean acidification · Eutrophication · Calcium carbonate saturation · Tokyo Bay · Anthoropgenic CO_2

1 Introduction

The uptake of anthropogenic carbon dioxide (CO_2) by the oceans alters carbonate chemistry of seawater to make the world's oceans more acidic (e.g., Caldeira and Wickett 2003). This so-called "ocean acidification" is expected to profoundly affect marine ecosystems and may threaten some organisms, including commercially important shellfish, corals and fishes (e.g., Gattuso and Hansson 2011; Branch et al. 2013). Of particular concern is the impact of ocean acidification on calcifying organisms, such as clams, mussels, oysters, sea urchins, abalones, corals etc., because the saturation state of calcium carbonate ($CaCO_3$) in seawater decreases as a result of ocean acidification. The $CaCO_3$ saturation state (Ω) with respect to either aragonite or calcite (Ωar or Ωca), the two major types of $CaCO_3$ produced by marine organisms, is expressed by the product of carbonate and calcium ions ($[CO_3{}^{2-}]$ and $[Ca^{2+}]$) in seawater relative to the stoichiometric solubility product (K'_{SP}, for aragonite or calcite) at a given temperature, salinity and pressure (Mucci 1983):

$$\Omega = \left[CO_3^{2-}\right]\left[Ca^{2+}\right] / K'_{sp}. \quad (1)$$

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When CO_2 is dissolved in seawater, carbonate ion (CO_3^{2-}) is consumed via a series of chemical reactions, summarized as follows:

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-. \quad (2)$$

This results in a decrease in Ω to make the seawater less favorable to precipitate $CaCO_3$. When Ω is <1, seawater is corrosive and therefore $CaCO_3$ will begin to dissolve in the absence of protective mechanisms. Indeed, studies have shown a reduction in survival, calcification, growth, development and abundance when calcifying organisms such as mollusks (bivalves) were exposed to elevated CO_2 and decreased Ω conditions (Kroeker et al. 2013 and references there in). It has also been revealed that larval stages of mollusks are extremely sensitive to acidification (Talmage and Gobler 2009; Kroeker et al. 2013). Some organisms, however, may be able to regulate their metabolism and calcification to compensate for increased seawater acidity, but at a substantial energetic cost (Wood et al. 2008). Therefore, this regulation is unlikely to be sustainable in the long term and may reduce energy for other important metabolic processes of calcifying organisms (Wood et al. 2008; Kroeker et al. 2013). Ocean acidification also positively or negatively affects reproduction, behavior or photosynthesis of a range of organisms, while effects are overall negative for calcifiers (Gattuso and Hansson 2011; Kroeker et al. 2013). Although the overall effects of ocean acidification on marine ecosystems need to be further investigated, ocean acidification and the decrease in Ω can have substantial consequences on fisheries and marine ecosystem services (e.g., Cooley and Doney 2009; Narita et al. 2012; Branch et al. 2013).

The coastal area is the main field for aquaculture and capture fisheries, especially for shellfish, as well as other ecosystem services. In coastal regions, however, distribution and seasonal variation of Ω is not well known, as it is strongly locally regulated by other natural and anthropogenic environmental processes, such as freshwater and carbon inputs from land, intensive mixing, eutrophication and resulting bottom hypoxia (Salisbury et al. 2008; Wootton et al. 2008; Feely et al. 2010; Provoost et al. 2010; Cai et al. 2011; Melzner et al. 2013; Duarte et al. 2013). Therefore, observations of Ω with other environmental parameters are essential for understanding and prediction of carbonate chemistry with increasing atmospheric CO_2 and the impact of ocean acidification on regional ecosystems. In the present paper, we first show observational results of seasonal variation in Ω in Tokyo Bay, a highly eutrophicated bay in Japan. We will focus on Ωar because aragonite is more soluble and thus has lower Ω values than calcite, and because aragonite constructs the larval shell of mollusks, including commercially important bivalves such as clams and oysters. Studies have shown that a decrease in Ωar in seawater or at the sediment–water interface results in an increase in mortality and decrease in growth of larval and juvenile bivalves (Green et al. 2004; Talmage and Gobler 2009). Based on observations, we will discuss processes affecting Ω in the bay. We also make an estimation of future changes in Ω in order to provide information on future progress of ocean acidification in the bay.

2 Study area

Tokyo Bay is a semi-enclosed bay located in central Japan, with an area of 922 km^2 and a mean depth of 19 m (Fig. 1). The bay is surrounded by highly urbanized areas and receives freshwater and nutrients from rivers with discharges from sewage treatment plants. This makes the bay one of the most eutrophicated coastal environments in the world. The annual primary production in Tokyo Bay is reported as one of the highest among the world's estuarine-coastal ecosystems (Cloen et al. 2014), even though nutrient inputs to the bay and concentrations in surface bay waters have significantly decreased since the 1980s (Furukawa and Okada 2006; Kanda et al. 2008; Kodama et al. 2010; Kodama and Horiguchi 2011). Because of high primary production and surface stratification, respiration of organic matter by bacteria often causes hypoxia/anoxia in the bottom water of the Tokyo Bay during summer (e.g., Ishii et al. 2008). The annual catches of fish and shellfish in the bay decreased from ~100,000 tons in the 1960s to ~20,000 tons in the 2000s, due to excessive eutrophication, hypoxia/anoxia, coastal reclamation and competition with newly introduced species (Furukawa and Okada 2006). At present, shellfish correspond to more than 60 % of the total catch. The nearshore areas of the bay are also popular fields for recreational clam gathering.

Ocean acidification in Tokyo Bay is expected to cause additional stresses on organisms living in this eutrophicated bay, with socioeconomic consequences. Furthermore, it has been pointed out that eutrophication can amplify ocean acidification (Cai et al. 2011; Melzner et al. 2013). Eutrophication in coastal waters increases heterotrophic remineralization of organic matter and produces more CO_2 in bottom water, which lowers Ω and also reduces the ability of seawater to buffer changes in pH. Therefore, we expect that Tokyo Bay is one of the regions in Japan most vulnerable to ocean acidification. However, there is no observational information on the state of Ω and its seasonal variation in Tokyo Bay or other coastal areas of Japan. It is speculated that Ω in the bay has large seasonal variability, due to freshwater input and extensive biological activities during summer and cooling during winter. The large seasonal variability should lead the bay water to reach to the

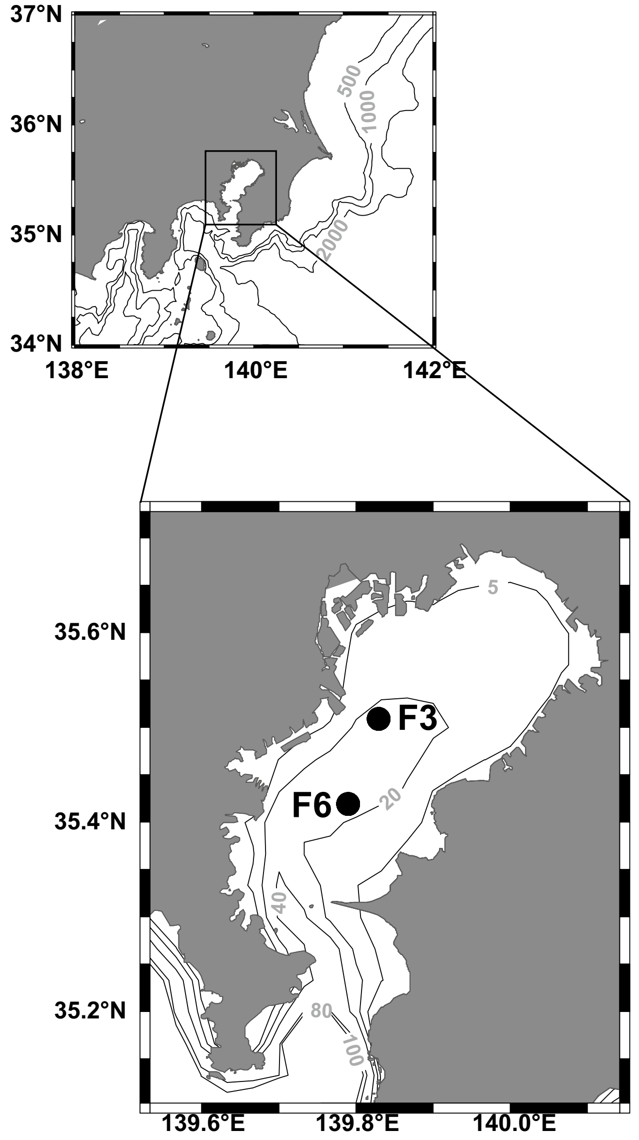

Fig. 1 Map of Tokyo Bay with sampling locations. *Gray lines* with *numbers* indicate bathymetry in meters

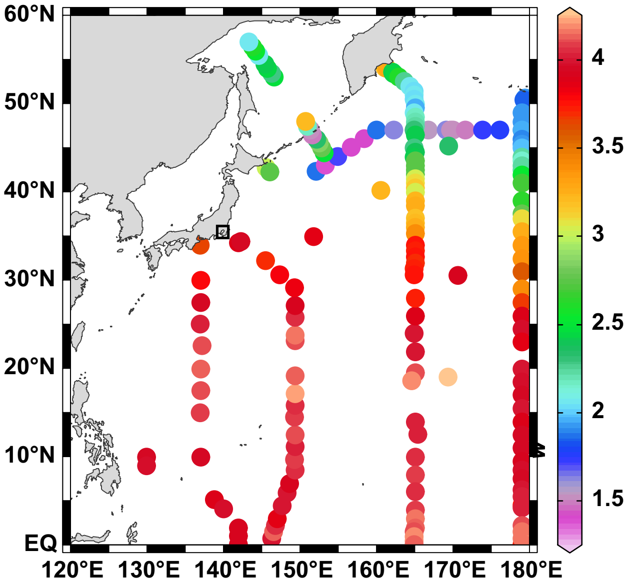

Fig. 2 Surface Ωar in the northeastern Pacific Ocean calculated from chemical data (DIC, TA and nutrients) in the GLODAP database (Key et al. 2004). Note that there are no data in the coastal region of Japan with depths shallower than 1000 m, and observations are from May to September only. A *black rectangle* in the map shows the location of Tokyo Bay

threshold, e.g. $\Omega = 1$, earlier than the open ocean, at least seasonally.

In the open ocean off Japan, some observational data of Ω are available. Distribution of surface Ωar in the open ocean region of the northeastern Pacific Ocean (Fig. 2) shows that Ωar is lower in the north, especially in the cyclonic western subarctic gyre, and is over 3.0 in the region south of 35.5°N where Tokyo Bay is located. This spatial variation reflects the fact that low temperature water has lower Ω ($CaCO_3$ and CO_2 dissolve more in colder water) and also upwelling of deeper water brings CO_2-enriched low Ω water toward the surface. A detailed and long-term observation in the subtropical North Pacific off the southern coast of Japan showed that Ωar of surface water is ~3.5 during the summer, but decreases to lower than 3.0 during the winter (at 33°40′N–34°00′N; Ishii et al. (2011)). In the western subarctic gyre further north, a similar seasonal pattern in surface Ωar was observed, but with a larger variation and lower values for both summer (~2.5) and winter (~1.3) (at ~45°N; Wakita et al. 2013). From these observations, the Ωar of waters in Tokyo Bay would be ~3 with a maximum value in summer, if there is no alternation of water properties by processes within the bay.

3 Observation and analysis

To estimate Ω of seawater, samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected in 8-L Niskin bottles mounted on a CTD rosette on the R/V Seiyo-maru of Tokyo University of Marine Science and Technology, monthly from April 2011 to January 2012 (except August 2011) at two stations in Tokyo Bay (Fig. 1). Station F3 and F6 are located at 35.51°N, 139.83°E and 35.42°N, 139.79°E, respectively. Bottom depths are 23 and 26 m for F3 and F6, respectively. Seawater samples were also collected for the analysis of nutrient and chlorophyll *a* concentrations. DIC of sample water was determined using a CO_2 extraction-coulometry method. TA was measured by using a spectrophotometric method (Yao and Byrne 1998). The DIC and TA values were calibrated against certified reference material (Batch 105) provided by Prof. A. G. Dickson (Scripps Institution of Oceanography). Pooled standard deviations of duplicate samples were 2.3 μmol kg^{-1} ($n = 10$) and 2.8 μmol kg^{-1} ($n = 13$) for DIC and TA, respectively. Unfortunately, we missed a sample and could not measure DIC and TA of bottom water at F6 in September. Nutrient concentrations were determined with an autoanalyzer system, a Quaatro-Marine 5ch (SEAL Analytical, Ltd, Fareham, UK), following the protocols for the Joint Global Ocean Flux Study (JGOFS 1996) and Kanda (1995) for ammonium analysis. Measured values were calibrated against standard reference materials for nutrient analysis from General Environmental Technos Co., Ltd., Japan. The detection limit of the system is 0.05 μmol L^{-1} for phosphate, 0.37 μmol L^{-1} for silicate, 0.10 μmol L^{-1} for nitrate, and 0.15 μmol L^{-1} for ammonium. Water samples for chlorophyll *a* measurement were filtered through precombusted (450 °C for 3 h) Whatmann GF/F filters. After the filtration, chlorophyllous pigments were extracted in N, N-dimethylformamide (DMF). Concentrations of chlorophyll *a* were determined by the fluorometric method (Suzuki and Ishimaru 1990) using a Turner Design Model TD-700 fluorometer.

Temperature, salinity and pressure were measured by a CTD (Falmouth Scientific Inc., Bourne, MA, USA). Sensor data have been scaled with pre-cruise calibrations from the sensor manufacturer. Changes in values between calibrations were less than 0.02, 0.02 °C, and 2 dbar for salinity, temperature, and pressure, respectively. Dissolved oxygen (DO) concentration was measured by a RINKO sensor (JFE Advantech Co., Ltd.), except in April 2011. Calibrations of the RINKO sensor performed for each cruise showed that the error between cruises was less than 3 %.

Observations of DIC, TA, nutrients, temperature, salinity and pressure were used to calculate Ω and partial pressure of CO_2 (pCO_2 with in situ temperature and pressure) by using the CO2sys program (Lewis and Wallace 1998) with constants of Lueker et al. (2000) for K_1 and K_2 and Dickson (1990) for $K\mathrm{SO}_4$. The uncertainty in both DIC and TA measurements can lead to an error of <0.06 in Ω and <32 μatm in pCO_2. In these calculations, we did not account for the contribution of dissolved organic matter (DOM) to TA: it has been shown that a bulk DOC acts as a proton acceptor and influences the acid–base system of seawater (e.g., Cai et al. 1998; Hernández-Ayon et al. 2007; Kim and Lee 2009). In open oceans, this contribution is generally much smaller than that of inorganic compounds, and is therefore negligible. In coastal waters, however, high concentrations of DOM due to high primary production and inputs from rivers can significantly contribute TA. For example, Cai et al. (1998) estimated organic contributions to TA ($\mathrm{TA_{org}}$) of <50 μmol kg^{-1} for waters in the coastal zone of Georgia (USA) with dissolved organic carbon (DOC, as a measure of DOM) concentrations of 300–750 μmol kg^{-1}. They also observed higher $\mathrm{TA_{org}}$ values up to 120 μmol kg,$^{-1}$ but only in a river estuary with very high DOC concentrations (>1000 μmol kg^{-1}). In the Baltic Sea, $\mathrm{TA_{org}}$ was estimated to be ~30 μmol kg^{-1} in waters with DOM of ~300 μmol kg^{-1} (Kuliński et al. 2014). Accordingly, the assumption of $\mathrm{TA_{org}} = 0$ can result in errors in calculations of Ω and pCO_2 in coastal waters. To estimate the order of this error, we assumed $\mathrm{TA_{org}}$ = ~20 μmol kg^{-1} in Tokyo Bay, based on the relationship between DOC and $\mathrm{TA_{org}}$ in the above-mentioned observations in coastal oceans and DOC concentrations of 80–180 μmol kg^{-1} at F3 and F6 stations (Kubo et al. 2015), although acid–base properties of DOM are regionally and temporally variable. A comparison between estimations with and without $\mathrm{TA_{org}}$ (TA-$\mathrm{TA_{org}}$) shows that 20 μmol kg^{-1} of $\mathrm{TA_{org}}$ results in an overestimation of Ω by ~8 % and an underestimation of pCO_2 by ~10 %, consistent with error estimations by Koeve and Oschlies (2012).

4 Results and discussions

4.1 Temperature, salinity, DO and chlorophyll *a*

Observations of temperature and salinity showed a strong stratification during summer (Fig. 3a, b). The salinity of the upper layer decreased from spring to summer by inputs of river runoff and precipitation, and reached a minimum of 15.9 and 27.3 in September at F3 and F6, respectively (Fig. 3b). At the bottom, salinity was 33.0–34.3, somewhat fresher than the water flowing into the bay from the open ocean (33.5–34.5) (Okada et al. 2007). Temperature increased from spring to summer at all depths and reached ~26.5 °C at the surface in early September at both stations. From October, atmospheric cooling and winds caused vertical mixing and resulted in a well-mixed water column with a temperature of ~10 °C in January. DO and chlorophyll *a* concentrations also showed distinct seasonal variations (Fig. 3c, d). Waters in the upper layer increased in DO and had high chlorophyll *a* concentration (7–40 μg L^{-1}) from June to November (also in May at F3), indicating active primary production. DO decreased in December and increased again in January. This coincides with the changes in chlorophyll *a* concentration, which decreased to 2 μg L^{-1} in December and increased again to 15–20 μg L^{-1} in January. High chlorophyll *a* in winter is sometimes observed in the inner part of the bay and has been attributed to the transport of phytoplankton cells from other parts of the bay, episodic stratification and favorable light conditions (Shibata and Aruga 1982; Nomura and Yoshida 1997). Nutrients are not considered to be the limiting factor for primary production in Tokyo Bay in winter (Shibata

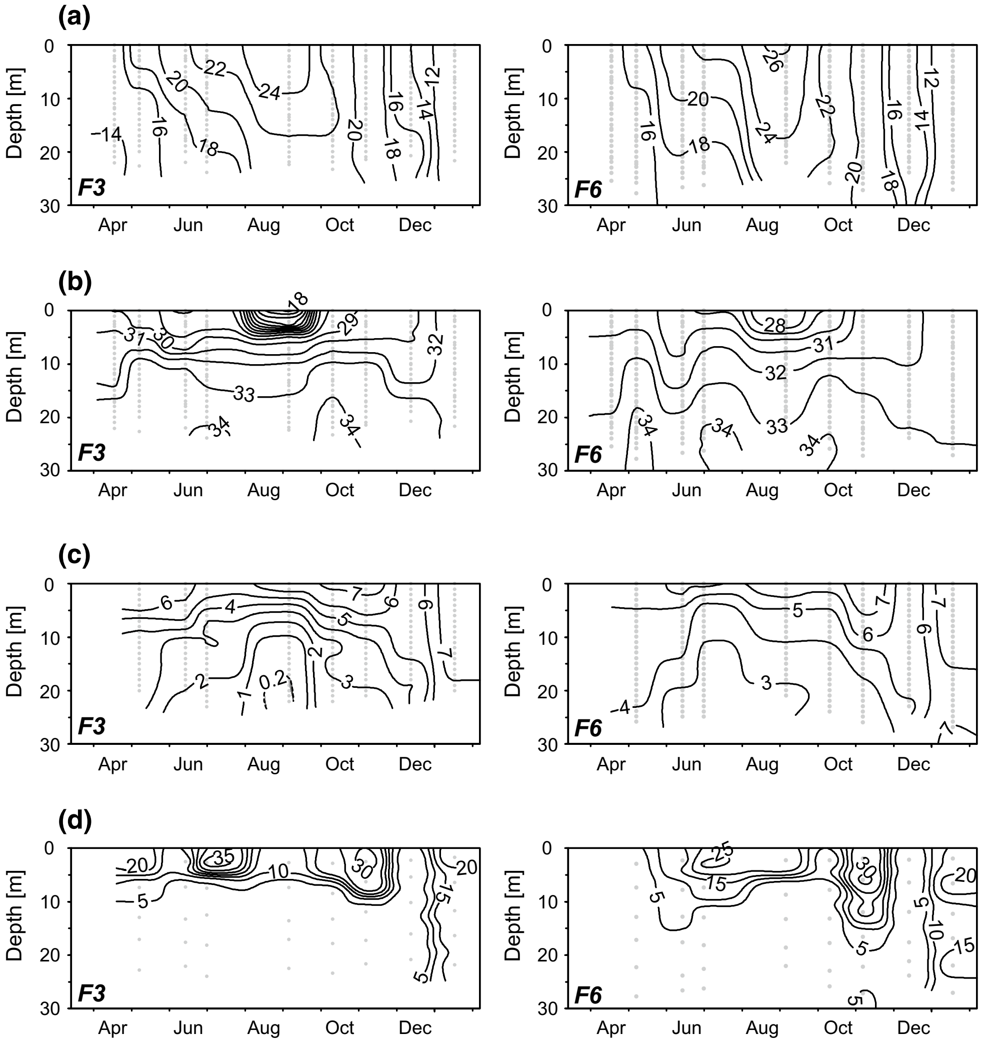

Fig. 3 Seasonal variations of temperature (**a**;°C), salinity (**b**), dissolved oxygen (DO; ml L^{-1}) (**c**) and chlorophyll *a* (**d**; µg L^{-1}) at stations F3 (*left*) and F6 (*right*)

and Aruga 1982; Bouman et al. 2010). In the bottom layer, DO was low throughout the year except in January, due to respiration and decomposition of organic matter produced in the upper layer and transported from land. The bottom water at F3 reached hypoxic condition ($\leq$2.0 ml L^{-1}) in July and severe hypoxia ($\leq$0.2 ml L^{-1}) in September. At F6, the minimum DO concentration was 2.1 ml L^{-1} observed in September. These observations showed that in 2011, F3 had a larger seasonal variability in surface salinity and bottom DO than F6. Previous studies have also shown larger seasonal variations at F3 than at F6 in salinity, nutrients, and chlorophyll *a* concentrations (Matsumura et al. 2001; Kanda et al. 2008). This is consistent with the fact that F3 is located in the innermost region of the bay, which directly receives massive amounts of freshwater, nutrients and organic matter from the land (e.g., Ninomiya et al. 1996; Kubo et al. 2015). Accordingly, the innermost region is characterized by large seasonal variations, strong stratification, high primary production, and frequent occurrence of hypoxic/anoxic waters in the water column (Shibata and Aruga 1982). Also, the seafloor of the innermost region is covered by silt and clay with high COD (chemical oxygen demand) and little benthic biomass, compared to the central region of the bay where F6 is located (Furukawa and Okada 2006; Kodama and Horiguchi 2011).

4.2 TA, DIC and pCO_2

Seasonal variations of carbonate parameters (Fig. 4) should be explained by the above-mentioned physical and biological conditions. At station F3, TA and DIC ranged from 1523 to 2290 µmol kg^{-1}, and from 1207 to 2160 µmol kg^{-1}, respectively. At F6, TA was between 2092 and 2283 µmol kg^{-1}, and DIC was between 1763 and 2092 µmol kg^{-1}. Note that

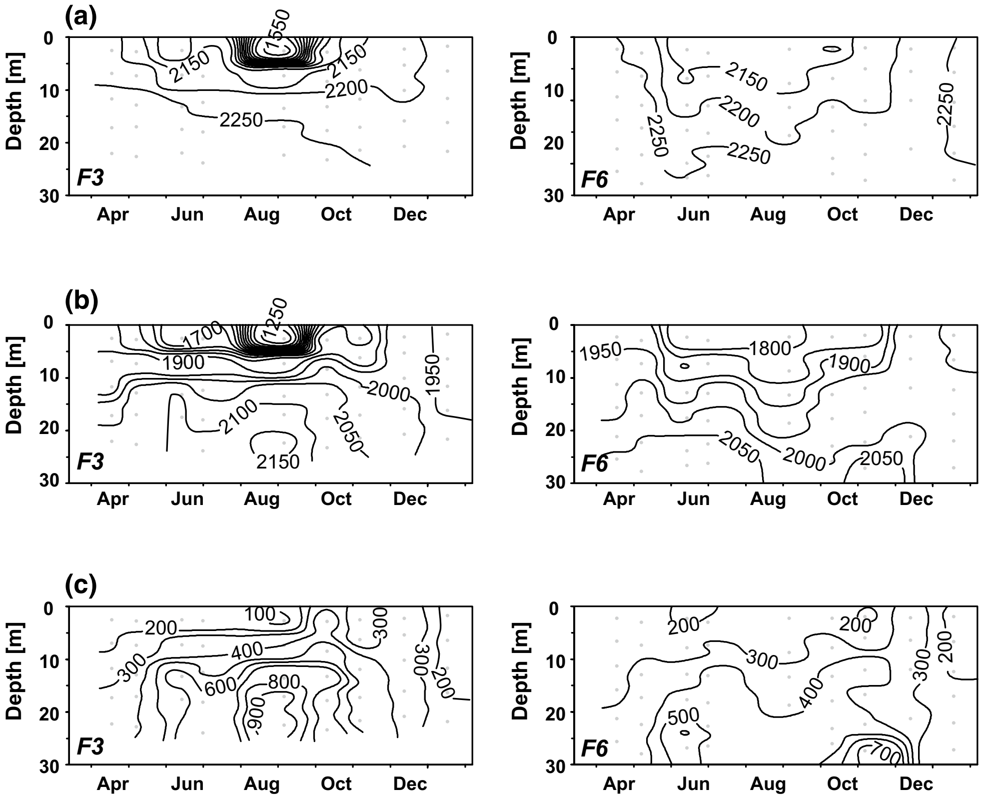

Fig. 4 Seasonal variations of TA (**a**), DIC (**b**), and pCO_2 (**c**) at stations F3 (*left*) and F6 (*right*)

normalization of TA and DIC to a constant salinity was not applied in this study because of the significant inputs of TA and DIC from rivers into Tokyo Bay. Variations are much larger than those in the open ocean (e.g., Wakita et al. 2013; Yasunaka et al. 2013). The lowest values observed at the surface of the F3 station in September correspond to the lowest salinity. Both TA and DIC correlated well linearly with salinity, and the coefficient of determination is 0.85 ($n = 95$) and 0.81 ($n = 94$), respectively, indicating that the mixing between freshwater and seawater is the main factor controlling seasonal variations of these parameters in the bay (Fig. 5). The intercept of salinity–TA regression line (1076 ± 97 μmol kg^{-1}) is close to that of Taguchi et al. (2009), who reported that salinity and TA in the bay can be expressed as a mixture of offshore water (North Pacific subtropical mode water; salinity = 34.82, TA = 2293 μmol kg^{-1}) and freshwater end-member with TA of 1006 μmol kg^{-1}. It is also close to TA in rivers flowing to Tokyo Bay; ~950 μmol kg^{-1} in Arakawa River (Kobayashi 1960) and 1094 μmol kg^{-1} in Tamagawa River (observed by ourselves in April 2011 at Futako Bridge, 18 km upstream from the river mouth). It should be noted that waters observed in April and May, as well as some summer surface waters, had higher TA values than expected from the regression line in the salinity-TA diagram (Fig. 5). This should reflect a seasonal variability in TA of river runoff and/or in relative contributions of river runoff and precipitation (TA = 0). Biological activity also alters TA, but to a smaller degree; assimilation of nitrate and denitrification increases TA and assimilation of ammonia and bacterial nitrification decreases TA (Brewer and Goldman 1976). The effect of these processes on TA can be evaluated by calculating the potential alkalinity (pA = TA + nitrate−ammonium). The difference between pA and TA was ~ ±20 μmol kg^{-1}. This means that nitrogen-related biological processes alter TA in Tokyo Bay by ± 20 μmol kg^{-1}. Formation and dissolution of calcium carbonate by calcifying organisms can also alter TA of seawater [one mole of $CaCO_3$ formation (dissolution) results in two moles of TA decrease (increase)]. For example, Shamberger et al. (2011) observed ~100 μmol kg^{-1} of daily TA fluctuation on a Hawaiian coral reef and Murata et al. (2006) found ~80 μmol kg^{-1} lower TA than expected from salinity in blooms of coccolithophorid in the Bering Sea. In the Tokyo Bay, shellfish are the major calcifier and calcifying plankton very rarely dominate in the bay (Yamada 1997). In our observations, bottom waters observed at 23 and 26 m in October at F6 showed lower TA values at salinity of ~34 by up to ~40 μmol kg^{-1} compared to other months (red crosses in Fig. 5a). This may be due to calcification at the bottom. However, it is not clear at the moment whether observed lower TA was due to calcification or not. Nevertheless, we

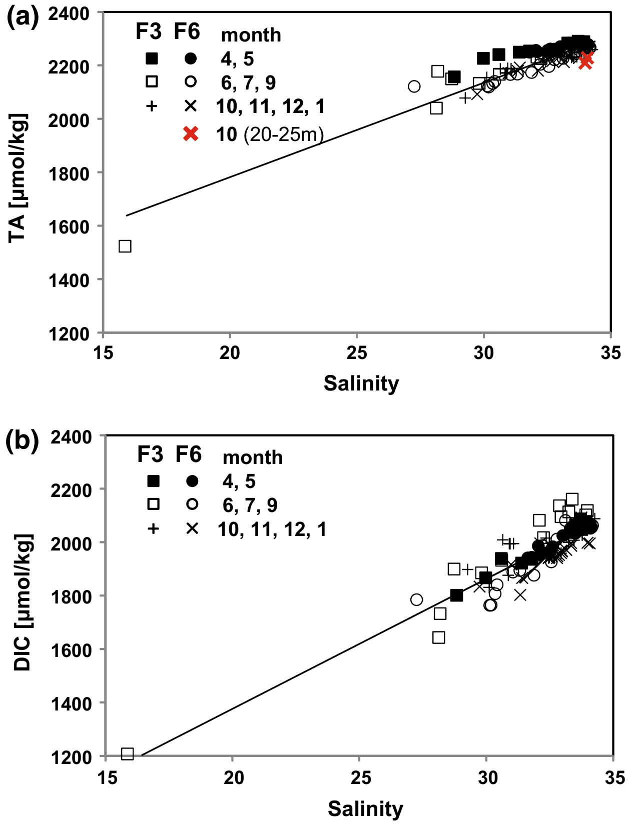

Fig. 5 Relationships between salinity and TA (**a**), and salinity and DIC (**b**). *Filled* and *open square* (*F3*) and *circles* (*F6*) are data observed in spring (April and May) and in summer (June to September), respectively. *Pluses* (*F3*) and *crosses* (*F6*) represents data from fall and winter (October to January). *Red crosses* in (**a**) indicate bottom water (23 and 26 m) observed in November at F6. *Black lines* in (**a**) and (**b**) indicate regression lines of TA = 35.456 × salinity + 1076.1 or DIC = 48.849 × salinity + 398.9, respectively

suppose that biological impacts on seasonal variation in TA are overall smaller than that of freshwater inputs, as suggested by the relatively good linear relationship between salinity and TA and the fact that it follows a mixing line between offshore water and freshwater end-member (Fig. 5a; Taguchi et al. 2009).

One can expect that freshwater end-member for DIC is closer to that for TA (1076 ± 97 µmol kg^{-1}), as bicarbonate ion (HCO_3^-) is a dominant carbonate species in freshwater. Actually, annual mean DIC observed in the lower Tamagawa river was ~1050 µmol kg^{-1} (Kubo et al. 2015). Furthermore, runoff into the bay can transport excess DIC due to a large contribution of effluent from sewage treatment plants (50 % of freshwater flux into Tokyo Bay) which have high pCO_2, high organic matter content and high DIC (~1600 µmol kg^{-1}; Kubo et al. 2015). However, the intercept of salinity-DIC relationship was as low as 399 ± 158 µmol kg^{-1}. This means that excess CO_2 from runoff has been removed on the way from river mouths to the study sites, probably in very low salinity area near the coast. The process of removal should be air-sea exchange and biological drawdown of CO_2. Consequently, freshening of surface water resulted in low DIC concentrations (Figs. 3b, 4b, 5b). In situ primary production further decreases DIC in surface waters. At the bottom, waters become enriched with DIC as produced organic matter settles and is respired by bacteria. This is more evident when pCO_2 is estimated from TA and DIC (Fig. 4c). The seawater pCO_2 was lower than that in the atmosphere (~400 µatm, Kubo, unpublished data in Tokyo Bay from 2007 to 2010) in the entire water column in January and in the upper layer throughout the year as a result of photosynthesis (in situ or in upstream region), except the upper layer in October at F3 (probably influenced by vertical mixing with deeper water) (Figs. 3c, d, 4c). On the other hand, pCO_2 in the bottom layer increases from May to August because of remineralization of organic matter. The lowest pCO_2 (82 µatm) was in the freshest surface water at F3 in September and the highest DIC (2160 µmol kg^{-1}) and pCO_2 (938 µatm) was observed in the anoxic bottom water at F3 in September (Fig. 4). Because of these biological impacts on CO_2, observed range in DIC was 1.2 and 1.7 times larger than in TA at F3 and F6, respectively. Variations in DIC, TA and pCO_2 are larger at F3 in the innermost bay than F6 in the central bay reflecting larger freshwater inputs and higher productivity/remineralization in the former region (Matsumura et al. 2001; Kanda et al. 2008; Kubo et al. 2015).

4.3 *Ω*

Figure 6 shows seasonal variation in *Ω*ar in Tokyo Bay. Despite its highly eutrophicated environment, waters at two stations in Tokyo Bay were oversaturated with respect to calcium carbonate throughout the year. Seasonal variation of *Ω*ar was large and almost mirrored pCO_2. From April to November, *Ω*ar was high in the upper layer and low in the bottom layer. A decrease in October is probably due to mixing with deeper water as increased pCO_2 at the surface suggests (Fig. 6). In December, *Ω*ar in the water column was the lowest but increased in January. These results suggest that photosynthesis and remineralization are major processes controlling seasonal variation of *Ω*ar in Tokyo Bay: photosynthesis removes CO_2 from seawater while remineralization releases CO_2 into seawater to increase and decreases *Ω*ar, respectively (Eqs. 1 and 2). The lowest value of 1.55 was observed in the anoxic and CO_2-enriched bottom water at F3 in September, as a result of organic matter remineralization. The highest *Ω*ar (5.12) was, on the other hand, observed at the surface of F3 in July, not in September when pCO_2 was the lowest. This is due to the heavy freshening in September which lowers *Ω*ar by reducing Ca^{2+} and CO_3^{2-} concentrations (Salisbury

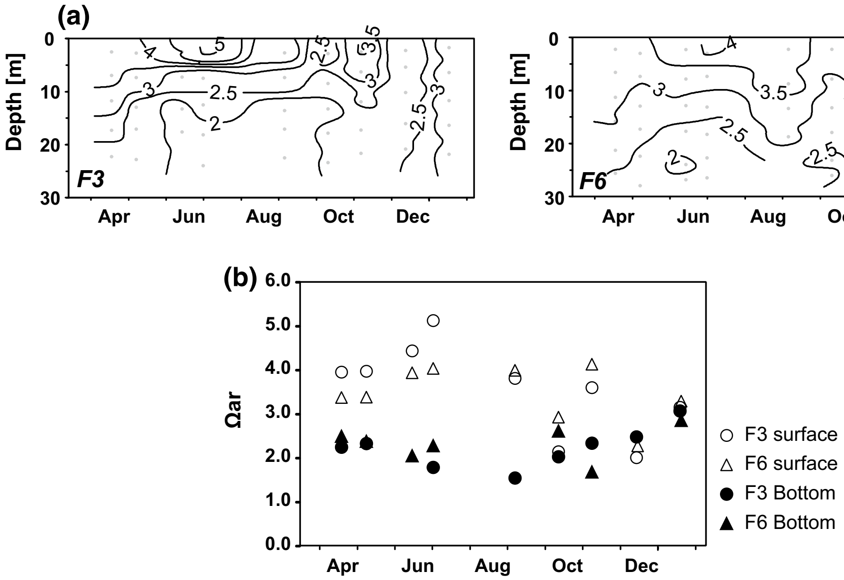

Fig. 6 **a** Seasonal variation of Ωar at stations F3 (*left*) and F6 (*right*). **b** Temporal changes in Ωar in uppermost (*open symbols*) and deepest (*filled symbols*) observations

et al. 2008; Yamamoto-Kawai et al. 2009, 2011). Therefore, the effect of photosynthesis was cancelled out by that of freshening in September. At F3, Ωar varied between 2.01 and 5.12 (Δ3.11) at the surface and 1.55–3.07 (Δ1.52) at the bottom. At F6, Ωar was 2.27–4.04 (Δ1.77) at the surface and was 1.68–2.85 (Δ1.17) at the bottom, although we missed a sample of bottom water in September at F6. The range of variation was larger at F3 than F6 as expected from the more active photosynthesis and remineralization in the innermost bay. When compared to the offshore subtropical waters (Ωar = 3.0–3.5; Ishii et al. 2011), waters in Tokyo Bay experiences much larger temporal variation in Ωar both at the surface and the bottom. The pattern of seasonal variation is similar to that of open ocean in the surface layer, high in spring and summer and low in winter, but there are additional significant effects of freshening (descreases Ωar), mixing with CO_2-enriched bottom water (decreases Ωar), and high primary production (increases Ωar). Bottom waters showed an opposite variation, low in summer and high in winter with an occasionally low value in November at F6 when pCO_2 was high (Fig. 6). Bottom water in summer showed much lower Ωar than in offshore where Tokyo Bay water originates (Figs. 2, 6). From these results, we conclude that Ω in Tokyo Bay is controlled by the freshwater input and photosynthesis at the surface and remineralization at the bottom.

Here, we try to estimate effects of human activity on Ω in the bay through regulation of freshwater and nutrient discharges. Okada et al. (2007) estimated an increase of freshwater input to the Tokyo Bay from 341 $m^3\ s^{-1}$ in 1947–1974 to 424 $m^3\ s^{-1}$ in 2002–2003, mostly due to introduction of freshwater to the metropolitan region from outside of the drainage basins. We roughly estimate the effect of the freshwater increase to Ω of the bay as follows. Assuming that offshore water with salinity = 34.82 and TA = 2293 μmol kg^{-1} (following Taguchi et al. 2009) mixes with freshwater with salinity = 0 and TA = 1076 μmol kg^{-1} to have salinity between 15 and 34.5, fraction of freshwater (f_{FW}) and TA in mixed waters are estimated to be 0.56–0 and 1605–2293 μmol kg^{-1}, respectively. We calculated Ωar of the mixed waters by assuming 2 dbar for pressure, 276 μatm for pCO_2 and 18 °C for temperature, which are average values of our observations in surface water at F3 and F6. Then, we reduced f_{FW} of the mixed water by 20 % ($f_{FW} \times 0.80$), based on the increase estimated by Okada et al. (2007), and recalculated salinity, TA, and then Ωar. Results show that the removal of 20 % of freshwater increases Ωar by up to 0.32. Note that effects of increases in nutrients or carbon discharges from land that should result in changes in biological activities and DO concentration are not considered here, as they should be included in the estimates of eutrophication effects as described below. Therefore, we estimate that the increase in freshwater input to the bay could have decreased Ωar by ~0.3. However, we suppose that Ωar in bay water was not actually decreased during the period from 1947–1974 to 2002–2003, because the expected decrease in salinity was not observed during this period despite an increase in freshwater discharge (Okada et al. 2007). This contradiction suggests a shorter residence time of freshwater in the bay, due to the decreased bay area, increased inflow of saline offshore water to the bay, and/

or increased discharge itself (Okada et al. 2007; Ando et al. 2003). Therefore, the effect of increased freshwater input on *Ω*ar and those of physical changes may have cancelled each other out. In other words, if the changes in physical condition are independent from the increased discharge, they could have increased *Ω*ar by 0.3.

Anthropogenic eutrophication, on the other hand, should have largely modified *Ω* in the bay. For example, Ishii et al. (2008) analyzed data of DO in Tokyo Bay from 1948 to 2005 and revealed that DO in summer bottom water in the innermost bay area was higher than 2.5 ml L^{-1} before 1956. but decreased to ~1.0 ml L^{-1} or lower in and after the 1960s. This change coincides with a sharp and large increase during the 1950s in COD in 1955-1975 data (Unoki and Kishino 1977, cited in Kawabe and Kawabe 1997), as well in numbers of red tide events in 1907–1995 (Nomura 1998). These indicate that a significant and rapid eutrophication occurred in the 1950/1960s. The decrease of DO by 1.5 ml L^{-1} (67 μmol kg^{-1}) corresponds to an increase by 46 μmol kg^{-1} of DIC when O_2:C stoichiometry of remineralization reaction was assumed to be −170:117 (Anderson and Sarmiento 1994). An addition of 46 μmol kg^{-1} of DIC to summer bottom water lowers *Ω*ar by about 0.45. Note that when the O_2/C ratio was varied within the theoretical range of 1–1.58 (Fraga et al. 1998), the change in DIC and *Ω*ar would be 42–67 μmol kg^{-1} and 0.4–0.6, respectively. At the surface, DO in summer was ~6.0 ml L^{-1} in the 1950s, and >7.5 ml L^{-1} after the 1950s due to enhanced photosynthesis, whereas the concentration in winter stayed nearly constant (Ishii et al. 2008). This should have resulted in an increase in summer surface water *Ω*ar by about 0.45, if other conditions stayed the same. Therefore, we roughly estimate that the eutrophication after the 1950s could have expanded seasonal variation of *Ω*ar in the innermost bay region by 15 % [0.45/(3.11−0.45)] and 40 % [0.45/(1.52−0.45)] at the surface and the bottom, respectively. Note that this can be an underestimation because we did not consider effects of denitrification in sediment or bottom water which increases DIC without changing DO and could have enhanced as a result of eutrophication, and air-sea exchange releases some of DO produced by photosynthesis in surface waters but has less impact on CO_2 due to a slower gas exchange rate for the latter. Also, temporal changes in neither photo-degradation of DOM to DIC nor TA_{org} were considered because of the lack of information.

4.4 *Ω* and atmospheric CO_2

In this section, we examine the effect of increased atmospheric CO_2 concentration on *Ω* in Tokyo Bay in order to provide some information on the future progress of ocean acidification in the bay. First of all, DIC is expressed as:

$$\mathrm{DIC} = \mathrm{C_{EQ}} + \left(\Delta\mathrm{C_{Diseq}} + \Delta\mathrm{C_{Bio}}\right) \tag{3}$$

where C_{EQ} is DIC of water in equilibrium with atmospheric CO_2 concentration when the water was last in contact with the atmosphere, ΔC_{Diseq} represents air-sea disequilibrium and ΔC_{Bio} is the change in DIC due to biological activity (cf. Gruber et al. 1996; Sabine et al. 2002; Yamamoto-Kawai et al. 2013). Using the CO2sys program (Lewis and Wallace 1998), C_{EQ} can be estimated from salinity, temperature, TA and atmospheric CO_2 concentration (xCO_2) (converted to pCO_2 at 100 % humidity and standard atmospheric pressure). The sum of latter two terms on the right hand side of the Eq. (3) is calculated by subtracting estimated C_{EQ} from DIC observed in 2011/2012. The Tokyo Bay is shallow enough to assume that all waters were very recently in contact with atmosphere and thus we used $xCO_2 = 394$ ppm, the mean xCO_2 at Mauna Loa for our observation period from April 2011 to January 2012 (NOAA/PMEL), for the calculation of C_{EQ} for our observation period. We should note that xCO_2 in the air over the Tokyo Bay can be different from that observed at Mauna Loa. A comparison of xCO_2 data between monthly observations from 2007 to 2010 in Tokyo Bay (Kubo, unpublished data) and monthly mean at Mouna Loa was from −18 to +35 ppm (Tokyo Bay–Mauna Loa). As for annual mean, the difference was only ~10 ppm. Therefore, we decided to use observations at Mauna Loa in 2011/2012, rather than observations in Tokyo Bay in different years. Assuming that salinity, temperature, and TA remains the same over time, we can estimate C_{EQ} of the bay water under the atmosphere with a given xCO_2. Then, with an assumption that ($\Delta C_{Diseq} + \Delta C_{Bio}$) also remains the same over time, DIC of the water under each xCO_2 can be estimated. Then, *Ω*ar was calculated from this estimated DIC and observed temperature, salinity and TA (Fig. 7).

It is shown that anthropogenic CO_2 has already decreased *Ω*ar of Tokyo Bay waters by about 0.6 from values in the preindustrial era with xCO_2 of 280 ppm. As discussed in the previous section, eutrophication should have also altered *Ω*ar in summer, to counteract and to aggravate the effect of ocean acidification at the surface and the bottom, respectively. Therefore, for summer seasons, preindustrial *Ω*ar could be lower for surface waters and higher for bottom waters than that presented in Fig. 7. If conditions other than xCO_2 remain the same as today in the future, *Ω*ar in both surface and bottom waters will be further reduced by 1.0–1.6 by the end of this century when xCO_2 reaches 1000 ppm with a high CO_2 emission scenario RCP8.5 in IPCC AR5 (Riahi et al. 2011). Surface waters in Tokyo Bay will remain oversaturated until the end of this century, but will be undersaturated at the beginning of the next century. Bottom water in the innermost bay region (F3) will experience seasonal undersaturation with respect

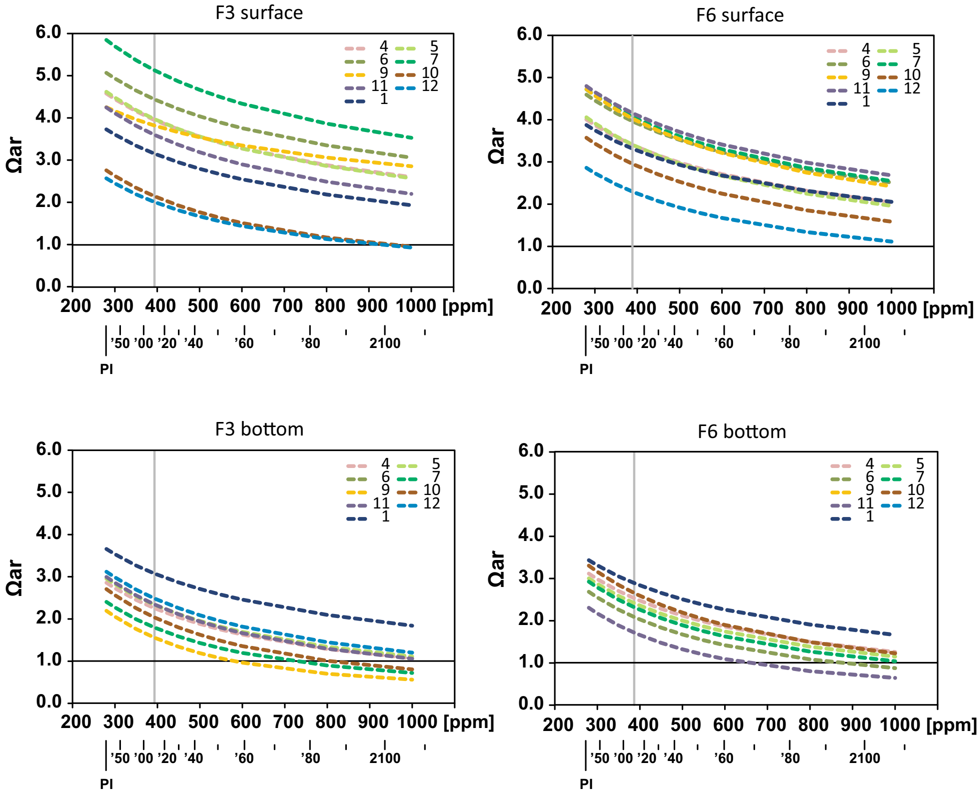

Fig. 7 Evolution of *Ω*ar in surface and bottom waters in each month with increasing xCO_2. Years for corresponding xCO_2 are also shown in *x*-axis [based on representative concentration pathway (RCP)8.5 scenario; Meinshausen et al. 2011]. PI represents preindustrial period. A *grey line* in each figure indicates conditions in 2011–2112. A *black line* shows the level when seawater is in equilibrium with aragonite (*Ω*ar = 1)

to aragonite when xCO_2 reaches to 600 ppm. For the middle part of the bay (F6), bottom water becomes seasonally undersaturated when xCO_2 exceeds 650 ppm. xCO_2 of 600 and 650 ppm can be reached as early as the years 2060 and 2070, respectively, in the RCP8.5 scenario. The year to reach undersaturation is about 50 years earlier in the bay than that expected in offshore waters. For instance, near surface waters south or southeast of Tokyo Bay are estimated to have *Ω*ar around 1.5 even when xCO_2 reaches 1000 ppm at the end of this century, and may reach undersaturation in the 2120s (Yara et al. 2012; Ishii et al. 2011). The present study suggests that this difference is caused by the large effect of remineralization on *Ω*ar in bottom water in the bay. Accordingly, an enhancement or reduction of eutrophication should alter the timing when waters are corrosive to aragonite. As a case study, we have estimated *Ω*ar in bottom water at F3 in September with doubled and without DIC change due to eutrophication (Fig. 8). For this calculation, 46 µmol kg^{-1} of DIC was assumed to represent the current eutrophication from the discussion above,

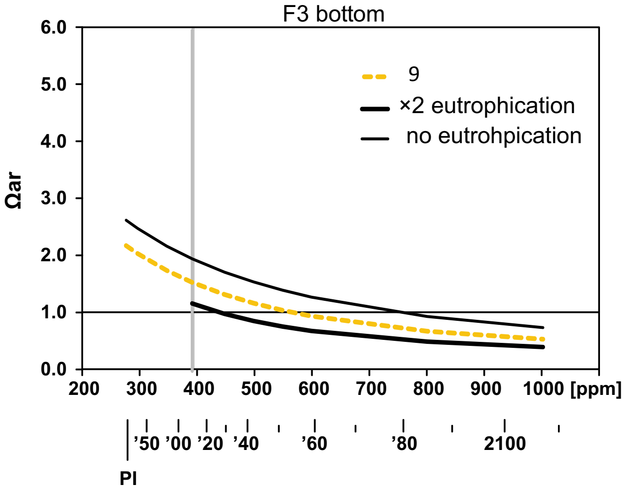

Fig. 8 Evolution of *Ω*ar in bottom water at F3 in September with increasing xCO_2 for cases with present eutrophication (*orange dashed line*), with doubled eutrophication (*thick black line*) and without eutrophication (*thin black line*). The doubled eutrophication case is applied only to the future prediction

and was added (doubled eutrophication) or removed (no eutrophication) in the ΔC_{Bio} term. Figure 8 indicates that enhancement or reduction of eutrophication could change the year to reach aragonite undersaturation by a few decades. It is also indicated in Fig. 8 that even if we could remove eutrophication from the bay, anthropogenic CO_2 will bring these water to be corrosive to aragonite by the year 2080.

5 Summary and conclusion

Monthly observation at two stations in Tokyo Bay revealed that Ωar in the bay varies much more than in offshore waters (cf. Ishii et al. 2011; Wakita et al. 2013). The very high primary production and resulting remineralization of organic matter in this shallow and eutrophicated bay are the major causes of such large variations. It should be declared that our observations are only from 1 year and may not represent typical conditions of Tokyo Bay. However, because this study is the first to report Ωar in Tokyo Bay, we believe that it is worth trying to quantify effects of different processes on Ωar, and to provide information on future changes in Ωar. Based on this standpoint, we estimated that eutrophication since the late 1950s has increased and decreased Ωar of summer bay waters by 0.45 or more at the surface and the bottom, respectively, in the innermost bay region. In the middle bay region, the effect of eutrophication on Ωar is smaller. Ocean acidification, on the other hand, affects Ωar at any depths and anywhere in this shallow bay. It is estimated that anthropogenic CO_2 has already decreased Ωar of the bay water by 0.6 since the preindustrial period. Therefore, in terms of Ωar, ocean acidification has a higher impact than eutrophication. If emission of CO_2 is continued at a high level as predicted by the IPCC RCP8.5 scenario (Riahi et al. 2011), bottom waters in the innermost region of the bay will reach seasonal undersaturation with respect to aragonite as early as 2060. In the middle bay region with less effect of eutrophication, bottom waters will experience seasonal undersaturation by 2070. Even when the effect of eutrophication is removed, bottom water in the innermost bay region will reach undersaturation by 2080. Eutrophication and hypoxia in Tokyo Bay are great concerns, and many efforts have been made to remedy these problems. Our results suggest that ocean acidification should also be considered as a serious problem as it can make the bay water to be corrosive to aragonite within 45 years at earliest, and many benthic organisms, including commercially important bivalves, rely on a planktonic early life stages with shells composed of aragonite. Furthermore, even when Ωar is still higher than 1.0, a decrease in Ωar can cause enhanced mortality and delayed development of larval bivalves because of the presence of amorphous calcium carbonate in their shells, which is substantially more soluble than aragonite (Talmage and Gobler 2009). Ocean acidification also affects other organisms. For example, increased CO_2 damages tissue of internal organs in some larval fish (Frommel et al. 2011) while it enhances growth of fleshy seaweeds (Kroeker et al. 2013 and references there in). An effect of ocean acidification on one species can progress to other species or to the ecosystem through the food web or by altering competitive balance between species (Kroeker et al. 2012). It is also pointed out that the concurrent effects of acidification and hypoxia are more severe than would be predicted by either individual stressor, and that even organisms insensitive to acidification alone could be negatively affected by acidification when concurrently exposed to hypoxic conditions (Gobler et al. 2014). Therefore, progress of ocean acidification could give an additional stress to the ecosystem of the Tokyo Bay, which is now suffering from eutrophication and hypoxia. Definitely we need more observations of Ω in Tokyo Bay to evaluate our estimations presented here. Also, observations in other coastal regions of Japan, together with investigations into responses of local ecosystems to ocean acidification are necessary in order to assess the impact of this ongoing global problem on local fisheries and marine ecosystem services in Japan.

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