# Seasonal variations in concentration and lability of dissolved organic carbon in Tokyo Bay

**A. Kubo[1], M. Yamamoto-Kawai[2], and J. Kanda[1]**

[1]Department of Ocean Sciences, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo, 108-8477, Japan.

[2]Center for Advanced Science and Technology, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo, 108-8477, Japan.

Correspondence to: A. Kubo (kuboatsushi0412@gmail.com)

**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. On average, recalcitrant DOC (RDOC), as a remnant of DOC after 150 days of bottle incubation, 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. Bioavailable DOC (BDOC) concentrations, defined as DOC minus RDOC, were lower than RDOC 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 autumn and winter because of freshwater input and biological production. The relative concentration of RDOC in the bay derived from phytoplankton, terrestrial, and open oceanic waters was estimated to be 9–10%, 21–32%, and 59–69%, respectively, based on 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 STP effluent entering the system. Tokyo Bay exported mostly RDOC to the open ocean because of remineralization of BDOC.

## 1. Introduction

The dissolved organic carbon (DOC) pool is the largest organic carbon reservoir in the ocean and 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., Carlson, 2002). Conversely, DOC in coastal waters consists of diverse mixtures of carbon with varying timescales of lability formed by primary production and materials of terrestrial origin. Riverine DOC export to the open ocean has been estimated to range from 0.21 to 0.25 PgC $yr^{-1}$ (Meybeck, 1993; Ludwig et al., 1996; Hedges et al., 1997; Cauwet, 2002) without considering loss or gain of DOC in coastal waters. 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). However, degradation of terrestrial DOC and biological production of DOC in coastal regions can significantly modify the flux of DOC to the open ocean. Dai et al. (2012) recently reported that riverine DOC export to the open ocean would be reduced to 0.17 PgC $yr^{-1}$ 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 lability, preferably from different environmental locations and different seasons, are needed.

In this study, we measured seasonal variations in the concentration and lability of DOC in Tokyo Bay, Japan, to evaluate the significance of DOC degradation to the carbon budget in coastal waters and carbon export to the open ocean. The bay is semi-enclosed, with an area of about 922 $km^2$ and a mean water depth of 19 m. The residence

57 time of water in the bay is estimated to be about 50 days (Takada et al., 1992). The bay
58 is located in central Japan and surrounded by metropolitan areas, with a total population
59 of about 26 million. Tokyo Bay represents typical highly urbanized coastal waters,
60 which are rapidly expanding worldwide (Nellemann et al., 2008). We also compared our
61 results with those obtained by Ogura (1975), who carried out an investigation of Tokyo
62 Bay in the 1970s and found that DOC in coastal waters could be divided into
63 bioavailable DOC (BDOC) and recalcitrant DOC (RDOC). Owing to his investigation,
64 BDOC and RDOC data from 1972 are available for Tokyo Bay.
65
66 **2. Materials and Methods**
67 Freshwater samples were collected two and eight times from the upper and lower
68 Arakawa River, respectively, and five times from effluent of the Shibaura sewage
69 treatment plant (STP; Figure 1) between December 2011 and October 2013. Water
70 samples were collected using a bucket, transferred into HCl acid-washed 1-L
71 polyethylene bottles and kept in the dark until being processed in the laboratory. The
72 bucket and sample bottles were rinsed three times with sample water before being filled.
73 Surface seawater of Tokyo Bay was collected in 8-L Niskin bottles mounted on a CTD
74 rosette on the R/V Seiyo-maru of Tokyo University of Marine Science and Technology
75 from January 2012 to December 2012 monthly at three stations (Figure 1). DOC and the
76 degradation experiment samples were filtered through GF/F filters (nominal pore size;
77 0.7 μm) that had been precombusted at 450°C for 3 h within 2 h of sample collection.
78 We assumed that GF/F filters allow the passage of a significant fraction of free-living
79 bacteria into DOC samples (e.g. Bauer and Bianchi, 2011); therefore, we did not add the
80 microbial community. Degradation experiment samples were then transferred to 500-

81 mL amber glass bottles and stored at room temperature (20°C) in total darkness until
82 analysis. The degradation experiments were conducted based on a total of seven
83 incubations (0, 5, 10, 20, 50, 100, and 150 days) per field sampling event. After
84 incubation, samples were dispensed into glass vials that had been pre-washed with HCl.
85 Freshwater samples were preserved with 6 mol $L^{-1}$ HCl at a concentration
86 corresponding to 1% of the volume, then stored in a refrigerator (5°C). Tokyo Bay
87 samples were frozen (–25°C) without adding HCl. DOC samples were measured at least
88 in triplicate with a TOC analyzer (TOC-$V_{CSH}$, Shimadzu, Kyoto, Japan). Potassium
89 hydrogen phthalate (Wako Pure Industries, Osaka, Japan) was used as a standard for
90 measurement of DOC.
91 Nutrient concentrations in freshwater and Tokyo Bay sites were high throughout the
92 year (Table S1 and S2). During summer, the phosphorus concentration generally
93 decreased and the nitrogen/phosphorus ratio was higher than the Redfield ratio of 16
94 (Redfield et al., 1963), suggesting that phosphorus acts as a limiting factor of primary
95 production at the bay. We did not add nutrients for the degradation experiment because
96 we assumed nutrients were not limiting the microbial growth. A degradation experiment
97 with phosphate ($KH_2PO_4$, 2 μmol $L^{-1}$) was conducted to ensure that phosphorus was not
98 a limiting factor in July 2012, at which time the concentration of phosphate was lowest
99 in the year (0.1μmol $L^{-1}$; Table S1 and S2). The results of the degradation experiment
100 with added phosphorus were not significantly different from those of the degradation
101 experiment without added phosphorus ($y=1.1x–8.2$, $R^2=0.97$, $p<0.05$).
102 RDOC was here defined as the concentration of DOC remaining at 150 days and
103 BDOC was obtained by subtracting RDOC from the initial DOC (Lønborg et al., 2009).
104 The degradation rate of DOC was described by a first-order exponential decay model

with a constant RDOC pool:

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

where DOC(t) is the amount of DOC remaining at time t (day), k is the degradation rate constant ($day^{-1}$), and RDOC is the remaining DOC pool after 150 days of incubation. BDOC is the bioavailable DOC (μmol $L^{-1}$) at the beginning of incubation and practically equals to subtraction of RDOC from initial DOC. Using BDOC and RDOC concentrations, k can be estimated by fitting the observed DOC(t) values to equation (1) 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,

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

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 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, 3h) Whatman GF/F filters. After filtration, chlorophyllous pigments were extracted using N, N-dimethylformamide, and the concentrations of chl *a* were determined by the

129 fluorometric method (Suzuki and Ishimaru, 1990) using a fluorometer (TD-700, Turner
130 Designs, Sunnyvale, CA, USA). Samples for particulate organic carbon (POC) were
131 filtered through precombusted (450°C, 3h) Whatman GF/F filters, after which the filters
132 were stored at –80°C until analysis. The samples for POC analyses were dried at 60°C
133 and acidified with vapor at 12 mol $L^{-1}$ HCl to remove carbonate before analysis. POC
134 were measured using a Hydra 20-20 isotope ratio mass spectrometer coupled to an
135 ANCA-GSL elemental analyzer (SerCon Ltd., Crewe, UK).
136
137 **3. Results and Discussion**
138 **3.1. Lability and sources of freshwater DOC flowing into Tokyo Bay**
139 The lowest chl *a*, DOC, and POC concentrations were observed at the upper
140 Arakawa River station, which is considered to be pristine (Table 1). The average
141 concentration of DOC was 38 μmol $L^{-1}$ at the upper Arakawa River station. Headstream
142 water sources in Japan are mostly surface runoff from neighboring watersheds and
143 ground water input through the mineral soil horizon before entering surface water
144 (Nakamura et al., 2011). The precipitation is characterized by very low DOC
145 concentrations (Avery et al., 2003). Ground water inputs through the mineral soil
146 horizon typically have low DOC concentrations because mineral soils have the ability to
147 adsorb a significant amount of DOC (Aitkenhead et al., 2003). Such low concentrations
148 of DOC in headstream waters have commonly been reported in Japan (e.g. Maki et al.,
149 2010), as well as in other countries (e.g. Yamashita et al., 2011). The results of the DOC
150 degradation experiments at the upper Arakawa River station are shown in Figure 2(a).
151 Rapid degradation of the labile pool was observed within the first 20 days of incubation.
152 Additionally, the mean concentration of RDOC was 25 μmol $L^{-1}$, and its mean

153 contribution to the total DOC was 67%. At the upper Arakawa River station, the
154 concentrations of DOC and RDOC were very low.

155 Relatively high temperatures and DOC values were observed at Shibaura STP,
156 while seasonal variations in chl *a* and POC were relatively small (Table 1). The average
157 concentration of DOC was 359 μmol $L^{-1}$, which was about nine times higher than the
158 value at the upper Arakawa River station. The annual mean concentration of RDOC was
159 278 μmol $L^{-1}$, while the mean contribution of RDOC to the total DOC was 78% (Figure
160 2(b)). The RDOC concentrations did not vary greatly between observation months, and
161 a good linear relationship was observed between BDOC and DOC ($R^2$=0.976, $p<0.001$,
162 slope=1.16), indicating that the seasonal variations in DOC were mostly due to
163 variations in the bioavailable fraction. Typically, STP effluents have high organic carbon
164 concentrations and a large bioavailable fraction (Servais et al., 1995; Servais et al.,
165 1999; Kaushal and Belt, 2012). In contrast, effluent of Shibaura STP showed a high
166 proportion of RDOC (67–93%). These findings suggest that most of the BDOC were
167 degraded before being discharged. This likely occurred because STPs in Japan conduct
168 secondary treatment, which consists of removal of wastewater suspended solids by
169 sedimentation and degradation of dissolved organic matter by activated sludge treatment
170 (Kadlec and Wallace, 2008).

171 Relatively high chl *a* and POC concentrations were observed at the lower Arakawa
172 River station (Table 1). The maximum concentrations of chl *a*, DOC, and POC were
173 observed in spring. The average concentration of DOC was 235 μmol $L^{-1}$, while the
174 annual mean concentration of RDOC was 149 μmol $L^{-1}$ and the mean contribution of
175 RDOC to the total DOC was 66% (Figure 2(c)). The concentrations of DOC were more
176 than six times higher than those at the upper Arakawa River station. High

177 concentrations of nutrients were also observed at the lower Arakawa River station (see
178 Table S1 and S2 in the auxiliary material), which was likely a result of inputs of DOC
179 and nutrients from STPs between observation sites. The RDOC concentrations did not
180 show large differences between observation months, and a good linear relationship
181 between BDOC and DOC was observed ($R^2$=0.942, p<0.001, slope=1.12), indicating
182 that the seasonal variations of DOC at the lower Arakawa River station were due to
183 variations in the bioavailable fraction.

184 Freshwater flowing into Tokyo Bay primarily consists of a mixture of river water
185 and STP effluent. The total discharge ratio of river water to STP effluent in the bay is
186 about 1:1 (Japan Sewage Works Association, 2010; Bureau of Sewerage, 2013).
187 Assuming that the ratio of river water to STP effluent is 1:1 and that data collected at
188 the upper Arakawa River station and Shibaura STP represent these two sources, the
189 average concentrations of RDOC and BDOC in freshwater would be 152 and 47 μmol
190 $L^{-1}$, respectively. These values are comparable with those observed at the lower
191 Arakawa River station (149 and 86 μmol $L^{-1}$, respectively). Arakawa River, which is the
192 largest river flowing into the bay, accounts for about 30% of the freshwater discharge
193 (Nihei et al., 2007a). Most rivers flowing into the bay have similar water quality
194 because of similar land use within the drainage basin (Nihei et al., 2007b); accordingly,
195 we can reasonably assume that observed RDOC and BDOC concentrations at the lower
196 Arakawa River station represent concentrations of total river water flowing into Tokyo
197 Bay.

198 Table 2 summarizes the first-order decay constants obtained by fitting the
199 exponential degradation of DOC with time. The annual average degradation constant
200 normalized to 15°C at the lower Arakawa River station was 0.031±0.005, which was

similar to other coastal waters (0.066±0.065; Lønborg and Álvarez-Salgado, 2012).

### 3.2. Tokyo Bay

Seasonal variations in temperature, salinity, chl *a*, POC, and DOC at the three stations in Tokyo Bay are presented in Figure 3. High values of temperature, chl *a*, POC, and DOC 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. DOC concentrations ranged from 81 to 182, 76 to 153, and 60 to 108 μmol $L^{-1}$ at stations F3, F6, and 06, respectively (Figure 4). The concentrations of DOC were generally lower than these at the lower Arakawa River station.

#### 3.2.1. Lability of DOC

The results of DOC degradation experiments at Tokyo Bay are shown in Figure 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 Figure 5. RDOC ranged from 70 to 120 μmol $L^{-1}$ at F3, 58 to 130 μmol $L^{-1}$ at F6, and 48 to 80 μmol $L^{-1}$ at 06. The mean contributions of RDOC to the total DOC were 81% at F3, 77% at F6 and 72% at 06. Both RDOC and BDOC showed similar seasonal variations as DOC, with high variations being observed in spring and summer and low in autumn and winter. The contribution of RDOC to the total DOC was higher than that of BDOC at all stations for the entire observation period. The RDOC concentrations of the surface water were significantly higher than those of the bottom water at 06 (see Table S3 in the auxiliary material). Thus, our

225 RDOC results likely include a fraction of semi-labile DOC. Degradation of this semi-
226 labile DOC fraction would occur by bacterial mineralization with longer time, photo-
227 degradation (Moran and Zepp, 1997; Opsahl and Benner, 1997; Obernosterer and
228 Benner, 2004), aggregation (Sholkovitz, 1976; Mulholland, 1981), and/or sorption to
229 particles (Chin et al., 1998; Kerner et al., 2003). However, the results of this study did
230 not change significantly when DOC were divided into BDOC, semi-labile DOC, and
231 RDOC. The lifetime of semi-labile DOC is about 1.5 years (Hansell, 2013), which is
232 considerably longer than the residence time of Tokyo Bay (Takada et al., 1992).
233 Therefore, in our analysis, there was no problem with inclusion of semi-labile DOC in
234 RDOC. In addition, Ogura (1975) only divided DOC into BDOC and RDOC; therefore,
235 we divided DOC in the same way to enable comparison with that study.
236 Table 3 summarizes the degradation constants of DOC for the bay surface waters.
237 The annual average degradation constants normalized to 15°C at F3, F6, and 06 were
238 0.128±0.014, 0.094±0.016, and 0.083±0.010, respectively. Most degradation constants
239 for the bay water were higher than those of freshwater (Tables 2 and 4). The half-lives
240 of BDOC were calculated from the degradation constant. The annual average half-lives
241 of BDOC at F3, F6, and 06 were 5.9, 8.5, and 10.0 days, respectively. BDOC produced
242 by phytoplankton in the bay water might have led to faster degradation rates because the
243 half-lives of BDOC were about five times faster than the residence time of the bay
244 water.
245 RDOC concentrations in Tokyo Bay were negatively correlated with salinity and
246 positively correlated with chl *a* (Table 4). In the bay, salinity was lower in spring and
247 summer than in autumn and winter (Figure 3) because of high freshwater input during
248 spring and summer. The freshwater RDOC concentration was higher than that of Tokyo

249 Bay water; therefore, a negative relationship between RDOC and salinity was observed.
250 RDOC is also produced directly by phytoplankton (Kragh and Søndergaard, 2009).
251 Hence, the positive relationship between RDOC and chl *a* observed in this study likely
252 reflected RDOC produced by phytoplankton.
253
254 **3.2.2. RDOC sources**
255 To estimate the sources of RDOC in Tokyo Bay, multiple linear regression analysis
256 with salinity and chl *a* as the independent variables was applied to all RDOC data
257 observed at three stations in Tokyo Bay. BDOC in Tokyo Bay was not well correlated
258 with salinity and chl *a* (Table 4), so multiple linear regression analysis was not applied
259 to the BDOC data. We obtained the following multiple linear regression equation
260 (Model I):
261
262 $$[\mathrm{RDOC}] = 259 - 5.96 \times [Sal] + 0.597 \times [Chla] \quad (3)$$
$$(r^2 = 0.79, P < 0.001, n = 35)$$
263
264 where [RDOC] is the RDOC concentration (μmol $L^{-1}$), [Sal] is salinity, and [Chla] is the
265 chl *a* concentration (μg $L^{-1}$) of each sample. The end-member of terrestrial RDOC
266 ([$RDOC_{terr\text{-}end}$]) was as follows when the salinity was 0;
267
268 $$[\mathrm{RDOC}_{terr-end}] = 259 + 0.597 \times [Chla_{river}] \quad (4)$$
269
270 where [$Chla_{river}$] is the chl *a* concentration (μg $L^{-1}$) at the freshwater site. The end-
271 member of terrestrial RDOC was higher than the average RDOC concentration at the

lower Arakawa River station (149 μmol $L^{-1}$) and was similar to that of Shibaura STP (278 μmol $L^{-1}$). The ratio of river water to STP effluent was 1:1 (Japan Sewage Works Association, 2010; Bureau of Sewerage, 2013) and data collected at the upper Arakawa River station and Shibaura STP represent these two sources (see section 3.1.). It is possible that freshwater inputs in Tokyo Bay were more strongly influenced by STPs than headstream waters. Alternatively, if we assume that the RDOC concentration at salinity=0 and chl *a*=0 was close to the average RDOC concentration actually observed at the lower Arakawa River station (149 μmol $L^{-1}$), we obtain the following multiple regression equation (Model II):

$$[\mathrm{RDOC}] = 149 - 2.65 \times [Sal] + 1.03 \times [Chla] \quad (5)$$

$$(r^2 = 0.71, P < 0.001, n = 35)$$

The end-member of terrestrial RDOC ([$RDOC_{terr\text{-}end}$]) is as follows when salinity is 0;

$$[\mathrm{RDOC}_{terr-end}] = 149 + 1.03 \times [Chla_{river}] \quad (6)$$

In this study, we assumed that [$Chla_{river}$] was 6.0 μg $L^{-1}$ (Ministry of the Environment: http://www.env.go.jp), which was the average value of surface waters in Arakawa River. Although [$Chla_{river}$] is usually lower than 10 μg $L^{-1}$ throughout the year, phytoplankton blooms occasionally persist (Ministry of the Environment: http://www.env.go.jp). Calculation of the RDOC sources using the minimum and maximum chl *a* concentration at the lower Arakawa River station (Table 1) resulted in estimated RDOC sources that did not differ significantly from the minimum and maximum concentrations.

The concentrations of RDOC in the open ocean ([$RDOC_{ocean\text{-}end}$]) can be estimated by assuming that salinity and chl *a* in the open ocean were 34.5 (Okada et al., 2007) and 1.0 μg $L^{-1}$, respectively (Japan Meteorological Agency: http://www.jma.go.jp/jma/index.html), which were the average values of surface waters offshore from Tokyo Bay. The [$RDOC_{ocean\text{-}end}$] values were 54.0 and 58.6 μmol $L^{-1}$ for Model I and II, respectively, which were comparable to the annual average RDOC concentration of the bottom water at 06 (see Table S3 in the auxiliary material). Following the method described Ogawa and Ogura (1990), we estimated the contributions of RDOC from different sources (RDOC from the open ocean [$RDOC_{ocean\ origin}$], terrestrial RDOC [$RDOC_{terr}$], and RDOC from phytoplankton [$RDOC_{phyto}$]) using two models of the multiple linear regression analysis. The RDOC concentrations can be expressed as follows:

$$[\mathrm{RDOC}] = [\mathrm{RDOC}_{phyto}] + [\mathrm{RDOC}_{ocean\ origin}] + [\mathrm{RDOC}_{terr}] \quad (7)$$

The equation describing RDOC derived from the open ocean ([$RDOC_{ocean\ origin}$]) is as follows:

$$[\mathrm{RDOC}_{ocean\ origin}] = [\mathrm{RDOC}_{ocean-end}] \times [Sal]/34.5 \quad (8)$$

The terrestrial RDOC ([$RDOC_{terr}$]) is as follows:

$$[\mathrm{RDOC}_{terr}] = [\mathrm{RDOC}_{terr-end}] \times (34.5 - [Sal])/34.5 \quad (9)$$

319 The RDOC derived from phytoplankton ([RDOC$_{phyto}$]) can be estimated from equation
320 (7):
321
322 $$[\mathrm{RDOC}_{phyto}] = [\mathrm{RDOC}] - [\mathrm{RDOC}_{ocean\ origin}] - [\mathrm{RDOC}_{terr}] \quad (10)$$
323
324 The relative concentrations of RDOC in the bay originating from phytoplankton,
325 terrestrial, and open oceanic waters at the three stations are presented in Table 5. The
326 results show that the open ocean is the major source of RDOC in Tokyo Bay. At station
327 F3, which is located close to land, terrestrial RDOC was comparable to that from the
328 open ocean. The concentration of terrestrial RDOC was higher than that of RDOC from
329 phytoplankton at all stations, even at the bay mouth.
330 The influx of terrestrial TOC (POC+DOC) from the rivers to Tokyo Bay was
331 estimated using a mass balance model ($8.1\times10^{10}$ gC year$^{-1}$; Yanagi et al., 1993), and the
332 DOC/TOC ratio in freshwater site was 0.62 (Kubo, unpublished data). Hence, the influx
333 of terrestrial DOC was estimated to be $5.0\times10^{10}$ gC year$^{-1}$ and RDOC accounted for
334 66% of terrestrial DOC (see section 3.1.; $3.3\times10^{10}$ gC year$^{-1}$). The efflux of TOC from
335 the surface bay to the open ocean was estimated using a mass balance model ($9.4\times10^{10}$
336 gC year$^{-1}$; Yanagi et al., 1993), and the DOC/TOC ratio in the surface bay mouth was
337 0.69 (Kubo, unpublished data). Hence, the efflux of DOC was estimated to be $6.5\times10^{10}$
338 gC year$^{-1}$ and RDOC accounted for 73% in the surface bay mouth (see section 3.2.;
339 $4.7\times10^{10}$ gC year$^{-1}$). Assuming that terrestrial and phytoplankton RDOC were exported
340 outside of the bay in the same ratio at the bay mouth (Table 5), Tokyo Bay exported
341 mostly terrestrial RDOC to the open ocean owing to the high concentration of terrestrial
342 RDOC and remineralization of BDOC. Moreover, the ratio of terrestrial RDOC input

343 into the bay ($3.3\times10^{10}$ gC $year^{-1}$) and terrestrial RDOC efflux to the open ocean
344 ($0.9\times10^{10}$ and $0.6\times10^{10}$ gC $year^{-1}$, respectively for Model I and II) was 28% and 17%,
345 respectively. Residual terrestrial RDOC in the bay may be removed from the water
346 column by photo-degradation (Moran and Zepp, 1997; Opsahl and Benner, 1997;
347 Obernosterer and Benner; 2004), aggregation (Sholkovitz, 1976; Mulholland, 1981),
348 and/or sorption to particles (Chin et al., 1998; Kerner et al., 2003).

349 The fate of terrestrial DOC in the coastal ocean and open ocean has long been the
350 subject of debate (Hedges et al., 1997). For example, biomarkers (e.g. lignin phenols)
351 and the stable carbon isotopic composition of DOC are commonly used to estimate the
352 contribution of terrestrial DOC to the open ocean (Druffel et al., 1992; Hedges et al.,
353 1997; Raymond and Bauer, 2001; Bauer and Bianchi, 2011). Lignin phenols analysis
354 indicated that terrestrial DOC comprises only a small fraction (4–10%) of the total DOC
355 in the open ocean (Meyers-Schulte and Hedges, 1986; Opshal and Benner, 1997; Hernes
356 and Benner, 2006). In addition, the stable carbon isotopic composition of DOC also
357 indicated that terrestrial DOC represents less than 10% of the total DOC (Bauer et al.,
358 2002). As a result, most terrestrial DOC is remineralized in coastal waters, and only a
359 small fraction is exported to the open ocean. In this study, terrestrial RDOC in the
360 surface bay mouth accounted for less than 20% of the total RDOC (Table 5). Although
361 these levels were slightly higher than those reported in previous studies using lignin
362 phenols and stable carbon isotopic compositions of DOC, they are probably reasonable
363 given that exported terrestrial RDOC were further diluted with open oceanic water once
364 outside the bay. Nevertheless, more complete information regarding the sources and
365 lability of DOC are important to enable a better understanding of the fate of DOC in the
366 coastal ocean and open ocean.

### 3.3. Change of DOC over four decades

Ogura (1975) investigated the concentrations of RDOC and BDOC in Tokyo Bay and freshwater sources flowing into the bay in the 1970s using GF/C filters (nominal pore size; 1.2 μm) to collect filtrate of degradation samples and found that the contribution of the DOC fraction from 0.45 μm (Millipore HA filter, Millipore Corp., Bedford, MA) to 1.2 μm was about 10% of the total DOC in Tokyo Bay. Ogawa and Ogura (1992) also showed that the low molecular weight DOC (< 10,000 Dalton; < 0.2 μm) in the bay comprised a major portion of the total DOC filtered by 1.2 μm (78–97%). Hence, the DOC fraction from 0.7 μm to 1.2 μm comprised a minor proportion of the DOC in Tokyo Bay. Ogura (1975) used a wet chemical oxidation method to measure the samples, while Ogawa and Ogura (1992) showed that both a wet chemical oxidation method and high temperature catalytic oxidation method for measuring DOC concentrations of Tokyo Bay waters generated similar results. Therefore, we assumed that our concentrations were comparable to those reported by Ogura (1975).

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 concentrations 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), indicating that 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

391 proportion of treated wastewater to the total freshwater inflow to the bay increased from
392 11% to 28% from 1970 to 2000 (National Institute for Land and Infrastructure
393 Management, 2004). Overall, these results indicate that the quantity of DOC flowing
394 into the bay has decreased, and the quality of DOC has become more recalcitrant owing
395 to an increase in STP effluent.

396 In Tokyo Bay, the concentrations of DOC at station F3 decreased from 287 μmol $L^{-1}$
397 in 1972 (Ogura, 1975) to 124 μmol $L^{-1}$ in 2012, most likely because of a decrease of
398 DOC discharge from rivers and a decrease in primary production (Yamaguchi and
399 Shibata, 1979; Yamaguchi et al., 1991; Bouman et al., 2010). The concentrations of
400 RDOC and BDOC observed in this study (100 μmol $L^{-1}$ and 24 μmol $L^{-1}$, respectively)
401 were lower than those estimated by Ogura (1975) in 1972 (165 μmol $L^{-1}$ and 100 μmol
402 $L^{-1}$, respectively). Conversely, the contribution of RDOC to the total DOC in this study
403 (80.6%) is higher than the value observed in 1972 (57.5%; Ogura, 1975). The
404 concentrations of RDOC and BDOC in Tokyo Bay have decreased because of a
405 decrease in DOC load from the land, especially for BDOC. As a result, the lability of
406 DOC has become more recalcitrant. In addition, decreasing nutrient loads in the bay
407 have caused decreasing primary production (Yamaguchi and Shibata, 1979; Yamaguchi
408 et al., 1991; Bouman et al., 2010). Therefore, DOC produced by phytoplankton should
409 also have decreased.

410

411 **4. Summary**

412 Rapid degradation of the labile pool was observed at freshwater sites and Tokyo Bay
413 within the first 20 days of incubation. BDOC are remineralized during the residence
414 time of the bay water. The contribution of RDOC to the total DOC was higher than that

of BDOC at all stations for the entire observation period, and accounted for 77% of the total. Accordingly, Tokyo Bay exported mostly terrestrial RDOC to the open ocean owing to 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 lability of DOC has become more recalcitrant because of improved sewage treatment. Since organic carbon degradation occurs at STPs before being discharged, DOC flowing into the bay has decreased, especially the BDOC.

**Acknowledgments**

We thank Ms. Chinatsu Oouchida, as well as other scientists, officers and crewmembers on board the R/V Seiyo-maru, for their help in sampling. This work was supported by a Grant-in-Aid for Scientific Research (C) (24510009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by a Canon Foundation grant.

**References**

Aitkenhead, J. A., McDowell, W. H., and Neff, J. C.: Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters, In "Aquatic Ecosystems: Interactivity of Dissolved Organic Matter" (Findlay, S. E. G., and Sinsabaugh, R. L., Eds.), pp. 25-70, Academic Press, San Diego, 2003.

Amon, R. M. W., and Benner, R.: Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, Geochim. Cosmochim. Ac., 60, 1783-1792, 1996.

439 Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin,
440 S. R., Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles
441 between land, oceans, and atmosphere, Front. Ecol. Emviron., 9, 53-60, 2011.
442 Avery Jr., G. B., Willey, J. D., Kieber, R. J., Shank, G. C., and Whitehead, R. F.: Flux
443 and bioavailability of Cape Fear River and rainwater dissolved organic carbon to
444 Long Bay, southeastern United States, Global Biogeochem. Cy., 17, 1042,
445 doi:10.1029/2002GB001964, 2003.
446 Bauer, J. E., and Bianchi, T. S.: Dissolved organic carbon cycling and transformation, In
447 "Treatise on estuarine and coastal science" (Wolanski, E., and McLusky, D. S.,
448 Eds.), vol. 5, pp. 7-67, Academic Press, Sam Diego, 2011.
449 Bauer, J. E., Druffel, E. R. M., Wolgast, D. M., and Griffin, S.: Temporal and regional
450 variability in sources and cycling of DOC and POC in the northwest Atlantic
451 continental shelf and slope, Deep-Sea Res. Pt II, 49, 4387-4419, 2002.
452 Bouman, H. A., Nakane, T., Oka, K., Nakata, K., Kurita, K., Sathyendranath, S., and
453 Platt, T.: Environmental controls on phytoplankton production in coastal
454 ecosystems: A case study from Tokyo Bay, Estuar. Coast. Shelf S., 87, 63-72, 2010.
455 Bureau of Sewerage: Management plan 2013, Bureau of Sewerage, Tokyo Metropolitan
456 Government, pp. 117, 2013 (in Japanese).
457 Carlson, C. A.: Production and removal processes, In "Biogeochemistry of Marine
458 Dissolved Organic Matter" (Hansell, D. A., and Carlson, C. A., Eds.), pp. 91-151,
459 Academic Press, San Diego, 2002.
460 Cauwet, G.: DOM in the coastal zone, In "Biogeochemistry of Marine Dissolved
461 Organic Matter" (Hansell, D. A., and Carlson, C. A., Eds.), pp. 579-609, Academic
462 Press, San Diego, 2002.

463 Chin, W. C., Orellana, M. V., and Verdugo, P.: Spontaneous assembly of marine
464 dissolved organic matter into polymer gels, Nature, 391, 568-572, 1998.
465 Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G.,
466 Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.:
467 Plumbing the global carbon cycle: integrating inland waters into the terrestrial
468 carbon budget, Ecosystems, 10, 171-184, 2007.
469 Dai, M., Yin, Z., Meng, F., Liu, Q., and Cai, W. J.: Spatial distribution of riverine DOC
470 inputs to the ocean: an updated global synthesis, Curr. Opin. Environ. Sustain., 4,
471 170-178, 2012.
472 Druffel, E. R. M., Williams, P. M., Bauer, J. E., and Ertel, J. R.: Cycling of dissolved
473 and particulate organic matter in the open ocean, J. Geophys. Res. Oceans, 97,
474 15639-15659, 1992.
475 Hansell, D. A.: Recalcitrant dissolved organic carbon fractions, Annu. Rev. Mar. Sci., 5,
476 3.1-3.25, 2013.
477 Hansell, D. A., Carlson, C. A., Repeta, D. J., and Schlitzer, R.: Dissolved organic matter
478 in the ocean: A controversy stimulates new insights, Oceanography, 22, 202-211,
479 2009.
480 Hedges, J., Keil., R. G., and Benner, R.: What happens to terrestrial organic matter in
481 the ocean?, Org. Geochem., 27, 195-212, 1997.
482 Hernes, P. J., and Benner, R.: Terrigenous organic matter sources and reactivity in the
483 North Atlantic Ocean and a comparison to the Arctic and Pacific oceans, Mar.
484 Chem., 100, 66-79, 2006.
485 Japan Sewage Works Association: Sewage statistics, 2010 (in Japanese).
486 Kadlec, R. H., and Wallace, S. D.: Treatment wetlands second edition, CRC Press, Boca

Raton, FL, pp. 1000, 2008.

Kaushal, S. S., and Belt, K. T.: The urban watershed continuum: evolving spatial and temporal dimensions, Urban Ecosys., 15, 409-435, 2012.

Kerner, M., Hohenberg, H., Ertl, S., Reckermann, M., and Spitzy, A.: Self-organization of dissolved organic matter to micelle-like microparticles in river water, Nature, 422, 150-154, 2003.

Kragh, T., and Søndergaard, M.: Production and decomposition of new DOC by marine plankton communities: carbohydrates, refractory components and nutrient limitation, Biogeochemistry, 96, 177-187, 2009.

Lønborg, C., and Álvarez-Salgado, X. A.: Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump, Global Biogeochem. Cy., 26, GB3018, doi:10.1029/2012GB004353, 2012.

Lønborg, C., Davidson, K., Álvarez-Salgado, X. A., and Miller, A. E. J.: Bioavailability and bacterial degradation rates of dissolved organic matter in a temperate coastal area during an annual cycle, Mar. Chem., 113, 219-226, 2009.

Ludwig, W., Probst, J. L., and Kempe, S.: Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochem. Cy., 10, 23-41, 1996.

Maki, K., Kim, C., Yoshimizu, C., Tayasu, I., Miyajima, T., and Nagata, T.: Autochthonous origin of semi-labile dissolved organic carbon in a large monomictic lake (Lake Biwa): carbon stable isotopic evidence, Limnology, 11, 143-153, 2010.

Meybeck, M.: C, N, P and S in rivers: From sources to global inputs, In “Interactions of C, N, P and S Biogeochemical Cycles and Global Change” (Wollast, R., Mackenzie, F. T., Chou, L., Eds), pp. 163-193. Springer-Verlag, Berlin, 1993.

Meyers-Schulte, K. J., and Hedges, J. I.: Molecular evidence for a terrestrial component

511 of organic matter dissolved in ocean water, Nature, 321, 61-63, 1986.
512 Moran, M. A., and Zepp, R.G.: Role of photoreactions in the formation of biologically
513 labile compounds from dissolved organic matter, Limnol. Oceanogr., 42, 1307-1316,
514 1997.
515 Moran, M. A., Sheldon, W. M. Jr., and Sheldon, J. E.: Biodegradation of riverine
516 dissolved organic carbon in five estuaries of the southeastern United States,
517 Estuaries, 22, 55-64, 1999.
518 Mulholland, P. J.: Formation of particulate organic carbon in water from a southeastern
519 swamp-stream, Limnol. Oceanogr., 26, 790-795, 1981.
520 Nakamura, T., Osaka, K., Hiraga, Y., and Kazama, F.: Nitrogen and oxygen isotope
521 composition of nitrate in stream water of Fuji River basin, J. Jpn. Assoc. Hydrol.
522 Sci., 41, 79-89, 2011 (in Japanese with English abstract).
523 National Institute for Land and Infrastructure Management: Information of port
524 environment, available at: http://www.nilim.go.jp/ (last access: June 25, 2013).
525 Nellemann, C., Hain, S., and Alder, J.: Rapid response assessment in dead water:
526 Merging of climate change with pollution, over-harvest, and infestations in the
527 world's fishing grounds, United Nations Environment Programme, pp.61, 2008.
528 Nihei, Y., Takamura, T., and Watanabe, N.: Issues on discharge monitoring in main
529 influence rivers into Tokyo Bay, J. Jpn. Soc. Civil Eng., 54, 1226-1230, 2007a (in
530 Japanese with English abstract).
531 Nihei, Y., Ehara, K., Usuda, M., Sakai, A., and Shigeta, K.: Water quality and pollutant
532 load in the Edo River, Ara River and Tama River, J. Jpn. Soc. Civil Eng., 54, 1221-
533 1225, 2007b (in Japanese with English abstract).
534 Obernosterer, I, and Benner, R.: Competition between biological and photochemical

processes in the mineralization of dissolved organic carbon, Limnol. Oceanogr., 49, 117-124, 2004.

Ogawa, H., and Ogura, N.: Source and behavior of organic carbon of seawater in Tokyo Bay, Chikyukagaku, 24, 27-41, 1990 (in Japanese with English abstract).

Ogawa, H., and Ogura, N.: Comparison of two methods for measuring dissolved organic carbon in sea water, Nature, 356, 696-698, 1992.

Ogura, N.: Further studies on decomposition of dissolved organic matter in coastal seawater, Mar. Biol., 31, 101-111, 1975.

Okada, T., Takao, T., Nakayama, K., and Furukawa, K.: Change in freshwater discharge and residence time of seawater in Tokyo Bay, J. Jpn. Soc. Civil Eng., 63, 67-72, 2007 (in Japanese with English abstract).

Opsahl, S., and Benner, R.: Distribution and cycling of terrigenous dissolved organic matter in the ocean, Nature, 386, 480-482, 1997.

Raymond, P. A., and Bauer, J. E.: Bacterial consumption of DOC during transport through a temperate estuary, Aquat. Microb. Ecol., 22, 1-12, 2000.

Raymond, P. A., and Bauer, J. E.: Riverine export of aged terrestrial organic matter to the North Atlantic Ocean, Nature, 409, 497-500, 2001.

Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of sea-water, In “The Sea” (Hill M. N., Eds.), pp. 26-77, Interscience, New York, 1963.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., Laruelle, G. G., Lauerwald, R., Luyssaert, S., Andersson, A. J., Arndt, S., Arnosti, C., Borges, A. V., Dale, A. W., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D. E., Leifeld, J., Meysman, F. J. R.,

559 Munhoven, G., Raymond, P. A., Spahni, R., Suntharalingam, P., and Thullner, M.:
560 Anthropogenic perturbation of the carbon fluxes from land to ocean, Nat. Geosci., 6,
561 597-607, 2013.
562 Servais, P., Barillier, A., and Garnier, J.: Determination of the biodegradable fraction of
563 dissolved and particulate organic carbon in waters, Ann. Limnol., 31, 75-80, 1995.
564 Servais, P., Garnier, J., Demarteau, N., Brion, N., and Billen, G.: Supply of organic
565 matter and bacteria to aquatic ecosystems through waste water effluents, Water Res.,
566 33, 3521-3531, 1999.
567 Sholkovitz, E. R.: Flocculation of dissolved organic and inorganic matter during the
568 mixing of river water and seawater, Geochim. Cosmochim. Ac., 40, 831-845, 1976.
569 Suzuki, R., and Ishimaru, T.: An improved method for the determination of
570 phytoplankton chlorophyll using N, N-Dimethylformamide, J. Oceanogr. Soc. Japan,
571 46, 190-194, 1990.
572 Takada, H., Ishiwatari, R., and Ogura, N.: Distribution of linear alkylbenzenes (LABs)
573 and linear alkylbenzene sulphonates (LAS) in Tokyo Bay sediments, Estuar. Coast.
574 Shelf S., 35, 141-156, 1992.
575 Yamaguchi, Y., and Shibata, Y.: Recent status of primary production in Tokyo Bay,
576 Bull. Coast. Oceanogr., 16, 106-111, 1979 (in Japanese).
577 Yamaguchi, Y., Satoh, H., and Aruga, Y.: Seasonal changes of organic carbon and
578 nitrogen production by phytoplankton in the estuary of river Tamagawa, Mar. Pollut.
579 Bull., 23, 723-725, 1991.
580 Yamashita, Y., Kloeppel, B. D., Knoepp, J., Zausen, G. L., and Jaffé, R.: Effect of
581 watershed history on dissolved organic matter characteristics in headwater streams,
582 Ecosystems, 14, 1110-1122, 2011.

583 Yanagi, T., Saino, T., Ishimaru, T., and Uye, S.: A carbon budget in Tokyo Bay, J.
584 Ocenogr., 49, 249-256, 1993.
585

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

587

588 Figure 2. Changes in dissolved organic carbon (μmol $L^{-1}$) in surface water of (a) the
589 upper Arakawa River station, (b) Shibaura STP, and (c) the lower Arakawa River
590 station. Error bars represent the standard deviations.

591

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

594

595 Figure 4. Changes in dissolved organic carbon (μmol $L^{-1}$) in surface water of (a) F3, (b)
596 F6, and (c) 06. Black square: January 2011; gray square: February 2011; white square:
597 March 2011; black diamond: April 2011; gray diamond: May 2011; white diamond:
598 June 2011; black triangle: July 2011; gray triangle: August 2011; white triangle:
599 September 2011; black circle: October 2011; gray circle: November 2011; white circle:
600 December 2011. Error bars represent the standard deviations.

601

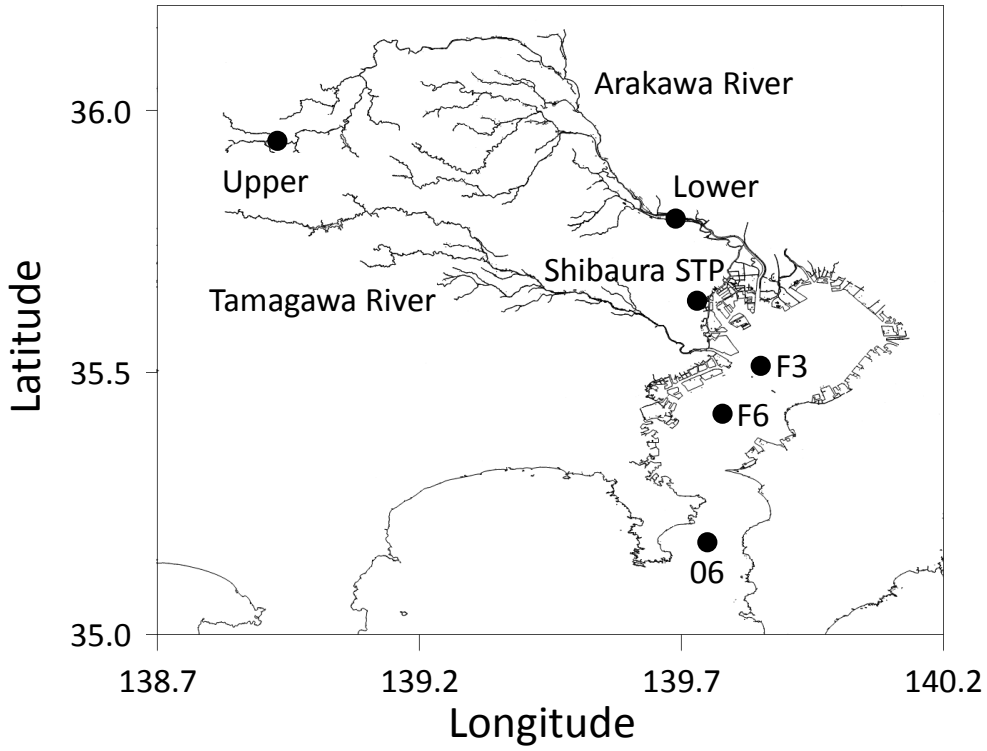
602 Figure 5. Seasonal variations in DOC (■), bioavailable DOC (BDOC; □), and
603 recalcitrant DOC (RDOC; ■) at station (a) F3, (b) F6, and (c) 06. Error bars represent
604 the standard deviations.

605

606

607

608




609

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

611

612

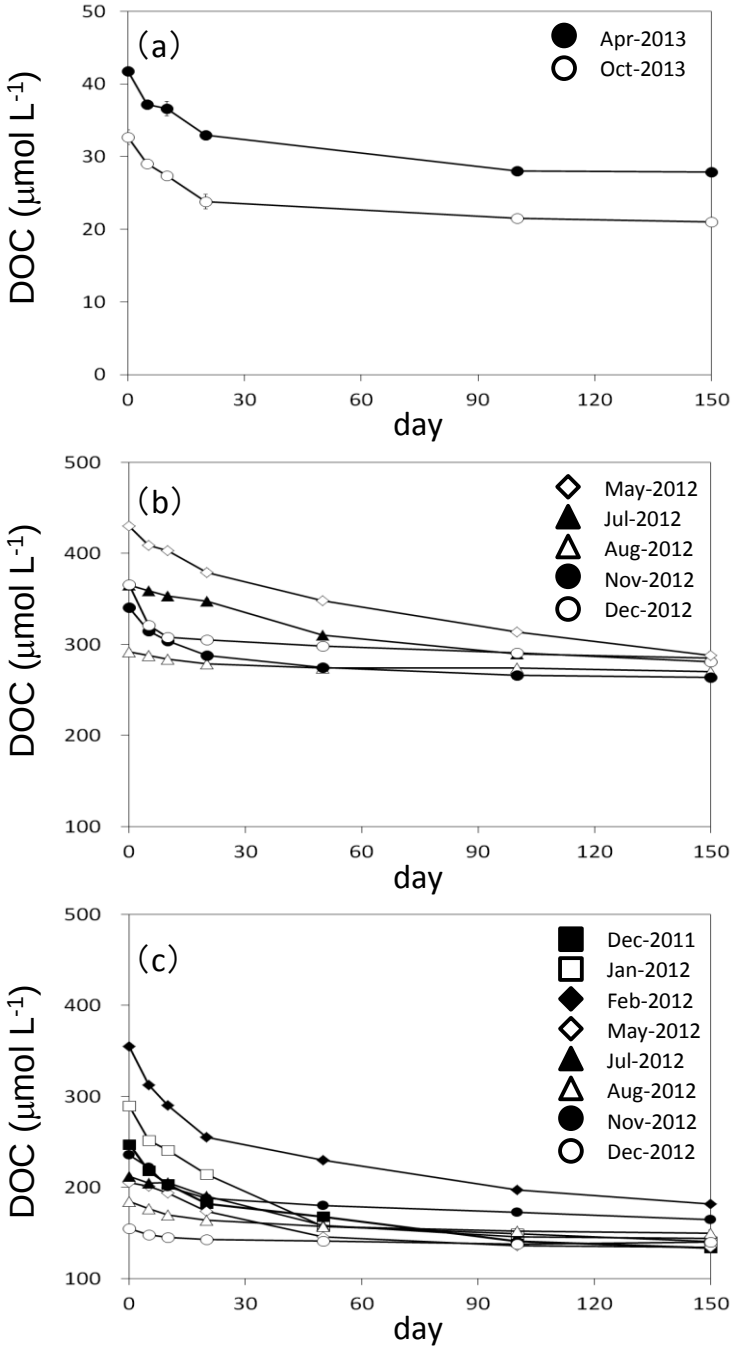
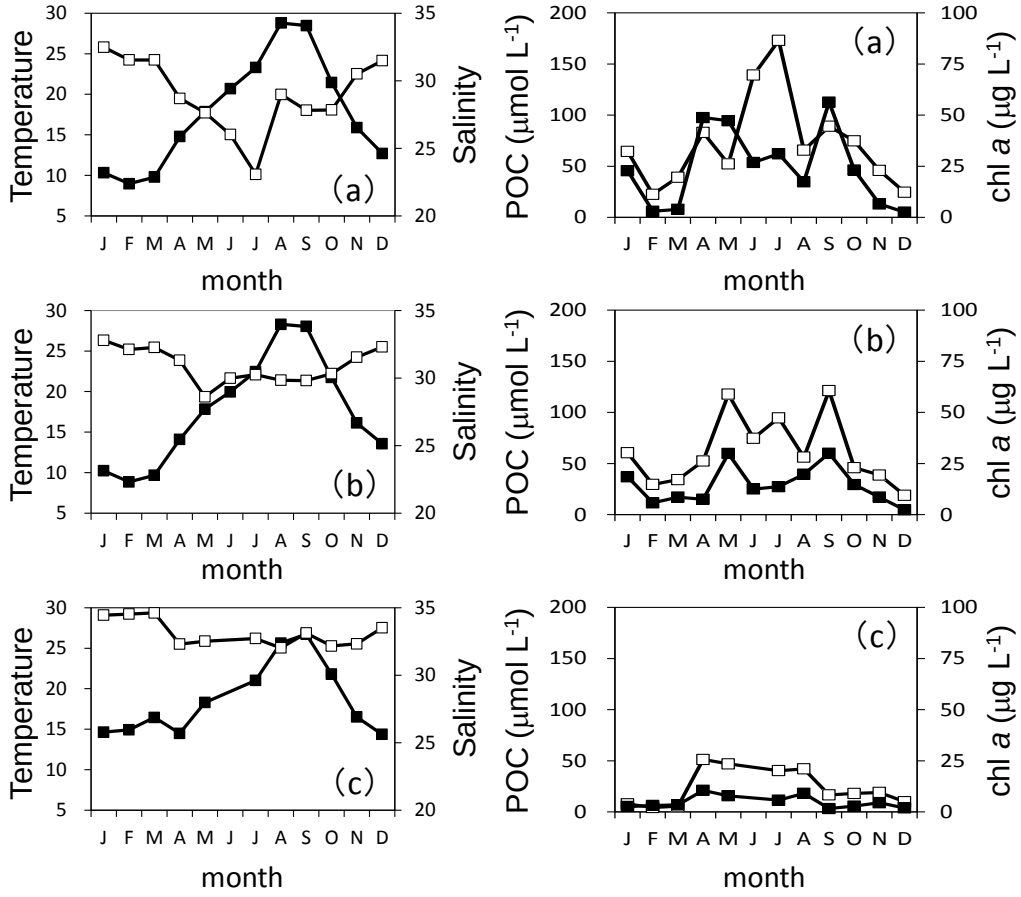



Figure 2. Changes in dissolved organic carbon (μmol $L^{-1}$) in surface water of (a) the upper Arakawa River station, (b) Shibaura STP, and (c) the lower Arakawa River station. Error bars represent the standard deviations.

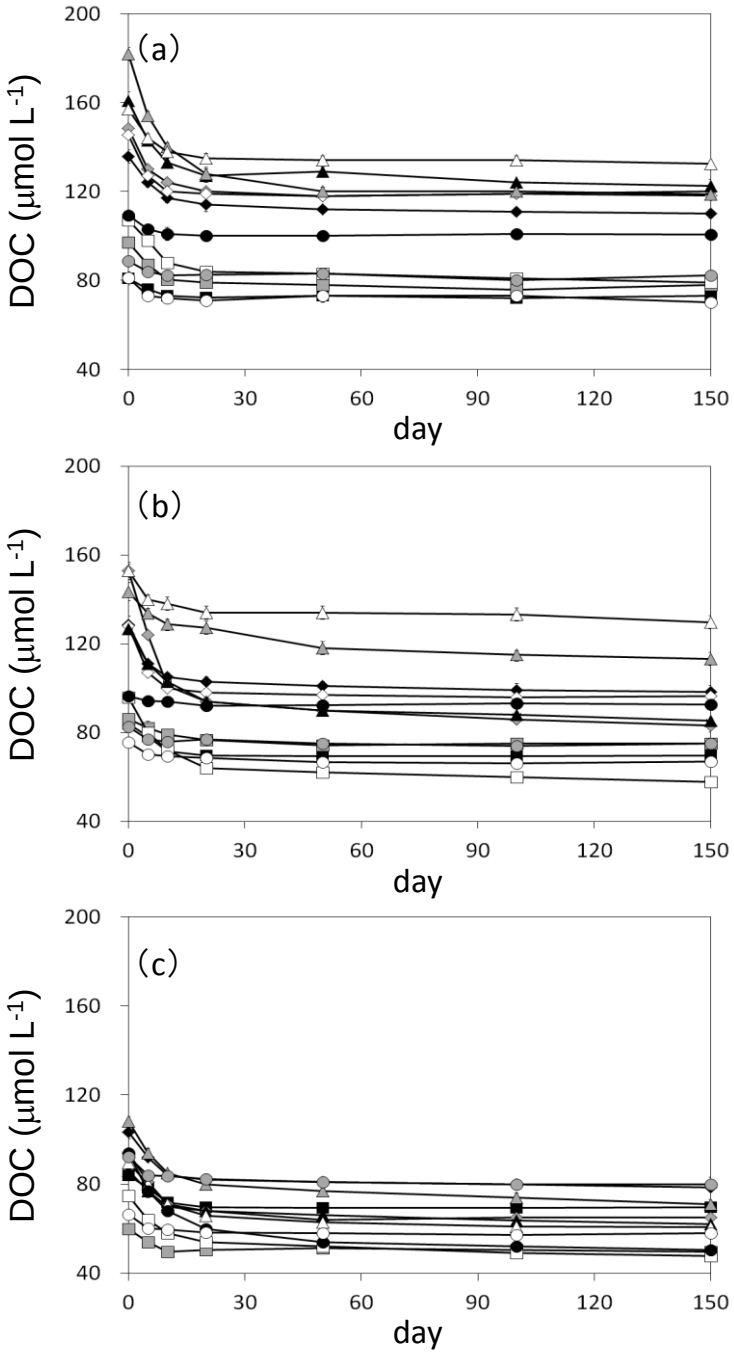



620

621 Figure 3. Seasonal variations in salinity (□), temperature (°C; ■), particulate organic

622 carbon (μmol $L^{-1}$ ; □), and chlorophyll *a* (μg $L^{-1}$; ■) at station (a) F3, (b) F6, and (c) 06.

623

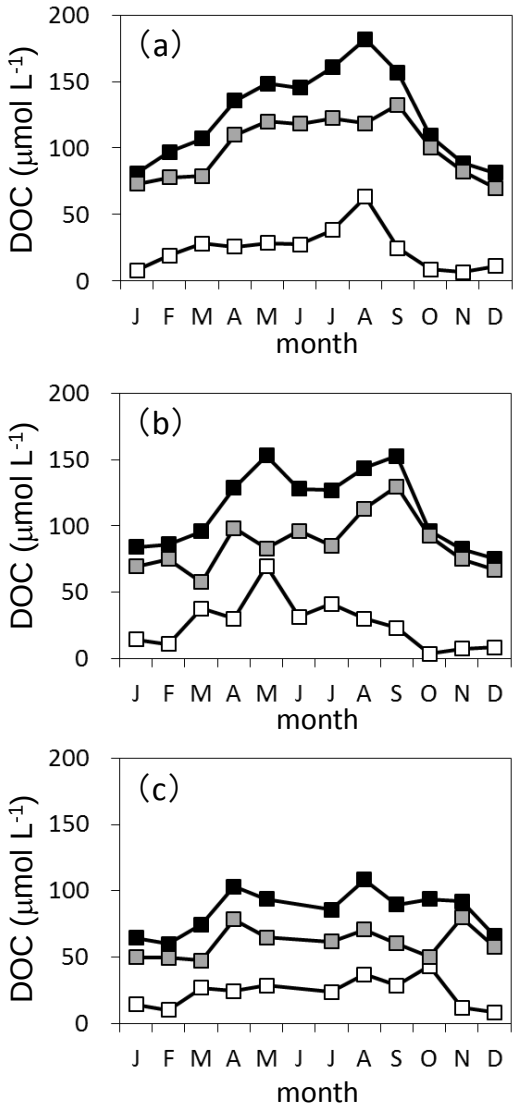



624
625

626 Figure 4. Changes in dissolved organic carbon (μmol $L^{-1}$) in surface water of (a) F3, (b)
627 F6, and (c) 06. Black square: January 2011; gray square: February 2011; white square:
628 March 2011; black diamond: April 2011; gray diamond: May 2011; white diamond:
629 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. Error bars represent the standard deviations.

636




637

638 Figure 5. Seasonal variations in DOC (■), bioavailable DOC (BDOC; □), and

639 recalcitrant DOC (RDOC; ■) at station (a) F3, (b) F6, and (c) 06. Error bars represent

640 the standard deviations.

641

642

643

644 Table 1

645 Temperature (°C), salinity, chl *a* concentrations (μg $L^{-1}$), DOC concentrations (μmol $L^{-1}$) ± standard deviation, and POC concentrations (μmol $L^{-1}$) at the upper Arakawa River (upper AR), the 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±0 | 13 |
| upper AR | Oct-2013 | 17.4 | 0.0 | 0.2 | 42±1 | 7 |
| lower AR | Dec-2011 | 12.1 | 0.6 | 2.0 | 247±4 | 178 |
| lower AR | Jan-2012 | 7.0 | 0.2 | 7.6 | 290±5 | 145 |
| lower AR | Feb-2012 | 7.2 | 0.2 | 49.3 | 355±3 | 313 |
| lower AR | May-2012 | 23.6 | 0.2 | 33.9 | 205±1 | 168 |
| lower AR | Jul-2012 | 24.2 | 0.2 | 1.5 | 213±2 | 84 |
| lower AR | Aug-2012 | 23.9 | 0.0 | 1.2 | 185±2 | 59 |
| lower AR | Nov-2012 | 17.4 | 0.2 | 2.0 | 236±2 | 63 |
| lower AR | Dec-2012 | 11.8 | 0.2 | 10.7 | 155±1 | 76 |
| Shibaura STP | May-2012 | 27.6 | 2.9 | 3.7 | 430±4 | 71 |
| Shibaura STP | Jul-2012 | 27.9 | 1.9 | 0.5 | 366±3 | 38 |
| Shibaura STP | Aug-2012 | 27.7 | 1.9 | 2.2 | 292±2 | 48 |
| Shibaura STP | Nov-2012 | 20.5 | 4.0 | 0.3 | 341±3 | 76 |
| Shibaura STP | Dec-2012 | 17.2 | 0.4 | 1.2 | 366±3 | 83 |

648

649

650

651

652

653 Table 2

654 Degradation constants for DOC ($k_{20}$) and normalized degradation constants at 15°C

655 ($k_{15}$) ± standard deviation at the upper Arakawa River (upper AR), the lower Arakawa

656 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±0.006 | 0.99 | 0.049±0.004 |
| upper AR | Oct-2013 | 0.053±0.007 | 0.98 | 0.036±0.005 |
| lower AR | Dec-2011 | 0.038±0.004 | 0.97 | 0.025±0.003 |
| lower AR | Jan-2012 | 0.040±0.004 | 0.99 | 0.027±0.003 |
| lower AR | Feb-2012 | 0.038±0.003 | 0.96 | 0.026±0.002 |
| lower AR | May-2012 | 0.028±0.004 | 0.99 | 0.019±0.003 |
| lower AR | Jul-2012 | 0.025±0.005 | 0.99 | 0.017±0.004 |
| lower AR | Aug-2012 | 0.045±0.010 | 0.99 | 0.031±0.007 |
| lower AR | Nov-2012 | 0.052±0.005 | 0.97 | 0.035±0.004 |
| lower AR | Dec-2012 | 0.110±0.014 | 0.97 | 0.071±0.010 |
| Shibaura STP | May-2012 | 0.019±0.005 | 0.99 | 0.013±0.004 |
| Shibaura STP | Jul-2012 | 0.021±0.006 | 0.99 | 0.014±0.004 |
| Shibaura STP | Aug-2012 | 0.040±0.021 | 0.97 | 0.027±0.015 |
| Shibaura STP | Nov-2012 | 0.062±0.006 | 0.99 | 0.042±0.004 |
| Shibaura STP | Dec-2012 | 0.110±0.005 | 0.92 | 0.072±0.004 |

657

658

659

660

661

662

663

664

665 Table 3

666 Degradation constants for DOC ($k_{20}$) and normalized degradation constants at 15°C

667 ($k_{15}$) ± standard deviation in Tokyo Bay (F3, F6, and 06). $R^2$ indicates coefficient of

668 determination.

| Station | Date | $k_{20}$ ($day^{-1}$) | $R^2$ | $k_{15}$ ($day^{-1}$) |
|---|---|---|---|---|
| F3 | Jan-2012 | 0.236±0.032 | 0.98 | 0.159±0.022 |
| F3 | Feb-2012 | 0.162±0.012 | 0.99 | 0.110±0.008 |
| F3 | Mar-2012 | 0.093±0.007 | 0.97 | 0.063±0.005 |
| F3 | Apr-2012 | 0.120±0.012 | 0.99 | 0.081±0.008 |
| F3 | May2012 | 0.203±0.009 | 0.99 | 0.137±0.006 |
| F3 | Jun-2012 | 0.286±0.007 | 0.99 | 0.193±0.005 |
| F3 | Jul-2012 | 0.127±0.010 | 0.97 | 0.086±0.007 |
| F3 | Aug-2012 | 0.109±0.005 | 0.99 | 0.074±0.004 |
| F3 | Sep-2012 | 0.153±0.010 | 0.99 | 0.103±0.007 |
| F3 | Oct-2012t | 0.301±0.025 | 0.98 | 0.203±0.017 |
| F3 | Nov-2012 | 0.269±0.024 | 0.87 | 0.182±0.017 |
| F3 | Dec-2012 | 0.221±0.019 | 0.97 | 0.149±0.014 |
| F6 | Jan-2012 | 0.150±0.016 | 0.98 | 0.101±0.011 |
| F6 | Feb-2012 | 0.095±0.020 | 0.99 | 0.064±0.014 |
| F6 | Mar-2012 | 0.100±0.003 | 0.99 | 0.067±0.002 |
| F6 | Apr-2012 | 0.151±0.011 | 0.98 | 0.102±0.008 |
| F6 | May2012 | 0.115±0.005 | 0.98 | 0.077±0.004 |
| F6 | Jun-2012 | 0.209±0.007 | 0.99 | 0.141±0.005 |
| F6 | Jul-2012 | 0.083±0.006 | 0.99 | 0.056±0.004 |
| F6 | Aug-2012 | 0.050±0.012 | 0.97 | 0.033±0.008 |
| F6 | Sep-2012 | 0.120±0.016 | 0.95 | 0.081±0.011 |
| F6 | Oct-2012t | 0.188±0.054 | 0.84 | 0.127±0.040 |
| F6 | Nov-2012 | 0.243±0.025 | 0.91 | 0.164±0.020 |
| F6 | Dec-2012 | 0.170±0.021 | 0.92 | 0.115±0.015 |
| 06 | Jan-2012 | 0.043±0.007 | 0.94 | 0.029±0.005 |
| 06 | Feb-2012 | 0.223±0.012 | 0.97 | 0.150±0.008 |
| 06 | Mar-2012 | 0.091±0.007 | 0.98 | 0.061±0.005 |
| 06 | Apr-2012 | 0.133±0.010 | 0.99 | 0.089±0.007 |
| 06 | May2012 | 0.134±0.007 | 0.99 | 0.090±0.005 |
| 06 | Jul-2012 | 0.089±0.010 | 0.97 | 0.060±0.007 |
| 06 | Aug-2012 | 0.085±0.006 | 0.97 | 0.057±0.004 |
| 06 | Sep-2012 | 0.094±0.008 | 0.99 | 0.063±0.006 |
| 06 | Oct-2012t | 0.085±0.005 | 0.99 | 0.057±0.004 |
| 06 | Nov-2012 | 0.146±0.021 | 0.94 | 0.098±0.014 |
| 06 | Dec-2012 | 0.240±0.013 | 0.87 | 0.162±0.009 |

669

670

671

672

673 Table 4

674 Correlation coefficients ($R^2$) of the significant ($p<0.05$) linear regressions between DOC

675 and hydrological data in Tokyo Bay (station F3, F6, 06, and total data). X indicates

676 dependent variable. n.s. indicates not significant.

| Station | X | Salinity | 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. |

677

678

679

680

681 Table 5

682 Relative concentration of RDOC (%) in Tokyo Bay derived from phytoplankton,

683 terrestrial, and open oceanic waters estimated from two multiple linear regressions.

| Station | Model I | | | Model II | | |
|---|---|---|---|---|---|---|
| | Phyto. | Terr. | Ocean | Phyto. | Terr. | Ocean |
| F3 | 13 | 42 | 46 | 15 | 29 | 57 |
| F6 | 9 | 34 | 56 | 10 | 23 | 67 |
| 06 | 4 | 20 | 77 | 5 | 12 | 83 |
| Total data | 9 | 32 | 59 | 10 | 21 | 69 |

684

685