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Seasonal variations in concentration and composition of dissolved organic carbon in Tokyo Bay

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Abstract

Concentrations of recalcitrant and bioavailable dissolved organic carbon (DOC) and their seasonal variations were investigated at three stations in Tokyo Bay, Japan, and in two freshwater sources flowing into the bay to evaluate the significance of DOC degradation for the carbon budget in coastal waters and carbon export to the open ocean. Recalcitrant DOC (RDOC) was differentiated from bioavailable DOC (BDOC) as a remnant of DOC after 150 days of bottle incubation. On average, RDOC accounted for 78 % of the total DOC in Shibaura sewage treatment plant (STP) effluent, 67 % in the upper Arakawa River water, 66 % in the lower Arakawa River water, and 78 % in surface bay water. RDOC concentrations were higher than BDOC at all stations. In freshwater environments, RDOC concentrations were almost constant throughout the year. In the bay, RDOC was higher during spring and summer than during autumn and winter. The relative abundance of RDOC in the bay derived from phytoplankton, terrestrial, and open oceanic waters was estimated to be 9 %, 33 %, and 58 %, respectively, by multiple regression analysis of RDOC, salinity, and chl *a*. In addition, comparison with previous data from 1972 revealed that concentrations of RDOC and BDOC have decreased by 33 % and 74 % at freshwater sites and 39 % and 76 % at Tokyo Bay, while the ratio of RDOC to DOC has increased. The change in DOC concentration and composition was probably due to increased amounts of sewage treatment plant effluent entering the system. Tokyo Bay exported DOC, mostly RDOC, to the open ocean because of remineralization of BDOC.

1 Introduction

Dissolved organic carbon (DOC) is the largest organic carbon reservoir in the ocean. The DOC pool in the ocean contains 662 Pg of carbon, which is roughly equivalent to that stored in the atmosphere in the form of carbon dioxide (Hansell et al., 2009). In open oceans, DOC production is ultimately constrained by primary production (e.g.,

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Carlson, 2002). Conversely, DOC in coastal waters consists of a diverse mixture of carbon formed by primary production and of terrestrial origin. Riverine DOC export to the open ocean has been estimated to range from 0.21 to 0.25 Pg C yr^{-1} (Meybeck, 1993; Ludwig et al., 1996; Hedges et al., 1997; Cauwet, 2002). Coastal waters are typically considered passive conduits in regional and global carbon budgets (Cole et al., 2007; Aufdenkampe et al., 2011; Regnier et al., 2013), and most studies have attempted to estimate DOC flux from land to the open ocean without considering loss or gain of DOC in coastal waters. However, degradation of terrestrial DOC and biological production of DOC in coastal regions can significantly modify the flux of DOC to the open ocean. Recently, Dai et al. (2012) reported that riverine DOC export to the open ocean would be reduced to 0.17 Pg C yr^{-1} if 10 % was degraded in coastal waters. However, their assumption of 10 % was based on the results of only a few bottle incubation experiments (Amon and Benner, 1996; Raymond and Bauer, 2000; Moran et al., 1999). Therefore, to better understand DOC export to the open ocean, experimental data describing DOC composition, preferably from different environmental locations and in different seasons, are needed.

In this study, we observed seasonal variations in the concentration and composition of DOC in Tokyo Bay, Japan. The bay is semi-enclosed, with an area of about 922 km^2 and a mean water depth of 19 m. The residence time of water in the bay is estimated to be about 50 days (Takada et al., 1992). The bay is located in central Japan and surrounded by metropolitan areas, with a total human population of about 26 million. Tokyo Bay represents typical highly urbanized coastal waters, which are rapidly expanding worldwide (Nellemann et al., 2008). We also compared our results with those obtained by Ogura (1975), who carried out an investigation of Tokyo Bay in the 1970s and found that DOC in coastal waters could be divided into bioavailable DOC (BDOC) and recalcitrant DOC (RDOC). Owing to his investigation, BDOC and RDOC data from 1972 are available for Tokyo Bay.

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2 Materials and methods

Freshwater samples were collected two and eight times from the upper and lower Arakawa River, respectively, and five times from effluent of Shibaura sewage treatment plant (STP; Fig. 1) between December 2011 and October 2013. Water samples were collected using a bucket, transferred into HCl acid-washed 1 L polyethylene bottles and kept in the dark until being processed in the laboratory. The bucket and sample bottles were rinsed three times with sample water before being filled. Surface seawater of Tokyo Bay was 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 from January 2012 to December 2012 monthly at three stations (Fig. 1). Both freshwater and seawater samples were filtered through GF/F filters that had been precombusted at 450 °C for 3 h, then transferred to 500 mL amber glass bottles and stored at room temperature (20 °C) in total darkness until analysis. The degradation experiments were conducted based on a total of seven incubations (0, 5, 10, 20, 50, 100, and 150 days) per each field sampling event. After incubation, samples were dispensed into glass vials that had been pre-washed with HCl. Freshwater samples were preserved with 6 mol L^{-1} HCl at a concentration corresponding to 1 % of the volume, then stored in a refrigerator (5 °C). Tokyo Bay samples were frozen (−25 °C) without adding HCl. DOC samples were measured at least in triplicate with a TOC analyzer (TOC-V_{CSH}, Shimadzu, Kyoto, Japan).

RDOC is defined as the concentration of DOC remaining at 150 days and BDOC is obtained by subtracting the RDOC from the initial DOC (Lønborg et al., 2009). The degradation rate of DOC is described by a first-order exponential decay model taking a RDOC pool into account:

$$\mathrm{DOC}(t) = \mathrm{BDOC} \cdot \exp(-k \cdot t) + \mathrm{RDOC} \quad (1)$$

where DOC(t) is the amount of DOC remaining at time t (day), k is the degradation rate constant (day^{-1}), and BDOC and RDOC are the concentrations of BDOC and

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RDOC (μmol L^{-1}). Using BDOC and RDOC concentrations obtained from 150 days of incubation, k can be estimated by fitting the observed DOC(t) values to the exponential model using Matlab 2012a. For comparison with the results reported by Lønborg and Álvarez-Salgado (2012), we used the following equation to normalize the degradation rate to the rate at 15 °C,

$$k(15\,^{\circ}\mathrm{C}) = k(T)\cdot(Q_{10})^{\frac{T-15}{10}} \quad (2)$$

where k(15 °C) and $k(T)$ are the degradation rate constants at 15 °C and T °C (20 °C for our experiment). Q_{10} is the temperature coefficient. In this study, we used a value of 2.2 based on Lønborg and Álvarez-Salgado (2012).

Temperature and salinity were measured in the field using a YSI EC 300 (YSI/Nanotech Inc., Yellow Springs, OH, USA) at freshwater sites and using a CTD (Falmouth Scientific Inc., Bourne, MA, USA) for sites in the bay. Water samples for chlorophyll *a* (chl *a*) measurement were filtered through precombusted (450 °C, 3 h) Whatmann GF/F filters. After filtration, chlorophyllous pigments were extracted using N,N-dimethylformamide (DMF), and concentrations of chl *a* were determined by the fluorometric method (Suzuki and Ishimaru, 1990) using a fluorometer (TD-700, Turner Designs, Sunnyvale, CA, USA). Samples for particulate organic carbon (POC) were filtered through precombusted (450 °C, 3 h) Whatmann GF/F filters, after which the filters were stored at −80 °C until analysis. The samples for POC analyses were dried at 60 °C and acidified with vapor at 12 mol L^{-1} HCl to remove carbonate before analysis. POC were measured using a Hydra 20–20 isotope ratio mass spectrometer (IRMS) coupled to an ANCA-GSL elemental analyzer (SerCon Ltd., Crewe, UK).

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3 Results and discussion

3.1 Composition and sources of freshwater DOC flowing into Tokyo Bay

The lowest chl *a*, DOC, and POC were observed at the upper Arakawa River station, which is considered to be pristine (Table 1). The average concentration of DOC was 38 µmol L^{-1} at the upper Arakawa River station. The results of the DOC degradation experiments at the upper Arakawa River station are shown in Fig. 2a. Rapid degradation of the labile pool was observed within the first 20 days of incubation. Additionally, the mean concentration of RDOC was 25 µmol L^{-1}, and its mean contribution to total DOC was 67 %. At the upper Arakawa River station, the concentrations of DOC and RDOC were very low.

At Shibaura STP, relatively high temperatures and DOC values were observed, while seasonal variations in chl *a* and POC were relatively small (Table 1). The average concentration of DOC was 359 µmol L^{-1}, which was about nine times higher than the value at the upper Arakawa River station. The annual mean concentration of RDOC was 278 µmol L^{-1}, while the mean contribution of RDOC to total DOC was 78 % (Fig. 2b). The RDOC concentrations did not vary greatly between observation months, and a good linear relationship between BDOC and DOC was observed (R^2 = 0.976, $p < 0.001$, slope = 1.16), indicating that the seasonal variation of DOC was mostly due to variations in the bioavailable fraction. Typically, STP effluents have high organic carbon concentrations and a large bioavailable fraction (Servais et al., 1995; Servais et al., 1999; Kaushal and Belt, 2012). In contrast, effluent of Shibaura STP showed a high proportion of RDOC (67–93 %). These findings suggest that most of the BDOC were degraded before being discharged, probably because STPs in Japan conduct secondary treatment.

A relatively high chl *a* and POC were observed at the lower Arakawa River station (Table 1). The maximum concentrations of chl *a*, DOC, and POC were observed in spring. The average concentration of DOC was 235 µmol L^{-1}, while the annual mean concentration of RDOC was 149 µmol L^{-1} and the mean contribution of RDOC to to-

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tal DOC was 66 % (Fig. 2c). The concentrations of DOC were more than six times those at the upper Arakawa River station, probably because of inputs of DOC from STPs between observation sites. The RDOC concentrations did not show large differences between observation months, and a good linear relationship between BDOC and DOC was observed ($R^2 = 0.942$, $p < 0.001$, slope = 1.12), indicating that the seasonal variations of DOC at the lower Arakawa River station were due to variations in the bioavailable fraction.

Freshwater flowing into Tokyo Bay primarily consists of a mixture of river water and STP effluent. The total discharge ratio of river water to STP effluent in the bay is about 1:1 (Japan Sewage Works Association, 2010; Bureau of Sewerage, 2013). Assuming that the ratio of river water to STP effluent is 1 : 1 and that data collected at the upper Arakawa River station and Shibaura STP represent these two sources, the average concentrations of RDOC and BDOC in freshwater would be 152 and 47 µmol L^{-1}, respectively. These values are comparable with those observed at the lower Arakawa River station (149, 86 µmol L^{-1}, respectively). Arakawa River, which is the largest river flowing into the bay, accounts for about 30 % of the freshwater discharge (Nihei et al., 2007a). Most rivers flowing into the bay have similar water quality because of similar land use of the drainage basin (Nihei et al., 2007b); accordingly, we can reasonably assume that observed RDOC and BDOC concentrations at the lower Arakawa River station represent concentrations of total river water flowing into Tokyo Bay.

Table 2 summarizes the first-order decay constants obtained by fitting the exponential degradation of DOC with time. The annual average degradation constant normalized to 15 °C at the lower Arakawa River station was 0.031, which was lower than that observed in other coastal waters (0.066; Lønborg and Álvarez-Salgado, 2012). These findings indicate that freshwater DOC flowing into Tokyo Bay is more recalcitrant than in other coastal systems.

In 1972, the average concentrations of DOC and RDOC were 561 and 224 (40 % of the total DOC) µmol L^{-1} in the freshwater environment of the lower Tamagawa River, which flows into Tokyo Bay (Ogura, 1975). The present DOC, RDOC, and BDOC con-

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centrations at the lower Arakawa River station are lower than those reported by Ogura (1975). During our calculations, we took into account the fact that the amount of freshwater discharge into the bay has increased by 24 % (Okada et al., 2007), the amount of RDOC and BDOC flowing into the bay would have decreased by 17 % and 68 %, respectively. Ogura (1975) also estimated a degradation constant of 0.087, which is much higher than that observed in the present study (Table 2). The proportion of treated wastewater to the total freshwater inflow to the bay increased from 11 % to 28 % from 1970 to 2000 (National Institute for Land and Infrastructure Management, 2004). Overall, these results indicate that the quantity of DOC flowing into the bay has decreased, and the quality of DOC has become more recalcitrant because of an increase of sewage treatment plant effluent.

3.2 Tokyo Bay

The seasonal variations of temperature, salinity, chl *a*, and POC at the three stations in Tokyo Bay are presented in Fig. 3. High temperature, chl *a*, and POC were observed during spring and summer, while low values were observed during autumn and winter. Salinity was higher during autumn and winter than spring and summer. Salinity showed the opposite seasonal pattern of temperature, chl *a*, and POC. DOC concentrations ranged from 81 to 182, 76 to 153, and 60 to 108 $\mu mol\,L^{-1}$ at stations F3, F6, and 06 stations, respectively (Fig. 4), with higher values being observed in spring and summer. DOC occurred in the order of F3 > F6 > 06. The concentrations of DOC at station F3 decreased from 287 $\mu mol\,L^{-1}$ in 1972 (Ogura, 1975) to 124 $\mu mol\,L^{-1}$ in 2012, most likely because of a decrease of DOC discharge from rivers and a decrease in primary production in the bay (Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Bouman et al., 2010).

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3.2.1 Composition of DOC

The results of DOC degradation experiments at Tokyo Bay are shown in Fig. 4. Rapid degradation of the labile pool occurred within the first 20 days of incubation, indicating that BDOC were remineralized during the residence time of the bay water. The seasonal variations in DOC, RDOC, and BDOC concentrations at the three stations in Tokyo Bay are shown in Fig. 5. RDOC ranged between 70 and 120 µmol L^{-1} at F3, 58 and 130 µmol L^{-1} at F6 and between 48 and 80 µmol L^{-1} at 06. The mean contributions of RDOC to DOC were 81 % at F3, 77 % at F6 and 72 % at 06. Both RDOC and BDOC showed similar seasonal variation to DOC, with high variations being observed in spring and summer and low in autumn and winter. The contribution of RDOC to DOC was higher than that of BDOC at all stations for the entire observation period. RDOC in Tokyo Bay was negatively correlated with salinity and positively correlated with chl *a* (Table 3).

When the seasonal change of RDOC is due to fluctuations in allochthonous input, a significant negative relationship between RDOC and salinity would be expected. Alternatively, when RDOC is produced directly by phytoplankton, a positive relationship between RDOC and chl *a* is expected (Kragh and Søndergaard, 2009). However, previous studies in coastal areas revealed no significant correlations between RDOC and salinity or chl *a* (Lønborg and Søndergaard, 2009; Lønborg et al., 2009; Lønborg et al., 2010). RDOC in Tokyo Bay was well correlated with salinity and chl *a*, indicating that allochthonous input and phytoplankton are major sources of RDOC in the bay.

Table 4 summarizes the degradation constants of DOC for the surface bay waters. The annual average degradation constants normalized to 15 °C at F3, F6, and 06 were 0.128, 0.094, and 0.083, respectively. Most values of degradation constants for the bay water were higher than those of freshwater (Tables 2 and 4). The half-lives of BDOC were calculated from the degradation constant. The annual average half-lives of BDOC at F3, F6, and 06 were 5.9, 8.5, and 10.0 days, respectively. BDOC produced by phytoplankton in the bay water might have led to faster degradation rates because

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the half-lives of BDOC were about five times faster than the residence time of the bay water. The degradation constants were higher than those observed in other coastal waters (0.066; Lønborg and Álvarez-Salgado, 2012).

3.2.2 RDOC sources

To estimate the sources of RDOC in Tokyo Bay, multiple linear regression analysis with salinity and chl *a* as independent variables was applied to all RDOC data observed at three stations in Tokyo Bay using the method described by Ogawa and Ogura (1990), which gave the following multiple regression equation:

$$[\mathrm{RDOC}\,(\mu\mathrm{mol\,L^{-1}})] = 259 - 5.96 \times [\mathrm{Sal}] + 0.597 \times [\mathrm{Chl}\ a\,(\mu\mathrm{g\,L^{-1}})] \quad (3)$$

$$\left(r^2 = 0.79, \quad P < 0.001, \quad n = 35\right)$$

where [RDOC] is the RDOC concentration, [Sal] is salinity, and [Chl *a*] is the chl *a* concentration of each sample. Based on the results of multiple regression analysis, we estimated the contributions of RDOC from different sources (RDOC from phytoplankton, RDOC from the open ocean, and terrestrial RDOC).

The equation describing RDOC derived from phytoplankton [$\mathrm{RDOC_{phyto}}$] is as follows:

$$[\mathrm{RDOC_{phyto}}] = 0.597 \times [\mathrm{Chl}\ a] \quad (4)$$

The concentrations of RDOC in the open ocean [$\mathrm{RDOC_{ocean}}$] can be estimated by assuming that chl *a* in the open ocean is $0\,\mu\mathrm{g\,L^{-1}}$ using the following equation:

$$[\mathrm{RDOC_{ocean}}] = 259 - 5.96 \times [\mathrm{Sal_{ocean}}] \quad (5)$$

where [$\mathrm{Sal_{ocean}}$] is the salinity of the open ocean water flowing into the bay. When [$\mathrm{Sal_{ocean}}$] = 35.0 (Ogawa and Ogura, 1990),

$$[\mathrm{RDOC_{ocean}}] = 50.4\,(\mu\mathrm{mol\,L^{-1}}) \quad (6)$$

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Here, concentrations of RDOC in the bay that originated from the open ocean [$RDOC_{ocean\ origin}$] can be estimated from:

$$\left[RDOC_{ocean\ origin}\right] = 50.4 \times [Sal]/35 \quad (7)$$

The concentration of RDOC derived from terrestrial origin [$RDOC_{terr}$] is estimated as:

$$\left[RDOC_{terr}\right] = (259 - 5.96 \times [Sal]) - 50.4 \times [Sal]/35 \quad (8)$$

The [$RDOC_{ocean}$] of 50.4 (standard error = 73) $\mu mol\,L^{-1}$ was comparable to the annual average RDOC concentration of the bottom water at 06 (see Table S1 in the auxiliary material). The terrestrial end-member of RDOC was 259 (standard error = 39) $\mu mol\,L^{-1}$. The annual mean concentration of RDOC at the lower Arakawa River station (149 $\mu mol\,L^{-1}$) was within three times the standard error of the terrestrial end-member (99 % confidence interval). The seasonal variations in RDOC derived from phytoplankton, terrestrial, and open oceanic waters at the three stations are presented in Fig. 6. The results show that [$RDOC_{ocean\ origin}$] is the major source of RDOC in Tokyo Bay. At station F3, which is located close to land, [$RDOC_{terr}$] was comparable to [$RDOC_{ocean\ origin}$]. Both $RDOC_{terr}$ and $RDOC_{phyto}$ were found to be higher during spring and summer than autumn and winter. The relative abundance of RDOC derived from phytoplankton, terrestrial, and open oceanic waters was estimated to be 9 %, 33 %, and 58 %, respectively. The concentration of terrestrial RDOC was higher than that of RDOC derived from phytoplankton at all stations throughout the year, even at the bay mouth. Accordingly, Tokyo Bay exported DOC, mostly terrestrial RDOC, to the open ocean because of the high concentration of terrestrial RDOC and remineralization of BDOC.

3.2.3 Change of DOC in four decades

The concentrations of RDOC and BDOC observed in this study (100 $\mu mol\,L^{-1}$ and 24 $\mu mol\,L^{-1}$, respectively) were lower than those estimated by Ogura (1975) in 1972

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(165 µmol L^{-1} and 100 µmol L^{-1}, respectively). The contribution of RDOC to total DOC in this study (80.6 %) is higher than the value in 1972 (57.5 %; Ogura, 1975). The concentrations of RDOC and BDOC in Tokyo Bay have decreased because of a decrease in DOC load from the land, especially for BDOC. As a result, the composition of DOC has become more recalcitrant. In addition, decreasing nutrient loads into the bay have caused decreasing primary production in the bay (Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Bouman et al., 2010). Therefore, autochthonous DOC should also have decreased.

4 Summary

A rapid degradation of the labile pool was observed at freshwater sites and Tokyo Bay within the first 20 days of incubation. BDOC are remineralized during the residence time of the bay water. The contribution of RDOC to DOC was higher than that of BDOC at all stations for the entire observation period, and accounted for 77 % of the total. In addition, RDOC sources ($RDOC_{phyto}$, $RDOC_{ocean\ origin}$, and $RDOC_{terr}$) could be estimated by multiple regression analysis between RDOC, salinity, and chl *a*. The concentration of terrestrial RDOC was higher than that of RDOC derived from phytoplankton at all stations throughout the year. Accordingly, Tokyo Bay exported DOC, mostly terrestrial RDOC, to the open ocean because of the high concentration of terrestrial RDOC and faster half-lives of BDOC relative to the residence time of the bay water. The concentrations of RDOC and BDOC have decreased in the last 40 years at freshwater sites and Tokyo Bay, during which time the composition of DOC has become more recalcitrant because of sewage improvement. Since organic carbon degradation occurs at STPs before being discharged, DOC flowing into the bay has decreased, especially the BDOC.

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Table 1. Temperature (°C), salinity, chl *a* ($\mu g\,L^{-1}$) concentrations, DOC ($\mu mol\,L^{-1}$) concentrations, and POC ($\mu mol\,L^{-1}$) concentrations at the upper Arakawa River (upper AR), lower Arakawa River (lower AR), and Shibaura STP stations.

Station	Date	Temp.	Sal.	chl *a*	DOC	POC
upper AR	Apr 2013	10.9	0.0	0.2	33	13
upper AR	Oct 2013	17.4	0.0	0.2	42	7
lower AR	Dec 2011	12.1	0.6	2.0	247	178
lower AR	Jan 2012	7.0	0.2	7.6	290	145
lower AR	Feb 2012	7.2	0.2	49.3	355	313
lower AR	May 2012	23.6	0.2	33.9	205	168
lower AR	Jul 2012	24.2	0.2	1.5	213	84
lower AR	Aug 2012	23.9	0.0	1.2	185	59
lower AR	Nov 2012	17.4	0.2	2.0	236	63
lower AR	Dec 2012	11.8	0.2	10.7	155	76
Shibaura STP	May 2012	27.6	2.9	3.7	430	71
Shibaura STP	Jul 2012	27.9	1.9	0.5	366	38
Shibaura STP	Aug 2012	27.7	1.9	2.2	292	48
Shibaura STP	Nov 2012	20.5	4.0	0.3	341	76
Shibaura STP	Dec 2012	17.2	0.4	1.2	366	83

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Table 2. Degradation constants for DOC (k_{20}) and normalized degradation constants at 15 °C (k_{15}) at the upper Arakawa River (upper AR), lower Arakawa River (lower AR), and Shibaura STP stations. R^2 indicates coefficient of determination.

Station	Date	k_{20} (day^{-1})	R^2	k_{15} (day^{-1})
upper AR	Apr 2013	0.072	0.99	0.049
upper AR	Oct 2013	0.053	0.98	0.036
lower AR	Dec 2011	0.038	0.97	0.025
lower AR	Jan 2012	0.040	0.99	0.027
lower AR	Feb 2012	0.038	0.96	0.026
lower AR	May 2012	0.028	0.99	0.019
lower AR	Jul 2012	0.025	0.99	0.017
lower AR	Aug 2012	0.045	0.99	0.031
lower AR	Nov 2012	0.052	0.97	0.035
lower AR	Dec 2012	0.110	0.97	0.071
Shibaura STP	May 2012	0.019	0.99	0.013
Shibaura STP	Jul 2012	0.021	0.99	0.014
Shibaura STP	Aug 2012	0.040	0.97	0.027
Shibaura STP	Nov 2012	0.062	0.99	0.042
Shibaura STP	Dec 2012	0.110	0.92	0.072

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Table 3. Correlation coefficients (R^2) of the significant ($p < 0.05$) linear regressions between DOC and hydrological data in Tokyo Bay (F3, F6, 06, and total data). n.s. indicates not significant.

Station	X	Sal.	chl *a*
F3	DOC	0.54	0.36
F3	RDOC	0.68	0.56
F3	BDOC	n.s.	n.s.
F6	DOC	0.74	0.64
F6	RDOC	0.64	0.59
F6	BDOC	0.37	0.31
06	DOC	0.81	0.51
06	RDOC	0.54	0.47
06	BDOC	0.29	n.s.
Total data	DOC	0.68	0.52
Total data	RDOC	0.73	0.62
Total data	BDOC	0.11	n.s.

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Table 4. Degradation constants for DOC (k_{20}) and normalized degradation constants at 15 °C (k_{15}) in F3, F6, and 06. R^2 indicates coefficient of determination.

Station	Date	k_{20} (day^{-1})	R^2	k_{15} (day^{-1})
F3	Jan 2012	0.236	0.98	0.159
F3	Feb 2012	0.162	0.99	0.110
F3	Mar 2012	0.093	0.97	0.063
F3	Apr 2012	0.120	0.99	0.081
F3	May 2012	0.203	0.99	0.137
F3	Jun 2012	0.286	0.99	0.193
F3	Jul 2012	0.127	0.97	0.086
F3	Aug 2012	0.109	0.99	0.074
F3	Sep 2012	0.153	0.99	0.103
F3	Oct 2012	0.301	0.98	0.203
F3	Nov 2012	0.269	0.87	0.182
F3	Dec 2012	0.221	0.97	0.149
F6	Jan 2012	0.150	0.98	0.101
F6	Feb 2012	0.095	0.99	0.064
F6	Mar 2012	0.100	0.99	0.067
F6	Apr 2012	0.151	0.98	0.102
F6	May 2012	0.115	0.98	0.077
F6	Jun 2012	0.209	0.99	0.141
F6	Jul 2012	0.083	0.99	0.056
F6	Aug 2012	0.050	0.97	0.033
F6	Sep 2012	0.120	0.95	0.081
F6	Oct 2012	0.188	0.84	0.127
F6	Nov 2012	0.243	0.91	0.164
F6	Dec 2012	0.170	0.92	0.115
06	Jan 2012	0.043	0.94	0.029
06	Feb 2012	0.223	0.97	0.150
06	Mar 2012	0.091	0.98	0.061
06	Apr 2012	0.133	0.99	0.089
06	May2012	0.134	0.99	0.090
06	Jul 2012	0.089	0.97	0.060
06	Aug 2012	0.085	0.97	0.057
06	Sep 2012	0.094	0.99	0.063
06	Oct 2012	0.085	0.99	0.057
06	Nov 2012	0.146	0.94	0.098
06	Dec 2012	0.240	0.87	0.162

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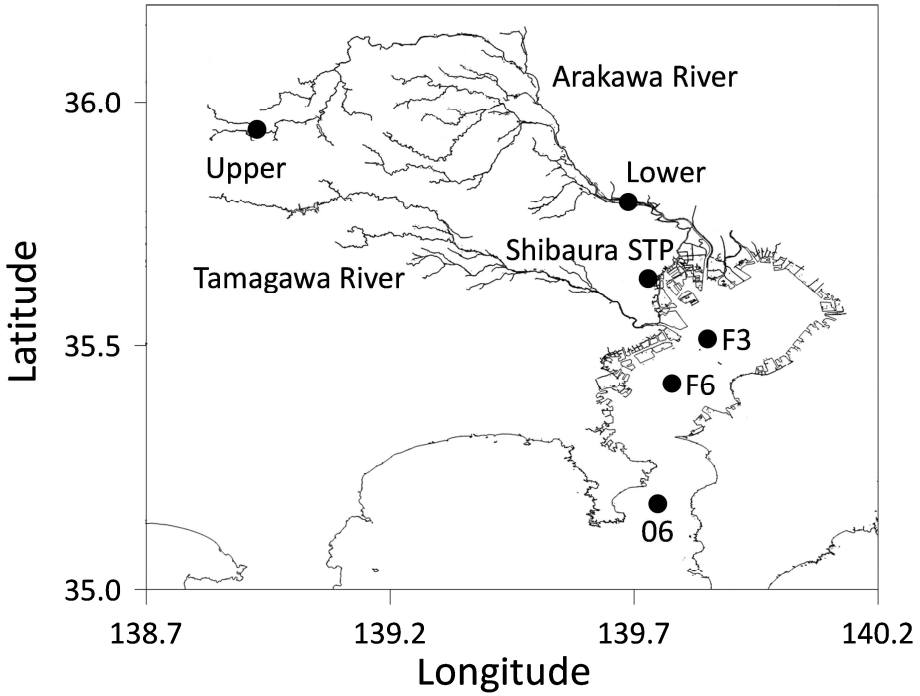

Figure 1. Map of Tokyo Bay. Locations of sampling sites are indicated by black circles.

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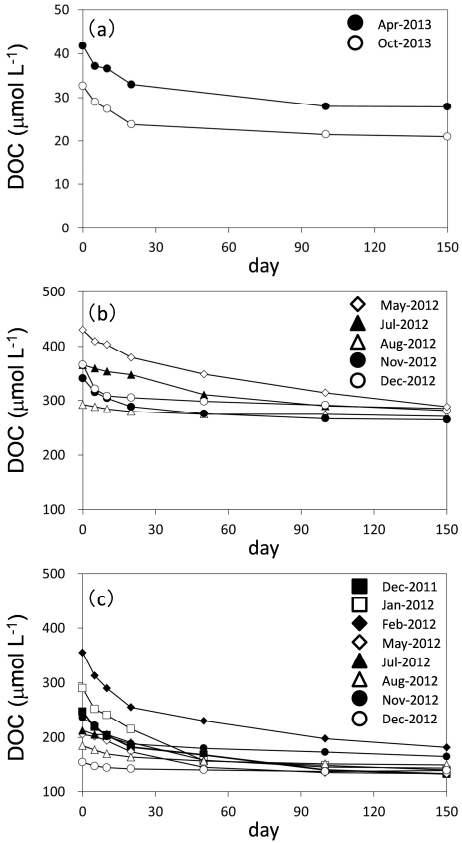

Figure 2. Changes in dissolved organic carbon (μmol L^{-1}) in surface water of **(a)** upper Arakawa River, **(b)** Shibaura STP, and **(c)** lower Arakawa River.

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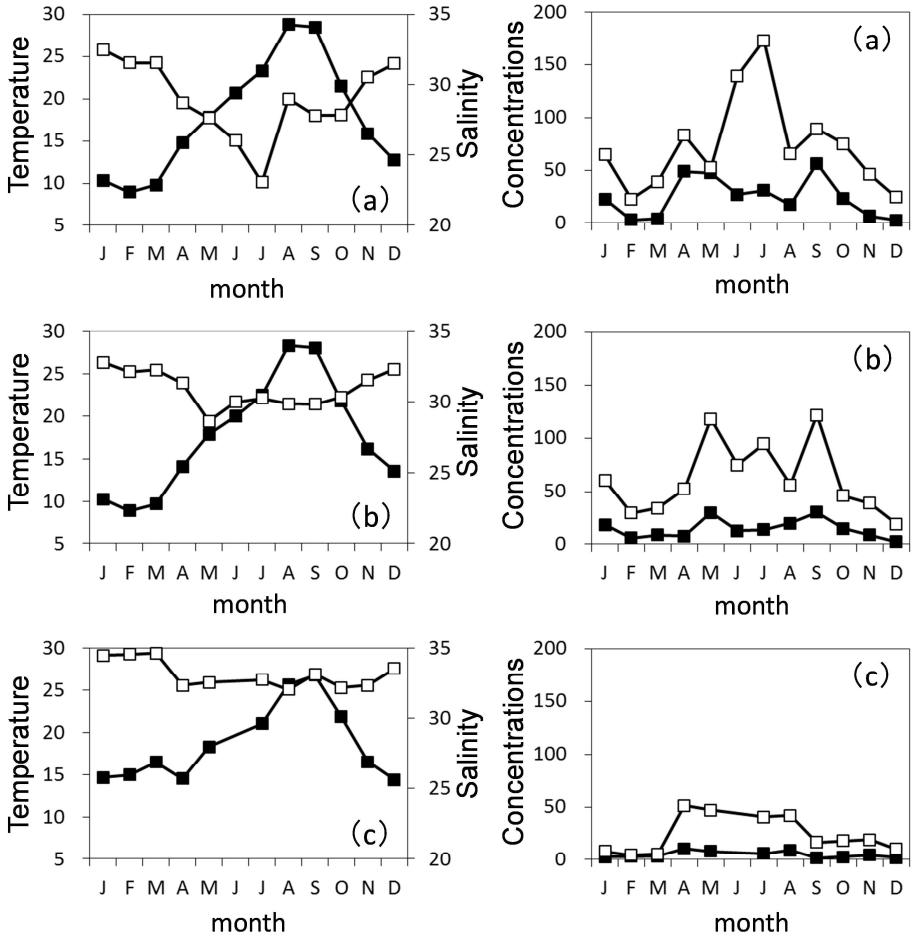

Figure 3. Seasonal variation of salinity (□), temperature (°C; ■), particulate organic carbon (μmol L^{-1}; □), and chlorophyll *a* (μg L^{-1}; ■) at station **(a)** F3, **(b)** F6, and **(c)** 06.

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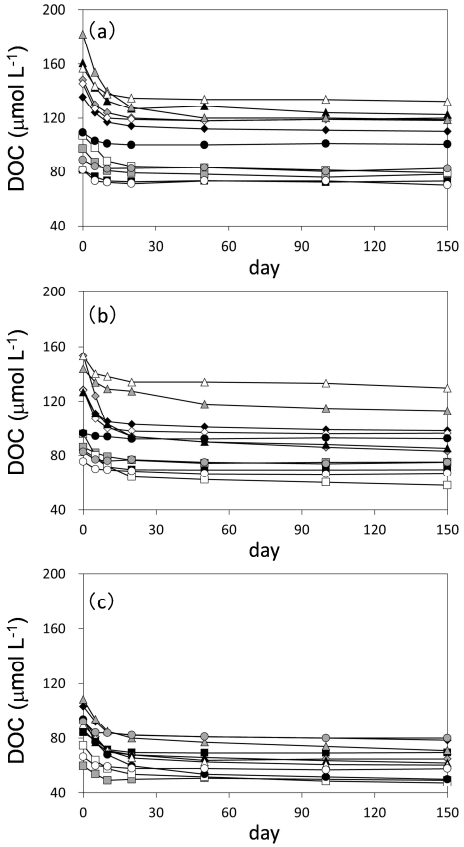

Figure 4. Changes in dissolved organic carbon (μmol L^{-1}) in surface water of **(a)** F3, **(b)** F6, and **(c)** 06. Black square: January 2011; gray square: February 2011; white square: March 2011; black diamond: April 2011; gray diamond: May 2011; white diamond: June 2011; black triangle: July 2011; gray triangle: August 2011; white triangle: September 2011; black circle: October 2011; gray circle: November 2011; white circle: December 2011.

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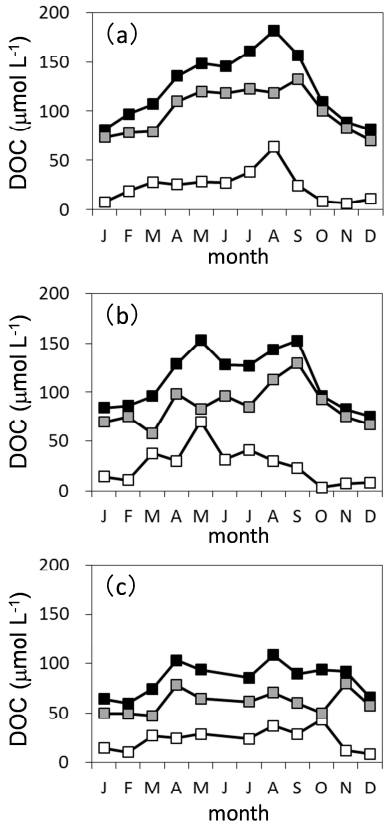

Figure 5. Seasonal variation of DOC (■), bioavailable DOC (BDOC; □), and Recalcitrant DOC (RDOC; ■) at station **(a)** F3, **(b)** F6, and **(c)** 06.

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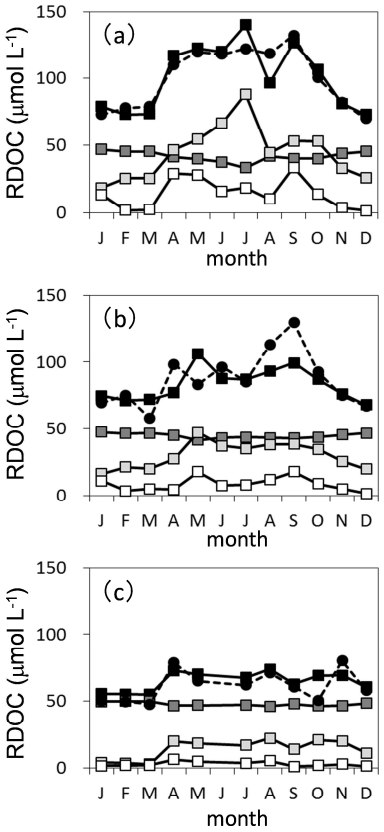

Figure 6. Seasonal variation of RDOC derived from phytoplankton (□), terrestrial (▒), and open oceanic waters (■). The black square (■) represents the total RDOC (μmol L^{-1}) estimated by multiple regression analysis. The black circle (•) with the dashed line represents the RDOC (μmol L^{-1}) determined by the incubation experiment.

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