Carbon cycling in Tokyo Bay

メタデータ	言語: English 出版者: 公開日: 2015-06-24 キーワード (Ja): キーワード (En): 作成者: 久保, 篤史 メールアドレス: 所属:
URL	https://oacis.repo.nii.ac.jp/records/1086

Doctoral Dissertation

CARBON CYCLING IN TOKYO BAY

March 2015

Graduate School of Marine Science and Technology

Tokyo University of Marine Science and Technology

Doctoral Course of Applied Marine Environmental Studies

Atsushi Kubo

CARBON CYCLING IN TOKYO BAY

By

Atsushi Kubo

This dissertation is submitted in partial fulfillment of

the requirements for the degree of

Doctor of Marine Science

Tokyo University of Marine Science and Technology

March 2015

Contents

Chapter 1. General Introduction

1.1. Global Carbon Reservoirs 2

1.2. Global Carbon Cycle 3

1.3. Carbon Cycle in Open Oceans 4

1.4. Carbon Cycle in Coastal Waters 6

Chapter 2. Description of Tokyo Bay

2.1. General Features 14

2.2. Water Environment 14

2.3. Sedimentary Environment 15

2.4. Purpose 17

Chapter 3. Biogeochemical Characteristics of the Water Column in Tokyo Bay

3.1. Introduction 25

3.2. Data and Methods 25

3.3. Results and Discussion 27

3.4. Summary 31

Chapter 4. Carbon Budget of Tokyo Bay Estimated by the Box Model

4.1. Introduction 51

4.2. Methods 52

4.2.1. Data for Box Model Analysis 52

4.2.1. Box Model Analysis 53

4.3. Results and Discussion 57
4.4. Summary 60

Chapter 5. Seasonal Variations and Sources of Sedimentary Organic Carbon in Tokyo Bay

5.1. Introduction 71
5.2. Materials and Methods 72
  5.2.1. Sample Collection 72
  5.2.2. Sample Analysis 73
5.3. Results 74
5.4. Discussion 75
  5.4.1. Seasonal Variation of Sedimentary Organic Carbon 75
  5.4.2. Sedimentary Organic Carbon Sources 76
    5.4.2.1. End-Member Estimation Using the TOC/TN Ratio (Model I) 77
    5.4.2.2. End-Member Estimation Using POC and Chl *a* Data (Model II) 78
    5.4.2.3. Sedimentary Organic Carbon Budget 79
5.5. Summary 80

Chapter 6. Nepheloid Layers and Lateral Carbon Export from Tokyo Bay Mouth

6.1. Introduction 96
6.2. Data 98
6.3. Results and Discussion 98
  6.3.1. Nepheloid Layer Distribution 98
  6.3.2. Quantifying Lateral Carbon Export in the Bottom Nepheloid Layer 99

6.4. Summary 101

Chapter 7. Seasonal Variations in Concentration and Lability of Dissolved Organic Carbon in Tokyo Bay

7.1. Introduction 115

7.2. Materials and Methods 116

7.3. Results and Discussion 119

7.3.1. Nutrient conditions in Tokyo Bay 119

7.3.2. Lability and Sources of Freshwater DOC Flowing into Tokyo Bay 119

7.3.3. Tokyo Bay 122

7.3.3.1. Lability of DOC 122

7.3.3.2. RDOC Sources 124

7.3.4. Change of DOC Over Four Decades 129

7.4. Summary 131

Chapter 8. Conclusions and Future Direction

8.1. Conclusions 150

8.2. Future Direction 151

Acknowledgments 157

References 159

Appendix 197

［課程博士・論文博士共通］

博士学位論文内容要旨
Abstract

専　攻 Major	応用環境システム学	氏　名 Name	久保　篤史
論文題目 Title	Carbon cycling in Tokyo Bay		

沿岸海域は、海洋全体の 10% にも満たない面積にも関わらず、炭素循環に大きな役割を果たしている。陸域起源の栄養塩が大量に供給されるため、沿岸海域で行われる一次生産は海洋全体の 20～30% を占めている。陸域起源有機物の供給に加え、内部生産由来の有機物が大量に供給されるため、沿岸海域で堆積する有機物量は海洋全体の約 80% を占めている。さらに、陸域起源有機物の分解による二酸化炭素生成と内部生産による二酸化炭素消費により溶存無機炭素濃度も大きく変動する。このように、沿岸海域における炭素循環は、陸域からの負荷と活発な生物活動によりダイナミックに変動している。しかし、沿岸海域における物質循環研究は栄養塩類に着目したものが多く、炭素循環について詳細に観測が行われた例は少ない。現在、世界人口の約 50% が沿岸域に住んでおり、大都市の大部分は沿岸域に位置している。沿岸域に位置した大都市の数は増加しており、2025 年までに現在の 2 倍になるといわれている。しかし、炭素循環研究が行われているのは人為起源炭素の影響が少ない海域が多く、大都市に隣接した沿岸海域に関する研究例はほとんどない。本研究では、世界的にみても巨大な都市である東京を流域に持つ東京湾における炭素循環を明らかにすることを目的とした。

本論文は 8 章からなっている。第 1 章では、研究の背景である海洋における炭素収支・炭素循環についてまとめた。第 2 章では、これまで東京湾で得られていた炭素循環に関する知見をまとめた。

第 3 章では、東京湾全域における溶存無機炭素、溶存有機炭素、粒状有機炭素の時空間変動を調べた。東京湾は春季から夏季にかけて水柱の成層化が進む。この時期は、表層で溶存有機炭素、粒状有機炭素、クロロフィル *a* が高濃度となっており、底層にいくにつれて減少していた。一方、溶存無機炭素は表層で低濃度、底層で高濃度となっていた。これらは陸域からの有機物負荷に加え、湾内での活発な生物活動による有機物生成および溶存無機炭素消費の影響であると考えられた。さらに、有機物が沈降し分解されることにより、底層では貧酸素水塊が形成され、溶存無機炭素が高濃度となっていた。一方、秋季から冬季にかけて水柱の鉛直混合が起き、成層構造は解消され、全てのパラメーターは鉛直的にほぼ均一となっていた。また、溶存有機炭素、粒状有機炭素、クロロフィル *a* 濃度は春季から夏季に比べて低くなっていた。

第 4 章では、第 3 章で得られたデータから東京湾におけるボックスモデルを作成し炭素収支を推定した。東京湾における純群集生産量は 19×10^{10} gC year^{-1} であった。これは、1970 年代から 1980 年代における純群集生産量の 3 分の 1 程度、1990 年代から 2000 年代の結果とほぼ同程度であった。これは、東京湾におけるクロロフィル *a* 濃度の長期変動と同様の傾向であった。東京湾における有機炭素の堆積量は 3.1×10^{10} gC year^{-1} であり、1980 年の堆積量と同程度であった。

第 5 章では、東京湾堆積物中の有機炭素含有量の季節変化を調べ、堆積物中の有機炭素含有量/有機窒素含有量比と炭素安定同位体比から有機炭素の起源推定を行った。有機炭素含有量は夏季に高く、冬季に低くなっていた。これは、水柱での内部生産と貧酸素水塊の影響によるものだと考えられた。内部生産の高い夏季に、底層への内部生産由来有機炭素の供給量が増加する。また、一部の有機炭素は貧酸素条件下で

は分解が進まないことが知られている。そのため、貧酸素水塊形成時には一部の有機炭素が分解されずに堆積物表層に蓄積していると考えられた。東京湾堆積物中の有機炭素の起源推定を行った結果、陸域起源有機炭素は約30%であり、堆積量は0.9×10^{10} gC year^{-1}であった。これは、陸域からの粒状有機炭素負荷量の約50%であった。一方、内部生産由来の有機炭素は約70% (2.2×10^{10} gC year^{-1}) であり、純群集生産量の約12%であった。

第6章では、湾口底層部に形成される高濁度層内の粒状有機炭素濃度から湾外への有機炭素輸送量を見積もった。高濁度層内の粒状有機炭素濃度は光束透過率と非常に良い相関がみられ、高濁度層の形成に粒状有機炭素が寄与していることが示唆された。また、高濁度層内の粒状有機炭素の炭素安定同位体比は湾口中層部の値より高く、湾内堆積物の炭素安定同位体比と同程度であった。沈降粒子中の有機物の炭素安定同位体比は表層で高く、底層にいくにつれ低下することが知られている。そのため、湾口表層で生成された有機物が沈降・分解を経て供給されたものではなく、東京湾堆積物の再懸濁により湾外へ流出しているものだと考えられた。この有機炭素輸送量を見積もったところ0.029×10^{10} gC year^{-1} であり、東京湾内における有機炭素堆積量の<1%であった。

第7章では、東京湾表層海水における易分解性溶存有機炭素と難分解性溶存有機炭素の季節変化を明らかにし、さらに難分解性溶存有機炭素の起源推定を行った。易分解性、難分解性溶存有機炭素共に春季から夏季にかけて高く、秋季から冬季にかけて低くなっていた。これは陸域起源の溶存有機炭素供給と内部生産由来の溶存有機炭素供給によるものだと考えられた。また、易分解性溶存有機炭素は東京湾海水の滞留時間に比べて非常に速い分解速度であったため、大部分が湾内で分解除去されていると考えられた。難分解性溶存有機炭素の時空間変動は、塩分とクロロフィル*a*によってある程度説明できることがわかった。そこで難分解性溶存有機炭素に対して、塩分とクロロフィル *a* を説明変数にとり、重回帰分析を行った。重回帰分析の結果から、難分解性溶存有機炭素の起源推定を行った。その結果、東京湾における難分解性溶存有機炭素は陸域起源、外洋水起源、植物プランクトン起源がそれぞれ21～32、59～69、8～10% であることが分かった。また、難分解性溶存有機炭素と易分解性溶存有機炭素濃度は1970年代と比べて39%、76%減少していた。東京湾における溶存有機炭素濃度の減少は東京湾流域で下水の整備が進んだことにより、流入する有機物量（特に易分解性溶存有機炭素）が減少したことと、湾内での内部生産量が低下したことによると考えられた。

第8章では、本研究で得られた成果についてまとめた。東京湾は陸域からの有機炭素負荷に加え、活発な生物活動により大量の有機炭素が生成していた。また、大気からの二酸化炭素吸収量と同程度の有機炭素が堆積していた。堆積物中の有機炭素は約70%が内部生産由来有機炭素であり、陸域起源有機炭素の寄与は約30%であった。また、湾口底層部では堆積物の再懸濁により高濁度層が形成していたが、湾外への有機炭素輸送量は堆積量に対して非常に少なかった。東京湾表層から湾外への溶存有機炭素輸送は大部分が陸域起源難分解性溶存有機炭素であり、易分解性溶存有機炭素は湾内で大部分が分解していた。

Chapter 1

General Introduction

1.1. Global Carbon Reservoirs

Carbon is present in all four domains of the natural environment, the lithosphere, the atmosphere, the biosphere, and the hydrosphere (Figure 1-1). It is estimated that 5000–10,000 PgC of carbon is stored in fossil fuels (Sundquist, 1993; Bianchi, 2007; Houghton, 2007). In the atmosphere, the smallest amount of carbon is present in the form of carbon dioxide (CO_2), with approximately 780 PgC being present in the 1990s (Sundquist, 1993; Houghton, 2007), although this value increased to 828 PgC in 2011. In addition, other carbon-containing gases (e.g., methane, carbon monoxide, and non-methane hydrocarbons) are either directly or indirectly important to the Earth's radiative balance (Houghton, 2007; IPCC, 2013). However, these gases are often ignored from the perspective of the global carbon balance (Houghton, 2007). A comparative amount of roughly 550 PgC is typically found in terrestrial biota (Sundquist, 1993; Houghton, 2007), while about 1200 PgC is stored in soil and 300 PgC in litter (Schlesinger, 1977; Houghton, 2007). Forests are particularly important as carbon reservoirs because trees hold much more carbon per unit area than other types of vegetation (Houghton, 2007). Terrestrial gross primary production (GPP) shows the largest global CO_2 flux of 120 PgC $year^{-1}$ (Beer et al., 2010; Guanter et al., 2014). The total amount of carbon in the ocean is approximately 38,000 PgC (Houghton, 2007; Hansell et al., 2009), most of which is in intermediate and deep waters, while only 700–1000 PgC is in direct contact with the atmosphere. The dissolved organic carbon (DOC) pool in the surface ocean (0–200 m) contains 47 PgC (Hansell et al., 2009), while living organisms contains only 3 PgC (Houghton, 2007; Hansell et al., 2009). There are also 3000–6000 PgC of reactive carbon within the open ocean sediments (Sundquist, 1993; Bianchi, 2007; Houghton, 2007), which, although important to determining the long-term concentration of CO_2 in the atmosphere and oceans, are less important to the short-term carbon cycle. Overall, the ocean contains about 70 times more carbon than the terrestrial biota and about 50 times more carbon than the atmosphere.

1.2. Global Carbon Cycle

The pre-industrial atmosphere was in a near steady-state with regard to the inputs and outputs of CO_2. However, these fluxes would not have been individually balanced because rivers transport around 0.7–0.8 PgC year^{-1} (Siegenthaler and Sarmiento, 1993) from the land into the ocean. To maintain a steady state, the vast majority of riverine carbon must have been outgassed to the atmosphere, making the ocean a net source of carbon in pre-industrial times (Watson and Orr, 2003).

Recent increases in atmospheric CO_2 have unbalanced the carbon exchanges of pre-industrial times (Siegenthaler and Sarmiento, 1993; Schimel et al., 2000). Anthropogenic activities have led to considerable anthropogenic emissions of CO_2 of ~11 PgC year^{-1} due to fossil-fuel combustion (8.3 PgC year^{-1}) and tropical deforestation (0.6–2.5 PgC year^{-1}) (Keeling, 1995; Siegenthaler and Sarmiento, 1993; IPCC, 2013). However, the amount of CO_2 has only accumulated at 3.2 PgC year^{-1} (Houghton, 2007), while the remaining anthropogenic CO_2 has been taken up in part by the oceans (1.4–2.0 PgC year^{-1}), which have become a net sink (Siegenthaler and Sarmiento, 1993; Toggweiler, 1995; Schimel et al., 2000; Watson and Orr, 2003; Keeling et al., 2005; Takahashi et al., 2009; Wanninkhof et al., 2013). A recent analysis that employed an ocean tracer based method (Gruber et al., 1996) to separate anthropogenic CO_2 from measured dissolved inorganic carbon (DIC) concentrations revealed a cumulative oceanic sink of 140 PgC for the period 1850–2000 (Joos et al., 1999). There were some left of “missing carbon sink” (Walsh et al., 1981; Siegenthaler and Sarmiento, 1993). The general consensus places the sink in the terrestrial biosphere (Siegenthaler and Sarmiento, 1993; Schimel et al., 2000; Keeling et al., 2005); however, the magnitude of the terrestrial carbon sink is difficult to quantify and is thus normally calculated indirectly or inferred from changes in the atmospheric and oceanic stable carbon isotope ratio of DIC (Keeling et al., 2005). Using the difference in land-use change and residual terrestrial sink, the world’s terrestrial ecosystems were found to be a net source of 40 PgC from 1850 to 2000 (Table 1-1). Based on the above results, the ocean is currently the largest sink in the anthropogenic carbon budget.

1.3. Carbon Cycle in Open Oceans

Organisms at the surface of the ocean take up CO_2 through photosynthesis, while particulate organic carbon (POC) sinks into the deep ocean, where it is almost completely respired by bacteria, returning it to DIC pools (Giering et al., 2014). This transfer of carbon from the surface to the deep ocean across the permanent thermocline, which is known as the biological pump (Sarmiento and Bender, 1994), exerts a strong influence on the air-sea exchange of CO_2 by decreasing the partial pressure of CO_2 (pCO_2) at the surface of the ocean (Watson and Orr, 2003). The fundamental factors limiting primary production in the ocean are light, nutrient supply, and trace element availability. Nutrient profiles show significant depletion near the surface and enrichment at depth due to the biological pump; therefore, upwelling or vertical mixing of nutrient rich water fuels phytoplankton growth (Raven and Falkowski, 1999). Global primary production can be estimated from satellite data using models based on chlorophyll biomass, temperature, and photosynthetically active radiation (Figure 1-2; Field et al., 1998). This satellite derived view (Figure 1-2) tends to show that high primary production occurs in regions of nutrient rich waters at the equator, high latitude, and coastal waters. The magnitude of global primary production has been estimated to be approximately 50 PgC year^{-1} (Field et al., 1998; Falkowski et al., 2003; Chavez et al., 2011). Freshly produced organic carbon is not only exported as a sinking flux, but also channeled through the grazing food chain, respired in the microbial loop, and stored as DOC (Figure 1-3; Azam et al., 1983; Azam, 1998). Based on sediment trap data, the flux that reached the aphotic zone comprises approximately 20–30% of primary production (Laws et al., 2000; Falkowski et al., 2003; Henson et al., 2011). The basis of the microbial food web is that large amounts of DOC are released extra-cellularly, primarily from prokaryotes and eukaryotes (Bjørnsen, 1988; Jumars et al., 1989; Nagata and Kirchman, 1990; Nagata and Kirchman, 1991; Nagata and Kirchman, 1992). This DOC returns to the main food chain via bacterial uptake, followed by flagellate and ciliate grazing. The microzooplankton can then be grazed on by macrozooplankton, resulting in channeling of the energy back to the classic grazing food chain. The microbial loop is a dynamic system driven by competition for nutrients between phytoplankton and bacteria (Cotner and Biddanda, 2002), predation (Fenchel, 1982), and viral infections (Riemann and Middelboe, 2002). The microbial loop appears to cycle approximately 10–20% of the DOC in any given system (Hedges, 2002).

The microbial carbon pump (MCP) has recently been proposed as a conceptual framework for understanding the role of microbial processes in recalcitrant DOC (RDOC) generation (Ogawa et al., 2001) and relevant carbon storage in the ocean (Figure 1-4; Jiao et al., 2010). Currently, long-term storage of carbon as RDOC is not explicitly addressed in the biological pump. Moreover, conventional interpretation of the biological pump emphasizes the vertical transport of carbon (either POC or DOC) from the euphotic zone to the deep ocean, whereas the MCP stresses the formation of RDOC, which can persist at any depth in the water column and in any regions, including the euphotic zone and coastal waters (Jiao et al., 2010). The MCP can be tested for sources and transformations of DOC, the production of RDOC, the underlying biogeochemical mechanisms, and the consequences for subsequent biogeochemical states of the ocean (Jiao et al., 2010; Stone, 2010; Jiao and Azam, 2011; Dang and Jiao, 2014).

1.4. Carbon Cycle in Coastal Waters

Coastal water is a dynamic region in which the land, rivers, open ocean, and atmosphere interact (Walsh, 1988; Wollast, 1998; Bianchi, 2007; Cai, 2011; Canuel et al., 2012). Although coastal waters comprise less than 10% of the surface ocean, they play a considerable role in biogeochemical cycles because they: (1) receive massive inputs of terrestrial organic matter, DIC, and nutrients through river discharge; (2) exchange large amounts of matter and energy with the open ocean; (3) constitute one of the most geochemically and biologically active areas of the biosphere; and (4) exchange large amounts of CO_2 with the atmosphere (Gattuso et al., 1998; Chen et al., 2013). For example, coastal waters account for 14–30% of the oceanic primary production, 80% of organic burial, 90% of sedimentary mineralization, and 75–90% of the oceanic sink of suspended river load (Mantoura et al., 1991; Pauly and Christensen, 1995; Field et al., 1998; Gattuso et al., 1998). Among sources of inorganic carbon, estuaries release CO_2 from the water to the atmosphere at levels corresponding to 6–31% (Chen and Borges, 2009; Laruelle et al., 2010; Cai, 2011; Chen et al., 2013; Laruelle et al., 2014) of the total open oceanic CO_2 uptake from the atmosphere (1.6 PgC year; Takahashi et al., 2009). In contrast, continental shelves take up CO_2 from the atmosphere at levels corresponding to 12–25% (Chen and Borges, 2009; Cai, 2011; Laruelle et al., 2014) of the total open oceanic CO_2 uptake from the atmosphere (1.6 PgC year; Takahashi et al., 2009). Thus, coastal water is disproportionately important to ocean carbon cycles and budgets. Despite its potential importance, the carbon budget of coastal waters has not been thoroughly investigated until recently (Moore et al., 1979; Mantoura and Woodward, 1983; Prahl and Coble, 1994; van Heemst et al., 2000; Cole et al., 2007; Maher and Eyre, 2012), and there have been few direct estimations of organic and inorganic carbon balance in coastal waters. In addition, most studies have focused on pristine coastal waters that have not been heavily impacted by human activity (Kemp et al., 1997; Maher and Eyre, 2012). However, carbon cycling is increasingly subject to human perturbation, and coastal waters are continuously modified by human activities through changing land and water uses, as well as increasing waste loading from economic activities (McManus, 2010). Today, over half of the world's population resides in urban areas, the majority of which are located in coastal zones (von Glasow et al., 2013). In 2009, 67% of all megacities were located in coastal areas, and this value is expected to increase by a factor of 2 by 2025 (United Nations, 2010). The Tokyo Metropolitan Area, which consists of Tokyo, Yokohama, Kawasaki, and Chiba, is the largest megacity in the world. Tokyo Bay is surrounded by this megacity. The total population of the drainage is about 29×10^6. Estimation of the carbon budget and cycling in this area surrounded by a megacity will improve our understanding of carbon cycling in coastal waters and the possible implications for urbanization in the future.

Table 1-1

The global carbon budget from 1850 to 2000 (modified from Hougton, 2007; Table 1).

Negative values indicate sink of carbon. Positive values indicate source of carbon.

	1850-2000 (PgC)	Reference
Emissions from fossil fuels and cement production	275	Keeling, 1973; Andres et al., 1999
Atmospheric increase	−175	IPCC,2013
Oceanic uptake	−140	Joos et al., 1999
Land-use change	156	Houghton, 2003
Residual terrestrial sink	−116	Houghton, 2007

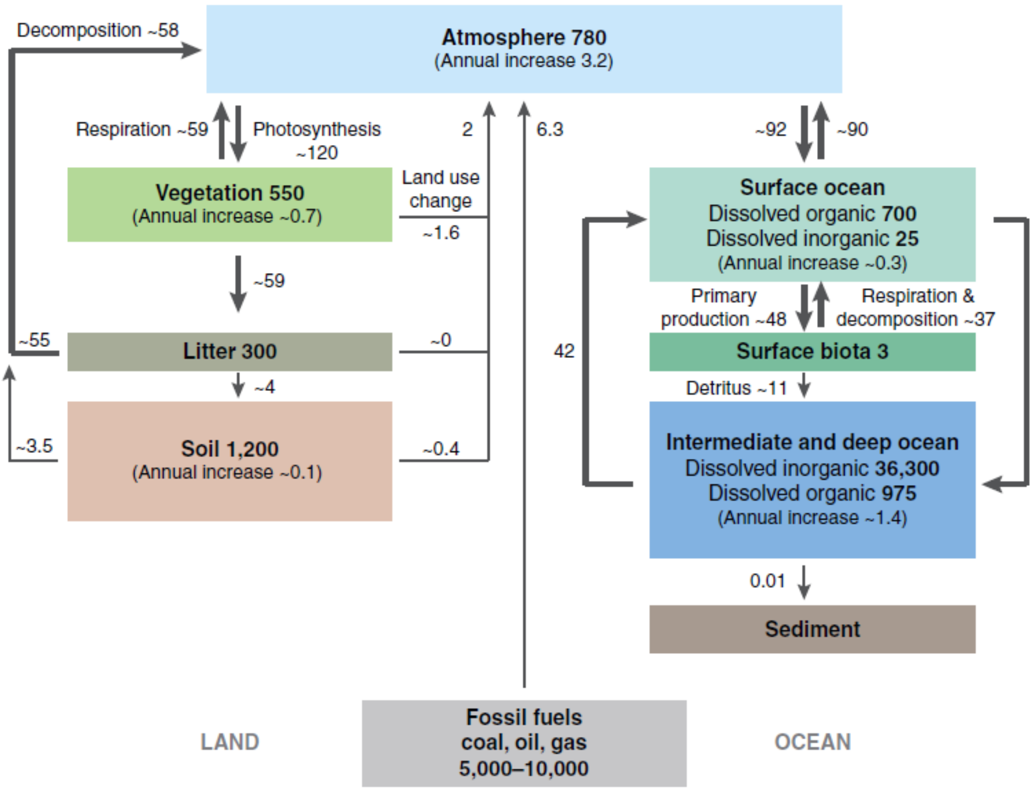

Figure 1-1
The global carbon cycle in the 1990s. Units are PgC or PgC year^{-1}. Arrows show flow of carbon (Houghton, 2007; Figure 1).

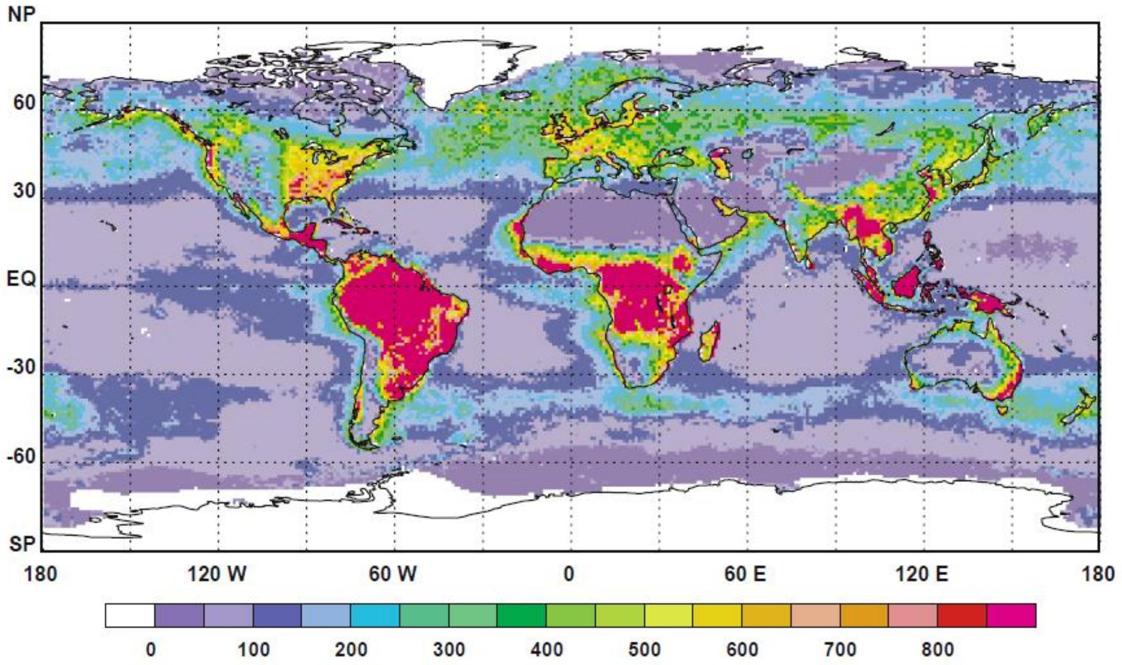

Figure 1-2
The global annual net primary production (NPP; gC m^{-2} year^{-1}) for the biosphere. Global NPP is 104.9 PgC year^{-1}, with 46.2% (48.5 PgC year^{-1}) contributed by the oceans and 53.8% (56.4 PgC year^{-1}) contributed by the land (Field et al., 1998; Figure 1).

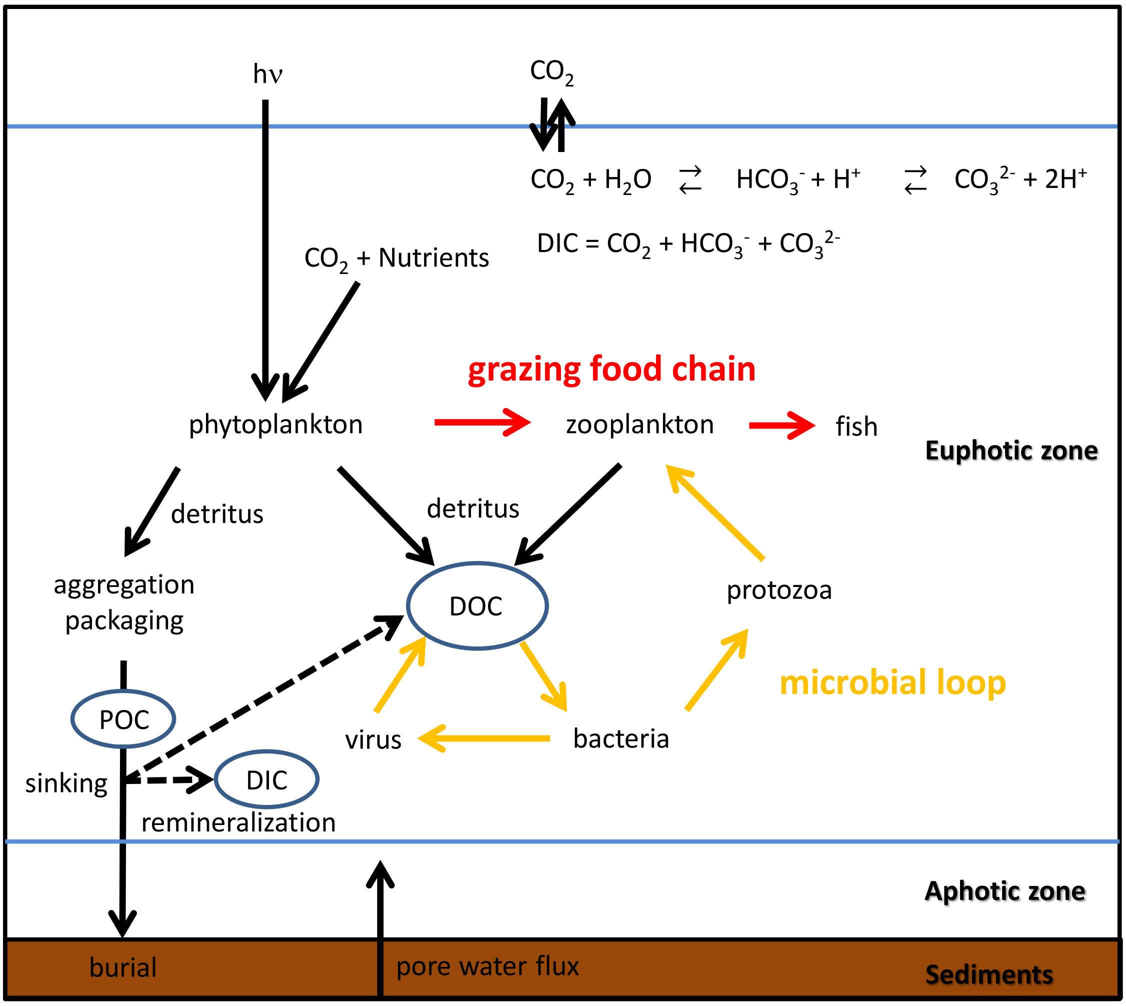

Figure 1-3
A simplified diagram of carbon flow including the grazing food chain and microbial loop. Arrows show flow of carbon.

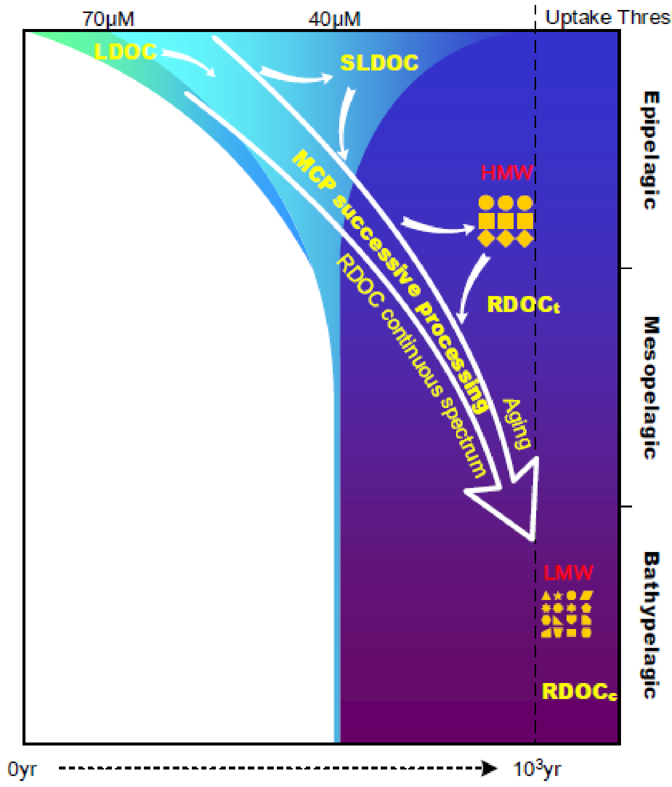

Figure 1-4
Linking RDOC at multiple dimensions: temporal (age) and spatial (depth) transformations of RDOC. Successive microbial processing of organic carbon results in the generation of RDOC of different recalcitrance and different potential residence time; MCP means microbial carbon pump, RDOCt means RDOC compounds that are resistant to microbial consumption in certain environments, but subject to further cleaving and decomposition when the situation changes; RDOCc composed of diverse small molecules which are inaccessible to microbial uptake due to their low concentration (Jiao et al., 2014; Figure 1).

Chapter 2

Description of Tokyo Bay

2.1. General Features

Tokyo Bay is located in central Japan, and the inner part of the bay is a semi-enclosed embayment with an area of about 920 km^2, a mean water depth of 19 m, and a water volume of about 17 km^3. The bay is connected to the North Pacific through the Uraga Strait (also referred to as the bay mouth). Although the bay mouth has an area of 400 km^2 (Figure 2-1), it is only 7 km wide, and water exchange between the bay and the open ocean is restricted. The residence time of the bay water is estimated to be 30–50 days (Unoki and Kishino, 1977; Okada et al., 2007). As shown in Figure 2-1, several rivers flow into the bay with a total discharge of rivers and the sewage treatment plants (STPs) directly into Tokyo Bay of 11 km^3 year^{-1} and 1.6 km^3 year^{-1}, respectively (Matsumura and Ishimaru, 2004), which is comparable to 75% of the bay volume. As a result, the water and sediments of Tokyo Bay are subject to various degrees of pollution due to the disposal of urban and industrial wastes and contaminated agricultural runoff.

2.2. Water Environment

Tokyo Bay has suffered from severe cultural eutrophication since the late 1950s. The input rate of organic matter and nutrients into the bay increased remarkably with human activities in the 1960s (Kamatani and Maeda, 1989), and this increase continued for the next two decades (Hattori et al., 1983; Ogawa and Ogura, 1990b). However, a law restricting the discharge of organic pollutants with high chemical oxygen demand (COD) was enacted in 1970. In addition, technical advances (e.g., improved sewage treatment and the use of phosphorus-free detergent) have reduced organic pollutant discharge into the bay (Hattori, 1983; Hattori et al., 1983). Hence, COD loading decreased significantly from 580 ton day^{-1} to 320 ton day^{-1} from 1980 to 2000 (Figure

2-2; Central Environmental Council, 2010). As a result, organic carbon concentrations in Tokyo Bay decreased from the late 1970s to the 1990s (Ogawa and Ogura, 1990b; Kawabe and Kawabe, 1997). Nutrient concentrations in Tokyo Bay have also decreased from the 1980s to the present (Esumi, 1979; Ogawa and Ogura, 1990b; Nomura, 1995; Ando et al., 1999; Matsumura et al., 2003; Ando et al., 2005; Kanda et al., 2008). As a result, primary production in surface water of the bay decreased by a factor of three from 1972 to 2002 (Funakoshi, 1974; Yamaguchi ant Shibata, 1979; Yamaguchi et al., 1991; Itoh, 2003; Bouman et al., 2010). However, phytoplankton growth is still not limited by nutrient concentrations, and phytoplankton blooms persist throughout the year. Hence, Tokyo Bay is a strong net sink for carbon dioxide because photosynthesis exceeds the degradation of terrestrial organic carbon in the system (Kubo, 2011; Kubo et al., in prep). The annual CO_2 flux in Tokyo Bay was calculated to be -5.2×10^{10} gC year^{-1} (Kubo et al., in prep; Figure 2-3). Moreover, anoxic bottom waters consistently appear in summer. Indeed, oxygen conditions in bottom waters have not improved since the 1980s, despite the decreasing nutrients and organic matter load from land (Ando et al., 2005; Ishii and Ohata, 2010).

2.3. Sedimentary Environment

The distribution of the sedimentation rate determined by the ^{210}Pb method in Tokyo Bay is presented in Figure 2-4 (Matsumoto, 1985). The sedimentation rates decrease southward and eastward from the northwest part of the bay. The bay mouth region contains no deposition and consists entirely of relict sand and tertiary rock. Conversely, the higher rate observed in the northwest region suggests dynamic depositional events caused by terrestrial substances carried by main rivers. The distribution of total organic carbon contents (TOC_{sed}; %) in the bay is presented in Figure 2-5 (Matsumoto, 1985). The TOC_{sed} had the same distribution as the sedimentation rate, the annual sedimentation rate was 4.2×10^{10} gC $year^{-1}$ and the average TOC_{sed} was about 3% for the entire bay in 1980 (Figure 2-2; Matsumoto, 1985), when organic carbon loading into the bay was largest.

Ishiwatari et al. (1983) pointed out that pollution by detergent started around the 1960s based on the vertical profile of alkylbenzenes in sediment cores. Contamination associated with large amounts of terrestrial and anthropogenic substances are an increasingly urgent concern in Tokyo Bay. Indeed, several studies have shown higher concentrations of coprostanol (indicator of fecal waste; Ogura and Ichikawa, 1983; Ogura, 1983), linear alkylbenzenesulphonates (indicator of synthetic detergent; Ishiwatari et al., 1983; Takada et al., 1992; Chalaux et al., 1995), trialkylamines (indicator of surface activating agent; Ishiwatari, 2003), fluorescent whitening agents (Hayashi et al., 2002; Managaki and Takada, 2005), perfluorooctanoate (indicator of surface activating agent; Ahrens et al., 2010; Sakurai et al., 2010; Zushi et al., 2011), and inositol hexaphosphate (indicator of soil; Suzumura and Kamatani, 1995) in the bay. In addition to terrestrial and anthropogenic substances, bay sediments receive and accumulate large amounts of organic matter produced by primary production in the water column (Wada et al., 1990; Ogawa and Ogura, 1990a; Ogawa et al., 1994; Ogawa and Ogura, 1997). Many of the terrestrial and planktonic substances decompose and regenerate in sediments during early diagenesis. Decomposition of organic matter is accompanied by oxygen depletion. In bottom waters oxygen depletion during summer and autumn leads to the release of nutrients and dissolved organic matter from sediments to bay waters; accordingly, sediments play significant roles as both sinks and sources of organic matter in the bay.

2.4. Purpose

Highly urbanized coastal aquatic systems are rapidly expanding worldwide (Nellemann et al., 2008). Therefore, it is essential to understand the carbon cycling and predict future carbon budgets in coastal waters so that the carbon budget in highly urbanized coastal waters can be understood.

This thesis was conducted to evaluate the carbon budget and cycling in Tokyo Bay, Japan, which is a typical highly urbanized coastal system.

There have been numerous reports of nutrients in Tokyo Bay, but few studies of both inorganic and organic carbon. Hence, the first objective of this thesis was to determine the spatial and temporal variations in the water column DIC, DOC, POC, and carbon isotope ratio of POC ($\delta^{13}C_{POM}$) of the entire Tokyo Bay (Chapter 3). In Chapter 4, the carbon budget was evaluated from a box-model using the data from Chapter 3.

The sedimentary organic carbon sources estimated from sedimentary carbon contents and their carbon isotope ratios were then elucidated (Chapter 5), and the boundary nepheloid layer carbon transport from the bay mouth to the deep ocean was measured (Chapter 6).

Finally, recalcitrant and bioavailable DOC in Tokyo Bay throughout the year was qualified and quantified (Chapter 7). In addition the results were compared with previous data generated by Ogura (1975) to determine how the lability of DOC in Tokyo Bay has changed with time.

Table 2-1

Results of the Mann-Kendall tests for the temporal trends of nutrients and chlorophyll *a* (Chl *a*). Decreasing and increasing trends with significance are shown as “-” and “+”, respectively. “**” indicate significance level at a=0.01 and “*” at a=0.05. “±” indicates that no significance trends are detected (Kanda et al., 2008; Table 1).

Depth (m)	F3						F6					
	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	$Si(OH)_4$	Chl *a*	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	$Si(OH)_4$	Chl *a*
0	–**	–*	–**	–**	–*	±	–**	±	–**	–*	–*	±
5	–**	–**	–**	±	–**	–*	–**	±	–*	±	–*	–**
10	–**	–**	–*	±	±	–**	–*	±	±	±	±	–**
15	–**	–**	–*	±	±	–**	–*	±	±	±	±	–**
20	–**	–*	±	±	±	–**	–**	±	±	±	±	–**
25							–*	+**	±	±	±	–*
integrated	–**	–**	–**	±	±	–**	–**	±	±	±	±	–*

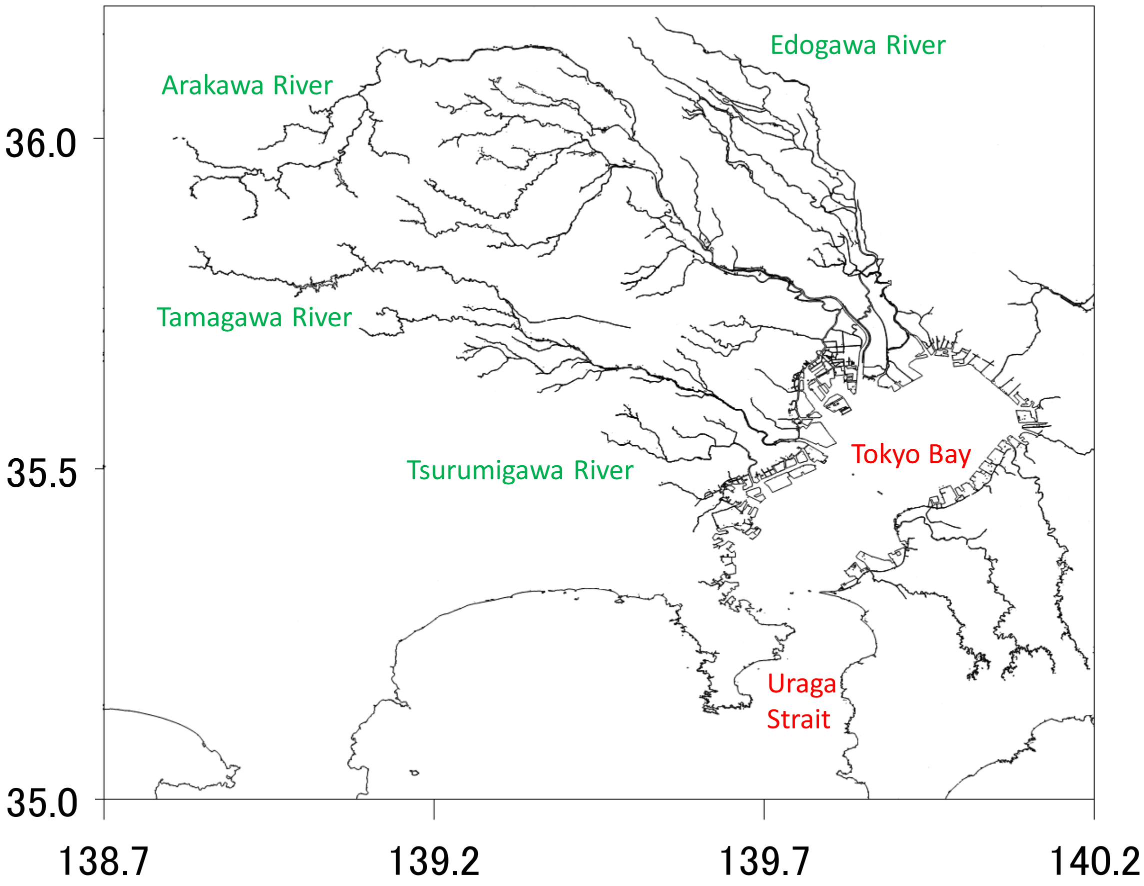

Figure 2-1
Map of Tokyo Bay.

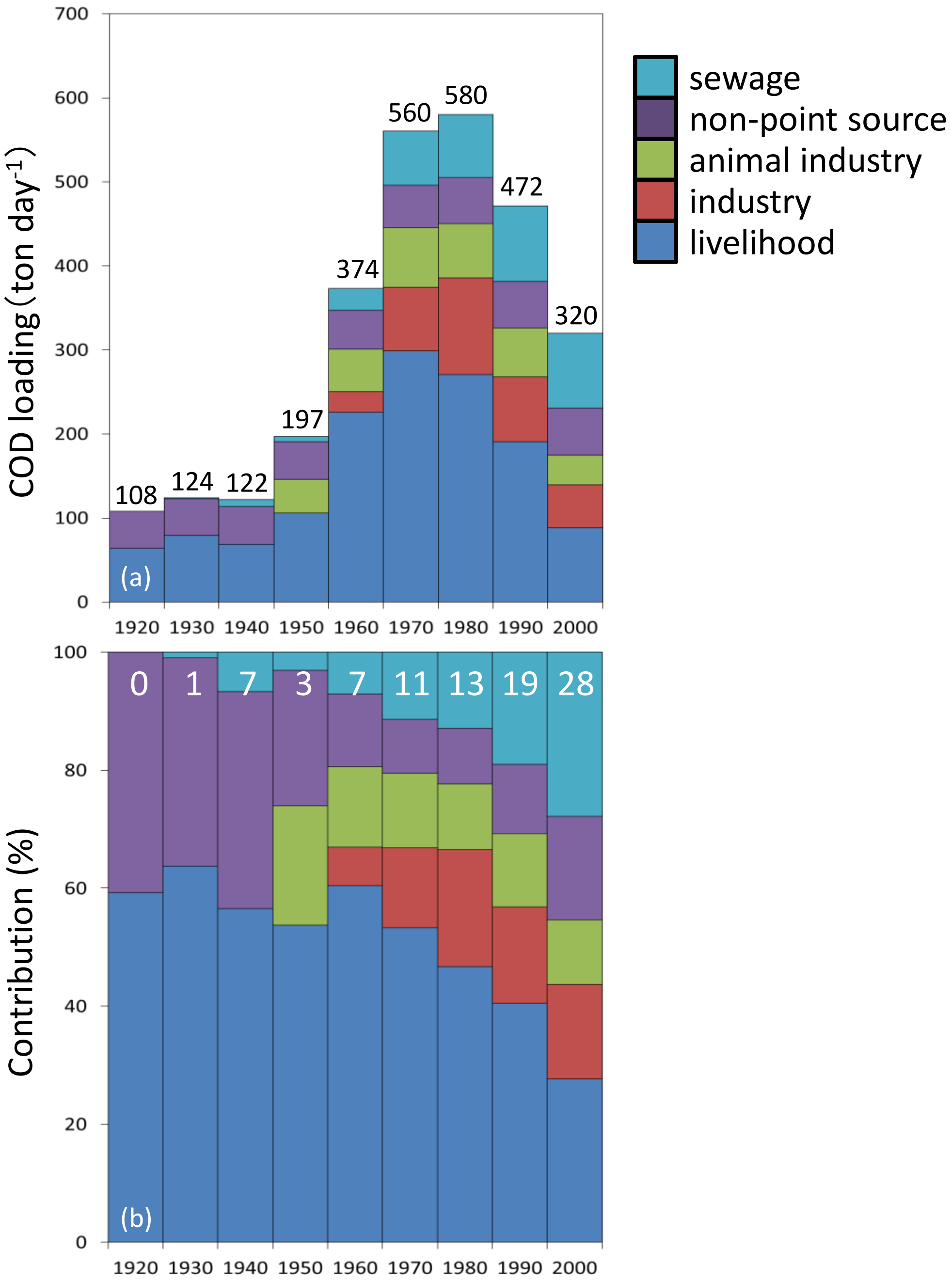

Figure 2-2

(a) COD loading into Tokyo Bay. Black numbers show total COD loading (ton day^{-1}).

(b) Contribution of each sources. White numbers show contribution of sewage (%) (This figures are based on the data of National Institute for Land and Infrastructure Management, 2004.)

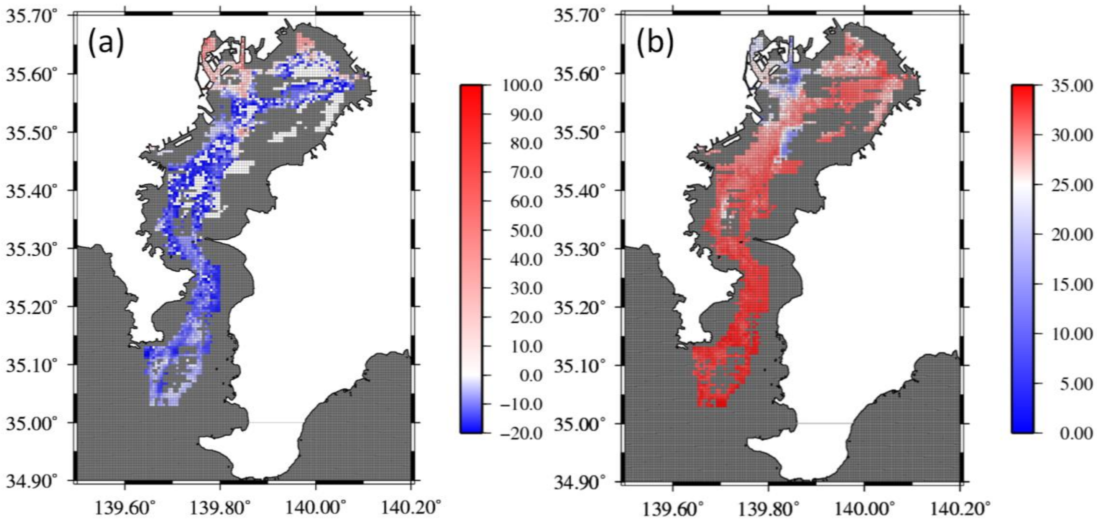

Figure 2-3
Map of (a) sea-air CO_2 flux (mmol C m^{-2} day^{-1}) and (b) salinity binned into 500 m × 500 m horizontal resolution grid. Positive flux values (red) represent outgassing of CO_2 to the atmosphere and negative values (blue) represent uptake (Kubo et al., in prep).

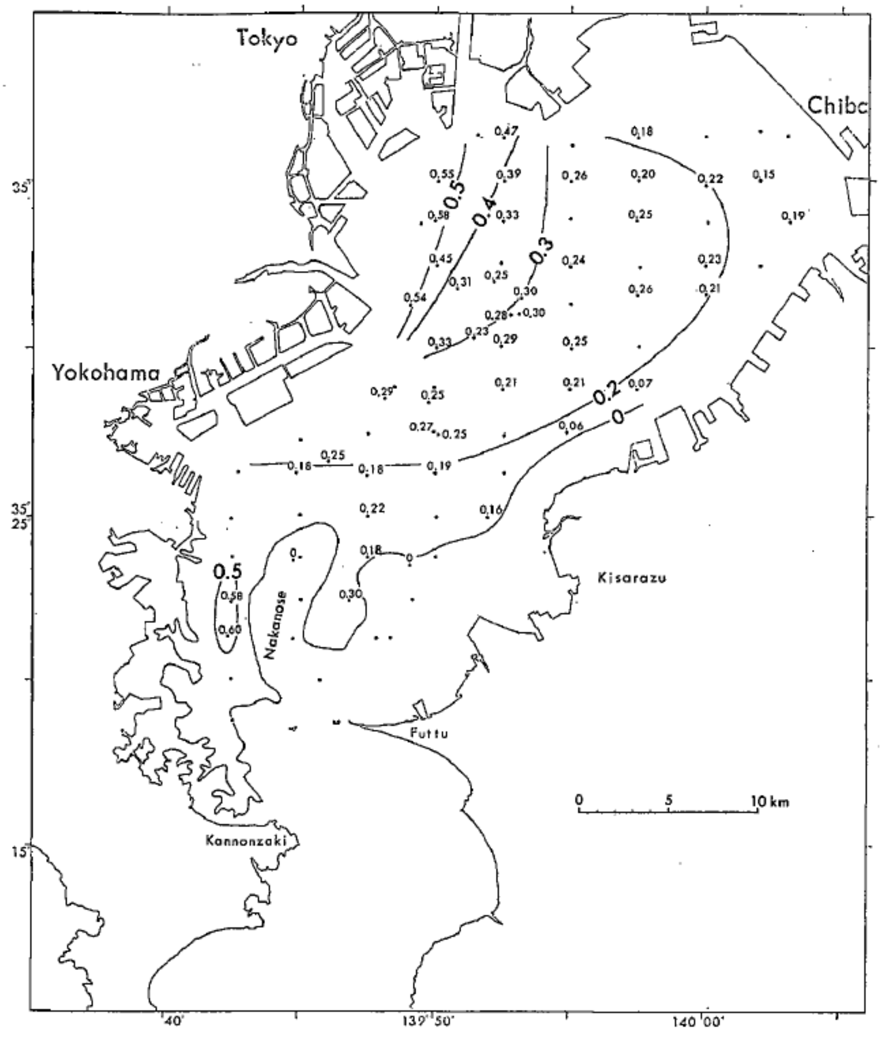

Figure 2-4
Sedimentation rates (g cm^{-2} year^{-1}) in Tokyo Bay during September 1980 and August 1981 determined by ^{210}Pb method (Matsumoto, 1985; Figure 2).

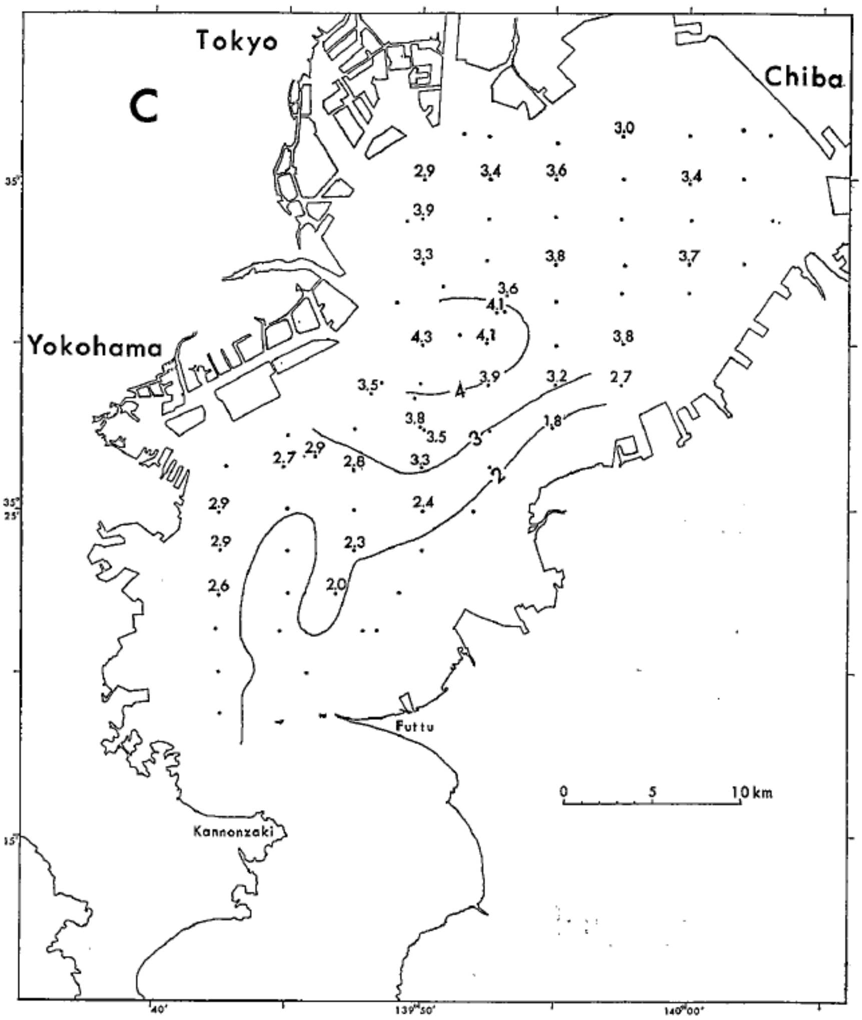

Figure 2-5
Distribution of total carbon contents (%) in the surface sediments (0-5 cm) of Tokyo Bay during September 1980 and August 1981 (Matsumoto, 1985; Figure 4) .

Chapter 3

Biogeochemical Characteristics of the Water Column in Tokyo Bay

3.1. Introduction

Coastal waters play a significant role in biogeochemical cycles because coastal areas act as interfaces for the exchange of organic and inorganic carbon between land and the open ocean. Moreover, coastal waters usually have very high biological productivity reflecting nutrient inputs from the land. Despite the great importance of coastal waters, their carbon budgets and cycles have not yet been clarified in detail (Kemp et al., 1997; Maher and Eyre, 2012).

The nitrogen and phosphorus budget for all of Tokyo Bay has already been reported (Matsukawa and Suzuki, 1985; Matsumura, 2000: Matsumura et al., 2002); however, there is no observation dataset for carbon in the entire the bay. Rather, organic carbon observations have only been carried out on the inner part of the surface of the bay throughout year (Ogura et al., 1975a, Ogura et al., 1975b, Ogura et al., 1986; Ogawa and Ogura, 1990a, Ogawa and Ogura, 1990b, Ogawa and Ogura, 1997; Suzumura et al., 2004; Maki et al., 2007) and the entire surface of the bay during summer (Suzumura and Ogawa, 2001). In addition, limited DIC observations were made by Yamamoto-Kawai et al. (in review) and Kubo et al. (in prep). Moreover, most river data for organic and inorganic carbon flowing into the bay are limited to data collected from the 1970s to the early 1990s, when the rivers were most polluted (Ogura et al., 1975a; Takada and Ogura, 1992; Takada et al., 1992; Ogawa and Ogura, 1997). Therefore, this chapter examines spatial and temporal variability of DIC, DOC, and POC to clarify the causes of carbon variations in Tokyo Bay.

3.2. Data and Methods

Freshwater and brackish water samples from the lower Arakawa River, the lower

Tamagawa River, the Shibaura STP effluent, and the Tokyo port entrance (TPE) station were collected monthly from May 2011 to May 2012 (Figure 3-1). Surface water samples were collected using a bucket, while temperature and salinity were measured in the field using a YSI EC 300 (YSI/Nanotech Inc., Yellow Springs, OH, USA). Moreover, seawater samples of Tokyo Bay were collected in 8-L Niskin bottles mounted on a CTD (Falmouth Scientific Inc., Bourne, MA, USA) rosette on the R/V Seiyo-maru from May 2011 to May 2012 monthly at eight stations (Figure 3-1). The CTD was lowered to within 5 m of the bottom. Dissolved oxygen (DO) was measured with a DO meter (Rinko-III ARO-CAV, JFE Advantech, Hyogo, Japan) onboard the CTD. DIC samples were fixed with 100 μL of $HgCl_2$ (JIS Special Grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan), then stored at room temperature until analysis, at which time they were analyzed at least in triplicate with a TOC analyzer (TOC-V_{CSH}; Shimadzu Corp., Kyoto, Japan) in IC (Inorganic Carbon) mode. Measured values were calibrated against standard reference material for DIC analysis of General Environmental Technos. DOC samples were filtered through pre-combusted (450°C for 3h) GF/F filters (nominal pore size; 0.7 μm, GE Healthcare Life Sciences, Piscataway, MJ, USA) and acidified with 300 μL of 6N HCl (Amino Acid Automated Analysis Grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan), then stored at 5°C until analysis. DOC samples were measured at least in triplicate with a TOC analyzer (TOC-V_{CSH}) in NPOC (Non-Purgeable Organic Carbon) mode. POC and $\delta^{13}C_{POM}$ samples were vacuum filtered through pre-combusted (450°C for 3h) GF/F filters, then wrapped in foil and frozen at −80°C until analysis. POC and $\delta^{13}C_{POM}$ samples were dried at 60°C and acidified with vapor at 12 mol L^{-1} HCl to remove carbonate before analysis. The filters were subsequently packed into tin foil (43×43 mm 168 mg, Elemental Microanalysis, Devon, UK). Prepared sample concentrations and stable isotope ratios were determined using a continuous flow isotope ratio mass spectrometer (ANCA-GSL, SerCon, Crewe, UK). Ratios of $^{13}C/^{12}C$ were expressed relative to the PeeDee Belemnite (PDB) standard after calculation as follows:

$$\delta^{13}\mathrm{C} = \left\{\left(\mathrm{R}_{\mathrm{sample}}/\mathrm{R}_{\mathrm{standard}}\right) - 1\right\} \times 1000 \qquad (3\text{-}1)$$

where $R = ^{13}C/^{12}C$. Machine drift during analyses was checked with L-α-alanine ($\delta^{13}C$ = −20.9‰; JIS Special Grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan) every five samples. Chlorophyll *a* (Chl *a*) samples were filtered through precombusted (450°C, 3h) GF/F filters. After filtration, chlorophyllous pigments were extracted using N, N-dimethylformamide (JIS Special Grade; Wako Pure Chemical Industries, Ltd., Osaka, Japan), and the concentrations of Chl *a* were determined by the fluorometric method (Suzuki and Ishimaru, 1990) using a fluorometer (TD-700, Turner Designs, Sunnyvale, CA, USA).

3.3. Results and Discussion

At freshwater sites, DOC was higher than that of Tokyo Bay (Tables 3-1–3-4), with the highest DOC being observed at the Shibaura STP. The values of DIC, POC, and $\delta^{13}C_{POM}$ were lower than those of Tokyo Bay (Tables 3-1–3-4). In addition, there were no distinct seasonal patterns of these parameters in freshwater sites. At the Shibaura STP, $\delta^{13}C_{POM}$ and Chl *a* were constant throughout the year.

The spatial distributions of temperature, salinity, and DO in Tokyo Bay during July 2011 and December 2011 are presented in Figures 3-2 and 3-3, respectively (all data are available in the Appendix Figure A1-1–1-8). In the inner surface water, temperature was higher and salinity was lower than in the central bay and bay mouth throughout the year. Moreover, significant seasonal stratification was observed in July. In the inner bay, the bottom oxygen concentration gradually decreased to almost zero from June to September. Bottom hypoxic water mass was widespread in August and September from the inner to the central bay. In contrast, the water was completely mixed from surface to bottom in the bay during December and February.

The spatial distributions of Chl *a*, DIC, DOC, POC, and $\delta^{13}C_{POM}$ in July 2011 and December 2011 are presented in Figures 3-4 and 3-5, respectively (all data are available in the Appendix Figure A1-9–1-16). In the surface water of the bay, Chl *a*, DOC, POC, and $\delta^{13}C_{POM}$ values were higher in July than December. In contrast, DIC concentrations were lower in July than December. In the bottom water, DIC concentrations were high throughout the year, especially during summer (see Appendix Figure A1-5). These distributions were inversely related to those of Chl *a*, DOC, POC, and $\delta^{13}C_{POM}$, and were more pronounced in the inner bay than the bay mouth.

In the surface water (<7.5 m), DIC concentrations were positively correlated with salinity during spring and summer ($y=41.8x+593$, $R^2=0.67$, $p<0.05$), while they were negatively correlated with Chl *a* during this period ($y=-6.5x+1917$, $R^2=0.51$, $p<0.05$) (Figure 3-6). In contrast, DIC concentrations were not significantly correlated with salinity or Chl *a* during autumn or winter. DOC concentrations were negatively correlated with salinity (spring and summer: $y=-4.2x+238$, $R^2=0.54$, $p<0.05$; autumn and winter: $y=-11.4x+456$, $R^2=0.58$, $p<0.05$) (Figure 3-7), while POC concentrations were positively correlated with Chl *a* (spring and summer: $y=2.8x+22$, $R^2=0.72$, $p<0.05$; autumn and winter: $y=1.7x+20$, $R^2=0.87$, $p<0.05$) (Figure 3-8). The freshwater DIC was lower and the DOC was higher than those of the bay (Tables 3-1–3-4), and a positive relationship between DIC and salinity and a negative relationship between DOC and salinity were observed. Phytoplankton also used DIC and produced organic matter; hence, a negative relationship between DIC and Chl *a*, and a positive relationship between POC and Chl *a* was observed. In contrast, DOC was not correlated with Chl *a*. When DOC is produced directly by phytoplankton, a positive relationship between DOC and Chl *a* is expected (Kragh and Søndergaard, 2009).

The POC/TOC ratio in the surface water was positively correlated with Chl *a* (Figure 3-9). Additionally, the POC/TOC ratio was usually below 50%, with the average POC/TOC ratio in the freshwater and surface water being 39% and 31%, respectively; however, this ratio was over 50% when the phytoplankton bloom occurred (Chl *a* > 30 μg L^{-1}). The $\delta^{13}C_{POM}$ was not correlated with salinity or Chl *a* (Figure 3-10), although constant vales of $\delta^{13}C_{POM}$ of around −16‰ were observed with high Chl *a*. These values were higher than the values of $\delta^{13}C_{POM}$ observed for the open ocean (about −20‰; Sharp, 2007); however, the highest value of $\delta^{13}C_{POM}$ was −14.0‰, which was similar to the theoretical value of $\delta^{13}C_{POM}$ observed for the phytoplankton bloom. A higher phytoplankton growth rate and lower CO_2 concentration in cells causes less isotope fractionation; therefore, the $\delta^{13}C_{POM}$ levels in phytoplankton deviate less from those in the open ocean and may reach a theoretical level of −11‰ (O’Leary, 1988). In addition, remarkably high $\delta^{13}C_{POM}$ values of around −13‰ have been reported in various eutrophic environments due to the rapid growth of phytoplankton (Ogura et al., 1986; Cifuentes et al., 1988; Takahashi et al., 1992; Ogawa and Ogura, 1997; Savoye et al., 2003). The POC/Chl *a* ratio was about 50 (Figure 3-11) when Chl *a* was higher than 10 μg L^{-1}, which was similar to the phytoplankton carbon content/Chl *a* ratio in coastal waters (58±7.7; Sun et al., 1994). In contrast, the POC/Chl *a* ratio at low Chl *a* concentrations was about 100–200 (Figure 3-11), which was a relatively high contribution of terrestrial organic carbon with high carbon contents (Hedges et al., 1986). The $\delta^{13}C_{POM}$ was about −17‰ when the POC/Chl *a* ratio was around 50, while the $\delta^{13}C_{POM}$ was lower when the POC/Chl *a* ratio was higher than 50. POC concentrations in the bay contributed to both terrestrial organic matter and organic matter derived from phytoplankton. In particular, the contribution of POC derived from phytoplankton was relatively high due to the high $\delta^{13}C_{POM}$ in the bay.

High Chl *a* concentrations were observed in November and January (see Appendix Figure A1-4). These results were reported previously for the inner bay, and have 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, 1995). Hirano (2014) recently showed that winter blooms in the bay were dominated by *Skeletonema japonicum*. Physiological characterization of *S. japonicum*, which can grow under low light conditions and in the presence of limited phosphorus (Lee, 2012), may be related to the winter blooms.

A good linear relationship between DIC and apparent oxygen utilization was observed in the bottom water during spring and summer ($y=0.70x+1976$, $R^2=0.50$, $p<0.05$). DIC in the bottom water was produced in situ by the biological oxidation of sinking organic carbon from the surface water because this was comparable to the stoichiometry of the remineralization reaction, which was assumed to be $C:O_2 = 117:170 \approx 0.69$ (Anderson and Sarmiento, 1994). Seasonal stratification prohibited contact with the bottom water and the atmosphere. As a result, high DIC concentrations were observed in the bottom water before vertical mixing. There was also a subsurface hypoxic water mass with high DIC concentration, in which the minimum oxygen concentration was observed immediately below the pycnocline and increased toward the bottom in September in the central bay (see Appendix Figure A1-5(e)). Fujiwara and Yamada (2002) showed that intrusion from the open ocean could potentially contribute to subsurface hypoxic water, which then moved out as a thin layer immediately under the pycnocline. The subsurface hypoxic water mass reached beyond the bay mouth without being exposed to the atmosphere. As a result, the water mass with high DIC also reached beyond the bay mouth without outgassing of CO_2 to the atmosphere. These characteristics are part of the reason that Tokyo Bay acts as a net sink for CO_2 in autumn (Kubo, 2011; Kubo, in prep.).

3.4. Summary

The seasonal and spatial variations in organic and inorganic carbon in Tokyo Bay were controlled by both terrestrial input and biological activity. In the surface water, the DIC concentrations were negatively correlated with salinity and positively correlated with Chl *a* during spring and summer. Additionally, DOC concentrations were negatively correlated with salinity and POC concentrations were positively correlated with Chl *a* throughout the year. In the bottom water, a good linear relationship between DIC and apparent oxygen utilization was observed during spring and summer owing to biological oxidation of sinking organic carbon from the surface water.

Table 3-1

Temperature (^oC), Salinity, DOC (μmol L^{-1}), POC (μmol L^{-1}), and $\delta^{13}C_{POM}$ (‰), DIC, and Chl *a* (μg L^{-1}) at the lower Arakawa River station.

Date	Temp. (^oC)	Sal.	DOC (μmol L^{-1})	POC (μmol L^{-1})	$\delta^{13}C_{POM}$ (‰)	DIC (μmol L^{-1})	Chl *a* (μg L^{-1})
May-2011	23.6	0.1	283	165	–32.6	1759	3.9
Jun-2011	24.3	0.1	232	113	–27.6	1544	9.9
Jul-2011	24.2	0.1	398	81	–25.5	1339	1.4
Aug-2011	23.9	0.0	185	56	–25.6	1244	1.1
Sep-2011	27.1	0.1	155	79	–29.2	1373	9.2
Oct-2011	19.0	0.1	187	74	–27.2	1258	4.7
Nov-2011	17.4	0.8	246	283	–25.1	1142	5.1
Dec-2011	10.7	0.1	236	60	–25.7	1536	2.0
Jan-2012	7.0	0.3	261	142	–27.9	1583	7.6
Feb-2012	9.3	0.1	338	310	–33.8	1711	42.3
Mar-2012	14.2	0.7	320	258	–33.1	1738	51.1
Apr-2012	19.0	1.3	301	212	–32.3	1764	56.8
Average	18.3	0.3	262	153	–28.8	1499	16.3

Table 3-2

Temperature (^{o}C), Salinity, DOC (μmol L^{-1}), POC (μmol L^{-1}), and $\delta^{13}C_{POM}$ (‰), DIC, and Chl *a* (μg L^{-1}) at the lower Tamagawa River station.

Date	Temp. (^{o}C)	Sal.	DOC (μmol L^{-1})	POC (μmol L^{-1})	$\delta^{13}C_{POM}$ (‰)	DIC (μmol L^{-1})	Chl *a* (μg L^{-1})
May-2011	23.2	0.2	162	65	–25.0	1110	5.4
Jun-2011	26.9	0.2	167	47	–25.4	1264	4.1
Jul-2011	21.4	0.1	203	48	–25.7	855	0.6
Aug-2011	23.7	0.0	263	71	–23.8	1245	4.3
Sep-2011	25.5	0.2	193	70	–23.1	1019	1.2
Oct-2011	19.3	0.1	111	22	–25.3	938	0.5
Nov-2011	17.4	0.1	138	108	–24.4	856	1.5
Dec-2011	11.5	0.6	121	18	–23.3	1018	0.4
Jan-2012	9.0	0.3	143	42	–25.7	1033	5.3
Feb-2012	10.9	1.2	150	106	–25.2	831	2.2
Mar-2012	15.7	0.7	170	92	–24.9	1074	5.3
Apr-2012	20.5	0.2	190	78	–24.6	1317	8.3
Average	18.8	0.3	168	64	–24.7	1047	3.3

Table 3-3

Temperature (^{o}C), Salinity, DOC (μmol L^{-1}), POC (μmol L^{-1}), and $\delta^{13}C_{POM}$ (‰), DIC, and Chl *a* (μg L^{-1}) at the Shibaura sewage treatment plant effluent.

Date	Temp. (^{o}C)	Sal.	DOC (μmol L^{-1})	POC (μmol L^{-1})	$\delta^{13}C_{POM}$ (‰)	DIC (μmol L^{-1})	Chl *a* (μg L^{-1})
May-2011	27.6	5.3	409	71	–24.0	1810	3.7
Jun-2011	26.4	2.2	410	42	–24.5	2218	0.8
Jul-2011	27.9	5.8	351	38	–24.5	2094	0.5
Aug-2011	27.7	1.9	292	48	–24.6	1545	2.2
Sep-2011	28.7	2.9	366	83	–29.7	1430	1.2
Oct-2011	24.4	7.0	341	53	–24.5	1291	0.8
Nov-2011	20.5	5.3	189	76	–24.5	1152	0.3
Dec-2011	17.7	2.9	288	134	–24.7	1475	0.6
Jan-2012	14.9	0.4	387	191	–24.8	1797	0.9
Feb-2012	17.2	1.2	305	79	–24.6	1364	0.1
Mar-2012	19.7	3.1	373	71	–24.0	1487	7.3
Apr-2012	22.2	4.9	441	63	–23.4	1610	14.4
Average	22.9	3.6	346	79	–24.8	1606	2.7

Table 3-4

Temperature (^{o}C), Salinity, DOC (μmol L^{-1}), POC (μmol L^{-1}), and $\delta^{13}C_{POM}$ (‰), DIC, and Chl *a* (μg L^{-1}) at Tokyo Port Entrance.

Date	Temp. (^{o}C)	Sal.	DOC (μmol L^{-1})	POC (μmol L^{-1})	$\delta^{13}C_{POM}$ (‰)	DIC (μmol L^{-1})	Chl *a* (μg L^{-1})
May-2011	19.3	26.3	147	64	–25.9	1923	10.1
Jun-2011	23.1	17.8	246	168	–20.3	1371	55.5
Jul-2011	27.2	23.0	198	435	–21.4	1496	189.4
Aug-2011	26.1	19.1	178	71	–22.6	1647	7.2
Sep-2011	25.3	11.1	154	40	–25.8	1288	1.5
Oct-2011	23.6	25.4	120	170	–22.0	1768	53.6
Nov-2011	21.1	25.5	171	109	–21.9	1725	38.1
Dec-2011	17.2	28.7	138	21	–25.0	2030	0.4
Jan-2012	11.0	29.8	110	86	–19.0	1957	19.1
Feb-2012	11.4	29.1	119	75	–20.5	1932	13.0
Mar-2012	11.7	28.3	127	64	–21.5	1906	7.0
Apr-2012	15.9	20.0	252	126	–22.4	1544	25.3
Average	19.4	23.7	163	119	–22.4	1716	35.0

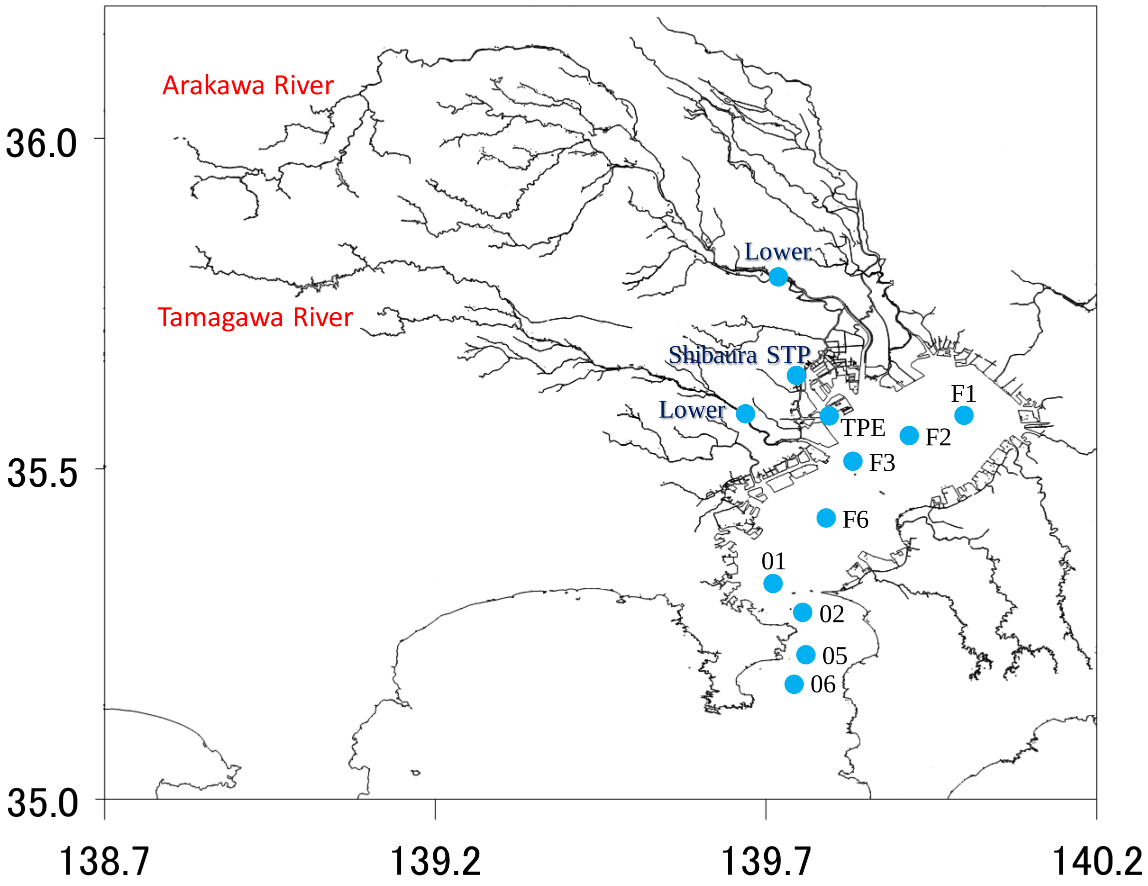

Figure 3-1
Map of Tokyo Bay. Locations of sampling sites are indicated by blue circles.

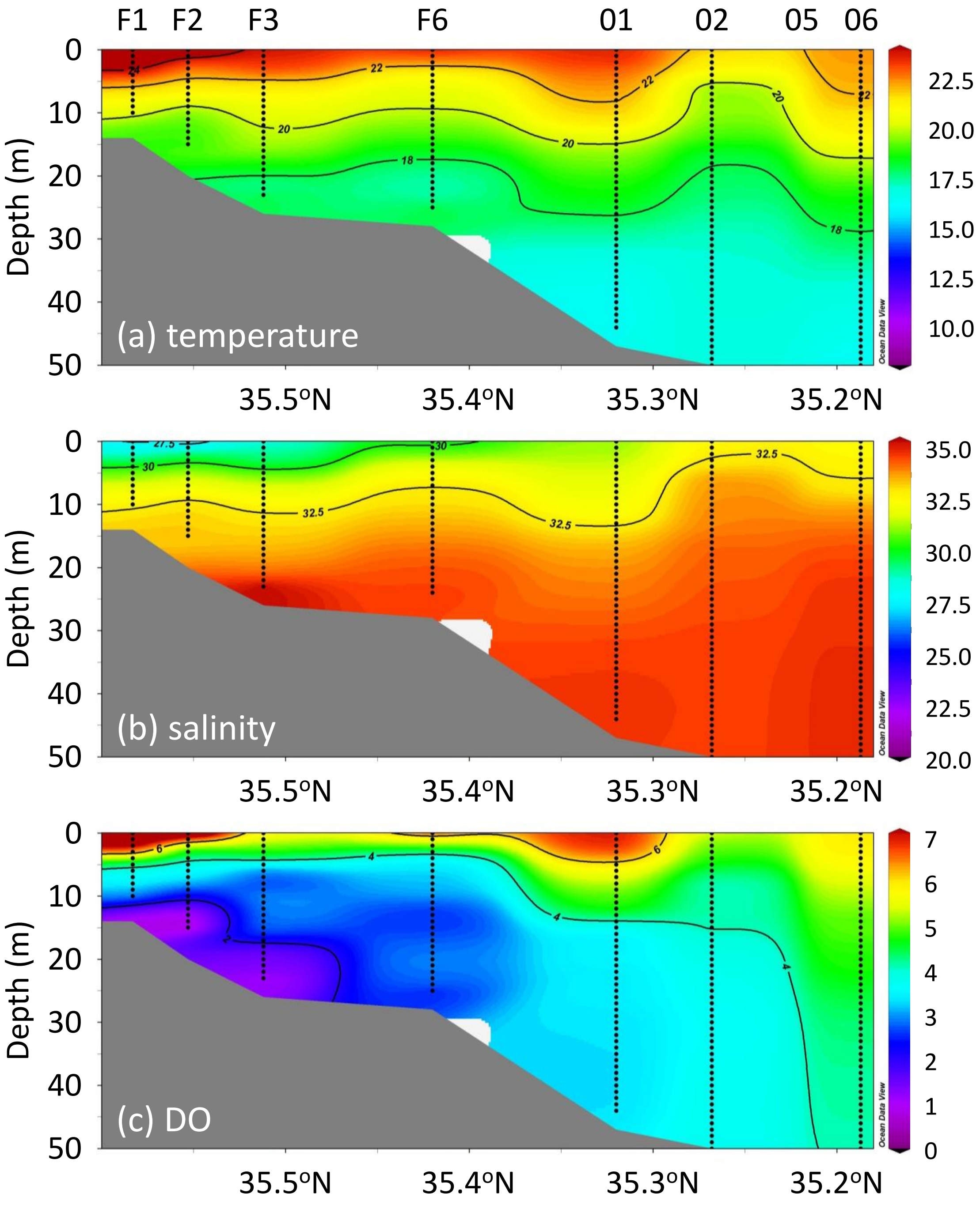

Figure 3-2
Spatial distribution of (a) temperature (°C), (b) salinity, and (c) DO (mL L^{-1}) in the upper 50 m of water column in July, 2011.

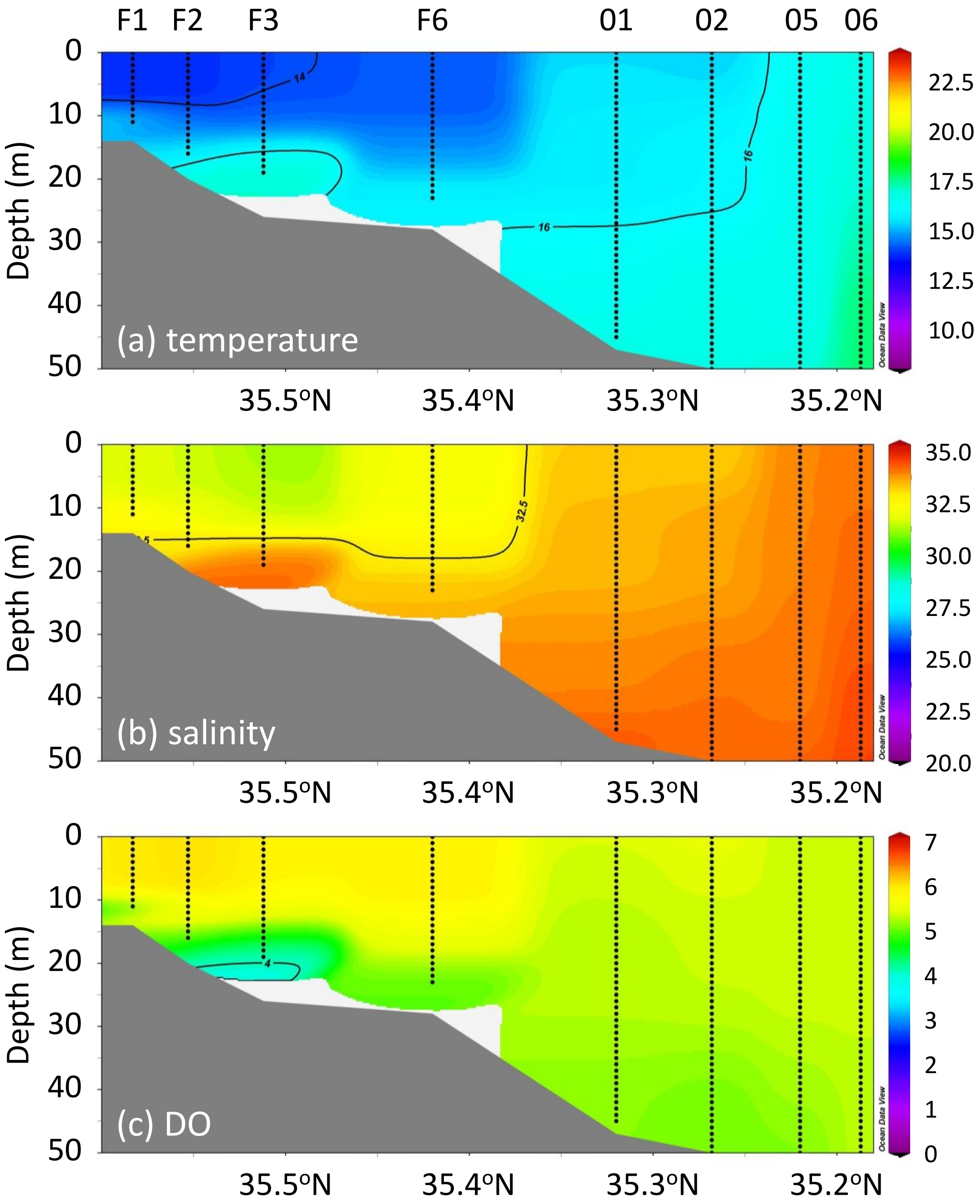

Figure 3-3
Spatial distribution of (a) temperature (°C), (b) salinity, and (c) DO (mL L^{-1}) in the upper 50 m of water column in December, 2011.

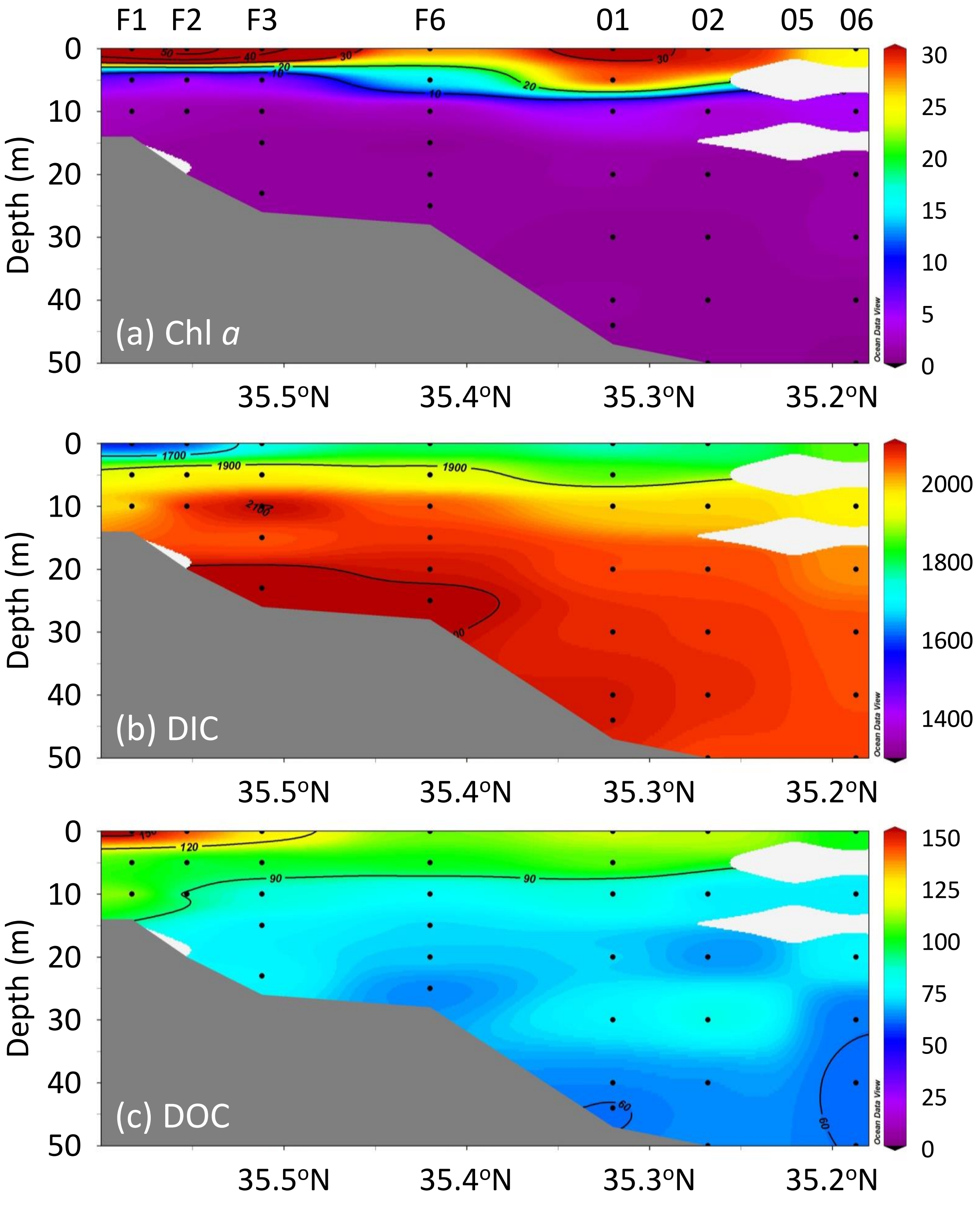

Figure 3-4

Spatial distribution of (a) Chl a (μg L^{-1}), (b) DIC (μmol L^{-1}), and (c) DOC (μmol L^{-1}) in the upper 50 m of water column in July, 2011.

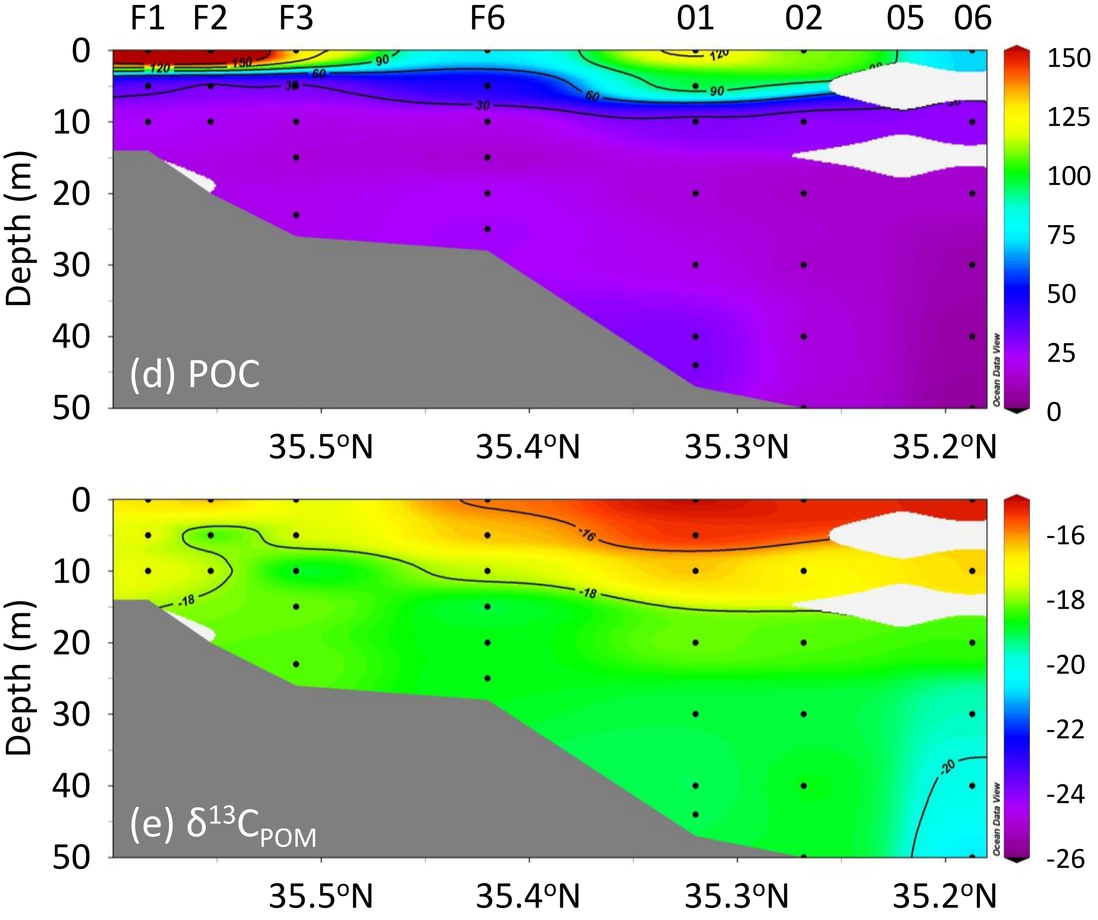

Figure 3-4 (continued)
Spatial distribution of (d) POC (μmol L^{-1}), and (e) $\delta^{13}C_{POM}$ (‰) in the upper 50 m of water column in July, 2011.

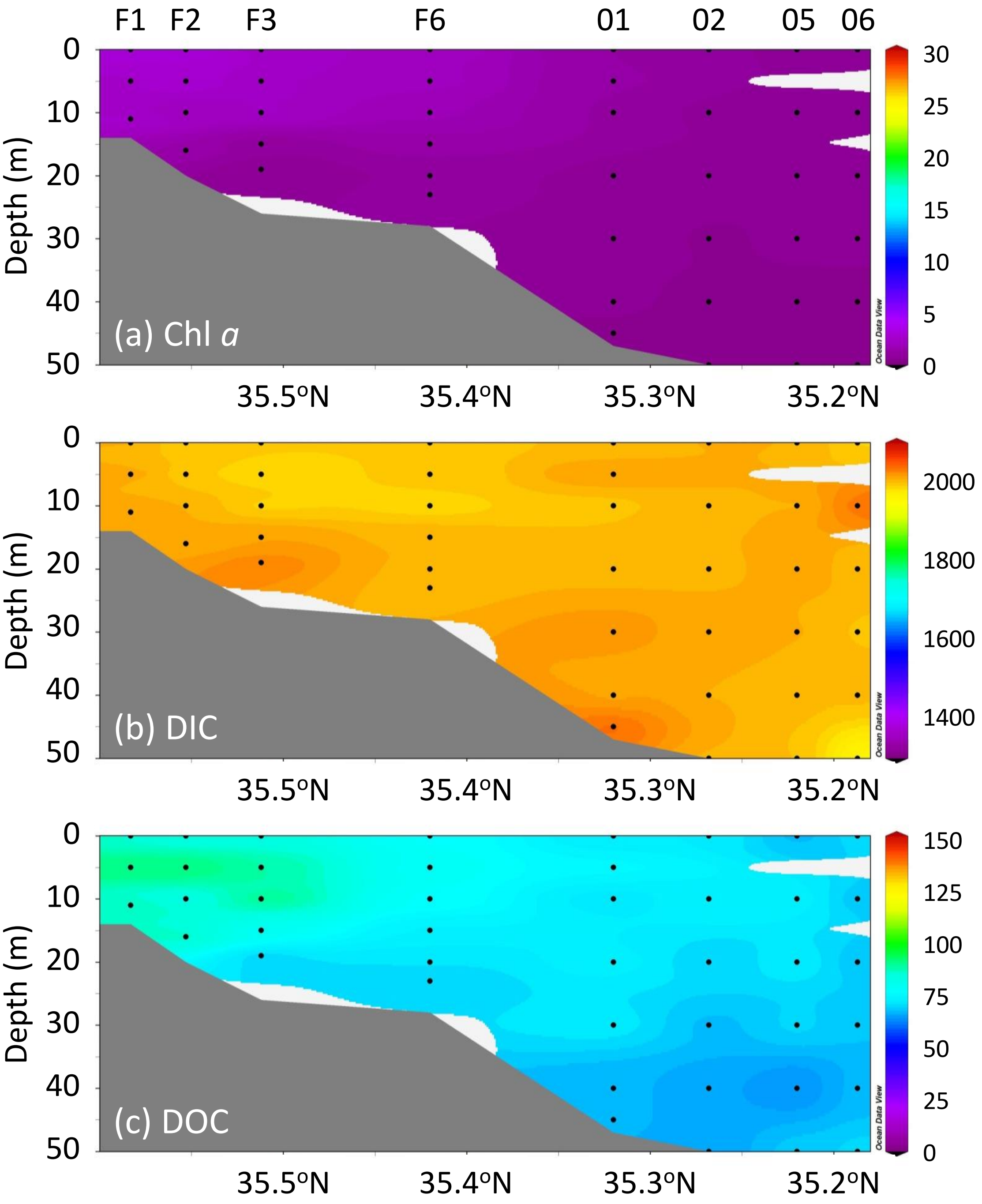

Figure 3-5
Spatial distribution of (a) Chl a (μg L^{-1}), (b) DIC (μmol L^{-1}), and (c) DOC (μmol L^{-1}) in the upper 50 m of water column in December, 2011.

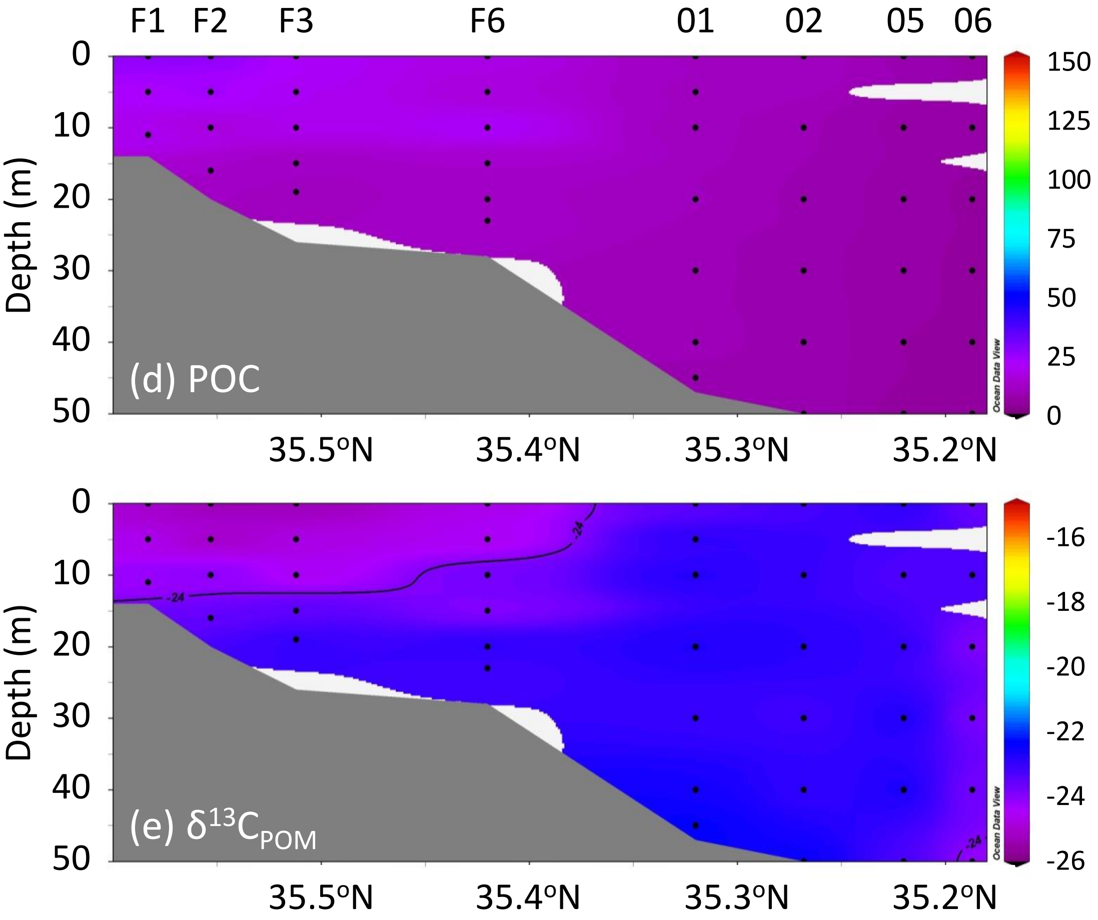

Figure 3-5 (continued)
Spatial distribution of (d) POC (μmol L^{-1}), and (e) $\delta^{13}C_{POM}$ (‰) in the upper 50 m of water column in December, 2011.

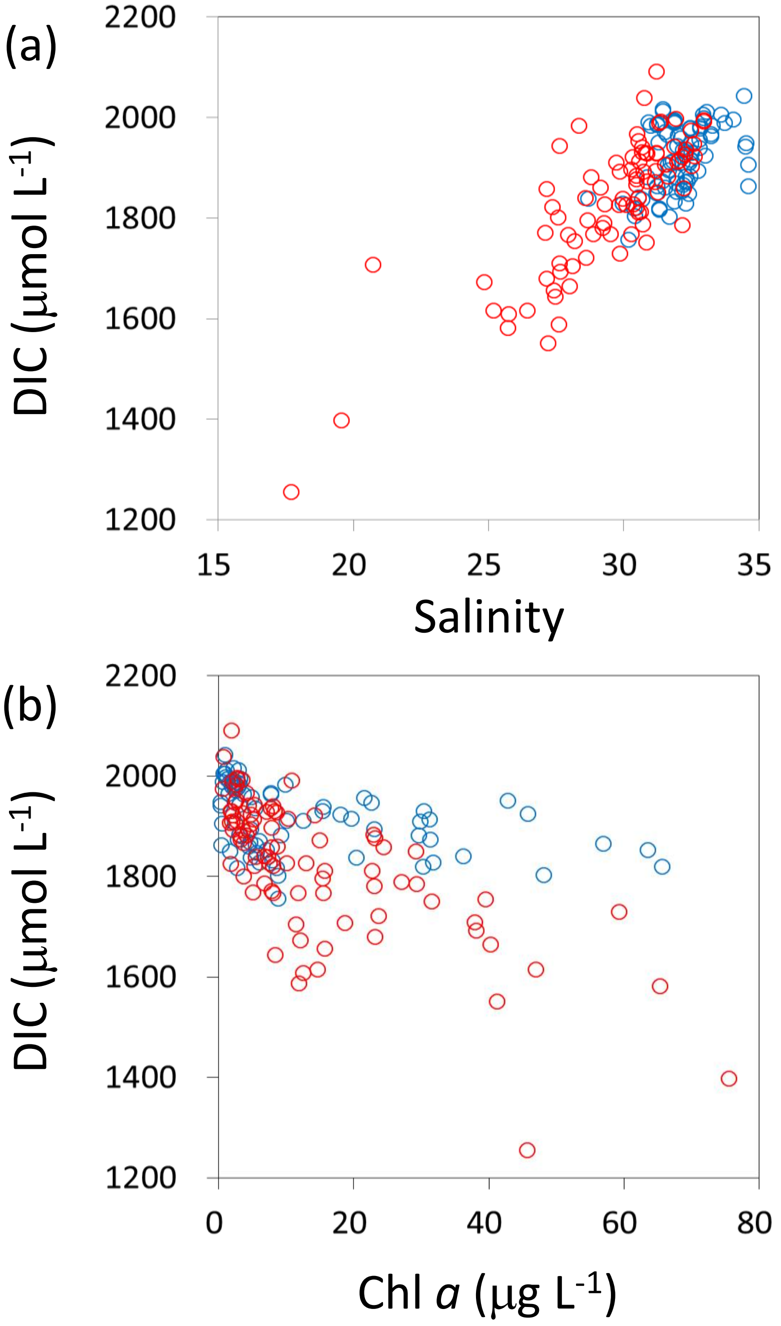

Figure 3-6
Variations in DIC with (a) salinity, and (b) Chl *a* in the surface water.
Red circles show data during spring and summer. Blue circles show data during autumn and winter.

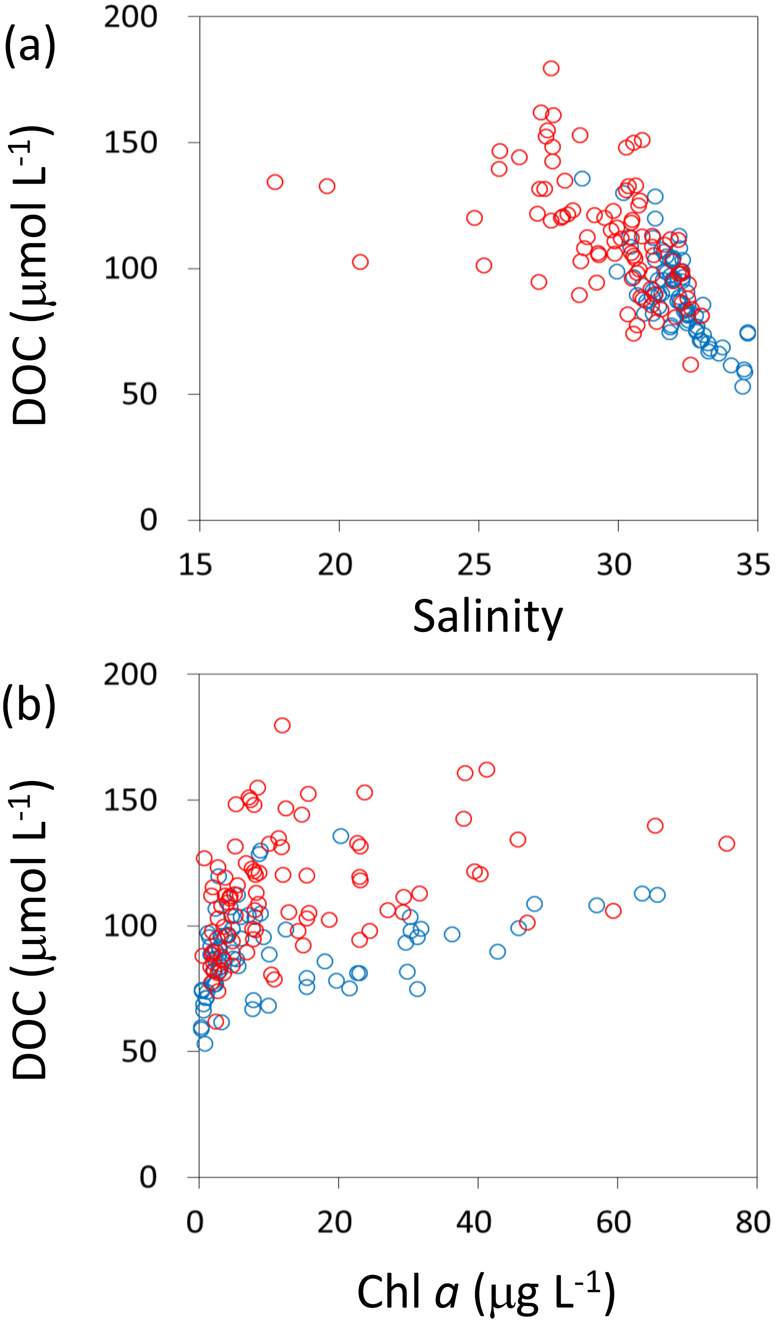

Figure 3-7
Variations in DOC with (a) salinity, and (b) Chl *a* in the surface water.
Red circles show data during spring and summer. Blue circles show data during autumn and winter.

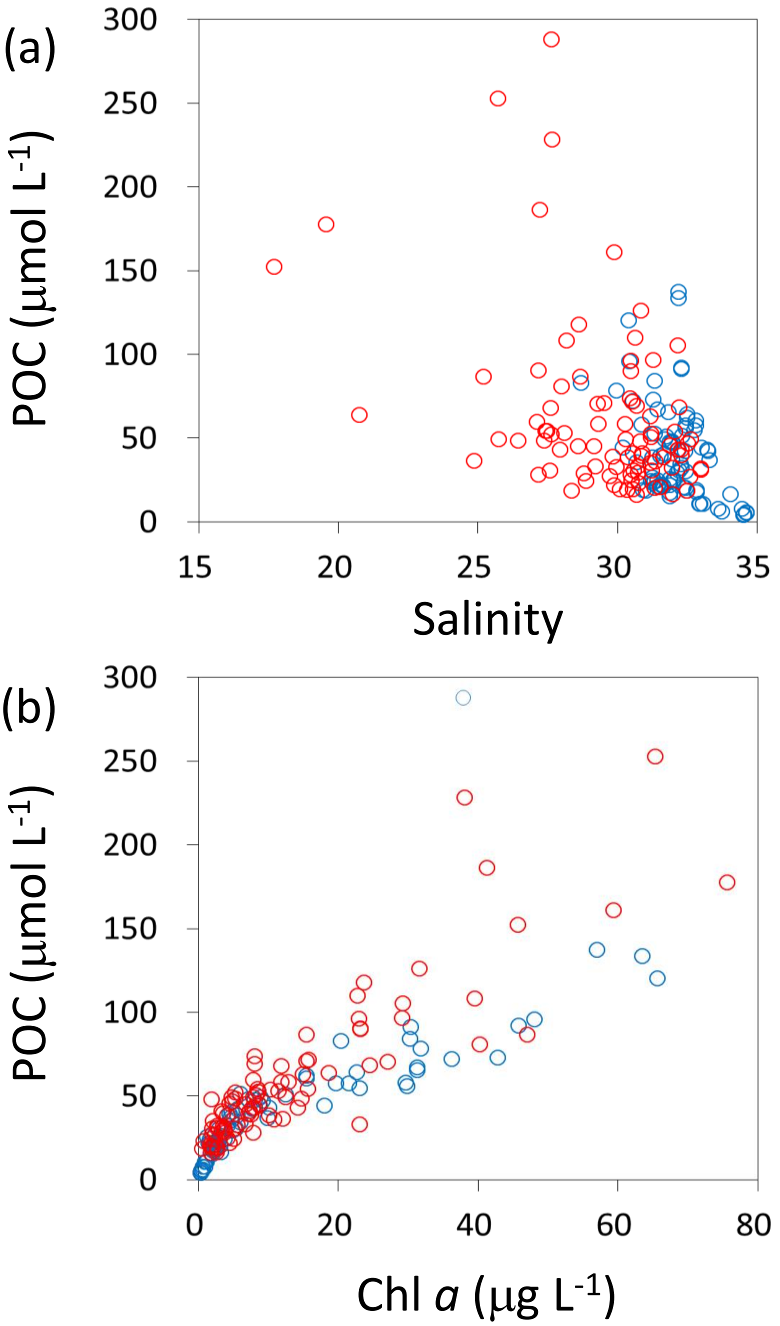

Figure 3-8
Variations in POC with (a) salinity, and (b) Chl *a* in the surface water.
Red circles show data during spring and summer. Blue circles show data during autumn and winter.

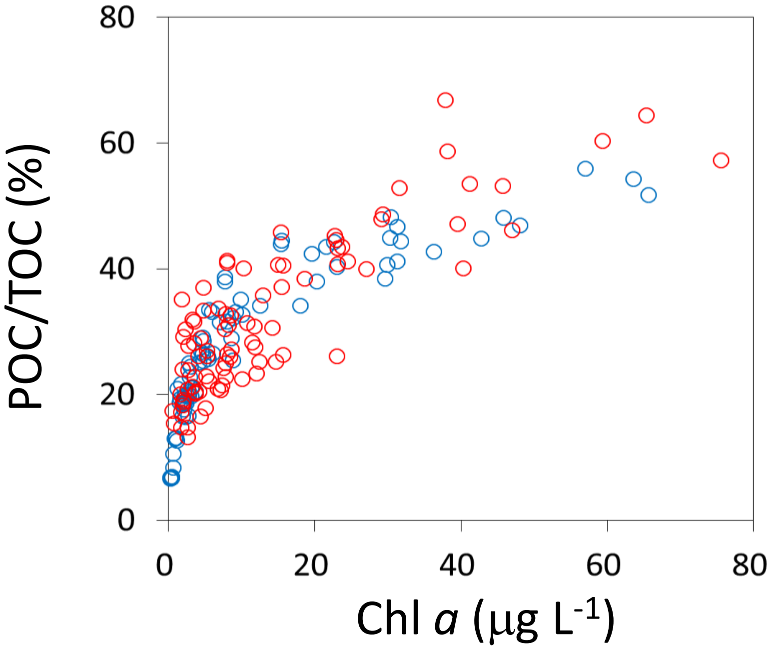

Figure 3-9
Variations in POC/TOC with Chl *a* in the surface water.
Red circles show data during spring and summer. Blue circles show data during autumn and winter.

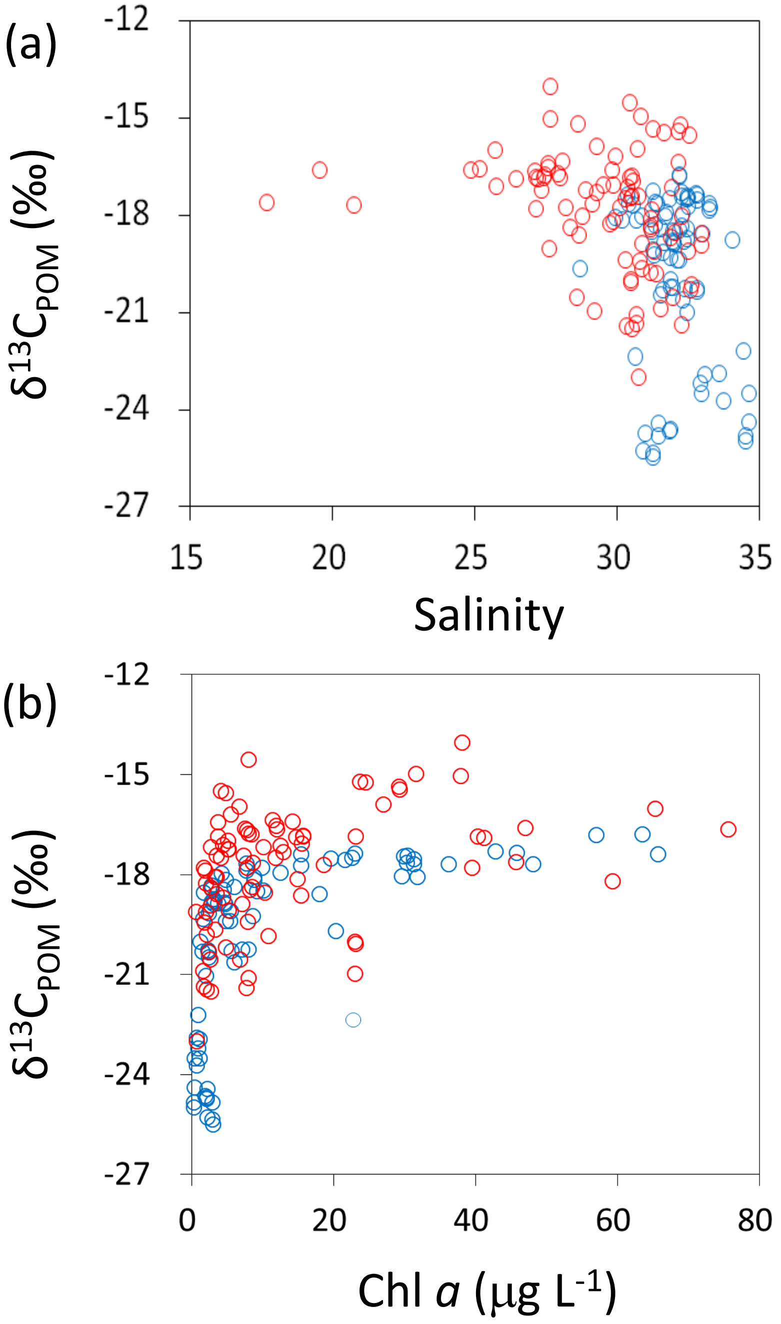

Figure 3-10
Variations in $\delta^{13}C_{POM}$ with (a) salinity, and (b) Chl *a* in the surface water. Red circles show data during spring and summer. Blue circles show data during autumn and winter.

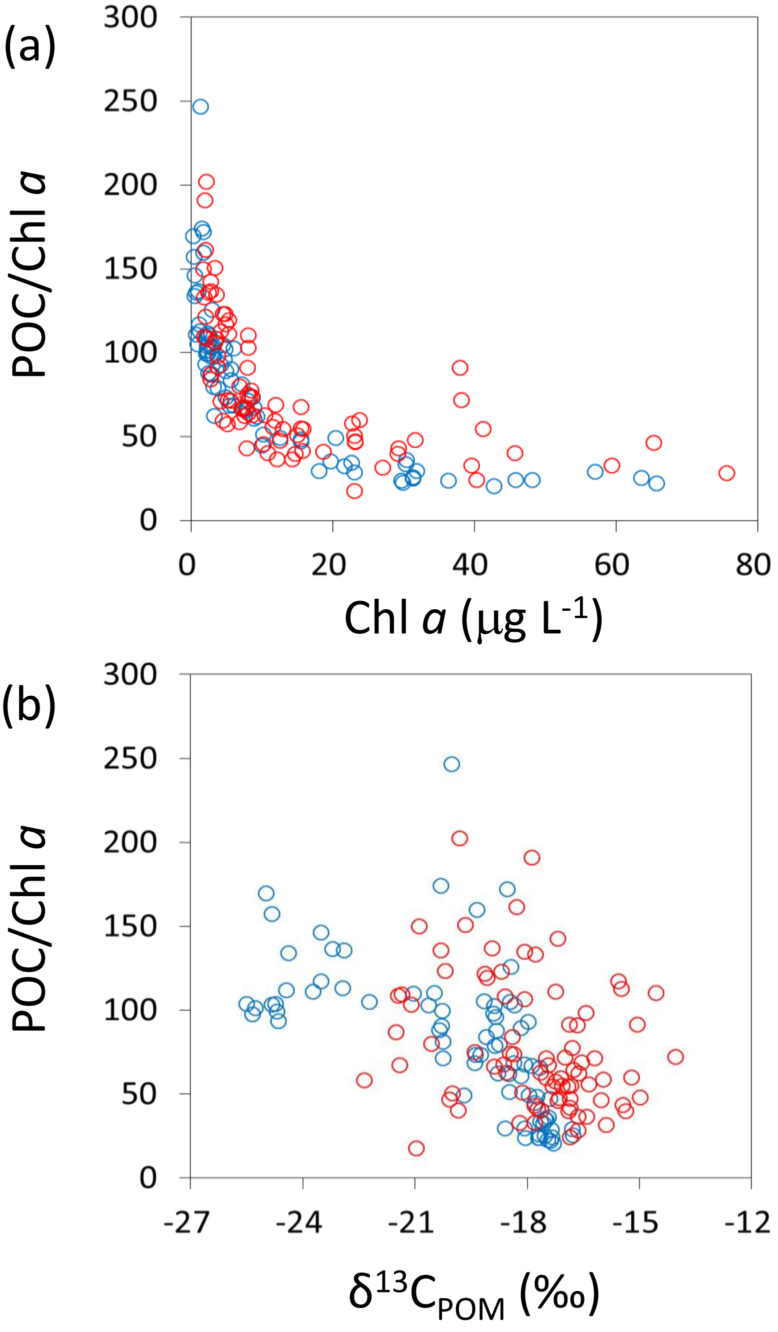

Figure 3-11
Variations in POC/Chl *a* with (a) Chl *a*, and (b) $\delta^{13}C_{POM}$ in the surface water.
Red circles show data during spring and summer. Blue circles show data during autumn and winter.

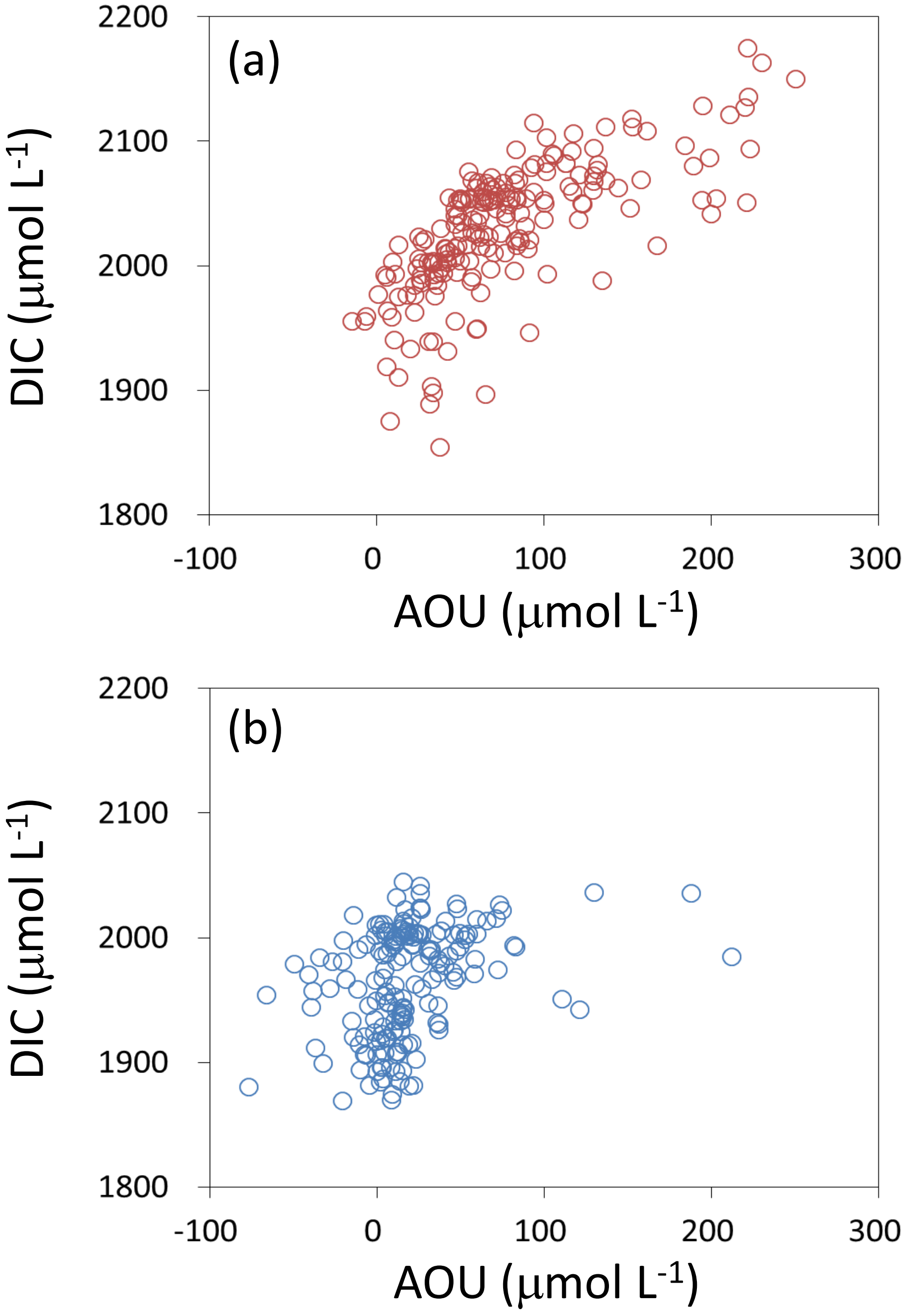

Figure 3-12
Variations in AOU with DIC in the bottom water. (a) Red circles show data during spring and summer, and (b) Blue circles show data during autumn and winter.

Chapter 4

Carbon Budget of Tokyo Bay Estimated by the Box Model

4.1. Introduction

Carbon budgets are critical to determining the flow of material within ecosystems. Several methods can be used to determine the material flows and budgets of coastal waters, including mass balance budgets (Nixon et al., 1995; Eyre and McKee, 2002; Maher and Eyre, 2012), diel changes in DO and DIC concentrations (Odum, 1956; Swaney et al., 1999; Gazeau et al., 2005), and box models (Gordon et al., 1996; Yanagi, 1999; Matsumura et al., 2002). All three methods have advantages and limitations. For example, mass balance methods based on the summation of measured/modeled individual flows are subject to errors associated with each individual flow, which can lead to significant uncertainty due to propagation errors (Smith, 1991). However, this method has the potential to provide detailed information regarding individual processes driving coastal carbon cycles. It is relatively easy to determine diel changes in DO and DIC to estimate net ecosystem metabolism, but these values are subject to uncertainties related to advective transport and atmospheric exchange rates (Swaney et al., 1999; Santos et al., 2011). Box models provide a well constrained integrated estimate of net community production (NCP); however, they generally do not provide detailed information at fine spatial and temporal scales (Kemp et al., 1997). In addition, many field observation data are required to conduct box model analyses. Reasonable consequences of nitrogen and phosphate budgets were obtained from monthly basis observation data (Matsukawa and Suzuki, 1985; Matsukawa and Sasaki, 1990; Yanagi, 1999; Matsumura et al., 2002; Yuk and Aoki, 2011). However, the carbon budgets of Tokyo Bay have not been estimated from box model analyses to date due to a lack of carbon data.

In this chapter, carbon budgets for Tokyo Bay were constructed based on carbon budgets estimated from the data provided in Chapter 3 and additional data as described in the next section.

4.2. Methods

4.2.1. Data for Box Model Analysis

The data for DIC and TOC (DOC+POC) in Tokyo Bay and freshwater sites are described in Chapter 3. Additional data for the box model included freshwater discharge amount, rainfall inputs of TOC, and air-sea CO_2 flux in surface waters. The methods and data are described in detail below.

The monthly amounts of freshwater discharge were estimated from precipitation (Japan Meteorological Agency: http://www.jma.go.jp/jma/index.html) and runoff rate according to Matsumura et al. (2003). Monthly loads of DIC and TOC (DOC+POC) were estimated from the average concentrations of the lower river water and discharge rate. The amounts of STP effluents were obtained from sewage statistics data (Japan Sewage Works Association, 2010). Monthly loads of DIC and TOC (DOC+POC) were estimated from the concentrations of Shibaura STP effluents and the discharge rate.

Rainfall samples for TOC were collected from the rooftops of nine buildings at Tokyo University of Marine Science and Technology in May 2011 and September 2011. The average concentration was 50.4 μmol L^{-1}, which was comparable to the global rain water concentrations (Willey et al., 2000; Avery et al., 2003; Avery et al., 2006; Coelho et al., 2008). Precipitation data were obtained from the Japan Meteorological Agency (available at http://www.jma.go.jp/jma/index.html). Monthly loads of TOC were estimated from the average concentration of rainwater and monthly precipitation.

Air-sea CO_2 flux data were obtained from Kubo (2011). Monthly averaged data are shown in Table 4-1.

4.2.2. Box Model Analysis

A simple advective-diffusive box model used for Tokyo Bay by Matsumura et al. (2002) was adopted. In this model, Tokyo Bay was divided into two-layered boxes by three cross sections (Figures 4-1 and 4-2). The two layers were separated by an interface situated 7.5 m deep according to Matsumura et al. (2002). Three cross sections were divided into an inner bay, central bay, and bay mouth region.

The balance equations of freshwater and salt for each box were expressed as:

1) Box 1

$$A_{13}U_{13} = A_{12}W_{12} + Q_{W1} \tag{4-1}$$

$$\begin{aligned} &V_1\frac{dS_1}{dt} + A_{13}U_{13}\frac{S_1 + S_3}{2} - A_{13}K_{H13}\frac{S_3 - S_1}{L_{13}} \\ &= A_{12}W_{12}\frac{S_1 + S_2}{2} + A_{12}K_{V12}\frac{S_2 - S_1}{L_{12}} \end{aligned} \tag{4-2}$$

2) Box 2

$$A_{12}W_{12} = -A_{24}U_{24} \tag{4-3}$$

$$\begin{aligned} &V_2\frac{dS_2}{dt} + A_{12}W_{12}\frac{S_1 + S_2}{2} + A_{12}K_{V12}\frac{S_3 - S_1}{L_{12}} \\ &= -A_{24}U_{24}\frac{S_2 + S_4}{2} + A_{24}K_{H24}\frac{S_4 - S_2}{L_{24}} \end{aligned} \tag{4-4}$$

3) Box 3

$$A_{35}U_{35} = A_{13}U_{13} + A_{34}W_{34} + Q_{W3} \tag{4-5}$$

$$\begin{aligned} &V_3\frac{dS_3}{dt} + A_{35}U_{35}\frac{S_3 + S_5}{2} - A_{35}K_{H35}\frac{S_5 - S_3}{L_{35}} \\ &= A_{13}U_{13}\frac{S_1 + S_3}{2} - A_{13}K_{H13}\frac{S_3 - S_1}{L_{13}} + A_{34}W_{34}\frac{S_3 + S_4}{2} + A_{34}K_{V34}\frac{S_4 - S_3}{L_{34}} \end{aligned} \tag{4-6}$$

4) Box 4

$$-A_{24}U_{24} + A_{34}W_{34} = -A_{46}U_{46} \tag{4-7}$$

$$\begin{aligned} &V_4\frac{dS_4}{dt} - A_{24}U_{24}\frac{S_2 + S_4}{2} + A_{24}K_{H24}\frac{S_4 - S_2}{L_{24}} + A_{34}W_{34}\frac{S_3 + S_4}{2} \\ &+A_{34}K_{V34}\frac{S_4 - S_3}{L_{34}} \\ &= -A_{46}U_{46}\frac{S_4 + S_6}{2} + A_{46}K_{H46}\frac{S_6 - S_4}{L_{46}} \end{aligned} \tag{4-8}$$

where A_{ij} is the area of the cross-section between box i and box j, U_{ij} and W_{ij} are the horizontal flow velocity and vertical flow velocity, respectively, Q_{wi} is the amount of freshwater discharge flowing into box i, V_i and S_i are the volume and average salinity of box i, dS_i/dt is the rate of change of the mean salinity with respect to the time, K_{Hij} and K_{Vij} are the horizontal diffusivity coefficient and vertical diffusivity coefficient between box i and j, and L_{ij} is the distance between box i and j. K_{H13} was assumed to be equal to K_{H24}, and K_{H35} was equal to K_{H46} according to Matsumura et al. (2002). Horizontal diffusivity was mainly dominated by tidal current; therefore, the square of K_H is proportional to tidal current (Tanimoto et al., 2001). The value of K_H was estimated from $K_{H35}=6.02\times K_{H13}$ by Unoki et al. (1980). Vertical diffusivity, K_{V34}, was estimated by K_{V12} and the density gradient ratio of box 3-4 and box 1-2 (Matsumura et al., 2002) because it was inversely proportional to density gradient (Tanimoto et al., 2001). Using the above equations, a linear equation with eight unknowns for U_{ij}, W_{ij}, K_{Hij}, and K_{Vij} was solved.

The DIC budgets in each box were calculated according to the following equation.

1) Box 1

$$\begin{aligned} \mathrm{P}_1 = -Q_{DX1} + V_1 \frac{dC_{DX1}}{dt} + A_{13}U_{13}\frac{C_{DX1}+C_{DX3}}{2} - A_{13}K_{H13}\frac{C_{DX3}-C_{DX1}}{L_{13}} \\ - A_{12}W_{12}\frac{C_{DX1}+C_{DX2}}{2} - A_{12}K_{V12}\frac{C_{DX2}-C_{DX1}}{L_{12}} + F_{DX1} \end{aligned} \tag{4-9}$$

2) Box 2

$$\begin{aligned} \mathrm{P}_2 = V_2 \frac{dC_{DX2}}{dt} + A_{24}U_{24}\frac{C_{DX2}+C_{DX4}}{2} - A_{24}K_{H24}\frac{C_{DX4}-C_{DX2}}{L_{24}} \\ + A_{12}W_{12}\frac{C_{DX1}+C_{DX2}}{2} + A_{12}K_{V12}\frac{C_{DX2}-C_{DX1}}{L_{12}} \end{aligned} \tag{4-10}$$

3) Box 3

$$\begin{aligned} \mathrm{P}_3 = -Q_{DX3} + V_3 \frac{dC_{DX3}}{dt} - A_{13}U_{13}\frac{C_{DX1}+C_{DX3}}{2} + A_{13}K_{H13}\frac{C_{DX3}-C_{DX1}}{L_{13}} \\ + A_{35}U_{35}\frac{C_{DX3}+C_{DX5}}{2} - A_{35}K_{H35}\frac{C_{DX5}-C_{DX3}}{L_{35}} \\ - A_{34}W_{34}\frac{C_{DX3}+C_{DX4}}{2} - A_{34}K_{V34}\frac{C_{DX4}-C_{DX3}}{L_{34}} + F_{DX3} \end{aligned} \tag{4-11}$$

4) Box 4

$$
\begin{aligned}
\mathrm{P}_4 = V_4 \frac{dC_{DX4}}{dt} - A_{24}U_{24}\frac{C_{DX2}+C_{DX4}}{2} + A_{24}K_{H24}\frac{C_{DX4}-C_{DX2}}{L_{24}} \\
+ A_{46}U_{46}\frac{C_{DX4}+C_{DX6}}{2} - A_{46}K_{H46}\frac{C_{DX6}-C_{DX4}}{L_{46}} \\
+ A_{34}W_{34}\frac{C_{DX3}+C_{DX4}}{2} + A_{34}K_{V34}\frac{C_{DX4}-C_{DX3}}{L_{34}}
\end{aligned}
\tag{4-12}
$$

where P_i is the DIC production in box i. Positive values are interpreted to be producing DIC in the water column via positive respiration, while negative values are interpreted as consuming DIC in the water column via positive organic matter production. Q_{DXi} is the DIC supply from the land to box i, C_{DXi} is the average DIC concentrations in box i, dC_{DXi}/dt is the rate of change of the mean DIC concentration with respect to time and F_{DXi} is the flux of carbon dioxide between air and box i.

Next, the TOC budgets in each box were calculated according to the following equation:

1) Box 1

$$
\begin{aligned}
\mathrm{D}_1 = Q_{TX1} - V_1\frac{dC_{TX1}}{dt} - A_{13}U_{13}\frac{C_{TX1}+C_{TX3}}{2} + A_{13}K_{H13}\frac{C_{TX3}-C_{TX1}}{L_{13}} \\
+ A_{12}W_{12}\frac{C_{TX1}+C_{TX2}}{2} + A_{12}K_{V12}\frac{C_{TX2}-C_{TX1}}{L_{12}} + R_{TX1}
\end{aligned}
\tag{4-13}
$$

2) Box 2

$$
\begin{aligned}
\mathrm{D}_2 = D_1 - V_2\frac{dC_{TX2}}{dt} - A_{24}U_{24}\frac{C_{TX2}+C_{TX4}}{2} + A_{24}K_{H24}\frac{C_{TX4}-C_{TX2}}{L_{24}} \\
- A_{12}W_{12}\frac{C_{TX1}+C_{TX2}}{2} - A_{12}K_{V12}\frac{C_{TX2}-C_{TX1}}{L_{12}} + R_{TX1}
\end{aligned}
\tag{4-14}
$$

3) Box 3

$$\begin{aligned}\mathrm{D}_3 = Q_{TX3} - V_3\frac{dC_{TX3}}{dt} + A_{13}U_{13}\frac{C_{TX1}+C_{TX3}}{2} - A_{13}K_{H13}\frac{C_{TX3}-C_{TX1}}{L_{13}} \\ - A_{35}U_{35}\frac{C_{TX3}+C_{TX5}}{2} + A_{35}K_{H35}\frac{C_{TX5}-C_{TX3}}{L_{35}} \\ + A_{34}W_{34}\frac{C_{TX3}+C_{TX4}}{2} + A_{34}K_{V34}\frac{C_{TX4}-C_{TX3}}{L_{34}} + R_{TX3}\end{aligned} \tag{4-15}$$

4) Box 4

$$\begin{aligned}\mathrm{D}_4 = \mathrm{D}_3 - V_4\frac{dC_{TX4}}{dt} + A_{24}U_{24}\frac{C_{TX2}+C_{TX4}}{2} - A_{24}K_{H24}\frac{C_{TX4}-C_{TX2}}{L_{24}} \\ - A_{46}U_{46}\frac{C_{TX4}+C_{TX6}}{2} + A_{46}K_{H46}\frac{C_{TX6}-C_{TX4}}{L_{46}} \\ - A_{34}W_{34}\frac{C_{TX3}+C_{TX4}}{2} - A_{34}K_{V34}\frac{C_{TX4}-C_{TX3}}{L_{34}} + R_{TX3}\end{aligned} \tag{4-16}$$

where D_i is the TOC precipitation or sediment in box i. In this equation, positive values are interpreted as precipitation or sedimentation to the lower box or sediment, while negative values are interpreted to be resuspension from the lower box or sediment. Q_{TXi} is the TOC supply from the land to box i, C_{TXi} is the mean TOC concentration in box i, dC_{TXi}/dt is the rate of change of the mean TOC concentration with respect to time and R_{TXi} is the TOC supply from the rain.

4.3. Results and Discussion

The annual loadings of DIC and TOC from the freshwater were 11.2×10^{10} gC year^{-1} and 4.9×10^{10} gC year^{-1}, respectively. DIC and TOC loadings were higher during spring and summer (13.1×10^{10} and 5.8×10^{8} gC year^{-1}, respectively) than autumn and winter (9.2×10^{10}, and 4.0×10^{8} gC year^{-1}, respectively). The annual load of TOC from rainwater was 0.084×10^{10} gC year^{-1}. Although TOC loading from rainwater was higher during spring and summer (0.102×10^{10} gC year^{-1}) than autumn and winter (0.066×10^{10} gC year^{-1}), this can be ignored from the perspective of the carbon budget in Tokyo Bay. Seasonal variations in DIC production and TOC deposition in each box are shown in Figure 4-3. At the bay surface water (Box 1 and 3), DIC was consumed throughout the year. In particular, highly negative values of DIC production were observed in the inner bay (Box 1) during spring and summer. A negative correlation was found between TOC depositions and DIC production, suggesting that active photosynthesis produced TOC, which was deposited to the bottom water. In contrast, DIC were produced throughout the year in the bottom water (Box 2 and 4) owing to TOC decomposition. TOC was deposited to the sediment throughout the year, except in the central bay during autumn and winter. A high deposition rate of TOC was observed in the inner bay during spring and summer, while resuspension of TOC was observed in the central bay during autumn and winter. The same pattern was shown in the nitrogen and phosphorus budgets from box model analysis in Tokyo Bay (Matsukawa and Sasaki, 1990; Matsumura et al., 2002).

The DIC budget in Tokyo Bay is shown in Figure 4-4. The annual NCP in the surface water was 19×10^{10} gC year^{-1}, which corresponded to 207 gC m^{-2} year^{-1}. NCP was higher during spring and summer (26.7×10^{10} gC year^{-1}) than autumn and winter (11.3×10^{10} gC year^{-1}). In contrast, DIC production in the bottom water was 9.0×10^{10} gC year^{-1}. DIC production was higher during spring and summer (10.2×10^{10} gC year^{-1}) than autumn and winter (7.7×10^{10} gC year^{-1}). Previous reports of primary production in Tokyo Bay were estimated using the ^{14}C or ^{13}C method (Funakoshi, 1974; Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Itoh, 2003; Bouman et al., 2010); thus, these values indicate primary production. Kitazawa et al. (2003) estimated that the NCP:

primary production ratio in the bay was 1.82, 1.85, and 1.92 in 1935, 1974, and 1994, respectively, while the NCP: primary production ratio in other autotrophic coastal waters was about 2.0 (Duarte and Cebrián, 1996; Cheng et al., 2000; Serret et al., 2002; Gazeau et al., 2005; Yamamoto et al., 2008; Maher and Eyre, 2012). Hence, a value of 2.0 was multiplied by the NCP data in this study. The results of this study were lower than those from the 1970s to 1980s, and similar to those from the 1990s and 2000s (Table 4-2; Funakoshi, 1974; Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Itoh, 2003; Bouman et al., 2010). These findings were consistent with the Chl *a* concentrations in surface water, which decreased from the 1970s to 1980s (Nomura, 1995), but not from the 1990s to the present (Kanda et al., 2008). Nevertheless, primary production in the bay was one of the highest values among coastal waters worldwide (Cloern et al., 2014).

The TOC budget for Tokyo Bay is shown in Figure 4-5. The annual deposition rate in the surface water was 13.4×10^{10} gC year^{-1}, with higher values being observed during spring and summer (20.4×10^{10} gC year^{-1}) than autumn and winter (6.3×10^{10} gC year^{-1}) owing to high TOC discharge from rivers and high primary production during spring and summer. TOC sedimentation in the bottom water was also higher during spring and summer (4.4×10^{10} gC year^{-1}) than autumn and winter (1.8×10^{10} gC year^{-1}). The average TOC sedimentation was 3.1×10^{10} gC year^{-1}, which is slightly lower than previously reported sedimentation rates for Tokyo Bay of 4.4 to 6.6×10^{10} gC year^{-1} (Table 4-3, Matsumoto, 1985; Nippon Foundation, 2001; Shimizu et al., 2005). The results of this study were slightly lower than those of previous studies. In fact, organic carbon and nutrient input from land decreased significantly from the 1970s to the present (Ogawa and Ogura, 1990b; Central Environmental Council, 2010; Kubo et al., 2014).

Decreasing nutrient loads in the bay have caused decreasing primary production (Funakoshi, 1974; Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Itoh, 2003; Bouman et al., 2010). As a result, the sedimentation rate of organic carbon was slightly decreased in the bay. TOC sedimentation in this study includes the annual efflux of DOC from sediment pore water, which can be estimated at about 0.23×10^{10} gC year^{-1} assuming the flux data was 34.2 μmol C m^{-2} hour^{-1} as reported by Yasui-Tamura et al. (in prep.) for Tamagawa River estuary and the muddy sediment area in the bay was 70% (Matsumoto, 1985). The annual efflux of DOC from sediment pore water was corresponded to 7% of TOC sedimentation in the bay (3.1×10^{10} gC year^{-1}).

The average organic carbon sedimentation: NCP ratio was 25% in the inner bay, with a higher value being observed during autumn and winter (43%) than spring and summer (20%) because biological oxidation activity was relatively high at high temperature, despite prevention of the organic decomposition in hypoxic water masses (see Chapter 5).

In this study, fish catches and shells were not considered, nor was dredging of sediment because these values comprised a minor proportion of organic carbon flow in the bay. The annual fish catch and shell carbon were estimated to be about 0.9×10^{6} gC year^{-1} (Kanto Regional Agricultural Administration Office, 2012), the carbon content of fish and shells was assumed to be 5% (Hendrixson et al., 2007). Additionally, the annual dredging of carbon was estimated to be 9.6×10^{6} gC year^{-1} (The Tokyo metropolitan area summit, 2012) if the carbon content of the sediment was assumed to be 3% (see Figures 2-5 and 5-1) and the density of sediment was 0.6×10^{-6} gC cm^{-3}.

4.4 Summary

The annual NCP in the surface water was 19×10^{10} gC year^{-1}, which was lower than that from the 1970s to the 1980s and similar to previous data from the 1990s and the 2000s (Table 4-2). These results were consistent with the Chl *a* concentration in surface waters from the 1970s to present. Annual TOC sedimentation was 3.1×10^{10} gC year^{-1}, which was comparable to the annual CO_2 flux between surface water and the atmosphere (5.2×10^{10} gC year^{-1}). The organic carbon sedimentation was slightly lower than that of previous studies, which likely reflected the significant decrease in organic carbon and nutrient input from land that has occurred since the 1970s. In addition, TOC sedimentation decreased because of organic carbon produced by phytoplankton in the bay.

Table 4-1

Averaged monthly air-sea CO_2 flux (10^{10} gC year^{-1}) during March 2007 and December 2010 in inner bay and central bay (Kubo, 2011). Positive flux values represent uptake of CO_2 from the atmosphere.

Month	Flux (10^{10} gC year^{-1})	
	inner bay	central bay
May	4.7	2.9
June	3.3	1.1
July	3.7	1.8
August	1.8	1.8
September	4.0	2.6
October	2.2	1.5
November	1.1	1.1
December	0.4	0.7
January	1.1	0.7
February	2.2	1.1
March	4.4	2.6
April	4.7	2.9

Table 4-2

Primary Production (gC m^{-2} $year^{-1}$) in Tokyo Bay.

Primary Production	Observation Year	Observation Stations	Observation Times	Method	Reference
1242	1972	6	3	^{14}C method	Funakoshi, 1974
2044	1988	1	11	^{14}C method	Yamaguchi et al., 1991
1242	1989	1	10	^{14}C method	Yamaguchi et al., 1991
366	1997	3	12	^{13}C method	Bouman et al., 2010
512	1998	3	12	^{13}C method	Bouman et al., 2010
500	2002	1	13	^{13}C method	Itoh, 2006
414	2011	–	–	Box Model	This Study

Table 4-3

Sedimentation Rate (10^{10} gC year^{-1}) in Tokyo Bay

Sedimentation Rates	Observation Year	Observation Stations	Method	Reference
4.2	1980	81	^{210}Pb method	Matsumoto, 1985
6.4	2000	7	^{210}Pb method	Nippon Foundation, 2001
4.9	2002	13	^{210}Pb method	Shimizu et al., 2005
3.1	2011	–	Box Model	This Study

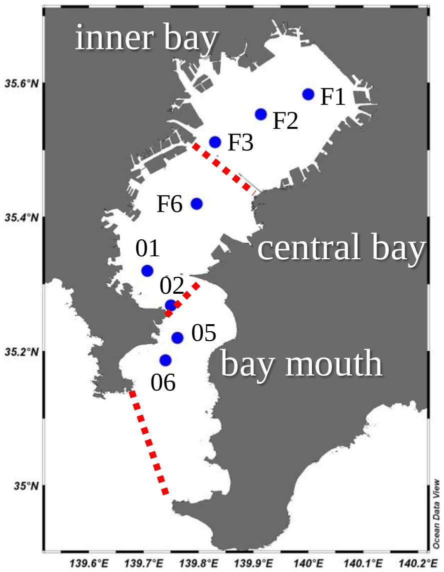

Figure 4-1
Observation points in Tokyo Bay.
Red broken lines show cross-sections of box model.

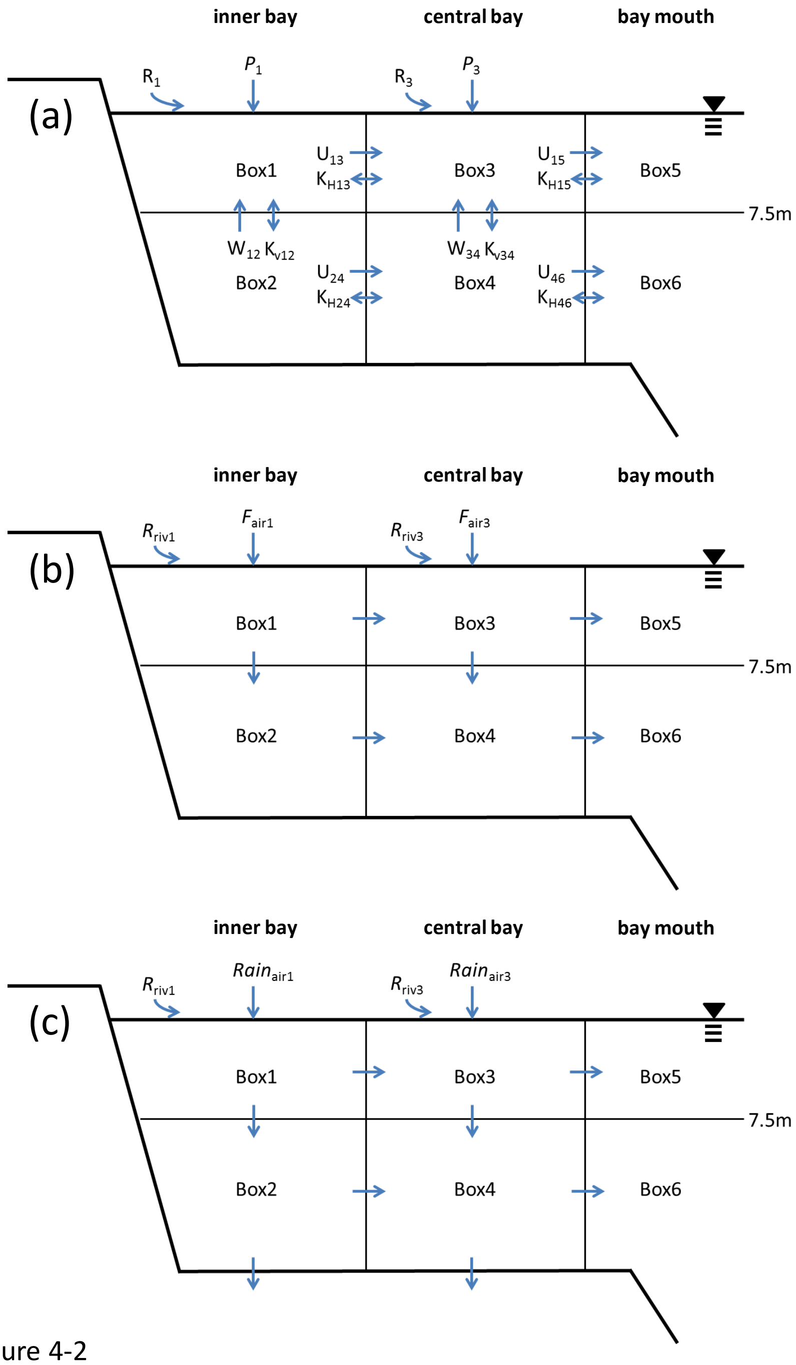

Figure 4-2
Horizontal and vertical divisions of box model and
(a) water budget, (b) DIC budget, (c) TOC budget

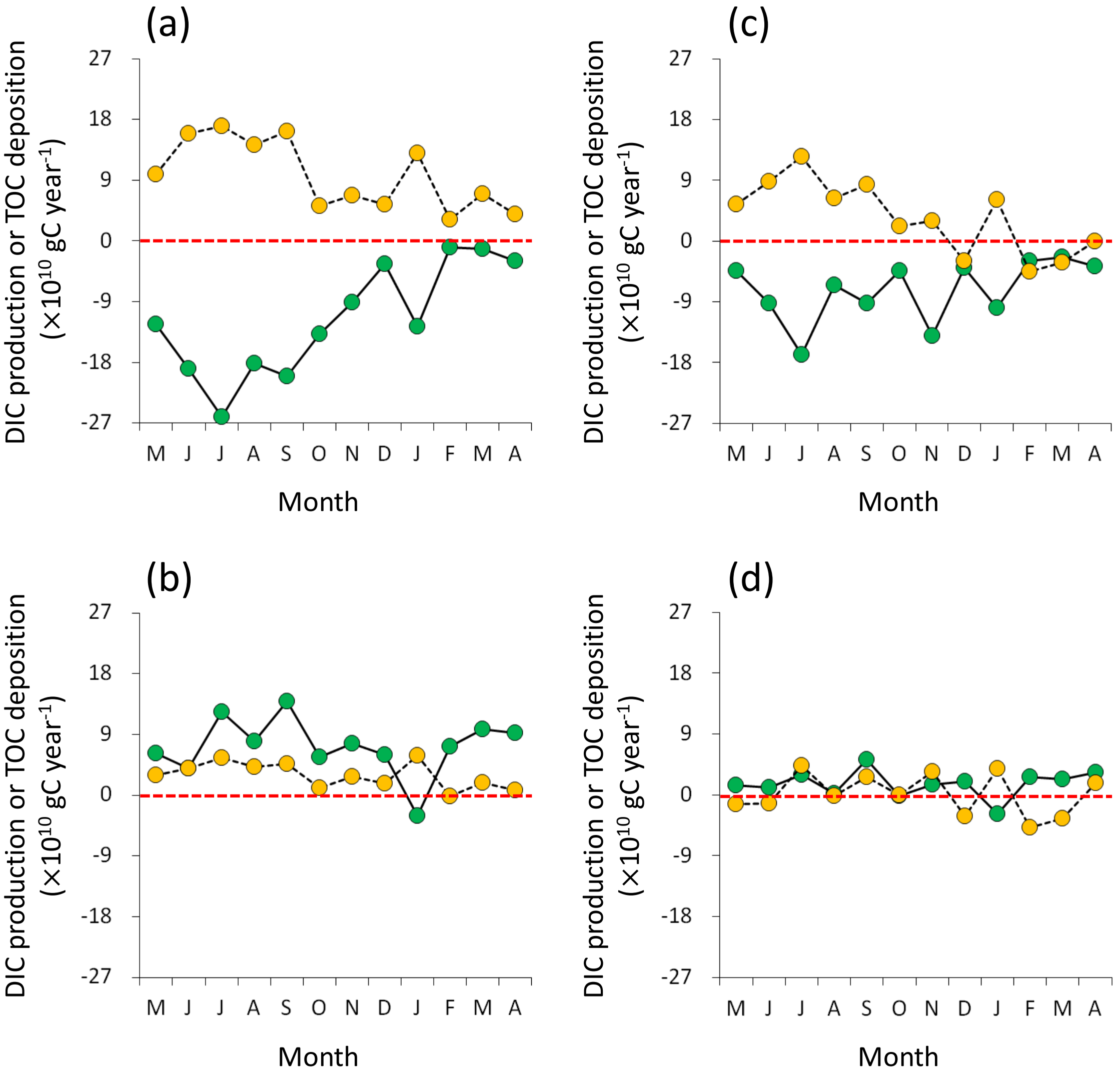

Figure 4-3
Month-to-month variation of DIC production (green) and TOC deposition (orange) in each box. Positive value indicate production of DIC and sedimentation of TOC. (a) box 1, (b) box 2, (c) box 3, and (d) box 4.

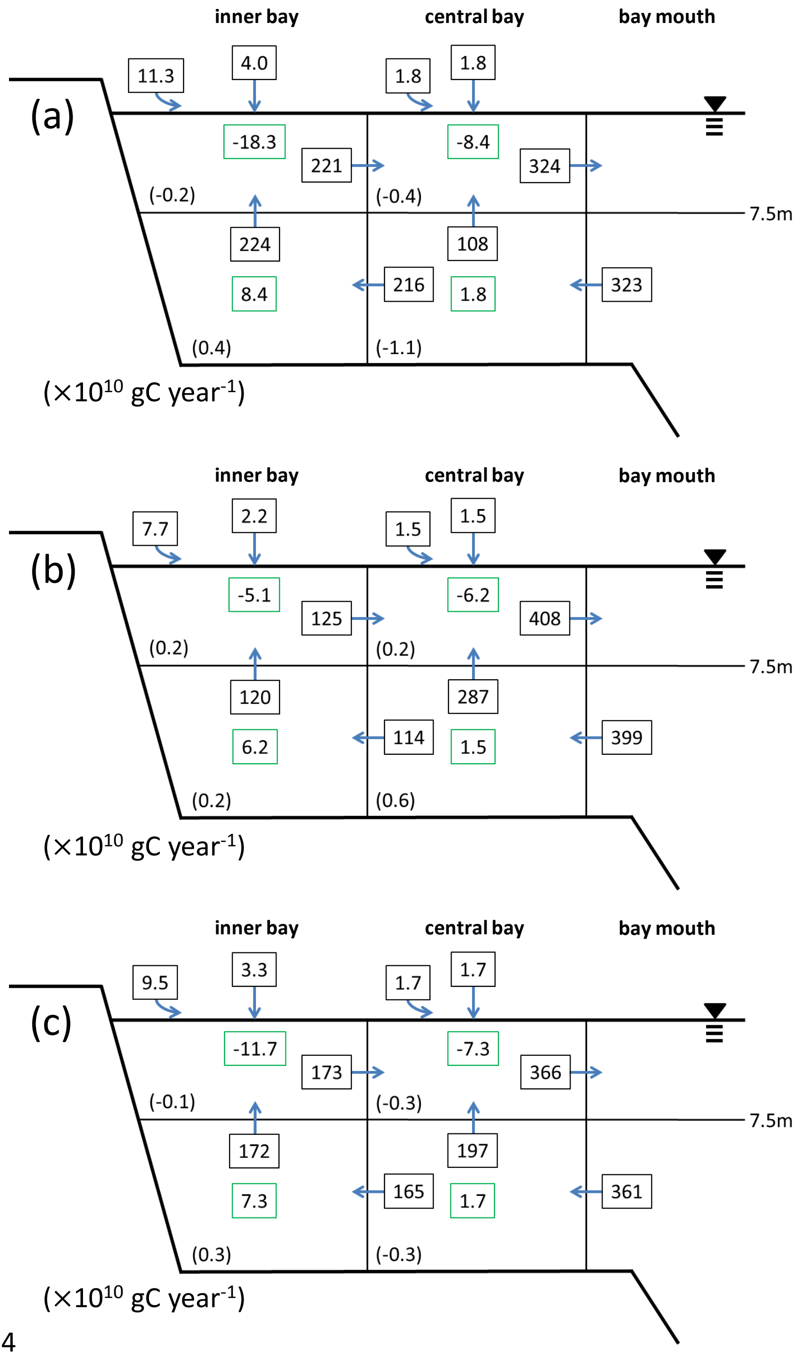

Figure 4-4
DIC budget in Tokyo Bay. (a) stratified season (May-October), (b) vertically mixed season (November-April), (c) through the year. Arrows denote direction of flux. Numbers with black square denote amount of carbon. Numbers with green square denote amount of biological uptake.

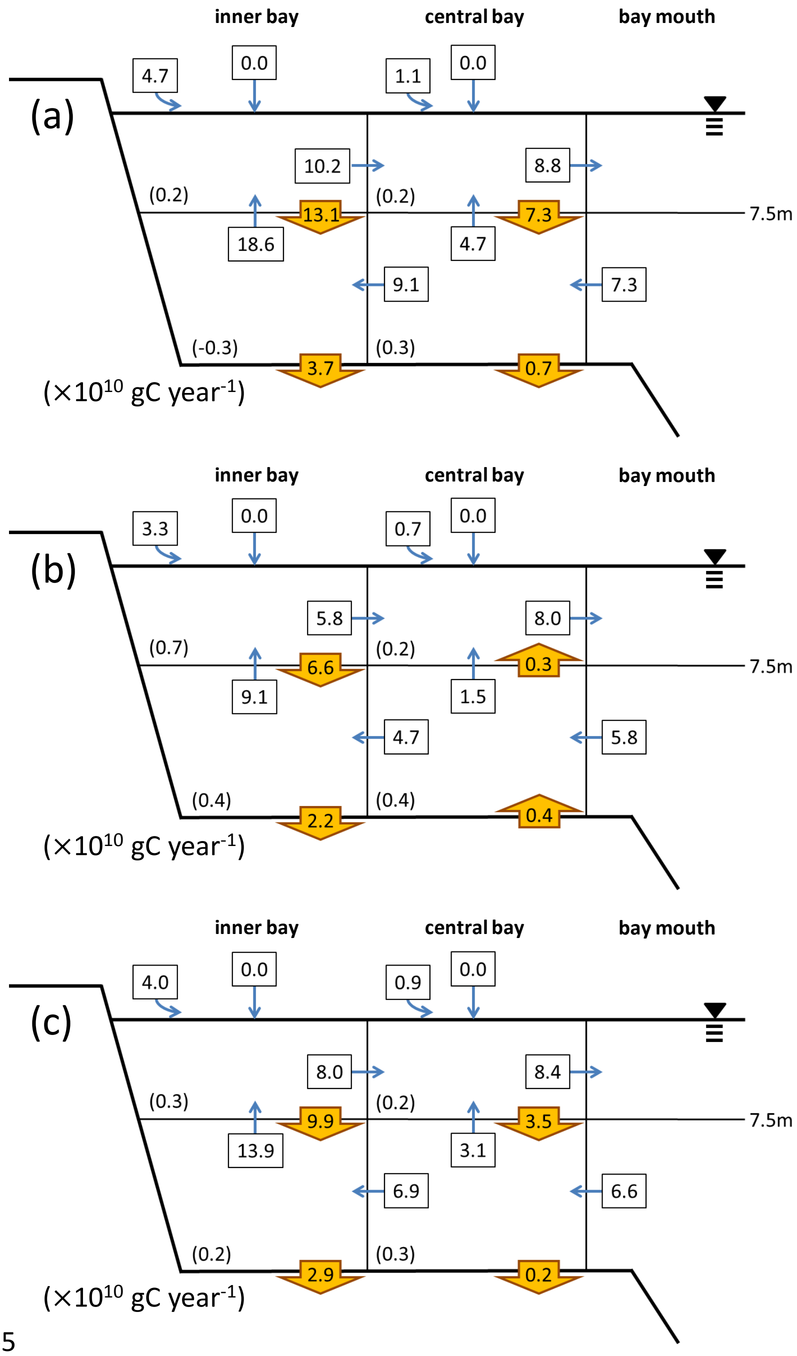

Figure 4-5

TOC budget in Tokyo Bay. (a) stratified season (May-October), (b) vertically mixed season (November-April), (c) through the year. Arrows denote direction of flux. Numbers with black square denote amount of carbon. Numbers with green square denote amount of biological uptake. Orange arrows denote direction of sedimentation or resuspension.

Chapter 5

Seasonal Variations and Sources of Sedimentary Organic Carbon in Tokyo Bay

5.1. Introduction

Coastal region sediments play an important role in global biogeochemical carbon cycles because they are recognized as the dominant reservoir for organic carbon burial in marine environments (Berner 1989; Hedges and Keil 1995). Sedimentary organic carbon in coastal waters can be supplied from both terrestrial sources and marine organisms (Heip et al., 1995; Artemyev, 1996). Knowledge of the sources of sedimentary organic carbon in coastal water and the factors controlling its distribution is essential to understanding the mechanisms of carbon cycling in the marine environment.

To elucidate the source and fate of organic matter in the marine environment, the elemental ratio of total organic carbon (TOC) to total nitrogen (TN) contents, which is usually expressed as TOC/TN, and stable carbon and nitrogen isotope ratios ($\delta^{13}C$ and $\delta^{15}N$, respectively) have been widely applied (Hedges and Parker, 1976; Peters et al., 1978; Thornton and McManus, 1994; Ogawa and Ogura, 1997; Naidu et al., 2000; Usui et al., 2006; Ramaswamy et al., 2008; Gao et al., 2012; Sarma et al., 2012; Krishna et al., 2013). In general, terrestrial organic matter can have a wide range of TOC/TN ratios (ca. 12–400; Hedges et al., 1986), while TOC/TN ratios of marine organic matter are less variable (ca. 4–9; Meyers, 1994; Tyson, 1995; Hedges et al., 1997; Twichell et al., 2002; Rumolo et al., 2011). Evaluation of isotope ratios indicates that terrestrial particulate organic matter (POM) has a depleted carbon isotope ratio ($\delta^{13}C_{POM}$) and nitrogen isotope ratio ($\delta^{15}N_{POM}$) when compared with marine POM (Vizzini et al., 2005). Typical isotope compositions of terrestrial POM have $\delta^{13}C_{POM}$ values ranging from −33 to −25‰ (e.g., Barth et al., 1998; Middelburg and Nieuwenhuize, 1998) and $\delta^{15}N_{POM}$ values ranging from 0 to 4‰ (Thornton and McManus, 1994). Typical $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ values of marine phytoplankton in temperate seas range from −22 to −18‰

(Peters et al., 1978; Wada et al., 1987; Middelburg and Nieuwenhuize, 1998) and 3 to 12‰ (Wada et al., 1987; Thornton and McManus, 1994), respectively. However, $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ values of marine POM often vary seasonally (Cifuentes, et al., 1988; Ogawa et al., 1994). Heavy $\delta^{13}C_{POM}$ has been reported in various types of eutrophic coastal waters (Cifuentes et al., 1988; Takahashi et al., 1992; Ogawa and Ogura, 1997) because of limited CO_2 diffusion from ambient water into algal cells (O'Leary, 1988). Therefore, the isotope ratio of surface sediments ($\delta^{13}C_{sed}$) may reflect seasonal variations in $\delta^{13}C_{POM}$. Reliable estimates of sedimentary organic carbon sources should take into account such seasonal variations; however, sedimentary organic carbon in coastal waters did not adequately account for temporal variability.

In this study, seasonal variations in TOC_{sed}, TN_{sed}, $\delta^{13}C_{sed}$, $\delta^{15}N_{sed}$, and chl *a* in the surface sediments of Tokyo Bay were observed. In addition, suspended POC in freshwater and seawater were measured to determine isotope values of terrestrial and marine end-members of POC throughout the year. These data were then used to assess the sedimentary organic carbon sources based on two end-member mixing models.

5.2. Materials and Methods

5.2.1. Sample Collection

Surface sediment and surface seawater samples of Tokyo Bay were collected monthly from May 2012 to 2013 on the R/V Seiyo-maru of Tokyo University of Marine Science and Technology. Surface sediment samples were collected using a multiple-corer (Rigo Co., Ltd., Tokyo, Japan) at station F3 and a gravity core sampler (HR type core sampler; Rigo Co., Ltd., Tokyo, Japan) at station F6 (Figure 5-1). The samples were cut into 0–1 cm sections, put into polyethylene bags, and stored at

−25°C until analysis. Surface seawater samples were collected at station F3 and F6 in Teflon-coated 8-L Niskin bottles mounted on a CTD rosette (Falmouth Scientific Inc., Bourne, MA, USA) with a chlorophyll fluorometer (SCF; Seapoint Sensors Inc., Exeter, NH, USA) and a DO sensor (RINKO-3 ARO-CAV; JFE Advantech Co., Ltd., Hyogo, Japan). Freshwater samples were collected monthly from the lower Arakawa River station and effluent of the Shibaura STP between May 2012 and April 2013 (Figure 5-1). 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. Both seawater and freshwater samples for suspended POM measurement were filtered through precombusted (450°C, 3h) Whatman GF/F filters, after which the filters were stored at −80°C until analysis.

5.2.2. Sample analysis

The sediment samples for TOC_{sed}, TN_{sed}, $\delta^{13}C_{sed}$, and $\delta^{15}N_{sed}$ analyses were freeze-dried, homogenized and powdered using a mortar and pestle. The analyses were preceded by treatment of samples with 1 mol L^{-1} HCl to remove carbonates. This process was repeated three times to ensure complete exclusion of carbonates. The water samples for suspended POC and $\delta^{13}C_{POM}$ analyses were dried at 60°C, then acidified with vapor at 12 mol L^{-1} HCl to remove carbonate before analysis. Sediment samples for TOC_{sed}, TN_{sed}, $\delta^{13}C_{sed}$, $\delta^{15}N_{sed}$, and water samples for suspended POC and $\delta^{13}C_{POM}$ were measured using a Hydra 20-20 isotope ratio mass spectrometer coupled to an ANCA-GSL elemental analyzer (SerCon Ltd., Crewe, UK). The sediment samples were measured in triplicate, and the mean values of the measurements were reported here. To prepare sediment samples for chlorophyll *a* (Chl *a*) analysis, about 0.2 g of freeze-dried homogenized sediments were sonicated with 8 mL of N, N-dimethyl formamide (Suzuki and Ishimaru, 1990) and pigments were extracted for 24 h at −20°C in the dark until analysis. Chl *a* was then measured using a fluorometer (TD-700, Turner Designs, Sunnyvale, CA, USA)

5.3. Results

Seasonal variations in TOC_{sed}, TN_{sed}, $\delta^{13}C_{sed}$, and $\delta^{15}N_{sed}$ in surface sediments in Tokyo Bay are presented in Figures 5-2 and 5-3. High values of TOC_{sed}, TN_{sed}, $\delta^{13}C_{sed}$, and $\delta^{15}N_{sed}$ were observed during summer, while low values were observed during other seasons. TOC_{sed} and TN_{sed} at station F3 were higher than or similar to that of station F6, while $\delta^{13}C_{sed}$ and $\delta^{15}N_{sed}$ were slightly lower than that of station F6.

Seasonal variations in Chl *a* in surface sediments are presented in Figure 5-4. Chl *a* in surface sediments ranged from 22.0 to 69.1 μg g^{-1} at station F3 and 9.2 to 33.2 μg g^{-1} at station F6. The maximum Chl *a* was reached in November at station F3. Seasonal variations of Chl *a* at station F3 differed slightly from the results of TOC_{sed}. In contrast, seasonal variations in Chl *a* at station F6 were similar to the results of TOC_{sed}.

Suspended POC and $\delta^{13}C_{POM}$ in surface water of the bay (station F3 and F6) and freshwater (the lower Arakawa River station and the Shibaura STP) are presented in Table 5-1. In surface water of the bay, high values of suspended POC and $\delta^{13}C_{POM}$ were observed during spring and summer, while low values were observed during autumn and winter. In freshwater sites, suspended POC values were similar to those of the bay, while relatively low values of $\delta^{13}C_{POM}$ were observed. At the lower Arakawa River station, there was no distinct seasonal pattern in suspended POC and $\delta^{13}C_{POM}$ values. At the Shibaura STP, there was no distinct seasonal pattern in suspended POC, while

$\delta^{13}C_{POM}$ was constant throughout the year.

5.4. Discussion

5.4.1. Seasonal Variations in Sedimentary Organic Carbon

A positive linear relationship between TOC_{sed} and TN_{sed} was observed in Tokyo Bay, and the intercept of the regression line passed very close to the origin (Figure 5-5). The contents of ammonium ions adsorbed onto clay minerals in surface sediments (Mackin and Aller, 1984) were low. Consequently, the measured TN_{sed} represents a reasonable estimate of organic nitrogen, and TOC_{sed}/TN_{sed} ratios can be used as a better proxy to estimate the sources of organic matter.

The TOC_{sed}/TN_{sed} ratios in the bay ranged from 9.2 to 11.8 at station F3 and from 8.8 to 10.5 at station F6 (Figure 5-6). The TOC_{sed}/TN_{sed} ratios were much lower than those of terrestrial organic matter (ca. 12–400; Hedges et al., 1986) and similar to those of marine organic matter (ca. 4–9; Meyers, 1994; Tyson, 1995; Hedges et al., 1997; Twichell et al., 2002; Rumolo et al., 2011). These findings indicate that surface sediments in the bay dominated by organic carbon derived from primary production rather than terrestrial organic matter.

High values of TOC_{sed} and $\delta^{13}C_{sed}$ were observed in summer, while low values were observed during other seasons. In the water column, high values of chlorophyll fluorescence (Figure 5-7), POC, and $\delta^{13}C_{POM}$ (Table 5-1) were also observed during summer. The large amount of organic carbon generated by primary production led to an increased flux of organic carbon to the sediments while also supporting bacterial organic degradation in the bottom waters, which led to anoxic bottom water in summer (Figure 5-8). Sedimentary organic carbon decomposition was mediated by a variety of aerobic and anaerobic microbial processes, which could progressively modify the bulk organic carbon composition because different fractions of organic carbon degrade at different rates (Zonneveld et al., 2010). In particular, some organic materials were degraded at similar rates in the presence or absence of oxygen, whereas other organic materials, which were mainly produced by phytoplankton as carbohydrate and amino acid with heavy $\delta^{13}C_{POM}$, were not decomposed without oxygen (Zonneveld et al., 2010). Hence, sedimentary organic carbon accumulates in surface sediment in summer. Vertical mixing was caused by atmospheric cooling in October, which resulted in a well-mixed water column during autumn and winter. As a result, organic materials with heavy $\delta^{13}C_{POM}$ decomposed gradually owing to oxygen levels in the bottom waters in autumn. Seasonal variations in Chl *a* at station F3 differed slightly from the TOC_{sed} values (Figures 5-2 and 5-4), with anaerobic degradation rates of Chl *a* being about 10 times lower than aerobic degradation rates (Sun et al., 1993). Hence, Chl *a* at station F3 did not decompose during summer and early autumn, resulting in continued accumulation of Chl *a* until November.

5.4.2. Sedimentary Organic Carbon Sources

To assess the relative proportions of terrestrial and marine organic carbon present in the sediments, a simple $\delta^{13}C$-based two end-member mixing model based on the work derived by Calder and Parker (1968) and Schultz and Calder (1976) was used. The contributions of terrestrial organic carbon (Ft) were estimated using the following equation:

$$\mathrm{Ft}\,(\%) = (\delta^{13}\mathrm{C_{mar}} - \delta^{13}\mathrm{C_{sed}})/(\delta^{13}\mathrm{C_{mar}} - \delta^{13}\mathrm{C_{terr}}) \times 100 \tag{5-1}$$

where $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$ are the marine and terrestrial end-member of the carbon isotope ratio respectively, and $\delta^{13}C_{sed}$ is carbon isotope ratio of sediment samples. Generally, most observations have assumed that the terrestrial end-member was −30.0 to −25.0‰, and the marine end-member was −23.5 to −19.0‰ (e.g., Liu et al., 2006; Yu et al., 2010; Gao et al., 2012; Sarma et al., 2012; Gireeshkumar et al., 2013; Krishna et al., 2013). However, $\delta^{13}C_{POM}$ was found to be about −16.0 to −13.0‰ in highly eutrophic coastal waters (Ogura et al., 1986; Cifuentes et al., 1988; Takahashi et al., 1992; Ogawa and Ogura, 1997; Mishima et al., 1999; Savoye et al., 2003). If a fixed value of the end-member is assigned to calculate the organic carbon origin, it will be difficult to obtain a reliable estimate of sedimentary organic carbon sources. Therefore, terrestrial and marine end-members were estimated using two approaches.

5.4.2.1. End-Member Estimation Using the TOC/TN Ratio (Model I)

The TOC_{sed}/TN_{sed} ratio distinguishes terrestrial organic matter and marine organic matter (Mishima et al., 1999). The linear regression between the TOC_{sed}/TN_{sed} ratio and the $\delta^{13}C_{sed}$ was shown in Figure 5-9. The regression equation was:

$$\begin{gathered}\delta^{13}\mathrm{C}_{sed} = -1.15 \times (TOC_{sed}/TN_{sed}) - 7.54 \\ (r^2 = 0.68, P < 0.001, n = 22)\end{gathered} \tag{5-2}$$

Based on this equation, the $\delta^{13}C_{mar}$ was estimated to be −15.1±0.8‰ at the two-sided 95% confidence bounds when the TOC/TN ratio was 6.63 (Redfield et al., 1963), while the $\delta^{13}C_{terr}$ was estimated to be −30.5±0.4‰ when the TOC/TN ratio of terrestrial organic matter was 20 (e.g., Saito et al., 1989).

5.4.2.2. End-Member Estimation Using POC and Chl *a* Data (Model II)

The values of $\delta^{13}C_{terr}$ can be estimated by suspended POC concentrations and the $\delta^{13}C_{POM}$ of the lower Arakawa River station and the Shibaura STP while considering the freshwater discharge ratio. The discharge of 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 in the drainage basin (Nihei et al., 2007b); accordingly, it can reasonably be assumed that the data at the lower Arakawa River station represent concentrations of total river water flowing into the bay. The total discharge ratio of the rivers and the STP effluents into the bay is 11:2 (Matsumura and Ishimaru, 2004); hence, the equation of $\delta^{13}C_{terr}$ is expressed as:

$$\begin{aligned}\delta^{13}C_{terr} &= \frac{[POC_{RIV}] \times 11}{([POC_{RIV}] \times 11 + [POC_{STP}] \times 2)} \times \delta^{13}C_{RIV} \\ &\quad + \frac{[POC_{STP}] \times 2}{([POC_{RIV}] \times 11 + [POC_{STP}] \times 2)} \times \delta^{13}C_{STP}\end{aligned} \tag{5-3}$$

where $[POC_{RIV}]$ and $[POC_{STP}]$ are suspended POC concentrations of the lower Arakawa River station and the Shibaura STP, respectively, and $\delta^{13}C_{RIV}$ and $\delta^{13}C_{STP}$ are the carbon isotope ratios of the lower Arakawa River station and the Shibaura STP, respectively.

We next assessed the suspended POC derived from terrestrial organic carbon in surface water of the bay. There were positive linear relationships between suspended POC and Chl *a* at station F3 and F6, respectively (Figure 5-10). Terrestrial POC

([POC$_{terr}$]) at station F3 and F6 can be estimated from the y-intercept of each linear regression equation as 18.1, 17.2, 14.8, and 12.9 (μmol L^{-1}), respectively (Figure 5-10). The equation of [POC$_{sample}$] is expressed as:

$$[POC_{sample}] = [POC_{mar}] + [POC_{terr}] \qquad (5\text{-}4)$$

where [POC$_{mar}$] is the POC concentration derived from marine POC. The isotope ratio of each sample ($\delta^{13}C_{sample}$) as measured at station F3 and F6 was expressed as:

$$\delta^{13}C_{\mathrm{sample}} = \frac{[POC_{mar}] \times \delta^{13}C_{mar} + [POC_{terr}] \times \delta^{13}C_{terr}}{([POC_{mar}] + [POC_{terr}])} \qquad (5\text{-}5)$$

The following equation can then be obtained from the above:

$$\delta^{13}C_{mar} = \frac{\left[POC_{sample}\right] \times \delta^{13}C_{sample} - [POC_{terr}] \times \delta^{13}C_{terr}}{[POC_{mar}]} \qquad (5\text{-}6)$$

The estimated values of monthly $\delta^{13}C_{terr}$ and $\delta^{13}C_{mar}$ determined from the above method are shown in Table 5-2. The estimated $\delta^{13}C_{terr}$ value was −29.3±0.8 (average ± standard error) ‰ on average, and the $\delta^{13}C_{mar}$ value was −15.2±1.8‰ (−14.8±0.5‰ at station F3 and −15.4±0.5‰ at station F6).

5.4.2.3. Sedimentary Organic Carbon Budget

The estimated values of $\delta^{13}C_{terr}$ were within the range of previous reports of −33.0 to −25.0‰ (Barth et al., 1998; Middelburg and Nieuwenhuize, 1998). In contrast, the estimated values of $\delta^{13}C_{mar}$ were comparable to phytoplankton $\delta^{13}C$ in Tokyo Bay (−15.7‰; Ogawa et al., 1994). The estimated maximum $\delta^{13}C_{mar}$ value from Model II was −11.7‰. The higher phytoplankton growth rate and lower CO_2 concentration in the cells causes less isotope fractionation; hence, the $\delta^{13}C_{POM}$ levels in phytoplankton deviate less from those in sea water and may reach a theoretical level of −11‰ (O'Leary, 1988). In addition, remarkably high $\delta^{13}C_{POM}$ values of around −13‰ have been reported in various eutrophic environments owing to rapid growth of phytoplankton (Ogura et al., 1986; Cifuentes et al., 1988; Takahashi et al., 1992; Ogawa and Ogura, 1997; Mishima et al., 1999; Savoye et al., 2003).

Table 5-3 shows the estimated contribution of terrestrial organic carbon (Ft; %) in the bay sediments from Model I and II. The contributions of terrestrial organic carbon were 27.3±4.3% for Model I and 29.2±3.5% for Model II in the bay, which was corresponded to $0.85\pm0.13\times10^{10}$ and $0.91\pm0.11\times10^{10}$ gC $year^{-1}$, respectively. This value was about 50% of the terrestrial POC flowing into the bay (1.9×10^{10} gC $year^{-1}$; see Chapter 4.3.). High terrestrial organic carbon contents were observed in the river mouth sediment (Ishiwatari et al., 1986; Ogawa et al., 1994). Hence, most terrestrial POC was probably sediment at the river mouth and the inner bay. The contributions of marine organic carbon were 72.7±4.3% for Model I and 70.8±3.35% for Model II in the bay, which was corresponded to $2.25\pm0.13\times10^{10}$ and $2.19\pm0.11\times10^{10}$ gC $year^{-1}$, respectively. This value was about 12% of the NCP in the bay (19×10^{10} gC $year^{-1}$; see Chapter 4.3.). Overall, the surface sediments in the bay were dominated by marine derived organic matter.

5.5. Summary

To identify sources of organic matter, seasonal variations in carbon and nitrogen contents and their stable isotopic values, and Chl *a* of the surface sediments were measured at two stations in Tokyo Bay. The TOC_{sed} and isotopic values indicate that organic carbon in surface sediment was controlled by terrestrial organic matter input, primary production in the bay, and hypoxic water in the bottom water during summer. The fraction of terrestrial and marine derived organic matter was estimated based on the $\delta^{13}C_{sed}$ value using the two end-member mixing model. The average contribution of terrestrial organic carbon was about 30% in the bay (0.9×10^{10} gC $year^{-1}$), which was about 50% of the terrestrial POC flowing into the bay (1.9×10^{10} gC $year^{-1}$). In contrast, the average contribution of marine organic carbon was about 70% in the bay (2.2×10^{10} gC $year^{-1}$), which was about 12% of the terrestrial POC flowing into the bay (19×10^{10} gC $year^{-1}$). Surface sediments in Tokyo Bay were dominated by marine derived organic matter.

Table 5-1

Particulate organic carbon concentrations (POC) and carbon isotope ratio values ($\delta^{13}C_{POC}$) in surface seawaters (station F3 and F6) and freshwaters ("Riv" means the lower Arakawa River station and STP means Shibaura Sewage Treatment Plant effluent).

Date	POC (μmol L^{-1})				$\delta^{13}C_{POC}$ (‰)			
	F3	F6	Riv	STP	F3	F6	Riv	STP
May-2012	52	118	135	85	–18.4	–16.0	–31.6	–24.4
Jun-2012	139	95	116	42	–18.4	–18.0	–27.6	–24.5
Jul-2012	173	95	93	61	–17.3	–15.4	–34.0	–24.0
Aug-2012	66	56	68	48	–16.4	–16.5	–25.6	–24.6
Sep-2012	89	121	76	83	–16.0	–16.4	–29.2	–25.0
Nov-2012	62	58	140	38	–18.8	–18.2	–25.1	–25.2
Dec-2012	60	47	88	42	–19.4	–20.1	–25.7	–25.0
Jan-2013	75	54	125	112	–19.7	–20.1	–27.9	–24.8
Feb-201	64	65	142	68	–18.9	–18.8	–33.8	–24.6
Mar-2013	58	60	122	45	–19.0	–19.0	–31.0	–24.4
Apr-2013	83	67	84	38	–18.1	–18.8	–32.3	–24.9

Table 5-2

Estimated carbon isotope values of terrestrial and marine end-member.

Date	Terrestrial end-member (‰)	Marine end-member (‰)	
		F3	F6
May-2012	–30.9	–11.7	–13.9
Jun-2012	–27.4	–17.0	–16.2
Jul-2012	–33.0	–15.4	–12.2
Aug-2012	–25.5	–12.9	–13.3
Sep-2012	–28.5	–12.8	–14.7
Nov-2012	–25.1	–16.4	–16.2
Dec-2012	–25.6	–16.9	–18.0
Jan-2013	–27.5	–17.4	–17.8
Feb-201	–33.0	–13.7	–15.2
Mar-2013	–30.6	–14.1	–15.8
Apr-2013	–31.7	–14.5	–15.7

Table 5-3

The contribution of terrestrial organic carbon (Ft; %) to the sedimentary organic matter.

Method	Terrestrial end-member (‰)	Marine end-member (‰)	Ft (%)
Model I	–30.5±0.4	–15.1±0.8	27.3±4.3
Model II	–29.3±0.5	–15.2±0.5	29.2±3.5

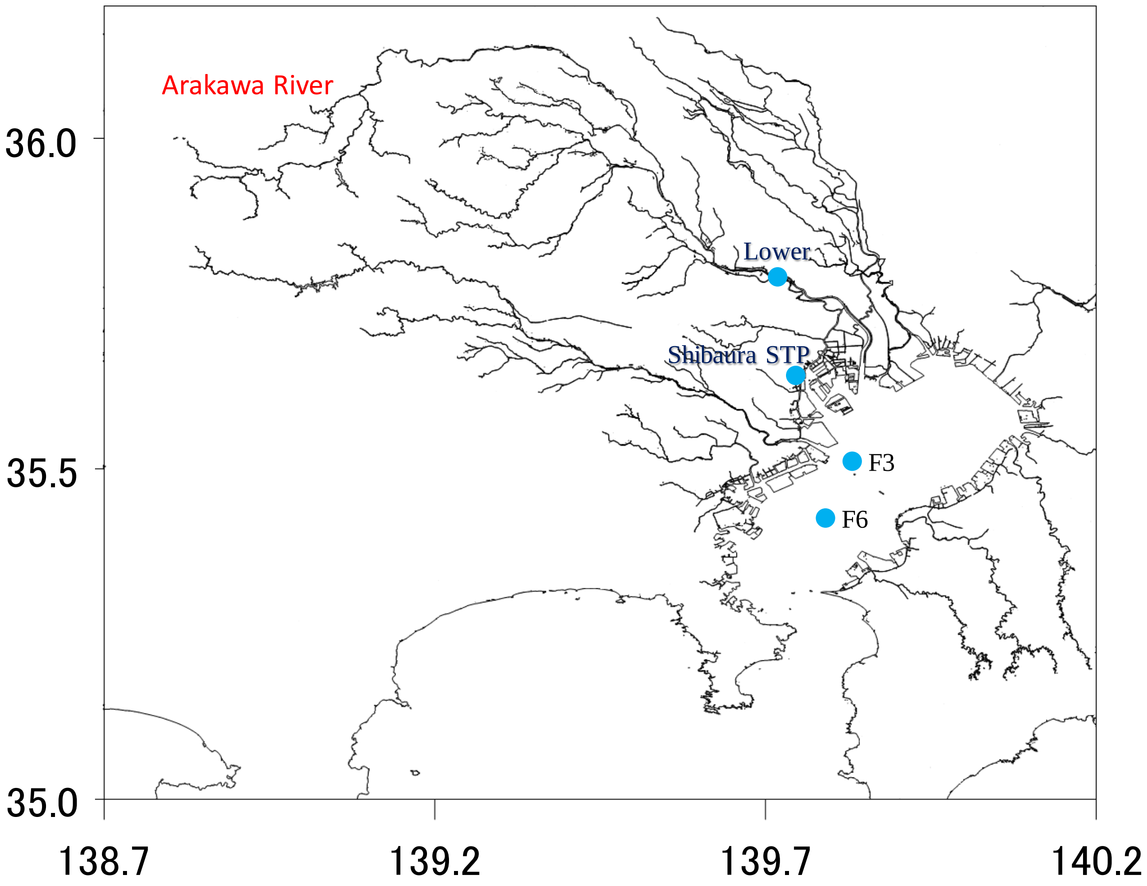

Figure 5-1
Map of Tokyo Bay. Locations of sampling sites are indicated by blue circles.

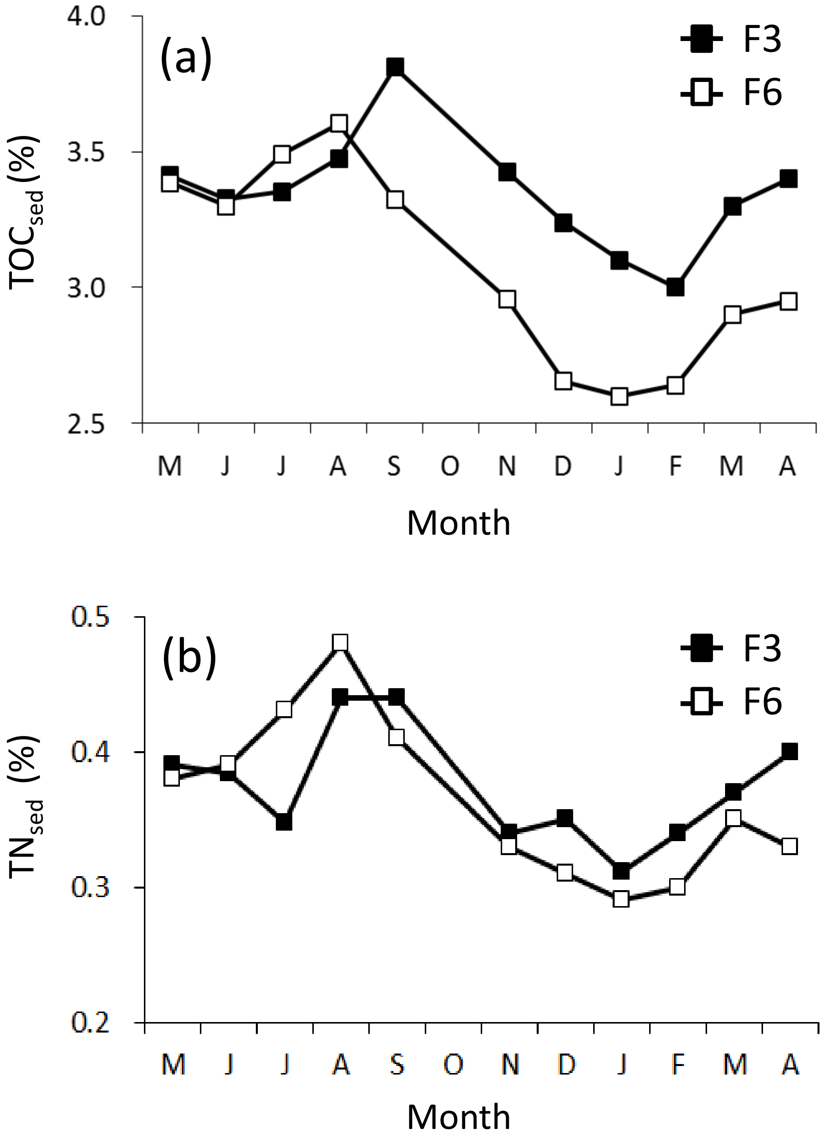

Figure 5-2
Seasonal variations of (a) TOC_{sed} (%) and (b) TN_{sed} (%) contents in surface sediments at F3 and F6 stations.

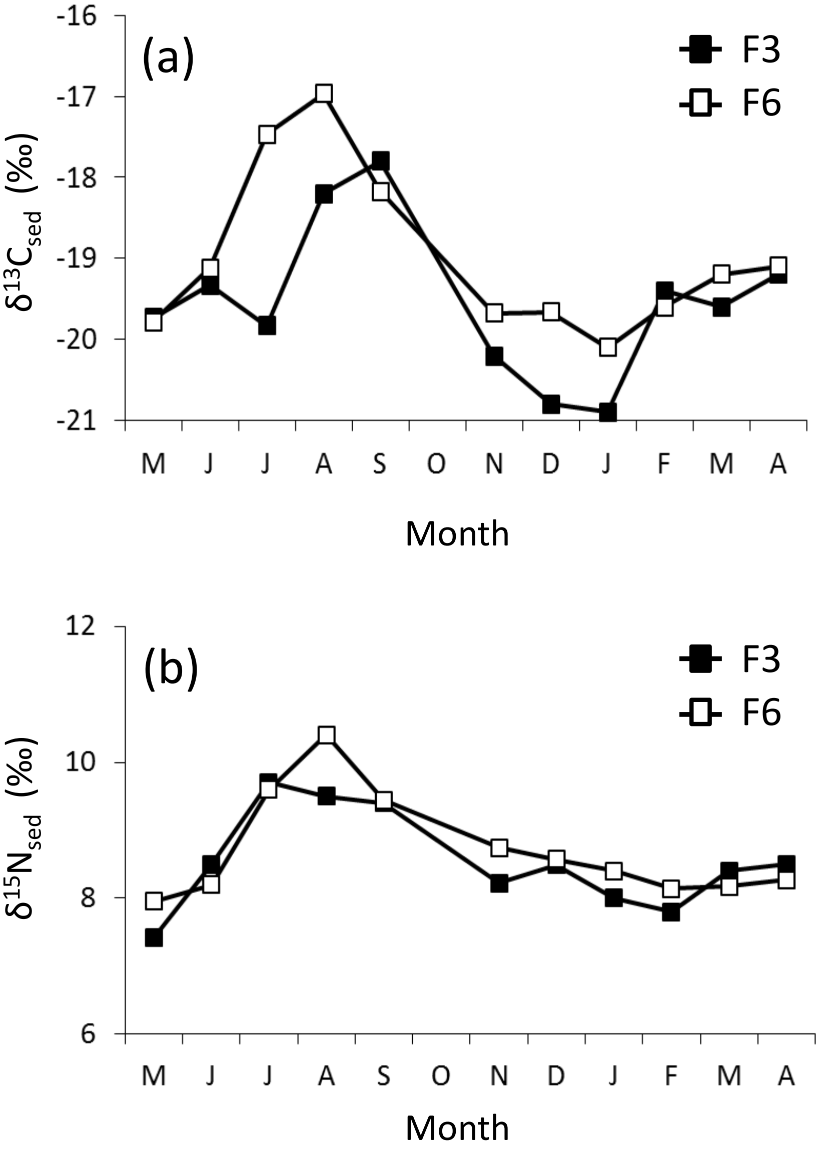

Figure 5-3
Seasonal variations of (a) $\delta^{13}C_{sed}$ (‰) and (b) $\delta^{15}N_{sed}$ (‰) values in surface sediments at F3 and F6 stations.

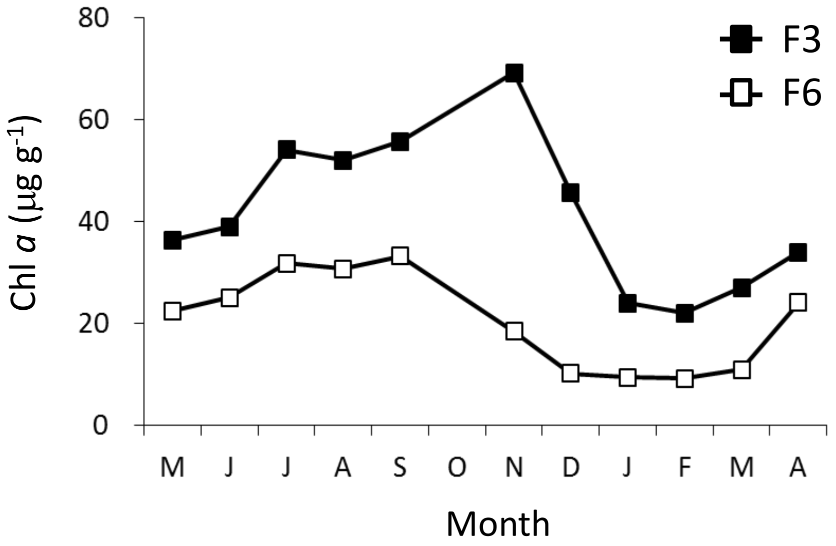

Figure 5-4
Seasonal variations of Chl *a* (μg g^{-1}) in surface sediments at station F3 and F6.

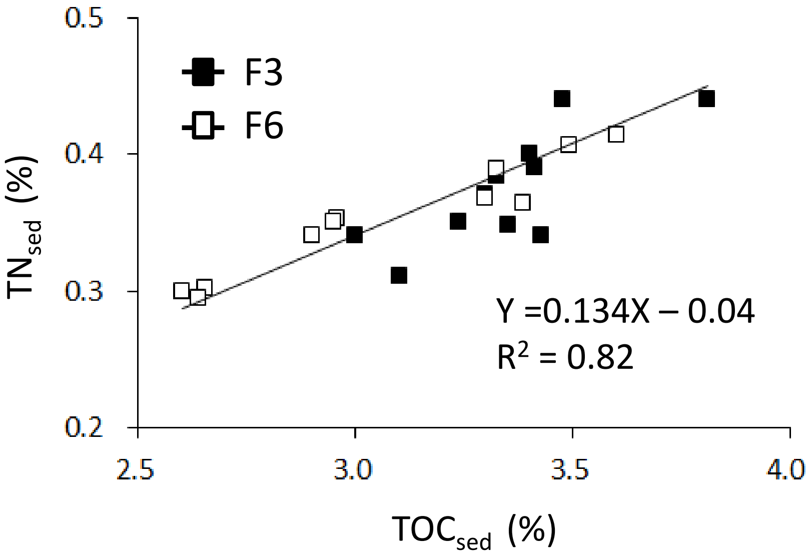

Figure 5-5
Relation between TOC$_{sed}$ (%) and TN$_{sed}$ (%) at the surface sediments of station F3 and F6. Black and white square show data at station F3 and F6, respectively.

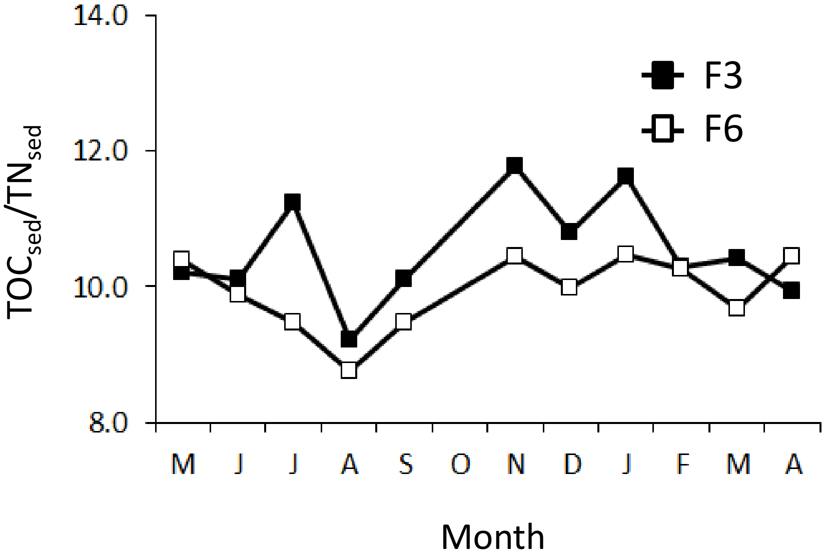

Figure 5-6
Seasonal variations of TOC_{sed}/TN_{sed} in surface sediments at station F3 and F6.

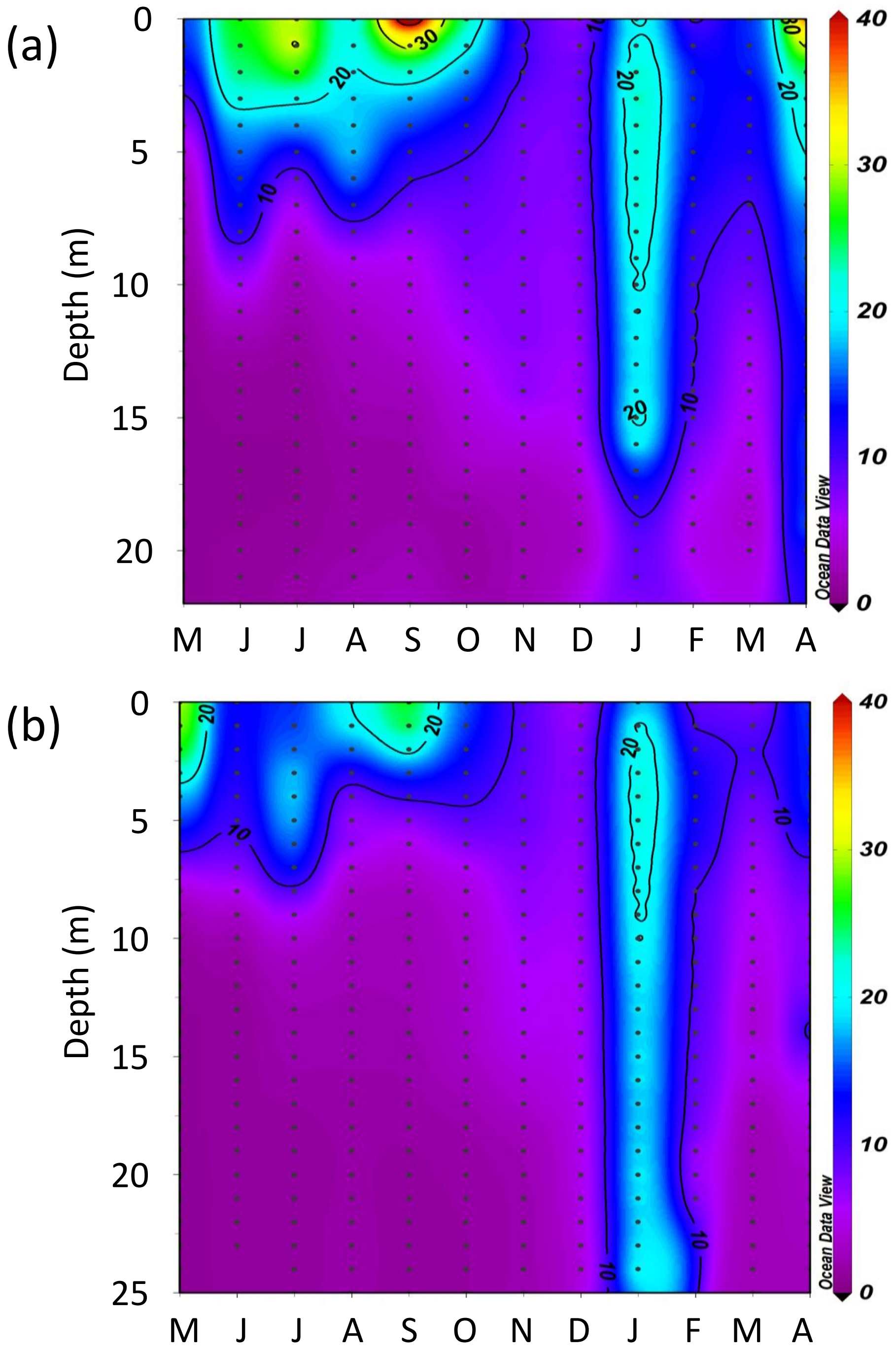

Figure 5-7
Contour plot of Chl a (μg L^{-1}) at (a) station F3 in 0-22 m layer and (b) station F6 in 0-25 m layer during observation period.

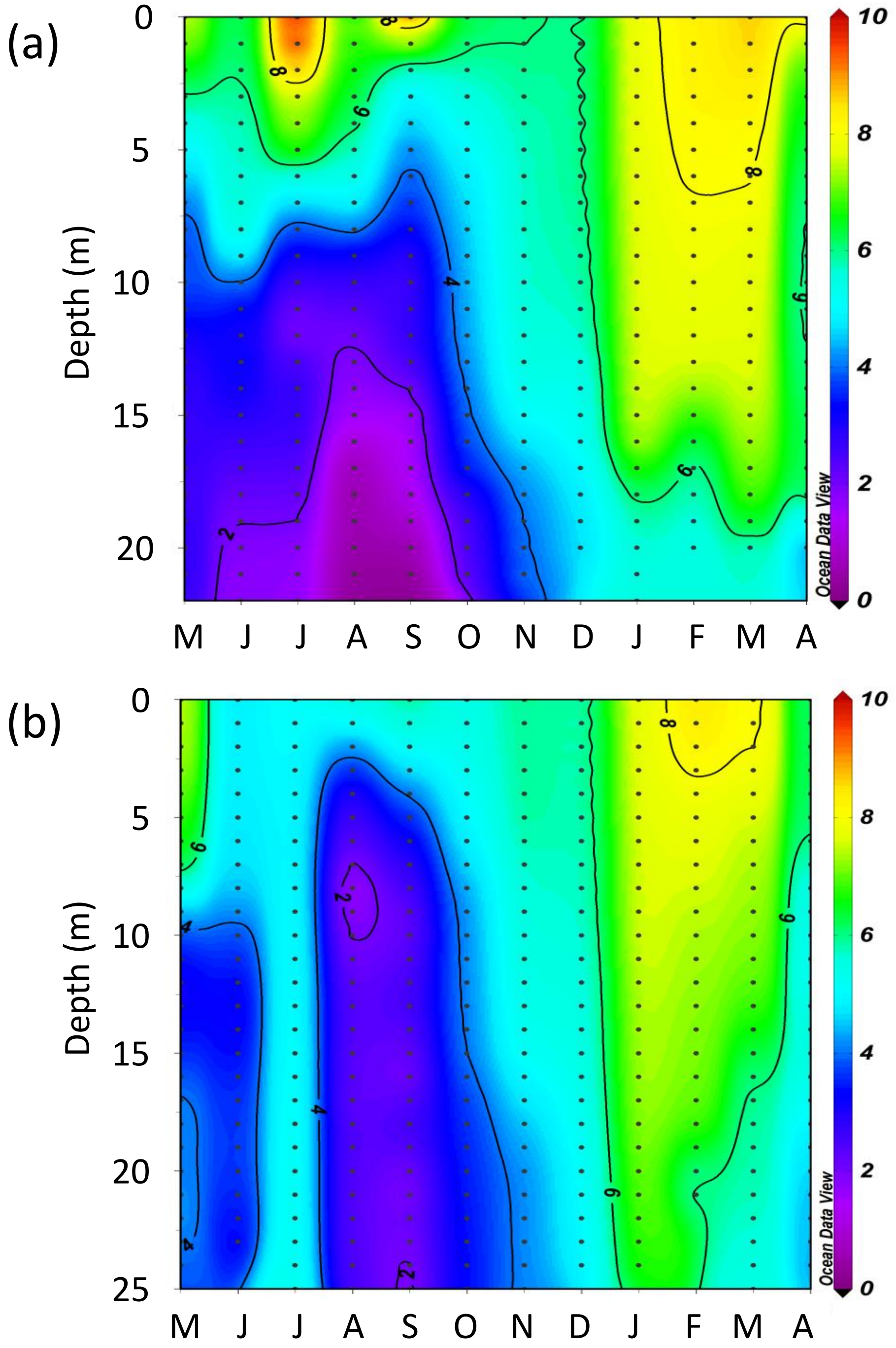

Figure 5-8
Contour plot of DO (mL L^{-1}) at (a) station F3 in 0-22 m layer and (b) station F6 in 0-25 m layer during observation period.

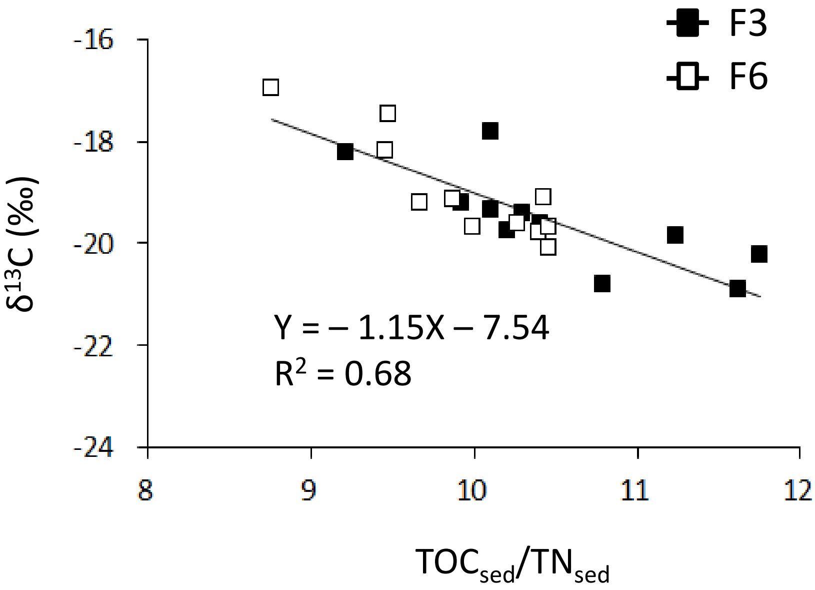

Figure 5-9

Relation between TOC_{sed}/TN_{sed} and $\delta^{13}C_{sed}$ (‰) at the surface sediments of station F3 and F6. Black and white square show data at station F3 and F6, respectively.

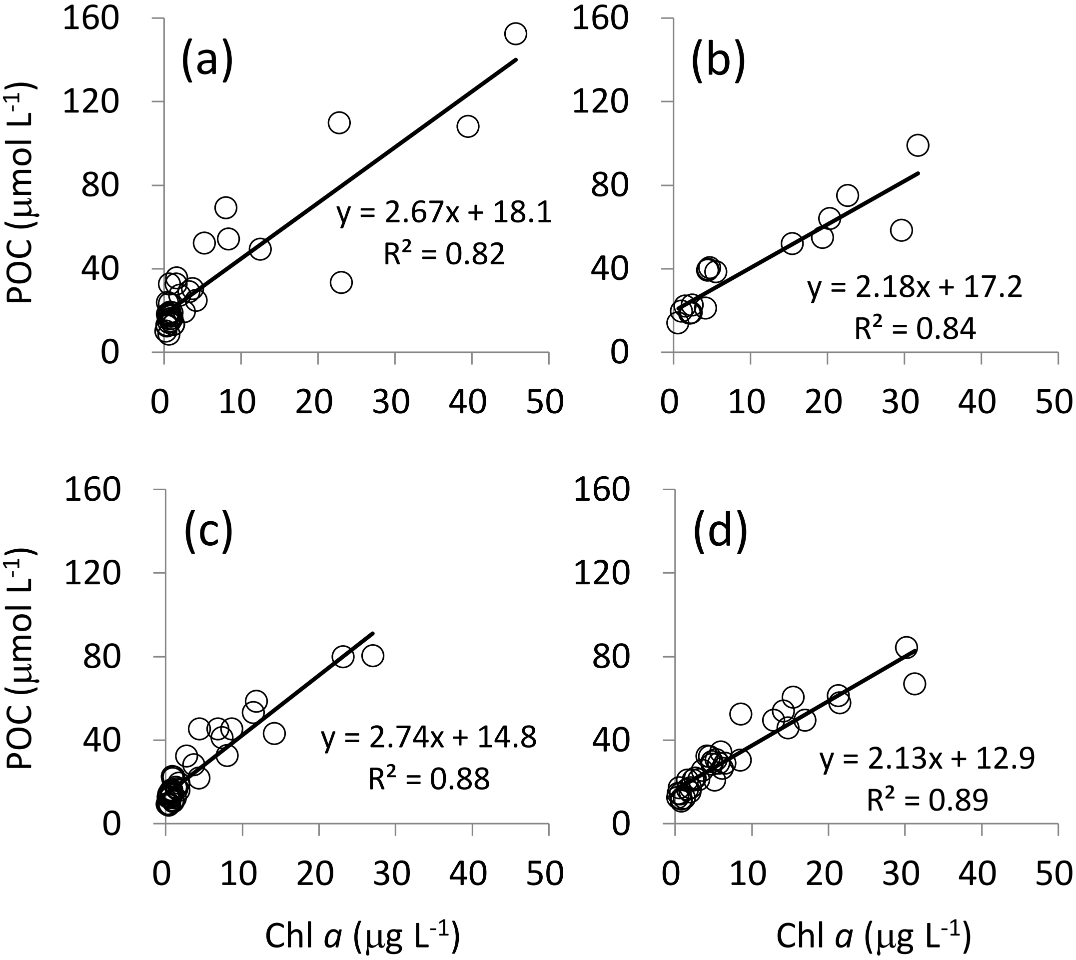

Figure 5-10

Relation between POC (μmol L^{-1}) and Chl *a* (μg L^{-1}) at station F3 (a, b) and F6 (c, d). (a, c): high freshwater discharge periods (during May and October), (b, d): low freshwater discharge periods (during November and April).

Chapter 6

Nepheloid Layers and Lateral Carbon Export from the Tokyo Bay Mouth

6.1. Introduction

Nepheloid layers are zones of elevated particulate concentration within the water column that are commonly found overlying continental shelves and slopes of the global ocean (Cacchione and Drake, 1986; Thomsen and van Weering, 1998; McCave and Hall, 2002; Rutgers van der Loeff et al., 2002; McPhee-Shaw et al., 2004). Nepheloid layers are usually observed near the surface, where they are associated with biological organic matter, and at the bottom of the water column (bottom nepheloid layer; BNL), where turbulence keeps particles in suspension while eroding and resuspending materials from the seafloor (Figure 6-1; Johnson et al., 2001; van Weering et al., 2001; Rutgers van der Loeff et al., 2002; Thomsen, 2002; van Weering and McCave, 2002; Inthorn et al., 2006). BNLs may extend from tens (McCave, 2002; McPhee-Shaw et al., 2004) to hundreds (Rutgers van der Loeff et al., 2002; Inthorn, 2006) of meters off the bottom, often exceeding the height of the well mixed benthic boundary layer. Particles in the BNL typically remain in suspension for periods of 1–2 months (Rutgers van der Loeff et al., 2002; Inthorn, 2006), their sinking characteristics being determined by aggregate formation (Thomsen and McCave, 2000) and a dynamic resuspension loop modulated by shear stresses (Thomsen and van Weering, 1998; Thomsen, 1999). In association with asymmetrical oscillations (barotropic tides and internal waves; Johnson et al., 2001; McCave et al., 2001; van Weering et al., 2001; Wollast, 2002; McPhee-Shaw et al., 2004; Monteiro et al., 2005), BNLs may propagate across the shelf, advecting with their load of suspended particulate matter and solutes. Long-distance lateral transport and alteration of organic matter in BNLs via resuspension-deposition cycles and microbial action have been thoroughly documented (Thomsen, 1999; Thomsen and McCave, 2000; McCave, 2002; Thomsen, 2002). Moreover, BNLs may become detached from the bottom in certain regions, particularly on continental slopes critical to internal tides, where they form intermediate nepheloid layers that tend to spread out laterally along isopycnals (Figure 6-2; Inthorn, 2006).

BNLs are important because they can form conduits for shelf-ocean exchange of biogeochemical constituents through their lateral advection (e.g., Wollast, 2002). This fact has been recognized by a host of continental margin flux studies conducted over a diverse range of oceanographic settings, including upwelling areas and western boundary currents (Falkowski et al., 1988; Walsh et al., 1988; Walsh, 1991; Biscaye et al., 1994). It has also been shown that the benthic carbon demand on the outer shelf and slope cannot be met by the vertical carbon flux. Therefore, lateral carbon transport, which typically occurs in BNLs, is a vital mechanism for sustaining the active benthos (Thomsen and van Weering, 1998; Thomsen, 1999; Rutgers van der Loeff et al., 2002; van Weering and McCave, 2002).

BNL is a ubiquitous feature of Tokyo Bay mouth (Yanagi et al., 1989; Yanagi et al., 1991; Yanagi et al., 1992; Yanagi, 1995). Yanagi et al. (1992) showed that the interaction between the tidal current and sudden changes in bottom topography at the shelf edge caused the effective transport of suspended matter from Tokyo Bay to the Pacific Ocean via a mechanism they termed the “Tidal Pump” (Figure 6-3). Moreover, Yanagi et al. (1995) observed that an intensified internal wave with an M_2 period above the shelf slope at the mouth of Tokyo Bay generated a bore-like water motion along the slope in the late flood tidal current, resuspended the settled particles on the slope and transported them upslope during one tidal cycle (Figure 6-4). It is important to quantify the material transport from the coastal waters to the open ocean with respect to global material cycling. However, the fate of suspended matter transported to the upslope direction has yet to be determined.

In this chapter, the BNLs of Tokyo Bay mouth were observed and the potential lateral export of POC was estimated.

6.2. Data

Hydrographic and biogeochemical data were collected during nine cruises of the R/V Seiyo-maru from May 2012 to January 2013 at station 06, 07, 08, 09, and 10 (Figure 6-5). At each station, the CTD was lowered to within 10 m of the bottom. Transmission data were collected with a Beam Transmittance Meter (Marine Systems Technology, 1060 Ti/1M) onboard the CTD. Water samples for POC were collected from each Niskin bottle from depths determined from the transmittance profile. The analysis methods for POC and $\delta^{13}C_{POM}$ are presented in Chapter 3.

6.3. Results and Discussion

6.3.1. Nepheloid Layer Distribution

Vertical distributions of temperature and salinity are presented in Figures 6-6 and 6-7. At the bay mouth, the surface water was mostly derived from coastal waters with low salinity (<34.0), while relatively high salinity water (>34.5) was found at about 100 m, where the water had a relatively high temperature that influenced salinity to a depth of 300 m. Relatively low salinity (<34.5) and temperature water derived from the western margin of the North Pacific Intermediate Water was found under the Kuroshio water (Talley, 1993; Senjyu et al., 1998).

Vertical distributions of transmittance, POC, and $\delta^{13}C_{POM}$ are presented in Figures 6-8–6-10. At the surface and bottom water, low transmittance was observed throughout the year (SNL and BNL, respectively). In contrast, intermediate water derived from Kuroshio Water was found to have high transmittance. In the SNL, transmittance values were higher during spring and summer than autumn and winter. In the BNL, there was no significant seasonal variation in transmission. The seasonal variation in the SNL and the lack of seasonality in the BNL strongly suggest that factors other than vertical input from surface primary production maintain the elevated particle concentrations in the BNL. A high POC concentration was observed in the BNL (Figure 6-9), and the transmittance of the BNL was negatively correlated with POC concentration (Figure 6-11). High $\delta^{13}C_{POM}$ values were observed in the SNL (−21‰) derived from phytoplankton production at the surface water, while intermediate water had low values of $\delta^{13}C_{POM}$ of about −24‰. In general, the $\delta^{13}C_{POM}$ values decreased downward owing to selective degradation of ^{13}C-rich molecules such as amino acids and/or carbohydrates during settling (Spiker and Hatcher, 1984; Nakatsuka et al., 1997). However, the $\delta^{13}C_{POM}$ was higher at the BNL than that of intermediate water at the BNL (Figure 6-12). In addition, these values were slightly lower than those in the inner bay sediments (see Chapter 5). This could have occurred when ^{13}C-rich molecules were decomposed during transportation from inner bay sediment (Sukigara and Saino, 2005; Sukigara and Saino, 2007). The POC in the BNL could include resuspension of bottom sediments by turbulence, as well as lateral advection of particles in the BNL from the highly productive inshore region.

6.3.2. Quantifying Lateral Carbon Export in the Bottom Nepheloid Layer

Yanagi et al. (1992) observed transmittance of the BNL and showed that it had a propagation speed of 14.5×10^3 m year^{-1}, which was comparable to the BNL length in the bay mouth. These findings strongly suggests that advection in the BNL could export POC to the deep ocean, as has been previously been suggested for Tokyo Bay (Yanagi et al., 1989; Yanagi et al., 1992; Noriki et al., 1997; Sukigara and Saino, 2005) and elsewhere (Walsh et al., 1981; Thomsen and van Weering, 1998; Madron et al., 2000; Hung et al., 2000; McCave et al., 2001; McCave and Hall, 2002; Inthorn et al., 2006; Swart et al., 2007; Waldron et al., 2009).

In this study, the lateral carbon export from the BNL to the deep ocean (E_{POC} gC year^{-1}) was estimated as follows:

$$E_{\mathrm{POC}} = \iiint_{BNL} dxdydz \times POC_{ave} \tag{6-1}$$

where $\iiint_{\mathrm{BNL}} dxdydz$ is the volume of the BNL (m^3) and $\mathrm{POC_{ave}}$ is the average POC concentration in the BNL (gC L^{-1}). $\iiint_{\mathrm{BNL}} dxdydz$ and $\mathrm{POC_{ave}}$ were assumed to have been estimated from a transmittance of less than 60%. The annual export of POC in the BNL was calculated to be 2.9×10^8 gC year^{-1}, which corresponds to only a tiny fraction (<1%) of organic carbon sedimentation in the inner bay (3.1×10^{10} gC year^{-1}; see Chapter 4.4). In this study, the flux of DOC was not considered in the BNL. The DOC profile showed a similar pattern as that of the open ocean (data not shown), in which DOC was high at the surface and decreased with depth (in BNLs; 44–53 μmol L^{-1}). Therefore, the potential lateral export of DOC from the BNL to the deep ocean was significantly lower than the POC flux. However, most continental shelves recognized that DOC export exceeds POC export fluxes off the coast of the United States, the East China Sea, and Benguela Shelf (Hung et al., 2000; Álvarez-Salgado et al., 2001; Hopkinson Jr. et al., 2002; Chen et al., 2003; Swart, 2008). If the DOC lateral export flux are similar to that of POC, organic carbon export fluxes will remain a small proportion of annual sedimentation in the inner bay.

6.4. Summary

The BNL was observed throughout the year at Tokyo Bay mouth. The transmittance data in the BNL were negatively correlated with POC concentration. The $\delta^{13}C_{POM}$ data also show that the POC in BNL was mainly controlled by lateral advection of particles from the highly productive inshore region. In addition, the lateral carbon export from the BNL to the deep ocean was estimated to be 2.9×10^{8} gC year^{-1}, and this lateral export flux corresponds to only a tiny fraction (<1%) of organic carbon sedimentation in the inner bay (3.1×10^{10} gC year^{-1}).

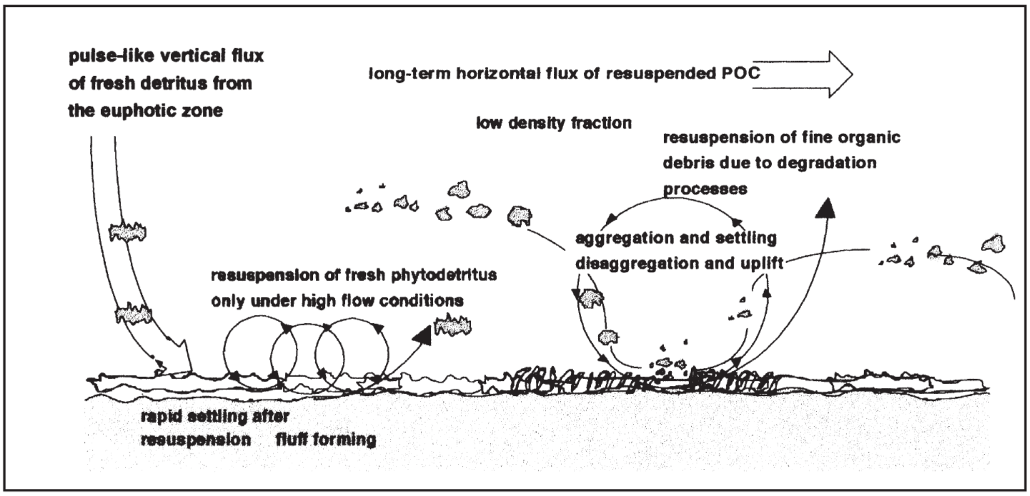

Figure 6-1
Schematic model of processes acting at different time scales that control the carbon input to the benthos at continental margins (Thomsen and van Weering, 1998; Figure ?)

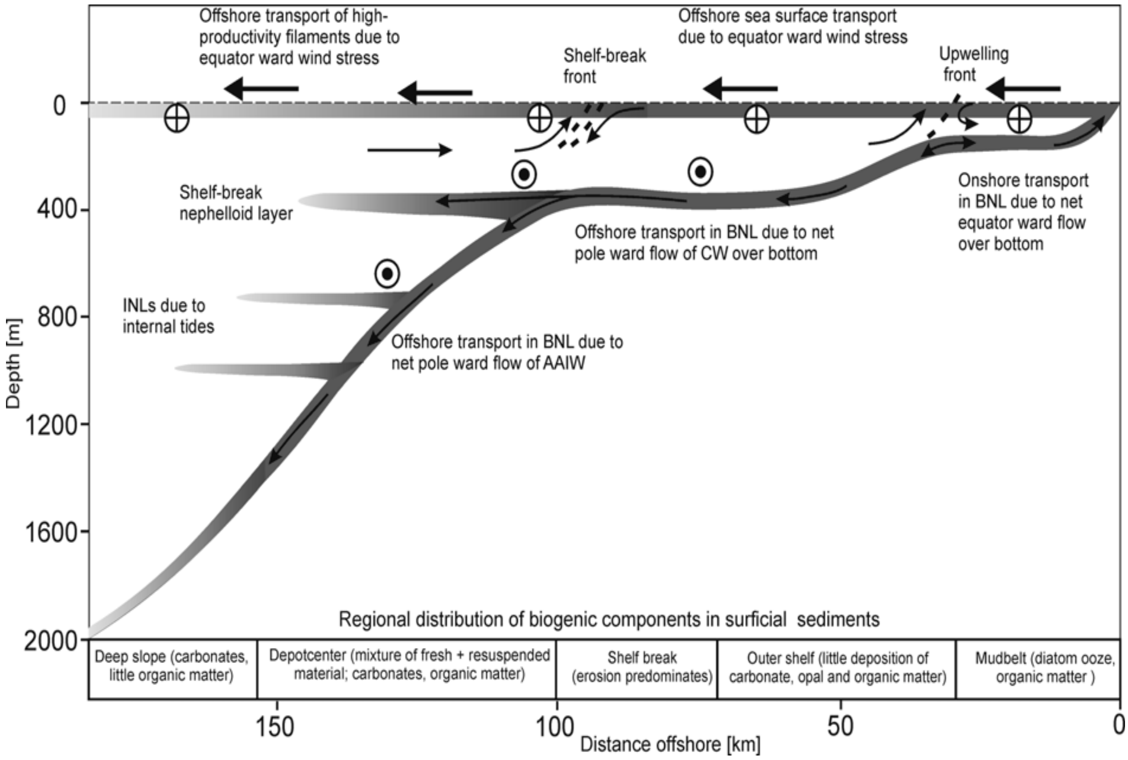

Figure 6-2
Conceptual model of the nepheloid layer distribution for the coastal waters offshore Namibia at 25.5°S. (Inthorn, 2006; Figure 2-9)

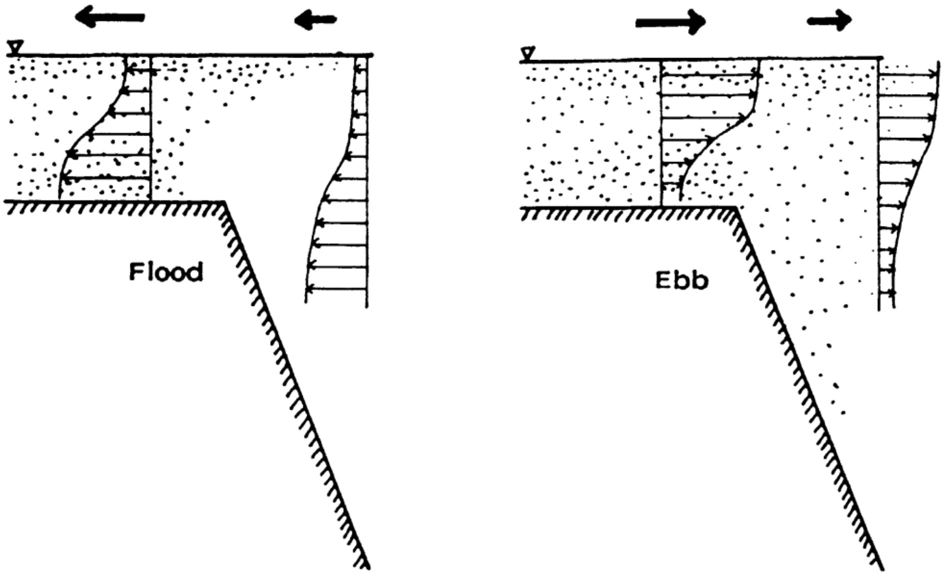

Figure 6-3
Schematic representation of tidal pump mechanism for transport of suspended matter across the shelf edge. Suspended matter above the shelf is transported to the shelf slope mainly at ebb tidal current (Yanagi et al., 1992; Figure 5)

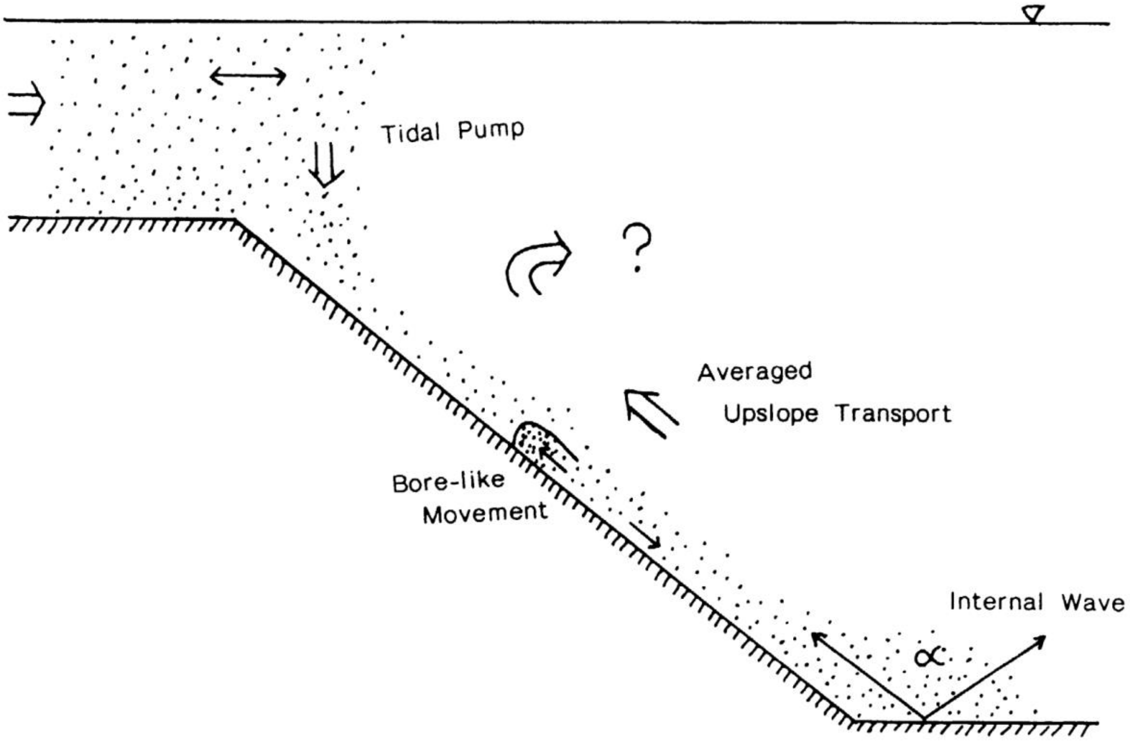

Figure 6-4
Schematic representation of suspended sediment transport at the shelf edge and shelf slope of Tokyo Bay. The concentration of suspended matter in the bottom turbid layer with the thickness of about 50 m is the highest in the late period of flood tidal current due to bore-like water movement of internal wave and suspended matter transport upslope in one-tidal cycle is missing in the long term (Yanagi et al., 1995; Figure 10)

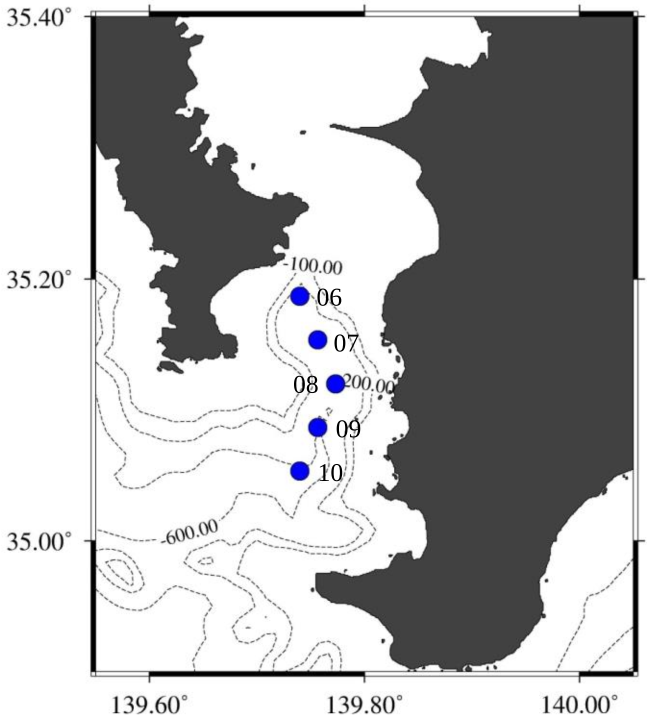

Figure 6-5
Map of Tokyo Bay mouth. Locations of sampling sites are indicated by blue circles.

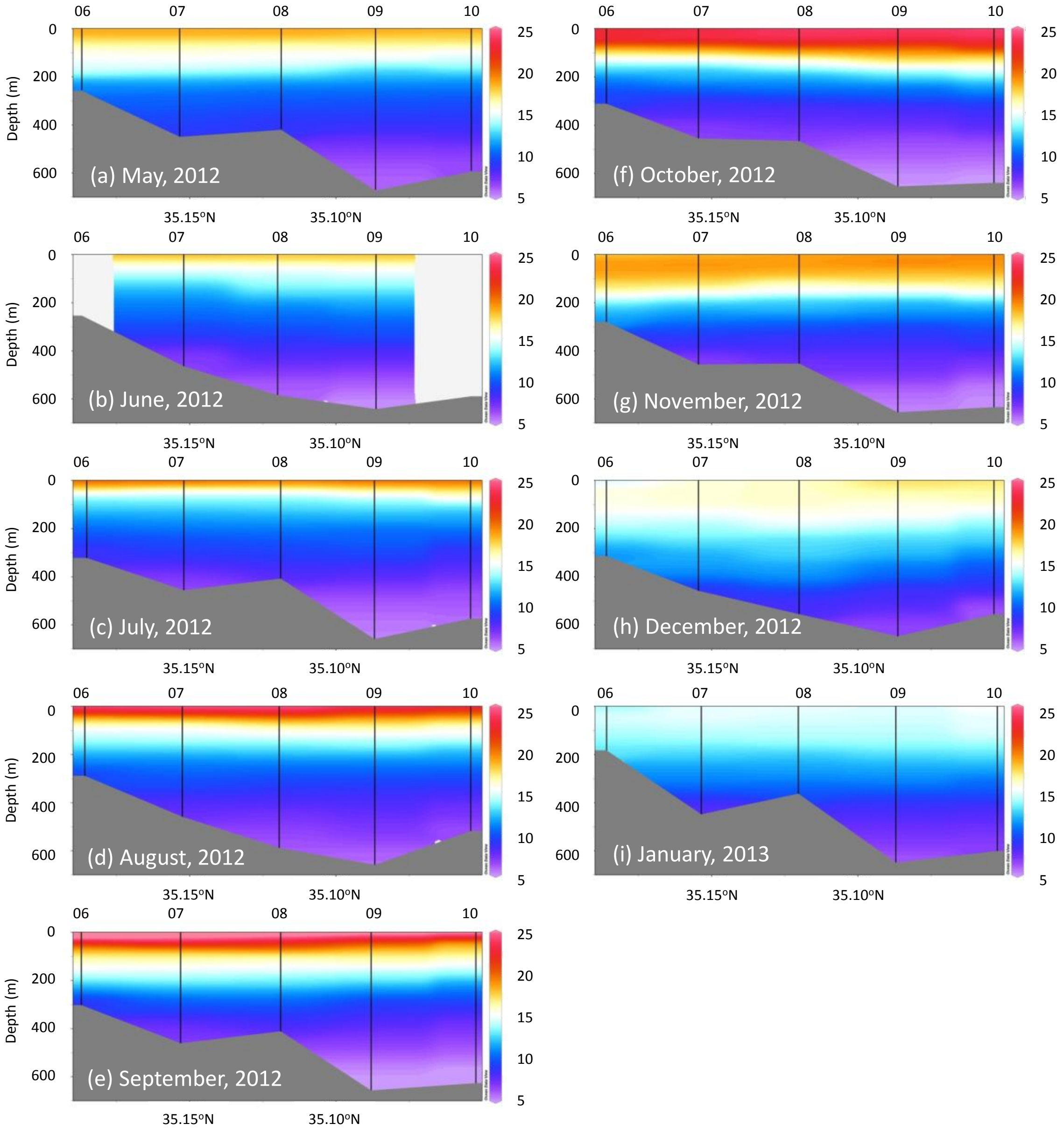

Figure 6-6
Spatial distribution of temperature (°C)

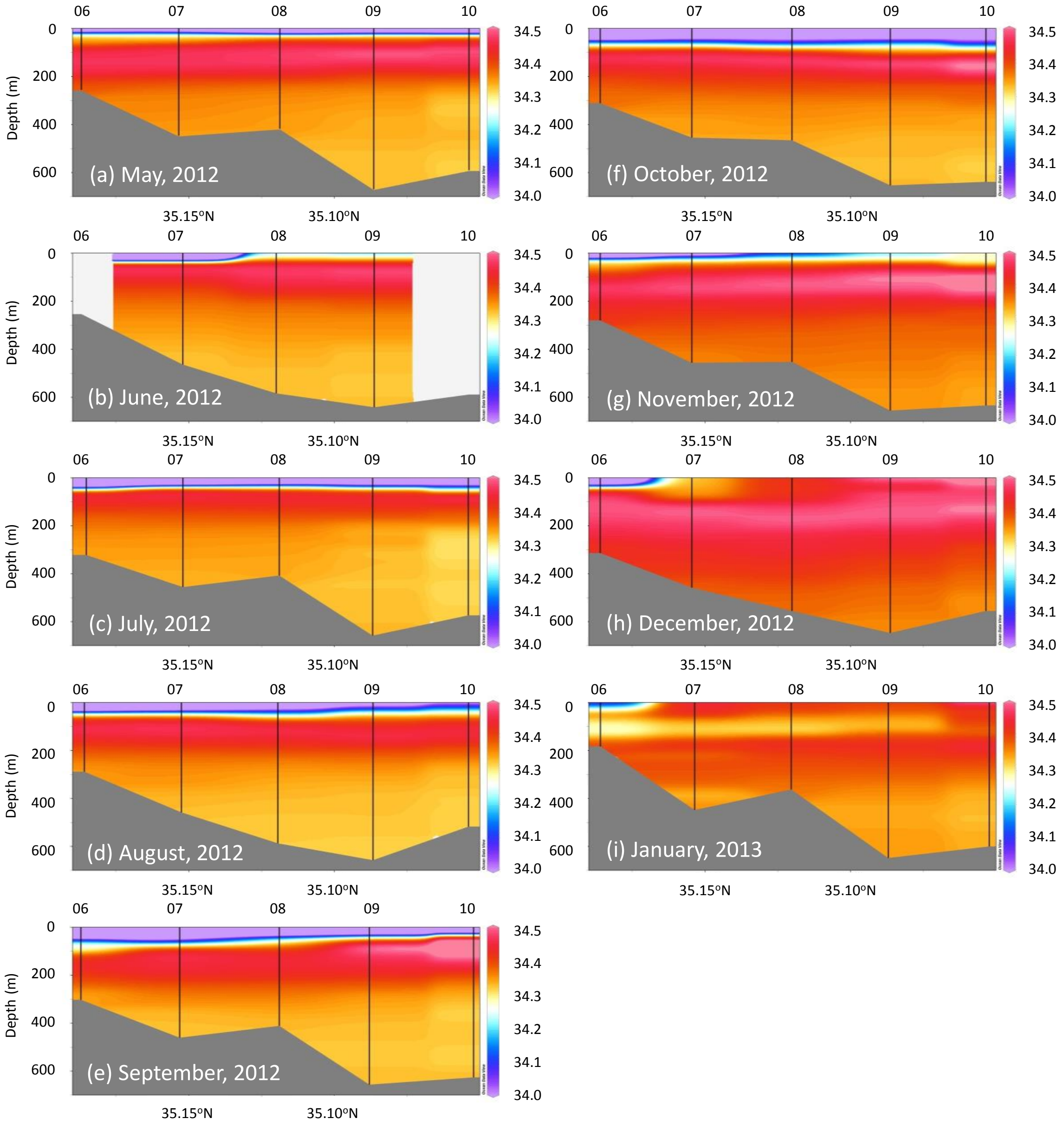

Figure 6-7
Spatial distribution of salinity

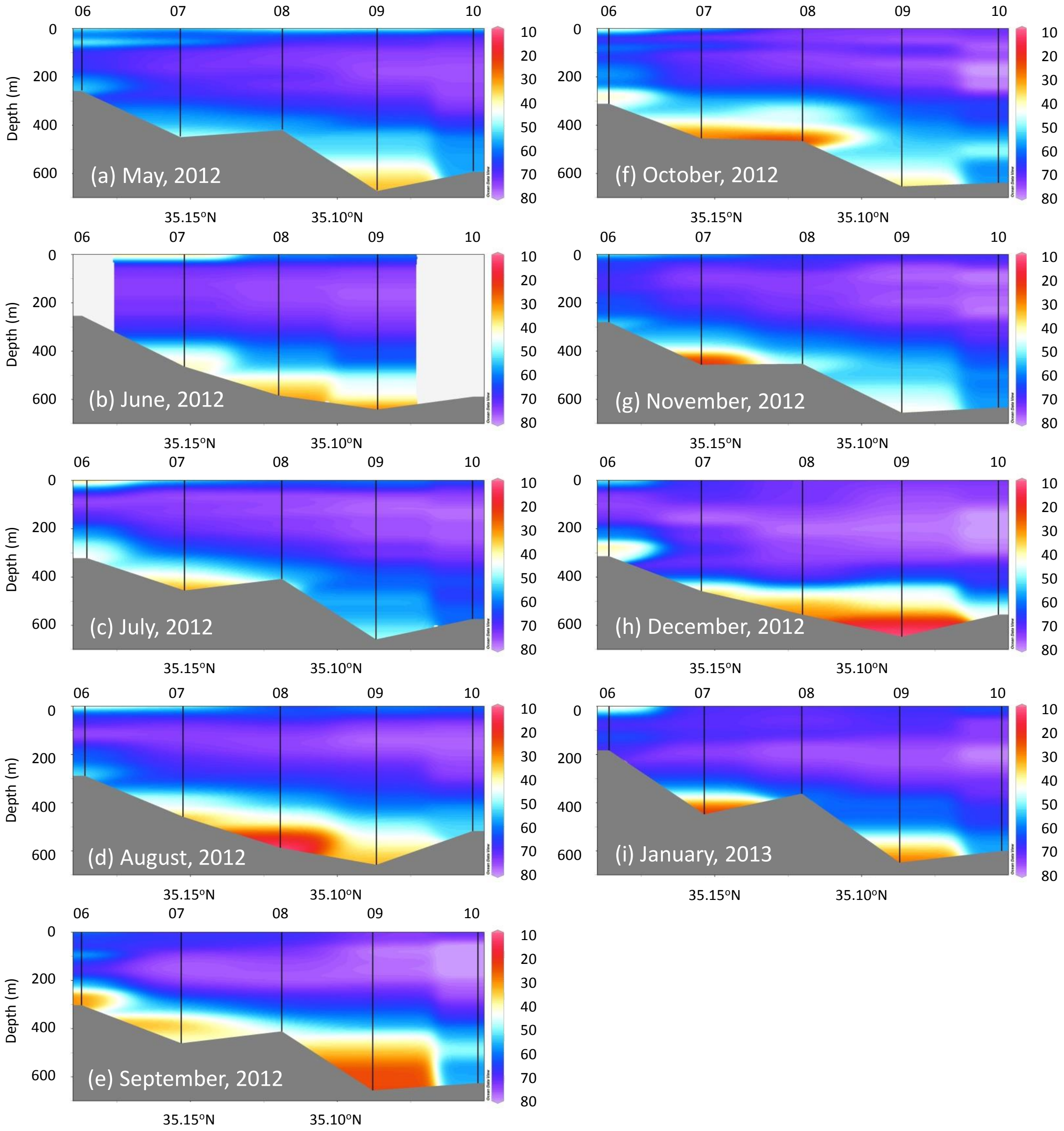

Figure 6-8
Spatial distribution of transmission (%)

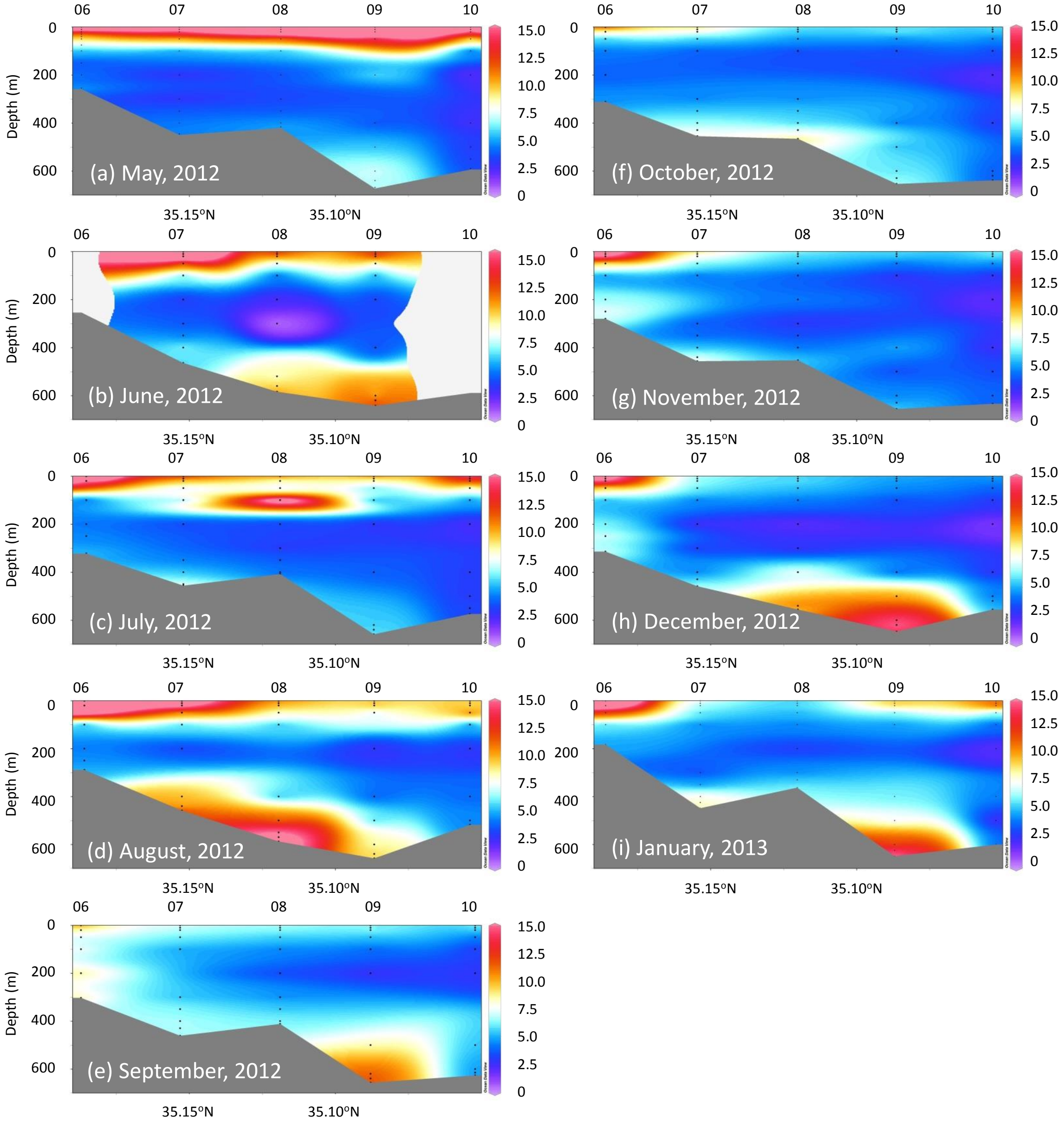

Figure 6-9
Spatial distribution of POC (μmol L^{-1})

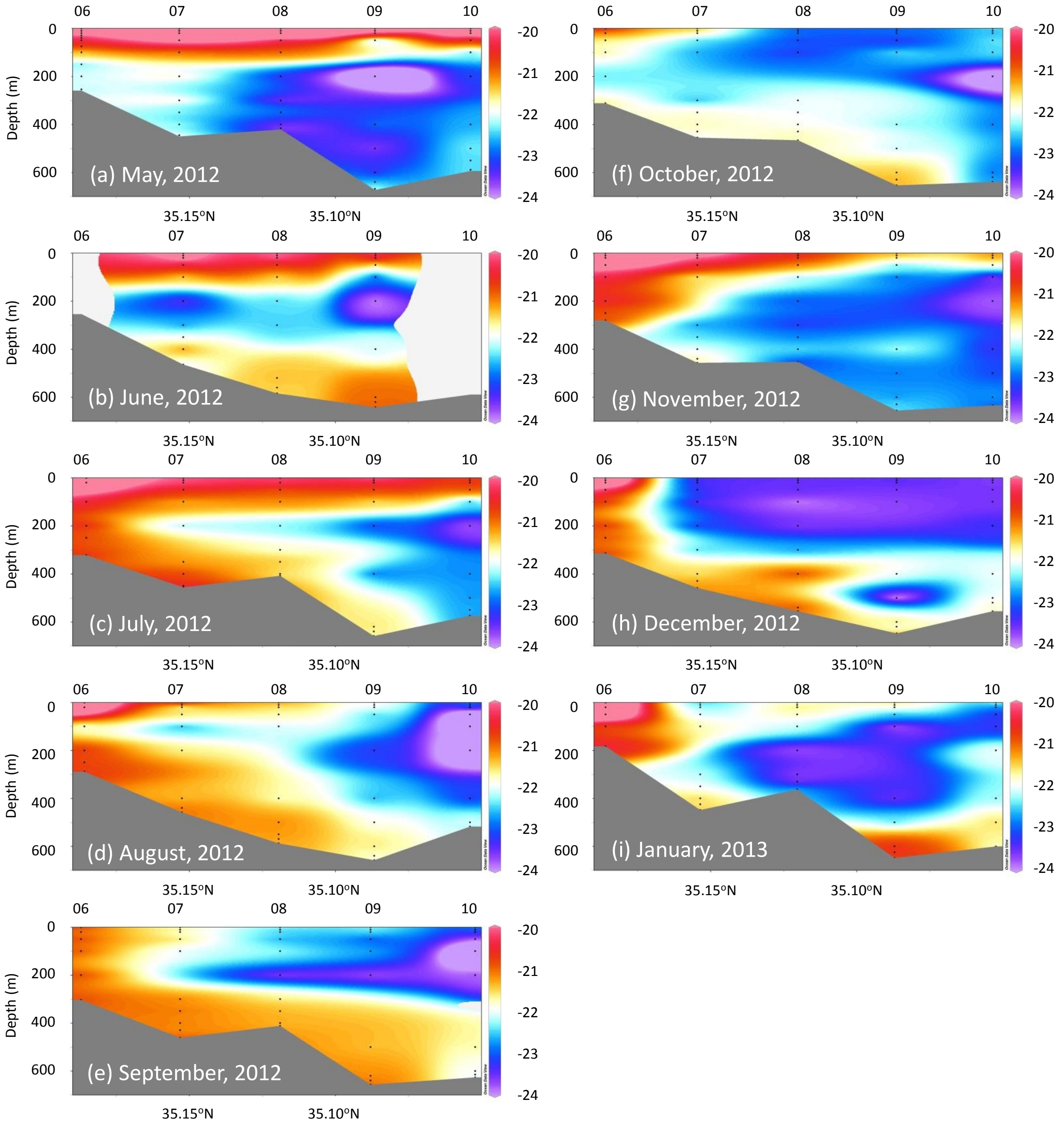

Figure 6-10
Spatial distribution of $\delta^{13}C_{POM}$ (‰)

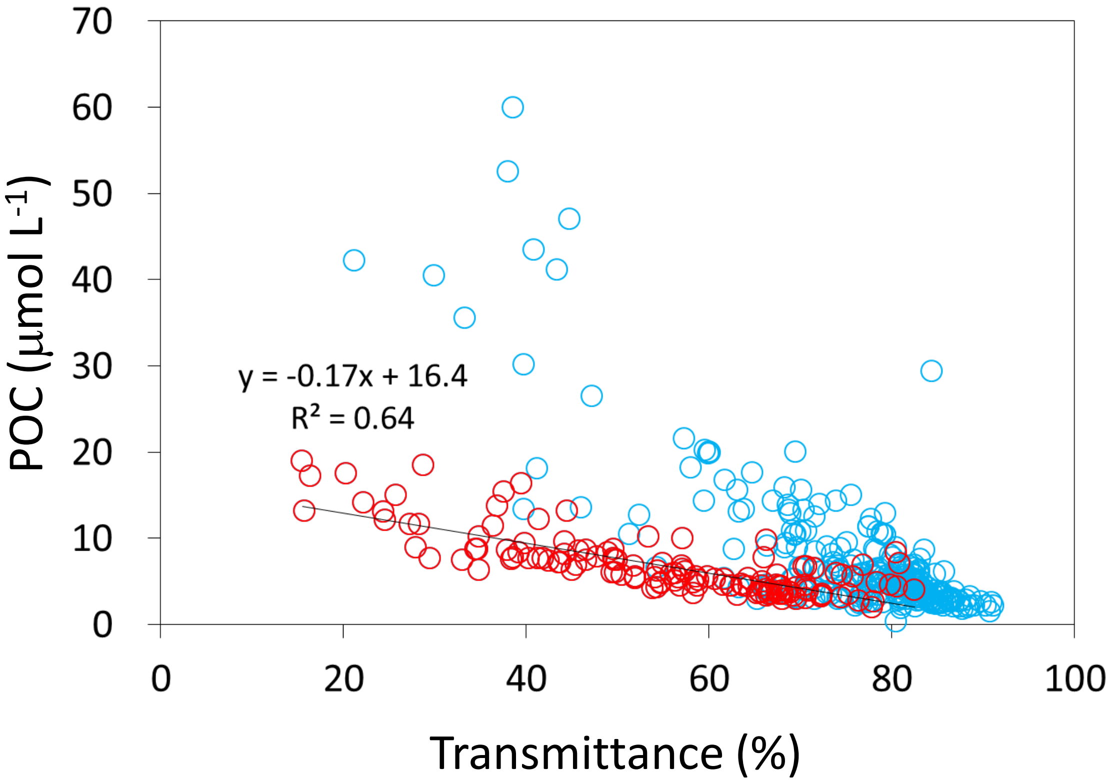

Figure 6-11
Variations in POC(µmol L^{-1}) with transmittance (%). Red circles show data in BNLs. Blue circles show data in surface and intermediate waters.

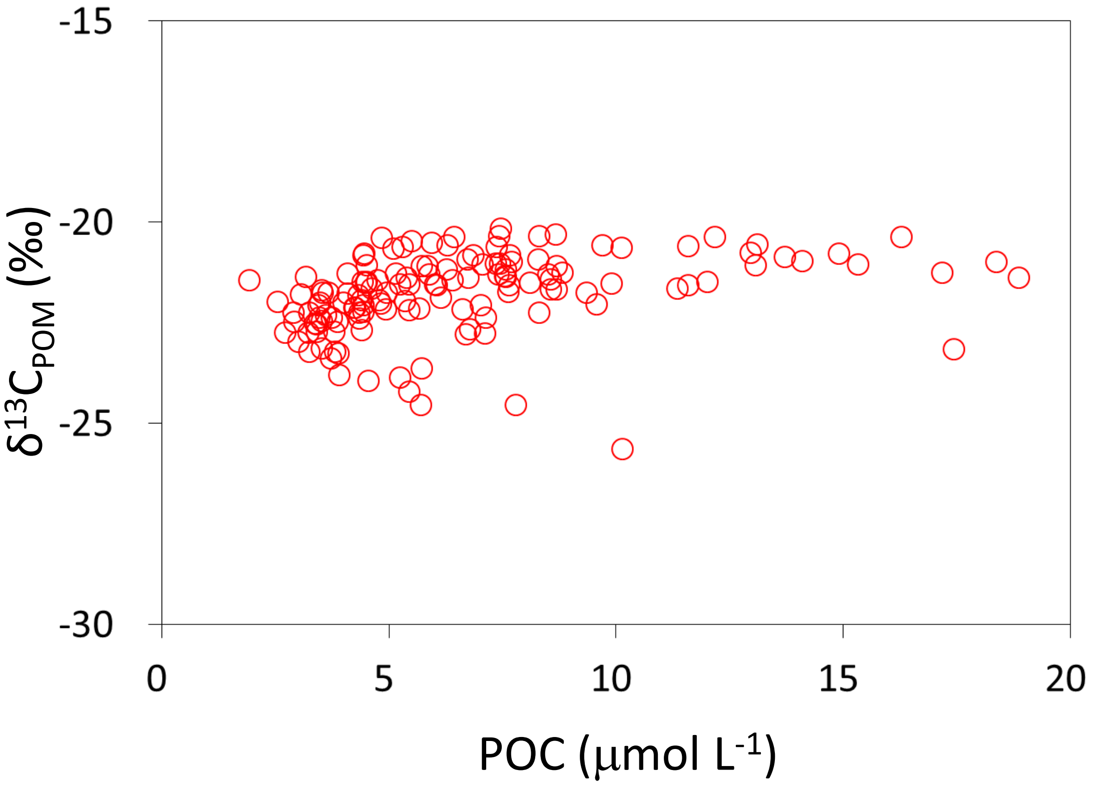

Figure 6-12
Variations in $\delta^{13}C_{POM}$ (‰) with POC (μmol L^{-1}) in BNLs.

Chapter 7

Seasonal Variations in Concentration and Lability of Dissolved Organic Carbon in Tokyo Bay

7.1. Introduction

The 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). In coastal waters, DOC 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 year^{-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 year^{-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 chapter, I measured seasonal variations in the concentration and lability of DOC in Tokyo Bay to evaluate the significance of DOC degradation to the carbon budget in coastal waters and carbon export to the open ocean. I 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 RDOC. Owing to his investigation, BDOC and RDOC data from 1972 are available for Tokyo Bay.

7.2. 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 the Shibaura STP (Figure 7-1) between December 2011 and October 2013. Freshwater 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. Within 2 h of after sample collection, the freshwater samples were carried back to the laboratory. DOC and the degradation experiment samples were filtered immediately after arrival in the laboratory through GF/F filters (nominal pore size; 0.7 μm) that had been precombusted at 450°C for 3 h. 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 (Figure 7-1). Within 1 h after sample collection, DOC and the degradation experiment samples were filtered through precombusted GF/F filters on board. Then, samples were kept in the dark and carried back to the laboratory within 4 h. I assumed that GF/F filters allow the passage of a significant fraction of free-living bacteria into DOC samples (e.g., Bauer and Bianchi, 2011). In addition, Tranvik and Höfle (1987) investigated the interactions between bacterial assemblages and DOC consumption using batch cultures and found that the DOC bioavailability was independent of the inoculum. Tanaka et al. (2011) also showed that mineralization rate of the BDOC fraction in coral reef was not different from natural waters and waters filtrated by GF/F, nevertheless the initial bacterial abundance in the incubated waters filtrated by GF/F was about 30-50% of bacteria abundance in natural waters. Therefore, I did not add the microbial community. I also did not add nutrients for the degradation experiment because I assumed nutrients were not limiting the microbial growth (see section 7.3.1.). Degradation experiment samples were then transferred to 600-mL amber glass bottles and stored at room temperature (20°C) in total darkness until analysis. The 100 mL headspace in each glass bottle contains about 900 μmol oxygen. The highest initial DOC concentration in this study was 430 μmol L^{-1} (Table 7-1). If I assume that one mole of oxygen is consumed when one mole of organic carbon is mineralized into CO_2, oxygen in headspace should have provided sufficient oxygen supply for heterotrophic decomposition by bacteria. The degradation experiments were conducted based on a total of seven incubations (0, 5, 10, 20, 50, 100, and 150 days) per field sampling event. After incubation, samples were dispensed into glass vials that had been pre-washed with HCl, pure water (Milli-Q water, Millipore Corp., Bedford, MA, USA), and then pre-combusted. Freshwater samples were preserved with 6 mol L^{-1} HCl at a concentration corresponding to 1% of the sample 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). Potassium hydrogen phthalate (Wako Pure Industries, Osaka, Japan) was used as a standard for measurement of DOC. DOC blank including pure water, instrument blank, and any carbon derived from vial was about 3 μmol L^{-1} in total.

RDOC was here defined as the concentration of DOC remaining at 150 days and

BDOC was obtained by subtracting RDOC from the initial DOC (Figure 7-2; Lønborg et al., 2009a, 2009b). The degradation rate of DOC was described by a first-order exponential decay model with a constant RDOC pool:

$$\mathrm{DOC(t)} = BDOC \cdot \exp(-k \cdot t) + RDOC \tag{7-1}$$

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 (7-1) using Matlab 2012a. For comparison with the results reported by Lønborg and Álvarez-Salgado (2012), I used the following equation to normalize the degradation rate to the rate at 15°C,

$$\mathrm{k(15°C)} = \mathrm{k(T)} \cdot (Q_{10})^{\frac{T-15}{10}} \tag{7-2}$$

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, I 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 Chl *a* and POC were also collected. The analysis method for Chl *a* and POC were presented in Chapter 3.

7.3. Results and Discussion

7.3.1. Nutrient Conditions in Tokyo Bay

Nutrient concentrations in freshwater and Tokyo Bay sites were high throughout the year (Table 7-2 and 7-3). During summer, the phosphorus concentration generally decreased and the nitrogen/phosphorus ratio was higher than the Redfield ratio of 16 (Redfield et al., 1963), suggesting that phosphorus acts as a limiting factor of primary production at the bay. A degradation experiment with phosphate (KH_2PO_4, 2 μmol L^{-1}) was conducted to ensure that phosphorus was not a limiting factor in July 2012, at which time the concentration of phosphate was lowest in the year (0.1μmol L^{-1}; Table 7-2 and 7-3). The results of the degradation experiment with added phosphorus were not significantly different from those of the degradation experiment without added phosphorus ($y=1.1x-8.2$, $R^2=0.97$, $p<0.05$). I did not add nutrients for the degradation experiment because I assumed nutrients were not limiting the microbial growth.

7.3.2. Lability and Sources of Freshwater DOC Flowing into Tokyo Bay

The lowest Chl *a*, DOC, and POC concentrations were observed at the upper Arakawa River station, which is considered to be pristine (Table 7-1). The average concentration of DOC was 38 μmol L^{-1} at the upper Arakawa River station. Headstream water sources in Japan are mostly surface runoff from neighboring watersheds and ground water input through the mineral soil horizon before entering surface water (Nakamura et al., 2011). The precipitation is characterized by very low DOC concentrations (Avery et al., 2003). Ground water inputs through the mineral soil horizon typically have low DOC concentrations because mineral soils have the ability to adsorb a significant amount of DOC (Aitkenhead et al., 2003). Such low concentrations of DOC in headstream waters have commonly been reported in Japan (e.g., Maki et al., 2010), as well as in other countries (e.g., Yamashita et al., 2011). The results of the DOC degradation experiments at the upper Arakawa River station are shown in Figure 7-3(a). Rapid degradation of the labile pool was observed within the first 20 days of incubation. Additionally, the average concentration of RDOC was 25 μmol L^{-1}, which was the lowest value in freshwater and Tokyo Bay sites and its contribution to the total DOC was 67%.

Relatively high temperatures and DOC values were observed at Shibaura STP, while seasonal variations in Chl *a* and POC were relatively small (Table 7-1). The average concentration of DOC was 355 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 the total DOC was 78% (Figure 7-3(b)). The RDOC concentrations did not vary greatly between observation months, and a significant linear relationship was observed between BDOC and DOC (R^2=0.976, p<0.001, slope=1.16), indicating that the seasonal variations in DOC were 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. This likely occurred because STPs in Japan conduct secondary treatment, which consists of removal of wastewater suspended solids by sedimentation and degradation of dissolved organic matter by activated sludge treatment

(Kadlec and Wallace, 2008).

Relatively high Chl *a* and POC concentrations were observed at the lower Arakawa River station (Table 7-1). 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 the total DOC was 66% (Figure 7-3(c)). The concentrations of DOC were more than six times higher than those at the upper Arakawa River station. High concentrations of nutrients were also observed at the lower Arakawa River station (see Table 7-2 and 7-3), which was likely a result of inputs of DOC and nutrients from STPs between observation sites. The RDOC concentrations did not show large differences between observation months, and a significant 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 and 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 within the drainage basin (Nihei et al., 2007b); accordingly, I 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 7-4 summarizes the first-order decay constants obtained by fitting the exponential degradation of DOC with time. The annual average degradation rate constant normalized to 15°C at the lower Arakawa River station was 0.031±0.005 d^{-1}, which was similar to other coastal waters (0.066±0.065 d^{-1}; Lønborg and Álvarez-Salgado, 2012).

7.3.3. Tokyo Bay

Seasonal variations in temperature, salinity, Chl *a*, POC, and DOC at the three stations in Tokyo Bay are presented in Figure 7-4. 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 7-4). The concentrations of DOC were generally lower than these at the lower Arakawa River station.

7.3.3.1. Lability of DOC

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 (Figure 7-5). The seasonal variations in DOC, RDOC, and BDOC concentrations at the three stations in Tokyo Bay are shown in Figure 7-6. 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 (Table 7-5). Thus, our RDOC results likely include a fraction of semi-labile DOC. Degradation of this semi-labile DOC fraction would occur by bacterial mineralization with longer time, photodegradation (Moran and Zepp, 1997; Opsahl and Benner, 1997; Obernosterer and Benner, 2004), aggregation (Sholkovitz, 1976; Mulholland, 1981), and/or sorption to particles (Chin et al., 1998; Kerner et al., 2003). However, the results of this study did not change significantly when DOC were divided into BDOC, semi-labile DOC, and RDOC. The lifetime of semi-labile DOC is about 1.5 years (Hansell, 2013), which is considerably longer than the residence time of Tokyo Bay (Takada et al., 1992). Therefore, in our analysis, there was no problem with inclusion of semi-labile DOC in RDOC. In addition, Ogura (1975) only divided DOC into BDOC and RDOC; therefore, I divided DOC in the same way to enable comparison with that study.

Table 7-6 summarizes the degradation constants of DOC for the bay surface waters. The annual average degradation rate constants normalized to 15°C at F3, F6, and 06 were 0.128±0.014, 0.094±0.016, and 0.083±0.010 d^{-1}, respectively. Most degradation rate constants for the bay water were higher than those of freshwater (Table 7-4). The half-lives of BDOC were calculated from the degradation rate constant. The annual average half-lives of BDOC at F3, F6, and 06 were 5.4, 7.4, and 8.4 days, respectively.

BDOC produced by phytoplankton in the bay water might have led to faster degradation rates because the half-lives of BDOC were about five times faster than the residence time of the bay water.

RDOC concentrations in Tokyo Bay were negatively correlated with salinity and positively correlated with Chl a (Table 7-7). In the bay, salinity was lower in spring and summer than in autumn and winter (Figure 7-4) because of high freshwater input during spring and summer. The freshwater RDOC concentration was higher than that of Tokyo Bay water; therefore, a negative relationship between RDOC and salinity was observed. RDOC is also produced directly by phytoplankton (Kragh and Søndergaard, 2009). Hence, the positive relationship between RDOC and Chl a observed in this study likely reflected RDOC produced by phytoplankton.

7.3.3.2. RDOC Sources

To estimate the sources of RDOC in Tokyo Bay, multiple linear regression analysis with salinity and Chl a as the independent variables was applied to all RDOC data observed at three stations in Tokyo Bay. BDOC in Tokyo Bay was not well correlated with salinity and Chl a (Table 7-7), so multiple linear regression analysis was not applied to the BDOC data. I obtained the following multiple linear regression equation (Model I):

$$\begin{gathered}[\mathrm{RDOC}\,] = (259 \pm 38) - (5.96 \pm 1.20) \times [Sal] + (0.597 \pm 0.20) \times [Chla] \\ (r^2 = 0.79, P < 0.001, n = 35)\end{gathered} \tag{7-3}$$

where [RDOC] is the RDOC concentration (μmol L^{-1}), [Sal] is salinity, and [Chla] is the chlorophyll *a* concentration (μg L^{-1}) of each sample. The end-member of terrestrial RDOC ([RDOC$_{terr\text{-}end}$]) was as follows when the salinity was 0;

$$[\mathrm{RDOC}_{terr-end}] = (259 \pm 38) + (0.597 \pm 0.20) \times [Chla_{river}] \qquad (7\text{-}4)$$

where [Chla$_{\mathrm{river}}$] is the Chl *a* concentration (μg L^{-1}) at the freshwater site. The end-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 7.3.1.). It is possible that freshwater inputs in Tokyo Bay were more strongly influenced by STPs than headstream waters. Alternatively, if I 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}), I obtain the following multiple regression equation (Model II):

$$\begin{aligned}&[\mathrm{RDOC}\ ] = 149 - (2.65 \pm 0.26) \times [Sal] + (1.03 \pm 0.40) \times [Chla] \\ &(r^2 = 0.71, P < 0.001, n = 35)\end{aligned} \qquad (7\text{-}5)$$

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

$$[\mathrm{RDOC}_{terr-end}] = 149 + (1.03 \pm 0.40) \times [Chla_{river}] \qquad (7\text{-}6)$$

In this study, I assumed that [Chla$_{\text{river}}$] 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$_{\text{river}}$] 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 7-1) 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 (Table 7-5). Following the method described Ogawa and Ogura (1990a), I 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:

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

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

$$[\mathrm{RDOC}_{ocean\ origin}] = [\mathrm{RDOC}_{ocean-end}] \times [Sal]/34.5 \tag{7-8}$$

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

$$[\mathrm{RDOC}_{terr}] = [\mathrm{RDOC}_{terr-end}] \times (34.5 - [Sal])/34.5 \tag{7-9}$$

The RDOC derived from phytoplankton ([RDOC$_{phyto}$]) can be estimated from equation (7-7):

$$[\mathrm{RDOC}_{phyto}] = [\mathrm{RDOC}] - [\mathrm{RDOC}_{ocean\ origin}] - [\mathrm{RDOC}_{terr}] \tag{7-10}$$

For each multiple linear regression equation (equation 7-3 and 7-5), the two-sided 95% confidence bounds of each coefficient and intercept were estimated. For the concentrations of RDOC originating from phytoplankton, terrestrial, and open oceanic waters, I estimated the upper and lower bounds by changing an equation within its error range. The relative concentrations of RDOC (%) with error in the bay originating from phytoplankton, terrestrial, and open oceanic waters at the three stations are presented in Table 7-8. The results show that the open ocean is the major source of RDOC in Tokyo Bay. At station F3, which is located close to land, terrestrial RDOC was comparable to that from the open ocean. The concentration of terrestrial RDOC was significantly higher than that of RDOC from phytoplankton at all stations, even at the bay mouth.

The influx of terrestrial DOC from the rivers to Tokyo Bay was estimated using a box model (see Chapter 4.3.; 3.0×10^{10} gC year^{-1}) and RDOC accounted for 66% of terrestrial DOC (see section 7.3.2.; 2.0×10^{10} gC year^{-1}). The efflux of DOC from the surface bay to the open ocean was estimated using a box model (see Chapter 4.3.; 5.8×10^{10} gC year^{-1}), and RDOC accounted for 73% in the surface bay mouth (see section 7.3.3.; 4.2×10^{10} gC year^{-1}). Assuming that terrestrial and phytoplankton RDOC were exported outside of the bay in the same ratio at the bay mouth (Table 7-8), Tokyo Bay exported mostly terrestrial RDOC to the open ocean owing to the high concentration of terrestrial RDOC and remineralization of BDOC. Moreover, the ratio of terrestrial RDOC input into the bay (2.0×10^{10} gC year^{-1}) and terrestrial RDOC efflux to the open ocean (0.8×10^{10} and 0.5×10^{10} gC year^{-1}, respectively for Model I and II) was 42% and 25%, respectively. Residual terrestrial RDOC in the bay may be removed from the water column by photodegradation (Moran and Zepp, 1997; Opsahl and Benner, 1997; Obernosterer and Benner; 2004), aggregation (Sholkovitz, 1976; Mulholland, 1981), and/or sorption to particles (Chin et al., 1998; Kerner et al., 2003).

The fate of terrestrial DOC in the coastal ocean and the open ocean has long been the subject of debate (Hedges et al., 1997). For example, biomarkers (e.g., lignin phenols) and the stable carbon isotopic composition of DOC are commonly used to estimate the contribution of terrestrial DOC to the open ocean (Druffel et al., 1992; Hedges et al., 1997; Raymond and Bauer, 2001; Bauer and Bianchi, 2011). Lignin phenols analysis indicated that terrestrial DOC comprises only a small fraction (4–10%) of the total DOC in the open ocean (Meyers-Schulte and Hedges, 1986; Opshal and Benner, 1997; Hernes and Benner, 2006). In addition, the stable carbon isotopic composition of DOC also indicated that terrestrial DOC represents less than 10% of the total DOC (Bauer et al., 2002). As a result, most terrestrial DOC is remineralized in coastal waters, and only a small fraction is exported to the open ocean. In this study, terrestrial RDOC in the surface bay mouth accounted for less than 20% of the total RDOC (Table 7-8). Although these levels were slightly higher than those reported in previous studies using lignin phenols and stable carbon isotopic compositions of DOC, they are probably reasonable given that exported terrestrial RDOC were further diluted with open oceanic water once outside the bay. Nevertheless, more complete information regarding the sources and lability of DOC are important to enable a better understanding of the fate of DOC in the coastal ocean and open ocean.

7.3.4. 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. Ogura (1975) conducted degradation experiment with short incubation time (about 50 days) relative to our experiment (150 days). However, BDOC can be consumed by bacteria over short periods (days to weeks; Lønborg and Álvarez-Salgado, 2012) and therefore, the remaining DOC pool after 150 days of incubation, used in equation (7-1), is not significantly different from RDOC concentration at 50 days. Actually, degradation rate constants calculated using data from the first 50 days (k_{50}) and those using all data from 150 days of experiment (k_{150}) are not significantly different ($k_{50}=0.90\times k_{150}+0.016$, $R^2=0.86$, $p<0.01$). Therefore, I assume that our degradation rate constants are comparable to those reported by Ogura (1975).

In 1972, the average concentrations of RDOC and BDOC were 224 and 337 μmol L^{-1} (40% and 60% of the total DOC, respectively) in the freshwater environment of the lower Tamagawa River, which flows into Tokyo Bay (Ogura, 1975). The present RDOC and BDOC concentrations at the lower Arakawa River station (149 and 86 μmol L^{-1}) are lower than those reported by Ogura (1975). If I assumed 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 rate constant (k_{15}) of 0.087 d^{-1}, which is much higher than that observed in the present study (Table 7-4). These changes are consistent with the fact that 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). Degradation of DOC at STPs before being discharged should lower BDOC fraction more than RDOC. Overall, our results indicate that the quantity of DOC flowing into the bay has decreased, and the quality of DOC becomes more recalcitrant.

In Tokyo Bay, the concentrations of DOC at station F3 decreased from 287 μmol L^{-1} in 1972 (Ogura, 1975) to 124 μmol L^{-1} in 2012, most likely because of a decrease of

DOC discharge from rivers and a decrease in primary production (Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Bouman et al., 2010). The concentrations of RDOC and BDOC observed in this study (100 μmol L^{-1} and 24 μmol L^{-1}, respectively) were lower than those estimated by Ogura (1975) in 1972 (165 μmol L^{-1} and 100 μmol L^{-1}, respectively). Conversely, the contribution of RDOC to the total DOC in this study (80.6%) is higher than the value observed 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, DOC becomes more recalcitrant. In addition, decreasing nutrient loads in the bay have caused decreasing primary production (Yamaguchi and Shibata, 1979; Yamaguchi et al., 1991; Bouman et al., 2010). Therefore, DOC produced by phytoplankton should also have decreased.

7.4. Summary

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 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 DOC becomes 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 fraction.

Table 7-1

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. Shibaura STP* indicates not conducted degradation experiment.

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*	Jan-2012	14.9	0.4	0.9	387±2	191
Shibaura STP*	Feb-2012	17.2	1.2	0.1	305±3	79
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

Table 7-2

Nutrient concentrations (μmol L^{-1}) at the upper Arakawa River (upper AR), the lower Arakawa River (lower AR), and Shibaura STP stations. Nutrient samples were filtered through cellulose acetate filters (DISMIC-25cs, 0.45μm pore size, Advantec, Tokyo, Japan), and stored at freezer (–25°C). Nutrient concentrations were determined with autoanalyzer systems, a Quaatro-Marine 5ch (SEAL Analytical, Ltd, Fareham, UK).

Station	Date	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	$Si(OH)_4$
upper AR	Apr-2013	0.0	36.2	0.1	0.2	170.1
upper AR	Oct-2013	0.0	33.4	0.1	0.2	160.6
lower AR	Dec-2011	302.4	124.8	7.2	9.4	257.4
lower AR	Jan-2012	88.3	145.2	9.8	4.2	283.3
lower AR	Feb-2012	148.2	132.8	9.9	2.5	230.1
lower AR	May-2012	274.4	102.1	0.8	9.8	240.3
lower AR	Jul-2012	202.8	189.1	9.4	6.8	244.3
lower AR	Aug-2012	170.1	242.1	8.8	7.0	217.3
lower AR	Nov-2012	94.4	120.4	7.0	3.1	246.9
lower AR	Dec-2012	47.4	81.5	7.5	3.4	101.2
Shibaura STP	May-2012	48.4	252.1	6.4	4.6	240.1
Shibaura STP	Jul-2012	91.8	209.4	7.1	8.1	230.4
Shibaura STP	Aug-2012	264.8	570.1	8.7	4.8	273.0
Shibaura STP	Nov-2012	28.4	66.7	5.8	4.0	81.7
Shibaura STP	Dec-2012	46.6	102.4	6.0	3.8	277.8

Table 7-3

Nutrient concentrations (μmol L^{-1}) at station F3, F6, and 06.

Station	Date	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	$Si(OH)_4$
F3	Jan-2012	1.7	22.4	2.3	0.2	1.3
F3	Feb-2012	16.4	27.7	2.7	1.0	10.5
F3	Mar-2012	2.4	25.1	10.8	0.5	5.6
F3	Apr-2012	7.6	26.2	3.0	0.3	7.4
F3	May-2012	9.7	19.1	2.5	0.7	33.2
F3	Jun-2012	0.3	28.4	4.0	0.8	53.3
F3	Jul-2012	0.4	28.8	2.6	0.1	38.0
F3	Aug-2012	0.4	1.7	0.3	0.1	2.4
F3	Sep-2012	1.8	2.8	0.5	0.3	3.9
F3	Oct-2012	4.4	24.1	2.7	1.1	22.9
F3	Nov-2012	5.6	27.8	3.7	1.4	22.1
F3	Dec-2012	11.6	30.4	4.7	1.9	38.9
F6	Jan-2012	1.1	16.6	1.9	0.2	0.4
F6	Feb-2012	8.7	21.3	2.0	0.5	6.0
F6	Mar-2012	2.1	20.9	6.7	0.4	2.1
F6	Apr-2012	2.5	16.6	2.3	0.2	5.1
F6	May-2012	0.3	20.8	2.2	0.1	26.8
F6	Jun-2012	0.5	10.4	2.6	0.3	36.9
F6	Jul-2012	0.6	1.1	0.2	0.1	2.9
F6	Aug-2012	2.6	2.1	0.5	0.4	9.7
F6	Sep-2012	0.3	0.5	0.2	0.2	1.9
F6	Oct-201	3.5	15.0	2.5	1.1	12.1
F6	Nov-2012	1.2	20.1	3.4	1.0	15.9
F6	Dec-2012	6.4	21.9	4.3	1.4	34.0
06	Jan-2012	0.6	8.8	0.3	0.5	10.0
06	Feb-2012	0.6	6.3	0.3	0.2	7.6
06	Mar-2012	0.3	4.6	0.2	0.2	5.6
06	Apr-2012	1.6	14.6	1.4	0.1	7.5

06	May-2012	0.2	1.0	0.6	0.1	4.2
06	Jul-2012	0.4	0.4	0.1	0.1	2.4
06	Aug-2012	1.0	1.8	0.4	0.2	6.4
06	Sep-2012	0.3	0.3	0.2	0.1	1.1
06	Oct-2012	1.0	7.4	1.0	0.7	7.4
06	Nov-2012	1.0	5.0	2.2	0.4	9.2
06	Dec-2012	1.6	10.4	3.0	0.7	18.4

Table 7-4

Degradation constants for DOC (k_{20}) and normalized degradation constants at 15°C (k_{15}) ± standard deviation at the upper Arakawa River (upper AR), the 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±0.006	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

Table 7-5

DOC, RDOC, DOC/RDOC, and salinity at station 06 bottom water (water depth is 300 m) in Tokyo Bay

Month	DOC (μmol L^{-1})	RDOC (μmol L^{-1})	RDOC/DOC (%)	Sal.
Jan-2012	54	40	75	34.4
Feb-2012	45	43	96	34.3
Mar-2012	54	45	83	34.4
Apr-2012	53	46	86	34.4
May-2012	59	57	98	34.4
Jul-2012	52	51	97	34.3
Aug-2012	52	40	77	34.3
Sep-2012	50	48	97	34.3
Oct-2012	51	48	97	34.4
Nov-2012	56	50	89	34.4
Dec-2012	48	43	90	34.4
Average	52	47	89	34.4

Table 7-6

Degradation constants for DOC (k_{20}) and normalized degradation constants at 15°C (k_{15}) ± standard deviation in Tokyo Bay (station 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±0.032	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	May-2012	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-2012	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	May-2012	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-2012	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	May-2012	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-2012	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

Table 7-7

Correlation coefficients (R^2) of the significant ($p<0.05$) linear regressions between DOC and hydrological data in Tokyo Bay (station F3, F6, 06, and total data). X indicates 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.

Table 7-8

Relative concentration of RDOC (%) ± error* in Tokyo Bay derived from phytoplankton, terrestrial, and open oceanic waters estimated from two multiple linear regressions. * see the chapter 7.3.3.2.

Station	Model I			Model II		
	Phyto.	Terr.	Ocean	Phyto.	Terr.	Ocean
F3	12±7	42±3	46±5	14±6	29±3	57±4
F6	8±6	35±3	57±5	10±6	23±2	67±3
06	4±4	20±4	76±4	5±4	12±2	83±4
Total data	8±6	32±3	59±5	10±5	21±3	69±4

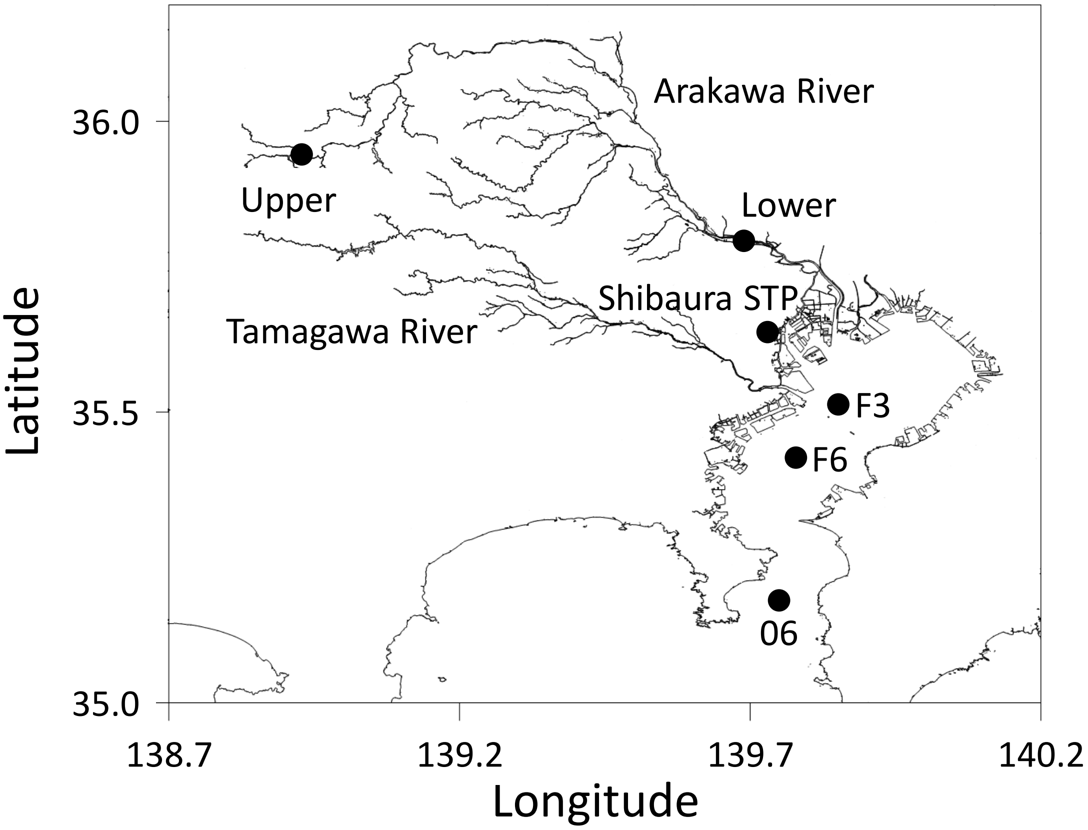

Figure 7-1
Map of Tokyo Bay. Locations of sampling sites are indicated by black circles.

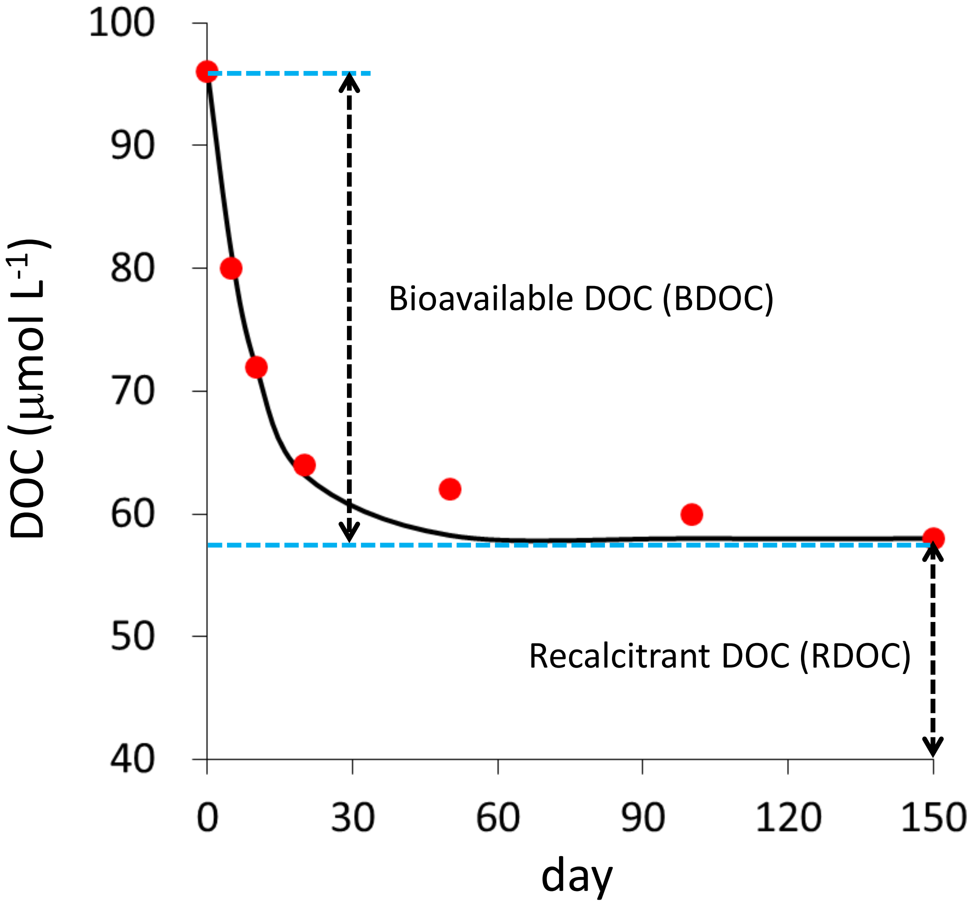

Figure 7-2
Time course of DOC concentrations during an incubation experiment with surface bay water at station F6 in March 2012. The exponential decay equation was fitted using the Marquardt-Levenberg algorithm implemented in the software Matlab 2012a. The BDOC and RDOC fractions are shown.

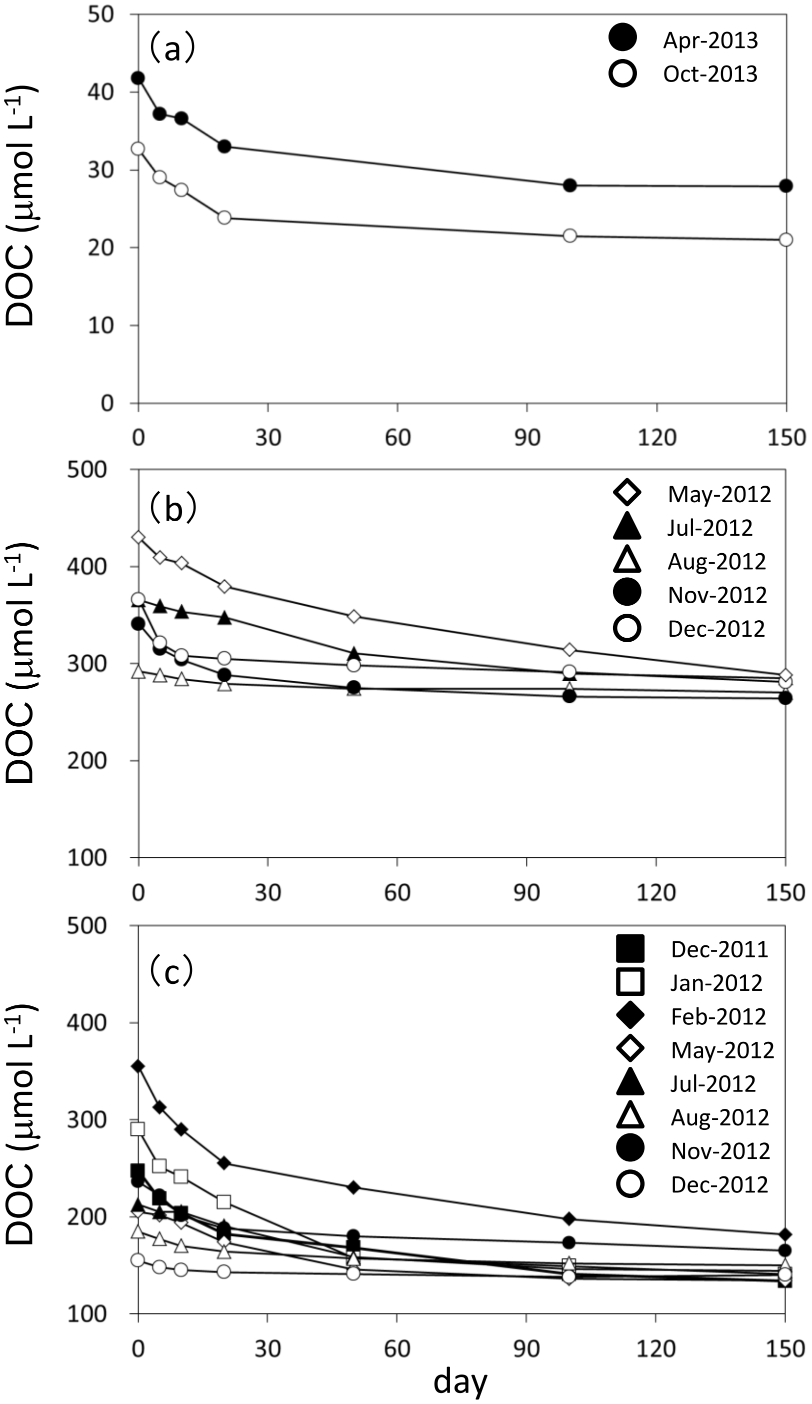

Figure 7-3
Changes in dissolved organic carbon (μmol L^{-1}) in surface water of (a) the upper Arakawa River, (b) Shibaura STP, and (c) the lower Arakawa River stations.

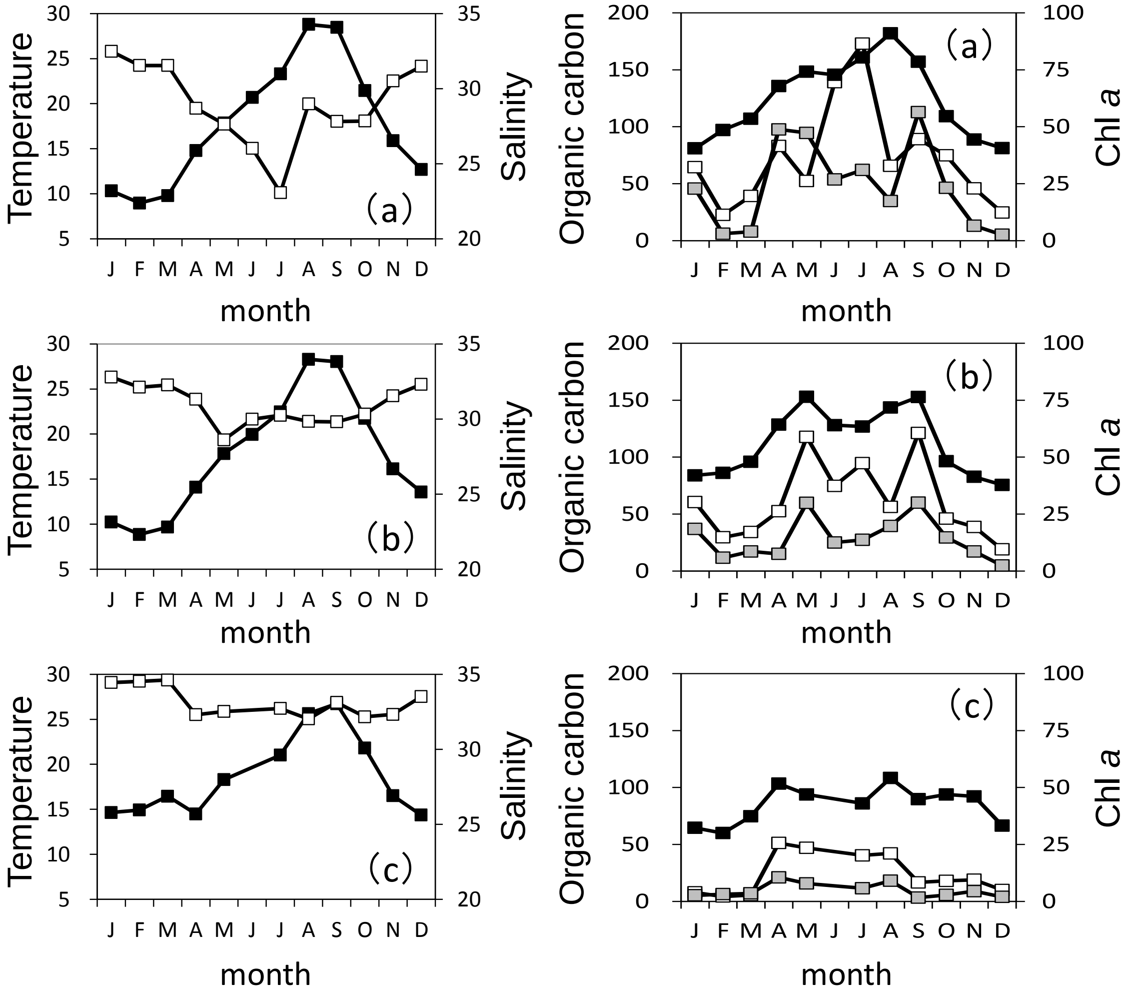

Figure 7-4
Seasonal variation of salinity (□), temperature (°C; ■), dissolved organic carbon (μmol L^{-1} ; ■), particulate organic carbon (μmol L^{-1} ; □), and chlorophyll *a* (μg L$^{-1;}$ ▨) at station (a) F3, (b) F6, and (c) 06.

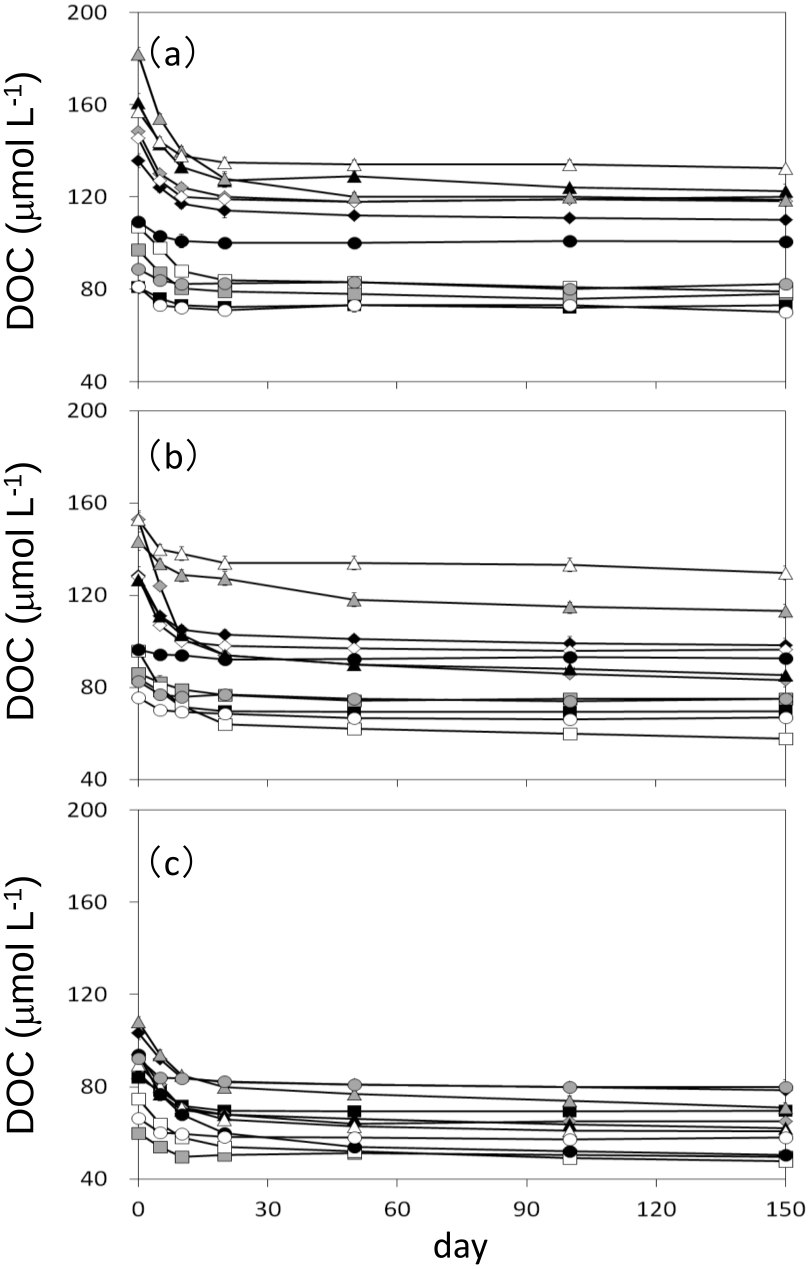

Figure 7-5

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. Error bars represent the standard deviations.

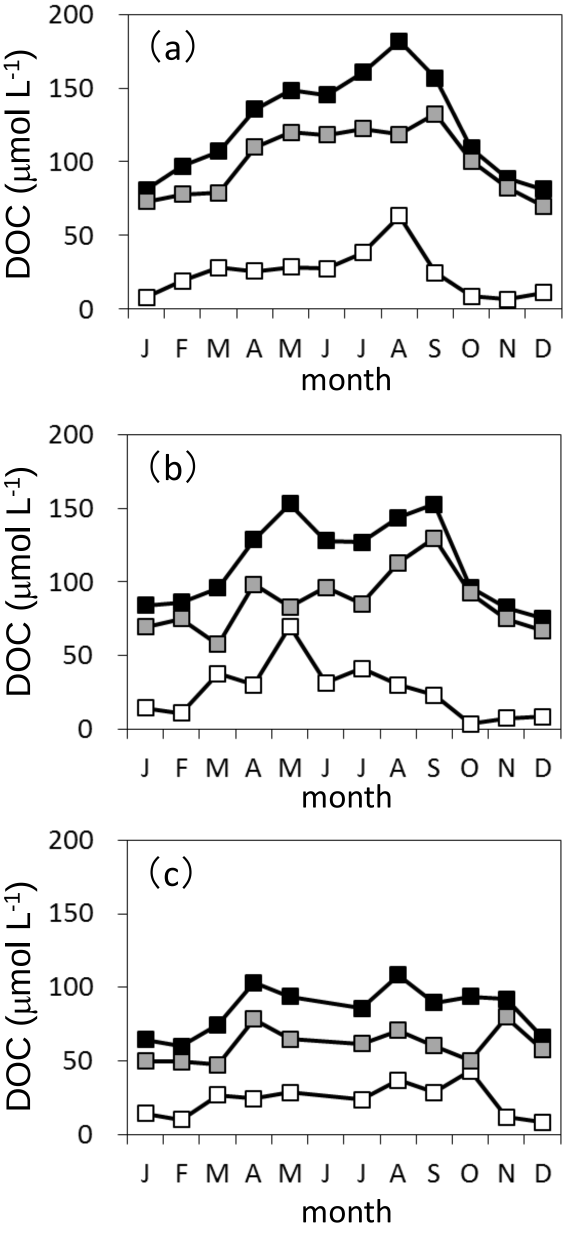

Figure 7-6
Seasonal variation of DOC (■), Bioavailable DOC (BDOC; □), and Refractory DOC (RDOC; ▨) at station (a) F3, (b) F6, and (c) 06.

Chapter 8

Conclusions and Future Direction

8.1. Conclusions

Although Tokyo Bay receives high organic carbon input from freshwater sources, it was found to be a net autotrophic system (see Chapter 4), as opposed to most coastal waters, which have been found to be heterotrophic (Smith and Hollibaugh, 1993; Gattuso et al., 1998; Caffrey, 2004). The results of this study also showed that the largest organic carbon sink was sedimentation (see Chapter 4), which was comparable to that of CO_2 influx from the atmosphere (Kubo, 2011; Kubo et al., in prep.). TOC_{sed} was dominated by organic carbon derived from primary production (see Chapter 5), and a small amount of sedimentary organic carbon was exported to the deep ocean as the BNL (see Chapter 6). Moreover, Tokyo Bay exported most 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.

There were alternations in the quantity and quality of carbon along the urbanizing watershed continuum with improved sewage treatment (Figures 8-1 and 8-2). POC and BDOC were significantly decreased at the STPs (see Chapter 7). Indeed, POC and BDOC input are currently about 2.3 and 4.2 times lower than they were in the 1970s, respectively, while RDOC is only about 1.4 times lower. Primary production in the present study was about three times lower than that in the 1970s (Funakoshi, 1974) because nutrient concentrations in the present were also about four times lower than those of the 1970s (Esumi, 1979). However, the sedimentation rate (see Chapter 4) and anoxic bottom water volume (Ishii and Ohata, 2010) did not differ greatly between the present and the 1970s. Hence, carbon was exported to the open ocean at greater levels than the present export amount and/or CO_2 was outgassed to the atmosphere. In the Elbe estuary, pCO_2 in 2007 was about three times lower than that in 1986, at which time

STPs had not been installed (Amann et al., 2012). These findings are similar to those observed for the Chesapeake Bay (Prasad et al., 2013) and Changjiang (Wang et al., 2007).

Expansion of urbanized areas with improved sewage treatment is occurring worldwide (Nellemann et al., 2008); therefore, understanding the impacts of urbanization on the carbon cycle will be equally important as predicting the impacts of changes in carbon cycling with urbanization.

8.2. Future Direction

In this study, the bulk DOC and POC budget and cycling in the water and sediment of Tokyo Bay was determined. Chemical characterization (e.g., lignin, carbohydrate, amino acid, and chromophobic DOM) and understanding the contributions of high and low molecular weight DOM to BDOC and RDOC is essential to identifying which compounds control the carbon dynamics in coastal waters. The fate of terrestrial DOC (e.g., lignin) has important ramifications for the global carbon cycle, but remains enigmatic (Hedges et al., 1997; Cauwet, 2002; Benner, 2004; Fichot and Benner, 2014). A third of terrestrial RDOC flowing into the bay is delivered to the open ocean, and residual terrestrial RDOC may be removed from the water column by photodegradation, aggregation, and sorption to particles (see Chapter 7). In particular, biological degradation and photodegradation influenced the terrestrial organic carbon balance (Fichot and Benner, 2014). Photochemical reactions break apart large aromatic-rich molecules like lignin and tannin into low molecular weight compounds that are rapidly utilized by microbes (Kieber et al., 1989; Kieber et al., 1997; Miller and Moran, 1997; Hernes and Benner, 2003; Dittmar et al., 2007). However, few studies have concurrently quantified all of the dominant bacterial degradation, photodegradation, partial photo-oxidation of DOC, and photostimulated bacterial respiration of partially photo-oxidized DOC (Benner and Opsahl, 2001; Cory et al., 2014; Fichot and Benner, 2014). Understanding the controls on the pathway of terrestrial DOC will improve our understanding of coastal and global carbon cycles.

Recently, the term boundless carbon cycle was introduced to designate the present-day lateral and vertical carbon fluxes from inland waters to the open ocean (Figure 8-3; Battin et al., 2009). Moreover, Regnier et al. (2013) extended this concept to all components (inland waters, estuaries, and coastal waters) of the global carbon cycle that are connected by the land-ocean aquatic continuum (Figure 8-4). However, the data are too sparse to fully resolve the diversity of inland waters, estuaries, and coastal waters. Global estimates of the carbon budget derived from high freshwater discharge lead to significant overestimation because they ignore low freshwater discharge areas (Borges, 2005; Cole et al., 2007; Jiang et al., 2008; Chen and Borges, 2009; Cai, 2011; Aufdenkampe et al., 2011; Butman and Raymond, 2011; Bauer et al., 2013; Raymond et al., 2013; Regnier et al. 2013; Abril et al., 2014). It should also be noted that sources, transport pathways, lability, and rates of degradation of organic carbon in highly urbanized areas represent important unknowns in aquatic systems. At present, this lack of understanding limits our ability to predict the present and future contribution of aquatic systems to the global carbon budget. Accordingly, future studies to quantify carbon fluxes in streams, rivers, and coastal waters are warranted.

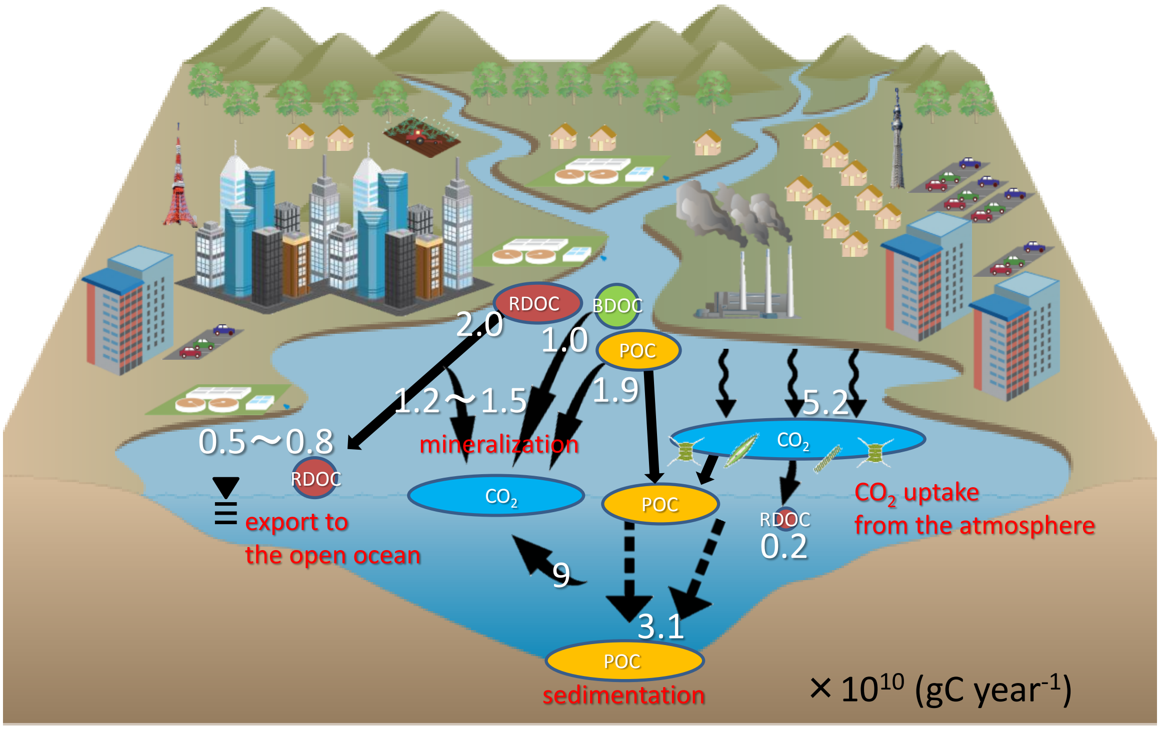

Figure 8-1
A conceptual model for carbon cycling in Tokyo Bay in the present. White numbers denote amount of carbon (× 10^{10} gC year^{-1}).

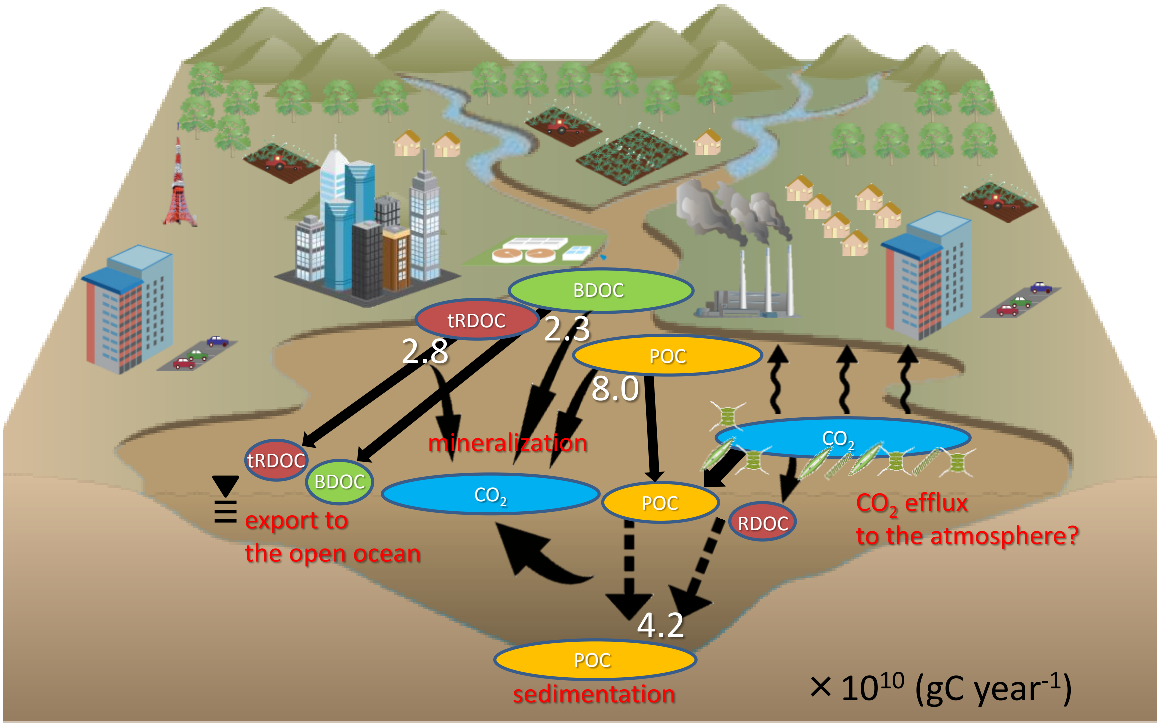

Figure 8-2
A conceptual model for carbon cycling in Tokyo Bay in 1970s. White numbers denote amount of carbon (×10^{10} gC year^{-1}).

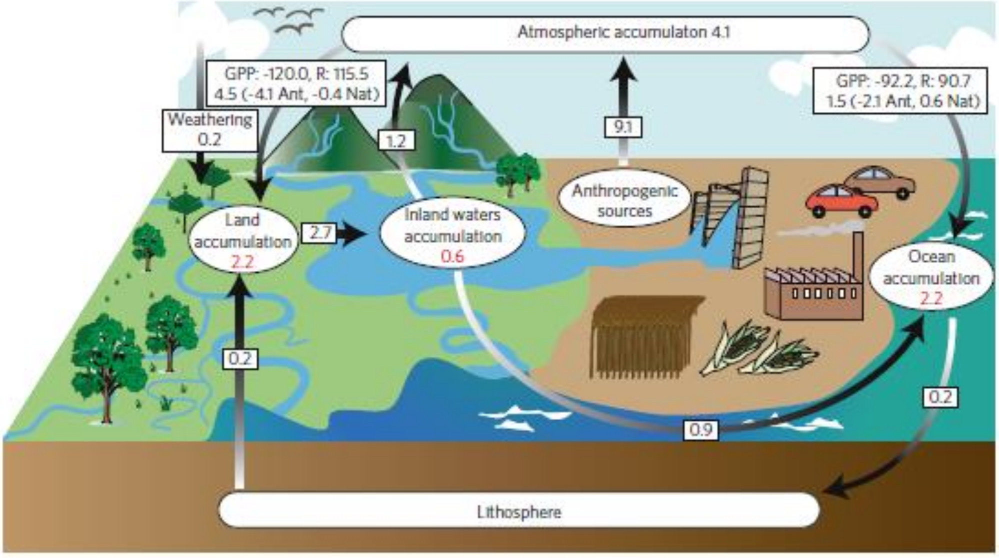

Figure 8-3
The 'boundless carbon cycle'. The schematic highlights carbon fluxes through inkand waters, and also includes pre-industrial and anthropogenic fluxes. Values are net fluxes between pools (black) or rates of change within pools (red); units are PgC year^{-1}; (Battin et al., 2009; Figure 1).

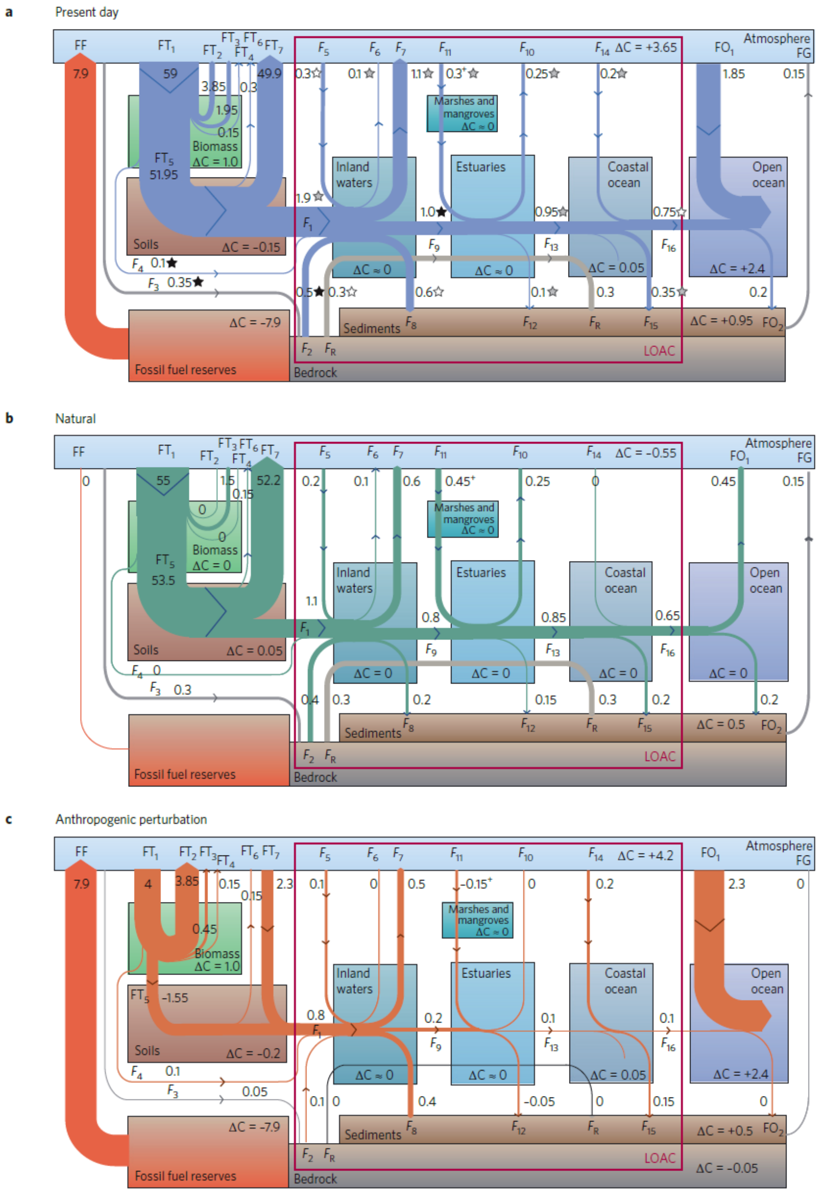

Figure 8-4
Global carbon budget and its anthropogenic perturbation. Estimates are shown for **a**, the preset day (2000-2010), **b**, the natural carbon cycle (-1750), and **c**, the anthropogenic perturbation only. All fluxes are in PgC year^{-1} (Regnier et al., 2013; Figure 1).

Acknowledgments

I would like to sincerely thank my thesis supervisor, Professor Jota Kanda, for his support and guidance. Throughout my undergraduate and graduate career, he has been a caring and insightful source of knowledge and encouragement. I also deeply appreciate the support from Associate Professor Michiyo Yamamoto-Kawai, who provided many suggestions regarding my study and manuscript development. Additionally, I thank Professor Yuji Tanaka for providing constructive comments on my study and writing. I am very grateful for Assistant Professor Fuminori Hashihama for his help in sampling and helpful comments regarding my study. I also thank all members of the chemical oceanography laboratory, especially Ms. Chinatsu Oouchida and Mr. Kentaroh Sugiyama for their assistance with sample collection.

I am very grateful to Professor Takashi Ishimaru and Assistant Professor Naho Horimoto-Miyazaki for their assistance sampling and helpful comments regarding my study. I also thank the officers and crewmembers of the R/V Seiyo Maru for assistance with sampling, as well as the staff of the Oceanographic Observation Center for coordinating observation and maintenance of CTD. Additionally, I thank Mr. Fuyuki Shibata at Marine Work Japan Ltd. for providing the DIC standard samples used in this study.

Financial support from the Canon Foundation is gratefully acknowledged. Additionally, I thank all project members of the Canon Foundation for Challenging Exploratory Research, especially Dr. Tomohiro Kuwae at the Port and Airport Research Institute, Associate Professor Hiroshi Ogawa at The University of Tokyo, Associate Professor Fumiyuki Nakajima at The University of Tokyo, and Dr. Masahiro Suzumura at the National Institute of Advanced Industrial Science and Technology for their

valuable comments on my study.

Finally, I thank my family for their encouragement and support of my education and work throughout my life.

References

Abril, G., Martinez, J.M., Artigas, L.F., Moreira-Turcq, P., Benedetti, M.F., Vidal, L., Meziane, T., Kim, J.H., Bernardes, M.C., Savoye, N., Deborde, J., Souza, E.L., Albéric, P., de Souza, M.F.L., and Roland, F.: Amazon River carbon dioxide outgassing fuelled by wetlands, Nature, 505, 395-398, 2014.

Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., and Ebinghaus, R.: Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan, Chemosphere, 79, 266-272, 2010.

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” (Editors, Findlay, S.E.G., and Sinsabaugh, R.L.), Academic Press, San Diego, pp. 25-70, 2003.

Alvarez-Salgado, X.A., Doval, M.D., Borges, A.V., Joint, I., Frankignoulle, M., Woodward, E.M.S., and Figueiras, F.G.: Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian upwelling system, Progress in Oceanography, 51, 321-337, 2001.

Amann, T., Weiss, A., and Hartmann, J.: Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality, Estuarine, Coastal and Shelf Science, 107, 112-121, 2012.

Amon, R.M.W., and Benner, R.: Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, Geochimica et Cosmochimica Acta, 60, 1783-1792, 1996.

Anderson, L.A., and Sarmiento, J.L.: Redfield rations of remineralization determined by nutrient data analysis, Global Biogeochemical Cycles, 8, 68-80, 1994.

Ando, H., Kashiwagi, N., Ninomiya, K., and Ogura, H.: Long-term trends of water quality in the coastal sea of Tokyo, Tokyo Metropolitan Research Institute Reports, 60-67, 1999.

Ando, H., Kashiwagi, N., Ninomiya, K., Ogura, H., and Kawai, T.: Changes in the state of water pollution in Tokyo Bay since 1980, Tokyo Metropolitan Research Institute Reports, 141-150, 2005.

Andres, R.J., Fielding, D.J., Marland, G., Boden, T.A., Kumar, N., and Kearney, A.T.: Carbon dioxide emissions from fossil-fuel use, 1751-1950, Tellus, 51, 759-765, 1999.

Artemyev, V.E.: Geochemistry of Organic Matter in River-Sea Systems, Kluwer Academic Publishers, Dordrecht, 190 pp., 1996.

Aufdenkampe, A.K., Mayorga, E., Raymondo, P.A., Melack, J.M., Doney, S.C., Alin, S.R., Aalto, R.E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Frontier in Ecology and the Environment, 9, 53-60, 2011.

Avery Jr., G.B., Willey, J.D., and Kieber, R.J.: Flux and bioavailability of Cape Fear River and rainwater dissolved organic carbon to Long Bay, southeastern United States, Global Biogeochemical Cycles, 17, 1042, 2003.

Avery Jr., G.B., Willey, J.D., and Kieber, R.J.: Carbon isotopic characterization of dissolved organic carbon in rainwater: Terrestrial and marine influence, Atmospheric Environment, 40, 7539-7545, 2006.

Azam, F.: Microbial control of oceanic carbon flux: The plot thickens, Sceince, 280, 694-696, 1998.

Azam, F., Fenchel, T., Field, J.G., Gray, J.S., Meyer-Reil, L.A., and Thingstad, F.: The ecological role of water-column microbes in the sea, Marine Ecology Progress Series, 10, 257-263, 1983.

Barth, J.A.C., Veizer, J., and Mayer, B.: Origin of particulate organic carbon in the upper St. Lawrence: isotopic constraints. Earth and Planetary Science Letters, 162, 111-121, 1998.

Battin, T.J., Luyssaert, S., Kaplan, L.A., Aufdenkampe, A.K., Richter, A., and Tranvik, L.: The boundless carbon cycle, Nature Geoscience, 2, 598-600, 2009.

Bauer, J.E., and Bianchi, T.S.: Dissolved organic carbon cycling and transformation, In “Treatise on Estuarine and Coastal Science” (Editors, Wolanski, E., and McLusky, D.S.), Academic Press, Sam Diego, vol. 5, pp. 7-67, 2011.

Bauer, J.E., Cai, W.J., Raymond, P.A., Bianchi, T.S., Hopkinson, C.S., and Regnier, P.A.G.: The changing carbon cycle of the coastal ocean, Nature, 504, 61-70, 2013.

Bauer, J.E., Druffel, E.R.M., Wolgast, D.M., and Griffin, S.: Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope, Deep-Sea Research Part II, 49, 4387-4419, 2002.

Beer, C., Reichstein, M., Tomelleri, E., Ciais, P., Jung, M., Carvalhais, N., Rödenbeck, C., Arain, M.A., Baldocchi, D., Bonan, G.B., Bondeau, A., Cescatti, A., Lasslop, G., Lindroth, A., Lomas, M., Luyssaert, S., Margolis, H., Oleson, K.W., Roupsard, O., Veenendaal, E., Viovy, N., Williams, C., Woodward, F., and Papale, D.: Terrestrial gross carbon dioxide uptake: global distribution and covariation with climate, Science, 329, 834-838, 2010.

Benner, R.: What happens to terrestrial organic matter in the ocean?, Marine Chemistry, 92, 307-310, 2004.

Benner, R., and Opsahl, S.: Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume, Organic Geochemistry, 32, 597-611, 2001.

Berner, R.A.: Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanerozoic time, Palaeogeogrphy, Palaeoclimatology, Palaeoecology, 75, 97-122, 1989.

Bianchi, T.S.: Biogeochemistry of Estuaries, Oxford University Press, New York, 683 pp., 2007.

Biscaye, P., Flagg, C., and Falkowski, P.G.: The Shelf Edge Exchange Processes experiment, SEEP-II: an introduction to hypotheses, results and conclusions, Deep-Sea Research II, 41, 231-252, 1994.

Bjørnsen, P.K.: Phytoplankton exudation of organic matter: Why do healthy cells do it?, Limnology and Oceanography, 33, 151-154, 1988.

Borges, A.V.: Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean?, Estuaries, 28, 3-27, 2005.

Bouman, H.A., Nakane, T., Oka, K., Nakata, K., Kurita, K., Sathyendranath, S., and Platt, T.: Environmental controls on phytoplankton production in coastal ecosystems: A case study from Tokyo Bay, Estuarine, Coastal and Shelf Sciencce, 87, 63-72, 2010.

Bureau of Sewerage: Management Plan 2013, Bureau of Sewerage, Tokyo Metropolitan Government, 117 pp., 2013 (in Japanese).

Butman, D., and Raymond, P.A.: Significant efflux of carbon dioxide from streams and rivers in the United States, Nature Geoscience, 4, 839-842, 2011.

Cacchione, D., and Drake, D.: Nepheloid layers and internal waves over continental shelves and slopes, Geo-Marine Letters, 6, 147-152, 1986.

Caffrey, J.M.: Factors controlling net ecosystem metabolism in U.S. estuaries, Estuaries, 27, 90-101, 2004.

Cai, W.J.: Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, Annual Review of Marine Science, 3, 123-145, 2011.

Calder, J.A., and Parker, P.L.: Stable carbon isotope ratios as indices of petrochemical pollution of aquatic system, Environmental Science and Technology, 2, 535-539, 1968.

Canuel, E.A., Cammer, S.S., Mclntosh, H.A., and Pondell, C.R.: Climate change impacts on the organic carbon cycle at the land-ocean interface, Annual Review of Earth and Planetary Sciences, 40, 685-711, 2012.

Carlson, C.A.: Production and removal processes, In “Biogeochemistry of Marine Dissolved Organic Matter” (Editors, Hansell, D.A., and Carlson, C.A.), Academic Press, San Diego, pp. 91-151, 2002.

Cauwet, G.: DOM in the coastal zone. In “Biogeochemistry of Marine Dissolved Organic Matter” (Editors, Hansell, D.A., and Carlson, C.A.), Academic Press, San Diego, pp. 579-609, 2002.

Central Environmental Council: Basic Direction of the 7th Total Water Pollutant Load Control Scheme, Ministry of the Environment Japan, 60 pp., 2010 (in Japanese).

Chalaux, N., Takada, H., and Bayona, J.M.: Molecular markers in Tokyo Bay sediments: sources and distribution, Marine Environmental Research, 40, 77-92, 1995.

Chavez, F.P., Messié, M., and Pennington, J.T.: Marine primary production in relation to climate variability and change, Annual Review of Marine Science, 3, 227-260, 2011.

Chen, C.T.A., and Borges, A.V.: Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2, Deep-Sea Research II, 56, 578-590, 2009.

Chen, C.T.A., Huang, T.H., Chen, Y.C., Bai, Y., He, X., and Kang, Y.: Air-sea exchanges of CO_2 in the world’s coastal seas, Biogeosciences, 10, 6509-6544, 2013.

Chen, C.T.A., Liu, K., and Macdonald, R.: Continental margin exchanges, In “Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change, (Editor, Fasham, M.J.R.), Springer-Verlag, Berlin, pp. 53-95, 2003.

Chen, W., and Wangersky, P.J.: Rates of microbial degradation of dissolved organic carbon from phytoplankton cultures, Journal of Plankton Research, 18, 1521-1533, 1996.

Chin, W.C., Orellana, M.V., and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, Nature, 391, 568-572, 1998.

Cifuentes, L.A., Sharp, J.H., and Fogel, M.L.: Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary, Limnology and Oceanography, 33, 1102-1115, 1988.

Cloern, J.E., Foster, S.Q., and Kleckner, A.E.: Phytoplankton primary production in the world’s estuarine-coastal ecosystems, Biogeosciences, 11, 2477-2501, 2014.

Coelho, C.H., Francisco, J.G., Nogueira, R.F.P., and Campos, M.L.A.M.: Dissolved organic carbon in rainwater from areas heavily impacted by sugar cane burning, Atmospheric Environment, 42, 7115-7121, 2008.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., and Melack, J.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171-184, 2007.

Cory, R.M., Ward, C.P., Crump, B.C., and Kling, G.W.: Sunlight controls water column processing of carbon in arctic fresh waters, Science, 345, 925-928, 2014.

Cotner, J.B., and Biddanda, B.A.: Small players, large role: Microbial influence on biogeochemical processes in pelagic aquatic ecosystems, Ecosystems, 5, 105-121, 2002.

Dai, M., Yin, Z., Meng, F., Liu, Q., and Cai, W.J.: Spatial distribution of riverine DOC inputs to the ocean: an updated global synthesis, Current Opinion in Environmental Sustainability, 4, 170-178, 2012.

Dang, H., and Jiao, N.: Perspectives on the microbial carbon pump with special reference to microbial respiration and ecosystem efficiency in large estuarine systems, Biogeosciences, 11, 3887-3898, 2014.

Dittmar, T., Whitehead, K., Minor, E.C., and Koch, B.P.: Tracing terrigenous dissolved organic matter and its photochemical decay in the ocean by using liquid chromatography/mass spectrometry, Marine Chemistry, 107, 378-387, 2007.

Druffel, E.R.M., Williams, P.M., Bauer, J.E., and Ertel, J.R.: Cycling of dissolved and particulate organic matter in the open ocean, Journal of Geophysical Research Oceans, 97, 15639-15659, 1992.

Duarte, C.M., and Cebrián, J.: The fate of marine autotrophic production, Limnology and Oceanography, 41, 1758-1766, 1996.

Esumi, H.: Water quality in Tokyo Bay (1972-1976), Bulletin on Coastal Oceanography Note, 16, 101-105, 1979 (in Japanese).

Eyre, B.F., and McKee, L.J.: Carbon, nitrogen, and phosphorus budgets for a shallow subtropical embayment (Moreton Bay, Australia), Limnology and Oceanography, 47, 1043-1055, 2002.

Falkowski, P.G., Flagg, C., Rowe, G., Smith, S., Whitledge, T., and Wirick, C.: The fate of a spring phytoplankton bloom: export or oxidation?, Continental Shelf Research, 8, 457-484, 1988.

Falkowski, P.G., Laws, E.A., Barber, R.T., and Murray, J.W.: Phytoplankton and their role in primary, new, and export production, In “Ocean Biogeochemistry” (Editor, Fasham, M.J.R.), Springer-Verlag, Berlin, pp. 99-122, 2003.

Fenchel, T.: Ecology of heterotrophic microflagellates. IV. Quantitative occurrence and importance as bacterial consumers, Marine Ecology Progress Series, 9, 35-42, 1982.

Fichot, C.G., and Benner, R.: The fate of terrigenous dissolved organic carbon in a river-influenced ocean margin, Global Biogeochemical Cycles, 28, 300-318, 2014.

Field, C.B., Behrenfeld, M.J., Randerson, J.T., and Falkowski, P.: Primary production of the biosphere: Integrating terrestrial and oceanic components, Science, 281, 237-240, 1998.

Fujiwara, T., and Yamada, Y.: Inflow of oceanic water into Tokyo Bay and generation of a subsurface hypoxic water mass, Journal of Geophysical Research, 107, doi:10.1029/2000JC000749, 2002.

Funakoshi, M., Nakamoto, N., and Hogetsu, K.: Primary production and the role of red tide in Tokyo Bay, Annual Report of Special Project Research, 72, 421-422, 1974 (in Japanese).

Gao, X., Yang, Y., and Wang, C.: Geochemistry of organic carbon and nitrogen in surface sediments of coastal Bohai Bay inferred from their ratios and stable isotopic signatures, Marine Pollution Bulletin, 64, 1148-1155, 2012.

Gattuso, J.P., Frankignoulle, M., and Wollast, R.: Carbon and carbonate metabolism in coastal aquatic ecosystems, Annual Review of Ecology, Evolution, and Systematics, 29, 405-434, 1998.

Gazeau, F.A., Borges, A.V., Barron, C., Duarte, C.M., Iversen, N., Middelburg, J.J., Delille, B., Pizay, M.D., Frankignoulle, M., and Gattuso, J.P.: Net ecosystem metabolism in a micro-tidal estuary (Randers Fjord, Denmark): Evaluation of methods, Marine Ecology Progress Series, 301, 23-41, 2005.

Giering, S.L.C., Sanders, R., Lampitt, R.S., Anderson, T.R., Tamburini, C., Boutrif, M., Zubkov, M.V., Marsay, C.M., Henson, S.A., Saw, K., Cook, Kathryn, and Mayor, D.J.: Reconciliation of the carbon budget in the ocean’s twilight zone, Nature, 507, 480-483, 2014.

Gireeshkumar, T.R., Deepulal, P.M., and Chandramohanakumar, N.: Distribution and sources of sedimentary organic matter in a tropical estuary, south west coast of India (Cochin estuary): A baseline study, Marine Pollution Bulletin, 66, 239-245, 2013.

Gordon, D.C., Boudreau, P.R., Mann, K.H., Ong, J.E., Silvert, W.L., Smith, S.V., Wattayakorn, G., Wulff, F., and Yanagi, T.: LOICZ biogeochemical modelling guidelines, LOICZ Reports and Studies 5, LOICZ core project of the international geosphere-biosphere programme: a study of global change of the international council of scientific unions, Netherland Institute for Sea Research, Taxel, Netherlands, 96 pp., 1996.

Gruber, N., Sarmiento, J.L., and Stocker, F.: An improved method for detecting anthropogenic CO_2 in the ocean, Global Biogeochemical Cycles, 10, 809-837, 1996.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J.A., Frankenberg, C., Huete, A.R., Zarco-Tejada, P., Lee, J.E., Moran, M.S., Ponce-Campos, G., Beer, C., Camps,-Valls, G., Buchmann, N., Gianelle, D., Klumpp, K., Cescatti, A., Baker, J.M., and Griffis, T.J.: Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence, Proceedings of the National Academy of Sciences, 111, E1327-E1333, 2014.

Hansell, D.A.: Recalcitrant dissolved organic carbon fractions, Annual Review of Marine Science, 5, 3.1-3.25, 2013.

Hansell, D.A., Carlson, C.A., Repeta, D.J., and Schlitzer, R.: Dissolved organic matter in the ocean, Oceanography, 22, 202-211, 2009.

Hattori, A.: Oceanographic features of Tokyo Bay. – water circulation, hydrography, and nutrient chemistry: an overview, Geochemistry, 17, 16-26, 1983 (in Japanese).

Hattori, A., Ohtsu, M., and Koike, I.: Distribution, metabolism and budgets of nitrogen in Tokyo Bay, Geochemistry, 17, 33-41, 1983 (in Japanese with English abstract).

Hayashi, Y., Managaki, S., and Takada, H.: Fluorescent whitening agents in Tokyo Bay and adjacent rivers: Their application as anthropogenic molecular markers in coastal environments, Environmental Science and Technology, 36, 3556-3563, 2002.

Hedges, J.: Why dissolved organic matter?, In “Biogeochemistry of Marine Dissolved Organic Matter” (Editors, Hansell, D.A., and Carlson, C.A.), Academic Press, San Diego, pp. 1-34, 2002.

Hedges, J., and Keil, R.G.: Sedimentary organic matter preservation: an assessment and speculative synthesis, Marine Chemistry, 49, 81-115, 1995.

Hedges, J., and Parker, P.L.: Land-derived organic matter in surface sediments from the Gulf of Mexico, Geochimica et Cosmochimica Acta, 40, 1019-1029, 1976.

Hedges, J., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., and Santos, U.M.: Compositions and fluxes of particulate organic material in the Amazon River, Limnology and Oceanography, 31, 717-738, 1986.

Hedges, J., Keil., R.G., and Benner, R.: What happens to terrestrial organic matter in the ocean?, Organic Geochemistry, 27, 195-212, 1997.

Heip, C.H.R., Goosen, N.K., Herman, P.M.J., Kromkamp, J., Middelburg, J.J., and Soetaerk, K.: Production and consumption of biological particles in temperate tidal estuaries, Oceanography and Marine Biology – An Annual Review, 33, 1-149, 1995.

Hendrixson, H.A., Sterner, R.W., and Kay, A.D.: Elemental stoichiometry of freshwater fishes in relation to phylogeny, allometry and ecology, Journal of Fish Biology, 70, 121-140, 2007.

Henson, S.A., Sanders, R., Madsen, E., Morris, P.J., Le Moigne, F., and Quartly, G.D.: A reduced estimate of the strength of the ocean’s biological carbon pump, Geophysical Research Letters, 38, L04606, 2011.

Hernes, P.J., and Benner, R.: Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments, Journal of Geophysical Research, 108, C9, 3291, 2003.

Hernes, P.J., and Benner, R.: Terrigenous organic matter sources and reactivity in the North Atlantic Ocean and a comparison to the Arctic and Pacific oceans, Marine Chemistry, 100, 66-79, 2006.

Hirano, H.: Species composition and seasonal variation of diatom in the center of Tokyo Bay, Graduation Thesis, Tokyo University of Marine Science and Technology, 28 pp., 2014 (in Japanese).

Hopkinson Jr., C.S., and Vallino, J., and Nolin, A.: Decomposition of dissolved organic matter from the continental margin, Deep-Sea Research II, 49, 4461-4478, 2002.

Houghton, R.A.: Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850-2000, Tellus, 55, 378-390, 2003.

Houghton, R.A.: Balancing the global carbon budget, Annual Review of Earth and Planetary Science, 35, 313-347, 2007.

Hung, J., Lin, P., and Liu, K.: Dissolved and particulate organic carbon in the southern East China Sea, Continental Shelf Research, 20, 545-569, 2000.

Inthorn, M.: Lateral particle transport in nepheloid layers – a key factor for organic matter distribution and quality in the Benguela high-productivity area, Doctor Thesis, University of Bremen, 124 pp., 2006.

Inthorn, M., Wagner, T., Scheeder, G., and Zabel, M.: Lateral transport controls distribution, quality, and burial of organic matter along continental slopes in high-productivity areas, Geology, 34, 205-208, 2006.

IPCC: ClimateChange 2013: The Scientific Basis, contribution of working group I to the fifth assessment report of the Intergovernmental Panel on Climate Change, Cambridge University Press, New York, 29 pp., 2013.

Ishii, M., and Ohata, S.: Variations in water quality and hypoxic water mass in Tokyo Bay, Bulletin on Coastal Oceanography, 48, 37-44, 2010 (in Japanese with English abstract).

Ishiwatari, R.: Characteristics and behavior of organic compounds in marine sediments, Bulletin of the Society of Sea Water Science, Japan, 57, 181-191, 2003.

Ishiwatari, R., Takada, H., Saito, H., and Yun, S.J.: Behavior of polluted organic matter in the estuarine region of Tokyo Bay: Polycyclic aromatic hydrocarbons and alkylbenzenes, Researches in organic geochemistry, 5, 51-55, 1986 (in Japanese).

Ishiwatari, R., Takada, H., and Yun, S.J.: Alkylbenzene pollution of Tokyo Bay sediments, Nature, 301, 599-600, 1983.

Itoh, Y.: Seasonal variations of light intensity – photosynthesis curve in Tokyo and Sagami Bay, Master Thesis, Tokyo University of Fisheries, 71 pp., 2003 (in Japanese).

Japan Sewage Works Association: Sewage Statistics, 2010 (in Japanese).

Jiang, L.Q., Cai, W.J., and Wang, Y.: A comparative study of carbon dioxide degassing in river- and marine-dominated estuaries, Limnology and Oceanography, 53, 2603-2615, 2008.

Jiao, N., and Azam, F.: Microbial carbon pump and its significance for carbon sequestration in the ocean, In “Microbial Carbon Pump in the Ocean” (Editors, Jiao, N., Azam, F., and Sanders, S.), Science/AAAS, Washington D.C., pp. 43-45, 2011.

Jiao, N., Herndl, G.J., Hansell, D.A., Benner, R., Kattner, G., Wilhelm, S.W., Kirchman, D.L., Weinbauer, M.G., Luo, T., Chen, F., and Azam, F.: Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean, Nature Reviews Microbiology, 8, 593-599, 2010.

Jiao, N., Robinson, C., Azam, F., Thomas, H., Baltar, F., Dang, H., Hardman-Mountford, N.J., Johnson, M., Kirchman, D.L., Koch, B.P., Legendre, L., Li, C., Liu, J., Luo, T., Luo, Y.W., Mitra, A., Romanou, A., Tang, K., Wang, X., Zhang, C., and Zhang, R.: Mechanisms of microbial carbon sequestration in the ocean – future research directions, Biogeosciences, 11, 5285-5306, 2014.

Johnson, D.R., Weidemann, A., and Pegau, W.S.: Internal tidal bores and bottom nepheloid layers, Continental Shelf Research, 21, 1473-1484, 2001.

Joos, F., Plattmer, G.K., Stocker, T.F., Marchal, O., and Schmittner, A.: Global warming and marine carbon cycle feedbacks on future atmospheric CO_2, Science, 284, 464-467, 1999.

Jumars, P.A., Penry, D.L., Baross, J.A., Perry, M.J., and Frost, B.W.: Closing the microbial loop: dissolved carbon pathway to heterotrophic bacteria from incomplete ingestion, digestion and absorption in animals, Deep-Sea Research, 36, 483-495, 1989.

Kadlec, R.H., and Wallace, S.D.: Treatment Wetlands second edition, CRC Press, Florida, 1000 pp., 2008.

Kamatani, A., and Maeda, M.: Distribution and budget of phosphorus in Tokyo Bay, Geochemistry, 23, 85-95, 1989 (in Japanese with English abstract).

Kanda, J., Chomthaison, P., Horimoto, N., Yamaguchi, Y., and Ishimaru, T.: Time-series variations in nutrient concentrations at two monitoring stations in Tokyo Bay, Journal of Japan Society on Water Environment, 31, 559-564, 2008 (in

Japanese with English abstract).

Kanto Regional Agricultural Administration Office: Annual Reports of Ministry of Agriculture, Forestry and Fisheries, 476 pp., 2012.

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

Kawabe, M., and Kawabe, M.: Temporal and spatial characteristics of chemical oxygen demand in Tokyo Bay, Journal of Oceanography, 53, 19-26, 1997.

Keeling, C.D.: Industrial production of carbon dioxide from fossil fuels and limestone, Tellus, 25, 174-198, 1973.

Keeling, C.D., Piper, S.C., Bacastow, R.B., Wahlen, M., Whorf, T.P., Heimann, M., and Meijer, H.A.: Atmospheric CO_2 and $^{13}CO_2$ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications, In “A Histrory of Atmospheric CO_2 and Its Effects on Plants, Animals, and Ecosystems” (Editors, Ehleringer, J.R., Cerling, T.E., and Dearing, M.D.), Springer-Verlag, Berlin, pp. 83-113, 2005.

Keeling, C.D., Whorf, T.P., Wahlen, M., and van der Plicht, J.: Interannual extreams in the rate of rise of atmospheric carbon dioxide since 1980, Nature, 375, 666-670, 1995.

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.

Kemp, W.M., Smith, E.M., Marvin-DiPasquale, M., and Boynton, W.R.: Organic carbon balance and net ecosystem metabolism in Chesapeake Bay, Marin Ecology Progress Series, 150, 229-248, 1997.

Kieber, R.J., Hydro, L.H., and Seaton, P.J.: Photooxidation of triglycerides and fatty acids in seawater: Implication toward the formation of marine humic substances, Limnology and Oceanography, 42, 1454-1462, 1997.

Kieber, D.J., McDaniel, J., and Mopper, K.: Photochemical source of biological substrates in sea water: implications for carbon cycling, Nature, 341, 637-639, 1989.

Kitazawa, D., Fujino, M., and Tabeta, S.: A numerical study on change in the marine environment of Tokyo Bay in the latest 70 years, Proceedings of 22nd International Conference on Offshore Mechanics and Arctic Engineering, 1, 791-798, 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.

Krishna, M., Naidu, S.A., Subbaiah, Ch.V., Sarma, V.V.S.S., and Reddy, N.P.C.: Distribution and sources of organic matter in surface sediments of the eastern continental margin of India, Journal of Geophysical Research Biogeoscience, 118, 1484-1494, 2013.

Kubo, A.: Spatial and temporal variations of pCO_2 in Tokyo Bay, Master Thesis, Tokyo University of Marine Science and Technology, 136 pp., 2011 (in Japanese).

Kubo, A., Maeda, Y., and Kanda, J.: Tokyo Bay as a significant net sink for carbon dioxide, in preparation.

Kubo, A., Yamamoto-Kawai, M., and Kanda, J.: Seasonal variations on concentration and lability of dissolved organic carbon in Tokyo Bay, Biogeosciences, 12, 269-279, 2015.

Laruelle, G.G., Dürr, H.H., Slomp, C.P., and Borges, A.V.: Evaluation of sinks and sources of CO_2 in the global coastal ocean using a spatially-explicit typology of estuaries and continental shelves, Geophysical Research Letters, 37, L15607, doi:10.1029/2010GL043691, 2010.

Laruelle, G.G., Lauerwald, R., Pfeil, B., and Regnier, P.: Regionalized global budget of the CO_2 exchange at the air-water interface in continental shelf seas, Global Biogeochemical Cycles, 28, 1199-1214, 2014.

Laws, E.A., Falkowski, P.G., Smith Jr., W.O., Ducklow, H., and McCarthy, J.J.: Temperature effects on export production in the open ocean, Global Biogeochemical Cycles, 14, 1231-1246, 2000.

Lee, K.: Molecular assessment of benthic diatom assemblages in Delaware's inland bays, Master Thesis, The University of Delaware, 180 pp., 2012.

Liu, M., Hou, L.J., Xu, S.Y., Ou, D.N., Yang, Y., Yu, J., and Wang, Q.: Organic carbon and nitrogen stable isotopes in the intertidal sediments from the Yangtze Estuary, China, Marine Pollution Bulletin, 52, 1625-1633, 2006.

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 Biogeochemical Cycles, 26, GB3018, doi:10.1029/2012GB004353, 2012.

Lønborg, C., and Søndergaard, M.: Microbial availability and degradation of dissolved organic carbon and nitrogen in two coastal areas, Estuarine, Coastal and Shelf Science, 81, 513-520, 2009a.

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, Marine Chemistry, 113, 219-226, 2009b.

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

Mackin, J.E., and Aller, R.C.: Ammonium adsorption in marine sediments, Limnology and Oceanography, 29, 250-257, 1984.

Madron, X.D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., and Buscail, R.: Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean), Oceanologica Acta, 23, 717-730, 2000.

Maher, D.T., and Eyre, B.D.: Carbon budgets for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO_2 flux, 26, GB1032, 2012.

Maki, H., Sekiguchi, H., Hiwatari, T., Koshikawa, H., Kohata, K., Yamazaki, M., Kawai, T., Ando, H., and Watanabe, M.: Influence of storm water and combined sewage overflow on Tokyo Bay, Environmental Forensics, 8, 173-180, 2007.

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.

Managaki, S., and Takada, H.: Fluorescent whitening agents in Tokyo Bay sediments: molecular evidence of lateral transport of land-derived particulate matter, Marine Chemistry, 95, 113-127, 2005.

Mantoura, R.F.C., and Woodward, E.M.S.: Conservative behavior of riverine dissolved organic carbon in the Seven Estuary: chemical and geochemical implications, Geochimica et Cosmochimica Acta, 47, 1293-1309, 1983.

Mantoura, R.F.C., Martin, J.M., and Wollast, R.: Ocean Margin Processes in Global Change, Wiley and Sons, Chichester, 486 pp., 1991.

Matsukawa, Y., and Sasaki, K.: Nitrogen budget in Tokyo Bay with special reference to the low sedimentation to supply ratio, Journal of the Oceanographical Society of Japan, 46, 44-54, 1990.

Matsukawa, Y., and Suzuki, T.: Box model analysis of hydrography and behavior of nitrogen and phosphorus in a eutrophic estuary, Journal of the Oceanographical Society of Japan, 41, 407-426, 1985.

Matsumoto, E.: Budgets and residence times of nutrients in Tokyo Bay, In “Marine and Estuarine Geochemistry” (Editors, Sigleo, A.C., and Hattori, A.), Lewis Publishers, Chelsea, pp. 127-136, 1985.

Matsumura, T.: Nutrient Budgets in Tokyo Bay, Doctor Thesis, Tokyo University of Fisheries, 69 pp., 2000 (in Japanese).

Matsumura, T., and Ishimaru, T.: Freshwater discharge and inflow loads of nitrogen and phosphorus to Tokyo Bay (from April 1997 to March 1999), Oceanography in Japan, 13, 25-36, 2004 (in Japanese with English abstract).

Matsumura, T., Horimoto, N., Xu, T., and Ishimaru, T.: Recent trends of nutrients in Tokyo Bay (1989-1998), La mer, 39, 19-32, 2003 (in Japanese).

Matsumura, T., Ishimaru, T., and Yanagi, R.: Nitrogen and phosphorus budgets in Tokyo Bay, Oceanography in Japan, 11, 613-630, 2002 (in Japanese with English abstract).

McCave, I.N.: Sedimentary settings on continental margins –an overview, In “Ocean Margin Systems” (Esitors, Wefer, G., Billett, D., Hebbeln, D., Jørgensen, B.B., Schlüter, M., and van Weering, T.C.E.), Springer-Verlag, Berlin, pp. 1-14, 2002.

McCave, I.N., and Hall, I.R.: Turbidity of waters over the Northwest Iberian continental margin, Progress in Oceanography, 52, 299-313, 2002.

McCave, I.N., Hall, I.R., Antia, A.N., Chou, L., Dehairs, F., Lampitt, R.S., Thomsen, L., van Weering, T.C.E. and Wollast, R.: Distribution, composition and flux of particulate material over the European margin at 47^{o}-50^{o}N, Deep-Sea Research II, 48, 3107-3139, 2001.

McManus, L.T.: Examining human impacts on global biogeochemical cycling via the coastal zone and ocean margins, In "Carbon and Nutrient Fluxes in Continental Margins" (Editors, Liu, K.K., Atkinson, L., Quiñones, R., and McManus, L.T.), Springer-Verlag, Berlin, pp. 497-514, 2010.

McPhee-Shaw, E.E., Sternberg, R.W., Mullenbach, B.M., and Ogston, A.S.: Observations of intermediate nepheloid layers on the northern California continental margin, Continental Shelf Research, 24, 693-720, 2004.

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" (Editors, Wollast, R., Mackenzie, F.T., and Chou, L.), Springer-Verlag, Berlin, pp. 163-193, 1993.

Meyers, P.A.: Preservation of elemental and isotopic source identification of sedimentary organic matter, Chemical Geology, 114, 289-302, 1994.

Meyers-Schulte, K.J., and Hedges, J.I.: Molecular evidence for a terrestrial component of organic matter dissolved in ocean water, Nature, 321, 61-63, 1986

Middelburg, J., and Nieuwenhuize, J.: Carbon and nitrogen stable isotopes in suspended matter and sediments from the Scheldt Estuary, Marine Chemistry, 60 217-225,

1998.

Miller, W.L., and Moran, M.A.: Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment, Limnology and Oceanography, 42, 1317-1324, 1997.

Mishima, Y., Hoshika, A., and Tanimoto, T.: Deposition rates of terrestrial and marine organic carbon in the Osaka Bay, Seto Inland Sea, Japan, determined using carbon and nitrogen stable isotope ratios in the sediment, Journal of Oceanography, 55, 1-11, 1999.

Monteiro, P., Nelson, G., van der Plas, A., Mabille, E., Bailey, G.W., and Klingelhoeffer, E.: Internal tide-shelf topography interactions as a forcing factor governing the large-scale distribution and burial fluxes of particulate organic matter (POM) in the Benguela upwelling system, Continental Shelf Research, 24, 1864-1876, 2005.

Moore, R.M., Burton, J.D., Williams, P.J.leB., and Young, M.L.: The behavior of dissolved organic material, iron and manganese in estuarine mixing, Geochimica et Cosmochimica Acta, 43, 919-926, 1979.

Moran, M.A., and Zepp, R.G.: Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter, Limnology and Oceanography, 42, 1307-1316, 1997.

Moran, M.A., Sheldon, W.M.Jr., and Sheldon, J.E.: Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States, Estuaries, 22, 55-64, 1999.

Mulholland, P.J.: Formation of particulate organic carbon in water from a southeastern swamp-stream, Limnology and Oceanography, 26, 790-795, 1981.

Nagata, T., and Kirchman, D.L.: Filtration-induced release of dissolved free amino acids: application to culture of marine protozoa, Marine Ecology Progress Series, 68, 1-5, 1990.

Nagata, T., and Kirchman, D.L.: Release of dissolved free and combined amino acids by bacterivorous marine flagellates, Limnology and Oceanography, 35, 433-443, 1991.

Nagata, T., and Kirchman, D.L.: Release of macromolecular organic complexes by heterotrophic marine flagellates, Marine Ecology Progress Series, 83, 233-240, 1992.

Naidu, A.S., Cooper, L.W., Finney, B.P., Macdonald, R.W., Alexander, C., and Semiletov, I.P.: Organic carbon isotope ratios ($\delta^{13}C$) of Arctic Amerasian continental shelf sediments, International Journal of Earth Sciences, 89, 522-532, 2000.

Nakamura, T., Osaka, K., Hiraga, Y., and Kazama, F.: Nitrogen and oxygen isotope composition of nitrate in stream water of Fuji River Basin, Journal of Japanese Association of Hydrological Sciences, 41, 79-89, 2011 (in Japanese with English abstract).

Nakatsuka, T., Handa, N., Harada, N., Sugimoto, T., and Imaizumi, S.: Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its $\delta^{15}N$, $\delta^{13}C$ and $\delta^{14}C$, Deep-Sea Research I, 44, 1957-1979, 1997.

National Institute for Land and Infrastructure Management: Information of port environment, 2004, available at: http://www.nilim.go.jp/ (last access: June 25, 2013) (in Japanese).

Nellemann, C., Hain, S., and Alder, J.: Rapid Response Assessment in Dead Water: Merging of Climate Change with Pollution, Over-Harvest, and Infestations in the World's Fishing Grounds, United Nations Environment Programme, 61 pp., 2008.

Nihei, Y., Takamura, T., and Watanabe, N.: Issues on discharge monitoring in main influence rivers into Tokyo Bay, Journal of Japan Society of Civil Engineers, 54, 1226-1230, 2007a (in Japanese with English abstract).

Nihei, Y., Ehara, K., Usuda, M., Sakai, A., and Shigeta, K.: Water quality and pollutant load in the Edo River, Ara River and Tama River, Journal of Japan Society of Civil Engineers, 54, 1221-1225, 2007b (in Japanese with English abstract).

Nippon Foundation: The Nippon Foundation Library, 2001, available at https://nippon.zaidan.info/index.html (last access: July 25, 2014) (in Japanese).

Nixon, S.W., Grange, S.L., and Nowicki, B.L.: An assessment of the annual mass balance of carbon, nitrogen, and phosphorus in Narragansett Bay, Biogeochemistry, 31, 15-61, 1995.

Nomura, H.: Long-term variations of environmental parameters in Tokyo Bay, central Japan, La mer, 33, 107-118, 1995 (in Japanese).

Noriki, S., Shimizu, M., Hamahara, K., Marita, H., Saino, T., and Yanagi, T.: Transportation of particulate material through the mouth of Tokyo Bay to the open ocean, Journal of Oceanography, 53, 571-577, 1997.

Obernosterer, I., and Benner, R.: Competition between biological and photochemical processes in the mineralization of dissolved organic carbon, Limnology and Oceanography, 49, 117-124, 2004.

Odum, H.T.: Primary production in flowing waters, Limnology and Oceanography, 1, 102-117, 1956.

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

Ogawa, H., and Ogura, N.: Fluctuation of the water quality of seawater in Tokyo Bay during 1980-1988, Geochemistry, 24, 43-54, 1990b (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.

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., and Benner, R.: Production of refractory dissolved organic matter by bacteria, Science, 292, 917-920, 2001.

Ogawa, H., Aoki, N., Kon, I., and Ogura, N.: Stable carbon isotope ratio of suspended particulate and sedimentary organic matter during the summer blooming in Tokyo Bay, Geochemistry, 28, 21-36, 1994 (in Japanese with English abstract).

Ogawa, N., and Ogura, N.: Dynamics of particulate organic matter in the Tamagawa Estuary and Inner Tokyo Bay, Estuarine, Coastal and Shelf Science, 44, 263-273, 1997.

Ogura, K.: Fate of coprostanol, an index of fecal pollution, in Tokyo Bay (1969-1972), Geochemistry, 17, 68-75, 1983 (in Japanese with English abstract).

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

Ogura, N., and Ichikawa, Y.: Coprostanol in sediments of Tokyo Bay, Geochemistry, 17, 76-81, 1983 (in Japanese with English abstract).

Ogura, N., Ambe, Y., Ogura, K., Ishiwatari, R., Mizutani, T., Satoh, Y., Matsushima, H., Katase, T., Ochiai, M., Tadokoro, K., Takada, T., Sugihara, K., Matsumoto, G., Nakamoto, N., Funakoshi, M., and Hanya, T.: Chemical composition of organic compounds present in water of the Tamagawa River, Japan Journal of Limnology, 36, 23-30, 1975a (in Japanese with English abstract).

Ogura, N., Kamatani, A., Nakamoto, N., Funakoshi, M., and Iwata, S.: Fluctuation of dissolved organic carbon in seawater of Sagami Bay during 1971-1972, Journal of the Oceanographical Society of Japan, 31, 43-47, 1975b.

Ogura, N., Kimura, K., Sekigawa, T., Yamada, K., and Minagawa, M.: Stable isotope ratios of particulate organic carbon in surface water at inner part of Tokyo Bay, Geochemistry, 20, 13-19, 1986 (in Japanese with English abstract).

Okada, T., Takao, T., Nakayama, K., and Furukawa, K.: Change in freshwater discharge and residence time of seawater in Tokyo Bay, Coastal Engineering, 63, 67-72, 2007.

O’Leary, M.: Carbon isotopes in photosynthesis, BioScience, 38, 328-336, 1988.

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

Pauly, D., and Christensen, V.: Primary production required to sustain global fisheries, Nature, 374, 255-257, 1995.

Peters, K.E., Sweeney, R.E., and Kaplan, I.R.: Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter, Limnology and Oceanography, 23, 598-604, 1978.

Prahl, F.G., and Coble, P.G.: Input and behavior of dissolved organic carbon in the Columbia River Estuary, In “Changes in Fluxes in Estuaries: Implications from Science and Management” (Editors Dyer, K.R., and Orth, R.J.), Olsen & Olsen, Fredensborg, pp. 451-457, 1994.

Prasad, M.B.K., Kaushal, S.S., and Murtugudde, R.: Long-term pCO_2 dynamics in rivers in the Chesapeake Bay watershed, Applied Geochemistry, 31, 209-215, 2013.

Ramaswamy, V., Gaye, B., Shirodkar, P.V., Rao, P.S., Chivas, A.R., Wheeler, D., and Thwin, S.: Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea, Marine Chemistry, 111, 137-150, 2008.

Raymond, P.A., and Bauer, R.: Bacterial consumption of DOC during transport through a temperate estuary, Aquatic Microbial Ecology, 22, 1-12, 2000.

Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503, 355-359, 2013.

Raven, J.A., and Falkowski, P.G.: Oceanic sinks for atmospheric CO_2, Plant, Cell and Environment, 22, 741-755, 1999.

Redfield, A.C., Ketchum, B.H., and Richards, F.A.: The influence of organisms on the composition of sea-water, In “The Sea” (Editor, Hill M.N.), Interscience, New York, pp. 26-77, 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., Munhoven, G., Raymond, P.A., Spahni, R., Suntharalingam, P., and

Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nature Geoscience, 6, 597-607, 2013.

Riemann, L., and Middelboe, M.: Viral lysis of marine bacterioplankton: Implications for organic matter cycling and bacterial clonal composition, Ophelia, 56, 57-68, 2002.

Rumolo, P., Barra, M., Gherardi, S., Marsella, E., and Sprovieri, M.: Stable isotopes and C/N ratios in marine sediments as a tool for discriminating anthropogenic impact, Journal of Environmental Monitoring, 13, 3399-3408, 2011.

Rutgers van der Loeff, M.M., Meyer, R., Rudels, B., and Rachor, E.: Resuspension and particle transport in the benthic nepheloid layer in and near Fram Strait in relation to faunal abundances and ^{234}Th depletion, Deep-Sea Research I, 49, 1941-1958, 2002.

Sakurai, T., Serizawa, S., Isobe, T., Kobayashi, J., Kodama, K., Kume, G., Lee, J.H., Maki, H., Imaizumi, Y., Suzuki, N., Horiguchi, T., Morita, M., and Shiraishi, H.: Spatial, phase, and temporal distributions of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in Tokyo Bay, Japan, Environmental Science and Technology, 44, 4110-4115, 2010.

Santos, I.R., Glud, R.N., Maher, D., Erler, D., and Eyre, B.D.: Diel coral reef acidification driven by porewater advection in permeable carbonate sands, Heron Island, Great Barrier Reef, Geophysical Research Letter, 38, L03604, 2011.

Sarma, V.V.S.S., Arya, J., Subbaiah, Ch.V., Naidu, S.A., Gawade, L., Kumar, P.P., and Reddy, N.P.C.: Stable isotopes of carbon and nitrogen in suspended matter and sediments from the Godavari estuary, Journal of Oceanography, 68, 307-319,

2012.

Sarmiento, J.L., and Bender, M.: Carbon biogeochemistry and climate change, Photosynthesis Research, 39, 209-234, 1994.

Savoye, N., Aminot, A., Treguer, P., Fontugne, M., Naulet, N., and Kérouel, R.: Dynamics of particulate organic matter $\delta^{15}N$ and $\delta^{13}C$ during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France), Marine Ecology Progress Series, 255, 27-41, 2003.

Saito, Y., Nishimura, A., and Matsumoto, E.: Transgressive sand sheet covering the shelf and upper slope off Sendai, Northeast Japan, Marine Geology, 89, 245-258, 1989.

Schimel, D., Melillo, J., Tian, H., McGuire, A.D., Kicklighter, D., Kittel, T., Rosenbloom, N., Running, S., Thornton, P., Ojima, D., Parton, W., Kelly, R., Sykes, M., Neilson, R., and Rizzo, B.: Contribution of increasing CO_2 and climate to carbon storage by ecosystems in the United States, Science, 287, 2004-2006, 2000.

Schlesinger, W. H.: Carbon balance in terrestrial detritus, Annual Review of Ecology and Systematics, 8, 51-81, 1977.

Schultz, D., and Calder, J.A.: Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments, Geochimica et Cosmochimica Acta, 40, 381-385, 1976.

Senjyu, T., Asano, N., Matsuyama, M., and Ishimaru, T.: Intrusion events of the intermediate Oyashio Water into Sagami Bay, Japan, Journal of Oceanography, 54, 29-44, 1998.

Serret, P., Fernandez, E., and Robinson, C.: Biogeographic differences in the net ecosystem metabolism of the open ocean, Ecology, 83, 3225-3234, 2002.

Servais, P., Barillier, A., and Garnier, J.: Determination of the biodegradable fraction of dissolved and particulate organic carbon in waters, Annals de Limnologie, 31, 75-80, 1995.

Servais, P., Garnier, J., Demarteau, N., Brion, N., and Billen, G.: Supply of organic matter and bacteria to aquatic ecosystems through waste water effluents, Water Research, 33, 3521-3531, 1999.

Sharp, Z.: Principles of Stable Isotope Geochemistry, Pearson Prentice Hall, Upper Saddle River, 344 pp., 2007.

Shibata, Y., and Aruga, Y.: Variations of Chlorophyll a concentration and photosynthetic activity of phytoplankton in Tokyo Bay, La mer, 20, 75-92, 1982.

Shimizu, J., Yamao, S., Nosaka, T., Noguchi, K., Mine, M., Matsumoto, K., Oichi, K., Tsutsumi, K., Miyamoto, T., and Ikeda, Y.: Distributions of sedimentary POPs (Persistent Organic Pollutants) in Tokyo Bay – Results from the survey of POPs in Tokyo Bay in 2002, Reports of Hydrographic and Oceanographic Research, 41, 35-50, 2005 (in Japanese with English abstract).

Sholkovitz, E.R.: Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, Geochimica et Cosmochimica Acta, 40, 831-845, 1976.

Siegenthaler, U., and Sarmiento, J.L.: Atmospheric carbon dioxide and the ocean, Nature, 365, 119-125, 1993.

Smith, S.V.: Stoichiometry of C:N:P fluxes in shallow-water marine ecosystems, In “Comparative Analyses of Ecosystems: Patterns, Mechanisms, and Theories” (Editors, Cole, J.J., Lovett, J., and Findlay, S.), Springer-Verlag, Berlin, pp. 259-286, 1991.

Smith, S.V., and Hollibaugh, J.T.: Coastal metabolism and the oceanic organic carbon balance, Reviews of Geophysics, 31, 75-89, 1993.

Spiker, E.C., and Hatcher, P.G.: Carbon isotope fractionation of sapropelic organic matter during early diagenesis, Organic Geochemistry, 5, 283-290, 1984.

Stone, R.: The invisible hand behind a vast carbon reservoir, Science, 328, 1476-1477, 2010.

Sukigara, C., and Saino, T.: Temporal variations of $\delta^{13}C$ and $\delta^{15}N$ in organic particles collected by a sediment trap at a time-series station off the Tokyo Bay, Continental Shelf Research, 25, 1749-1767, 2005.

Sukigara, C., and Saino, T.: Monitoring of particle transport from Tokyo Bay to the open ocean, Bulletin on Coastal Oceanography, 45, 51-59, 2007 (in Japanese with English abstract).

Sun, M.Y., Aller, R.C., and Lee, C.: Spatial and temporal distributions of sedimentary chloropigments as indicators of benthic processes in Long Island Sound, Journal of Marine Research, 52, 149-176, 1994.

Sun, M.Y., Lee, C., and Aller, R.C.: Laboratory studies of oxic and anoxic degradation of chlorophyll-a in Long Island Sound sediments, Geochimica et Cosmochimica Acta, 57, 147-157, 1993.

Sundquist, E.T.: The global carbon dioxide budget, Science, 259, 934-941, 1993.

Suzuki, R., and Ishimaru, T.: An improved method for the determination of phytoplankton chlorophyll using N, N-Dimethylformamide, Journal of the Oceanographical Society of Japan, 46, 190-194, 1990.

Suzumura, M., and Kamatani, A.: Origin and distribution of inositol hexaphosphatase in estuarine and coastal sediments, Limnology and Oceanography, 40, 1254-1261,

1995.

Suzumura, M., and Ogawa, H.: Distribution of organic carbon, nitrogen, and phosphorus in surface seawater of Tokyo Bay in summer, Bulletin on Coastal Oceanography, 38, 119-129, 2001 (in Japanese with English abstract).

Suzumura, M., Kokubun, H., and Arata, N.: Distribution and characteristics of suspended particulate matter in a heavily eutrophic estuary, Tokyo Bay, Japan, Marine Pollution Bulletin, 49, 496-503, 2004.

Swaney, D.P., Howarth, R.W., and Butler, T.J.: A novel approach for estimating ecosystem production and respiration in estuaries: Application to the oligohaline and mesohaline Hudson River, Limnology and Oceanography, 44, 1509-1521, 1999.

Swart, S.: Lateral carbon export from the southern Benguela upwelling system, University of Cape Town, Master Thesis, 177 pp., 2008.

Swart, S., Waldron, H.N., and Hutchings, L.: Evidence of carbon transport between shelf and slope waters in the Benguela upwelling system, African Journal of Marine Science, 29, 137-139, 2007.

Takada, H., and Ogura, N.: Removal of linear alkylbenzensulfonates (LAS) in the Tamagawa Estuary, Marine Chemistry, 37, 257-273, 1992.

Takada, H., Ishiwatari, R., and Ogura, N.: Distribution of linear alkylbenzenes (LABs) and linear alkylbenzene-sulphonates (LAS) in Tokyo Bay sediments, Estuarine, Coastal and Shelf Science, 35, 141-156, 1992.

Takahashi, K., Wada, E., and Sakamoto, M.: Carbon isotope ratio and photosynthetic activity of phytoplankton in the eutrophic Mikawa Bay, Japan, Ecological Research, 7, 355-361, 1992.

Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D.C.E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T.S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C.S., Delille, B., Bates, N.R., and de Baar, H.J.W.: Climatological mean and decadal change in surface pCO_2, and net sea-air CO_2 flux over the global oceans, Deep-Sea Research II, 56, 554-577, 2009.

Talley, L.D.: Distribution and formation of North Pacific Intermediate Water, Journal of Physical Oceanography, 23, 517-537, 1993.

Tanaka, Y., Ogawa, H., and Miyajima, T.: Production and bacterial decomposition of dissolved organic matter in a fringing coral reef, Journal of Oceanography, 67, 427-437, 2011.

Tanimoto, T., Hoshika, A., Mishima, Y., and Yanagi, T.: Budget of suspended materials and nutrients in Osaka Bay, Oceanography in Japan, 10, 397-412, 2001.

The Tokyo metropolitan area summit: The sediment observation of Tokyo Bay, 45 pp., 2012 (in Japanese).

Thomsen, L.: Processes in the benthic boundary layer at continental margins and their implication for the benthic carbon cycle, Journal of Sea Research, 41, 73-86, 1999.

Thomsen, L.: The benthic boundary layer, In “Ocean Margin Systems” (Esitors, Wefer, G., Billett, D., Hebbeln, D., Jørgensen, B.B., Schlüter, M., and van Weering, T.C.E.), Springer-Verlag, Berlin, pp. 143-155, 2002.

Thomsen, L., and McCave, I.: Aggregation processes in the benthic boundary layer at the Celtic Sea continental margin, Deep-Sea Research I, 47, 1389-1404, 2000.

Thomsen, L., and van Weering, T.C.E.: Spatial and temporal variability of particulate matter in the benthic boundary layer at the N.W. European Continental Margin (Goban Spur), Progress in Oceanography, 42, 61-76, 1998.

Thornton, S.F., and McManus, J.: Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland, Estuarine, Coastal and Shelf Science, 38, 219-233, 1994.

Toggweiler, J.R.: Anthropogenic CO_2: the natural carbon cycle reclaims center stage, Reviews of Geophysics, 33, 1249-1252, 1995.

Tranvik, L.J., and Höfle, M.G.: Bacterial growth in mixed cultures on dissolved organic carbon from humic and clear waters, Applied and Environmental Microbiology, 53, 482-488, 1987.

Tyson, R.V.: Sedimentary Organic Matter: Organic Facies and Palynofacies, Chapman and Hall, London, 615 pp., 1995.

Twichell, S.C., Meyers, P.A., and Diester-Haass, L.: Significant of high C/N ratios in organic-carbon-rich Neogene sediments under the Benguela Current upwelling system, Organic Geochemistry, 33, 715-722, 2002.

United Nations: World Urbanization Prospects: The 2009 revision, United Nations Department of Economic and Social Affairs/Population Division, 47 pp., 2010.

Unoki, S., and Kishino, M.: Water exchange in inland waters, Costal Engineering, 24, 486-490, 1977 (in Japanese).

Unoki, S., Okazaki, M., and Nagasgima, H.: Circulation flow and hydrographic conditions in Tokyo Bay, Technical Report of the Physical Oceanography

Laboratory, The Institute of Physical and Chemical Research, 89 pp., 1980.

Usui, T., Nagao, S., Yamamoto, M., Suzuki, K., Kudo, I., Montani, S., Noda, A., and Minagawa, M.: Distribution and sources of organic matter in surficial sediments on the shelf and slope off Tokachi, western North Pacific, inferred from C and N stable isotopes and C/N ratios, Marine Chemistry, 98, 241-259, 2006.

van Heemst, J.D.H., Megens, L., Hatcher, P.G., and de Leeuw, J.W.: Nature, origin and average age of estuarine ultrafiltered dissolved organic matter as determined by molecular and carbon isotope characterization, Organic Geochemistry, 31, 847-857, 2000.

van Weering, T.C.E., and McCave, I.: Benthic processes and dynamics at the NW Iberian margin: an introduction, Progress in Oceanography, 52, 123-128, 2002.

van Weering, T.C.E., de Stigter, H., Balzer, W., Epping, E., Graf, G., Hall, I., Helder, W., Khripounoff, A., Lohse, L., McCave, I., Thomsen, L., and Vangriesheim, A.: Benthic dynamics and carbon fluxes on the NW European continental margin, Deep-Sea Research II, 48, 3191-3221, 2001.

Vizzini, S., Savona, B., Caruso, M., Savona, A., and Mazzola, A.: Analysis of stable carbon and nitrogen isotopes as a tool for assessing the environmental impact of aquaculture: a case study from the western Mediterranean, Aquaculture International, 13, 157-165, 2005.

von Glasow, R., Jickells, T.D., Baklanov, A., Carmichael, G.R., Church, T.M., Gallardo, L., Hughes, C., Kanakidou, M., Liss, P.S., Mee, L., Raine, R., Ramachandran, P., Ramesh, R., Sundseth, K., Tsunogai, U., Uematsu, M., and Zhu, T.: Megacities and large urban agglomerations in the coastal zone: Interactions between atmosphere, land, and marine ecosystems, AMBIO, 42, 13-28, 2013.

Wada, E., Kabaya, Y., Tsuru, K., and Ishiwatari, R.: ^{13}C and ^{15}N abundance of sedimentary organic matter in estuarine areas of Tokyo Bay, Japan, Mass Spectroscopy, 38, 307-318, 1990.

Wada, E., Minagawa, M., Mizutani, H., Tsuji, T., Imaizumi, R., and Karasawa, K.: Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, Japan, Estuarine, Coastal and Shelf Science, 25, 321-336, 1987.

Waldron, H.N., Monteiro, P.M.S., and Swart, N.C.: Carbon export and sequestration in the southern Benguela upwelling system: lower and upper estimate, Ocean Science, 5, 711-718, 2009.

Walsh, J.J.: Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen, Nature, 350, 53-55, 1991.

Walsh, J.J., Biscaye, P., and Csanady, G.: The 1983-1984 shelf edge exchange processes (SEEP)-I experiment: hypotheses and highlights, Continental Shelf Research, 8, 435-456, 1988.

Walsh, J.J., Rowe, G., Iverson, R.L., and McRoy, C.P.: Biological export of shelf carbon is a sink of the global CO_2 cycle, Nature, 291, 196-201, 1981.

Wang, F., Wang, Y., Zhang, J., Xu, H., and Wei, X.: Human impact on the historical change of CO_2 degassing flux in River Changjiang, Geochemical Transactions, 8, 7-16, 2007.

Wanninkhof, R., Park, G.H., Takahashi, T., Sweeney, C., Feely, R., Nojiri, Y., Gruber, N., Doney, S.C., McKinley, G.A., Lenton, A., Le Quéré, C., Heinze, C., Schwinger, J., Graven, H., and Khatiwala, S.: Global ocean carbon uptake: magnitude, variability and trends, Biogeosciencess, 10, 1983-2000, 2013.

Watson, A.J., and Orr, J.C.: Carbon dioxide fluxes in the global ocean, In “Ocean Biogeochemistry” (Editor, Fasham, M.J.R.), Springer-Verlag, Berlin, pp. 121-144, 2003.

Willey, J.D., Kieber, R.J., Eyman, M.S., and Avery Jr., G.B.: Rainwater dissolved organic carbon: Concentrations and global flux, Global Biogeochemical Cycles, 14, 139-148, 2000.

Wollast, R.: Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, In “The Sea” (Editor, Goldberg, E.D.), Interscience, New York, pp. 213-252, 1988.

Wollast, R.: Continental margins –review of geochemical settings, In “Ocean Margin Systems” (Esitors, Wefer, G., Billett, D., Hebbeln, D., Jørgensen, B.B., Schlüter, M., and van Weering, T.C.E.), Springer-Verlag, Berlin, pp. 15-31, 2002.

Yamaguchi, Y., and Shibata, Y.: Recent status of primary production in Tokyo Bay, Bulletin of Coastal Oceanography, 16, 106-111, 1979 (in Japanese).

Yamaguchi, Y., Satoh, H., and Aruga, Y.: Seasonal changes of organic carbon and nitrogen production by phytoplankton in the estuary of river Tamagawa, Marine Pollution Bulletin, 23, 723-725, 1991.

Yamamoto-Kawai, M., Kawamura, N., Ono, T., Kosugi, N., Kubo, A., Ishii, M., and Kanda, J.: Calcium carbonate saturation and ocean acidification in Tokyo Bay, Japan, in reviewed.

Yamamoto, T., Hiraga, N., Takeshita, K., and Hashimoto, T.: An estimation of net ecosystem metabolism and net denitrification of the Seto Inland Sea, Japan, Ecological Modelling, 215, 55-68, 2008.

Yamashita, Y., Kloeppel, B. D., Knoepp, J., Zausen, G. L., and Jaffé, R.: Effect of watershed history on dissolved organic matter characteristics in headwater streams, Ecosystems, 14, 1110-1122, 2011.

Yanagi, T.: Material transport models from Tokyo Bay to the Pacific Ocean, Biogeochemical Processes and Ocean Flux in the Western Pacific, In "Biogeochemical Processes and Ocean Flux in the Western Pacific" (Editors, Sakai, H., and Nozaki, Y.), Terra Scientific Publishing Company, Tokyo, pp. 563-574, 1995.

Yanagi, T.: Seasonal variations in nutrient budgets of Hakata Bay, Japan, Journal of Oceanography, 55, 439-448, 1999.

Yanagi, T., Okada, S., Ishimaru, T., and Saino, T.: Behavior of high turbidity water outflow from Tokyo Bay in summer, La mer, 29, 45-51, 1991.

Yanagi, T., Shimizu, M., Saino, T., and Ishimaru, T.: Tidal pump at the shelf edge, Journal of Oceanography, 48, 13-21, 1992.

Yanagi, T., Tamaru, H., Ishimaru, T., and Saino, T.: Intermittent outflow of high-turbidity bottom water from Tokyo Bay in summer, La mer, 27, 34-40, 1989.

Yasui-Tamura, S., Kanda, J., Usui, T., and Ogawa, H.: Seasonal variations of pore water dissolved organic matter and nutrients in coastal sediments in Tokyo Bay, in preparation.

Yu, F., Zong, Y., Lloyd, J.M., Huang, G., Leng, M.J., Kendrick, C., Lamb, A.L., and Yim, W.W.S.: Bulk organic $\delta^{13}C$ and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China, Estuarine, Coastal and Shelf Science, 87, 618-630, 2010.

Yuk, J.H., and Aoki, S.: Nitrogen and phosphorus budgets of Hamana Bay, Japan, Journal of Coastal Research, 64, 1510-1514, 2011.

Zonneveld, K.A.F., Versteegh, G.J.M., Kasten, S., Eglinton, T.I., Emeis, K.C., Huguet, C., Koch, B.P., de Lange, G.J., de Leeuw, J.W., Middelburg, J.J., Mollenhauer, G., Prahl, F.G., Rethemeyer, J., and Wakeham, S.G.: Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record, Biogeosciences, 7, 483-511, 2010.

Zushi, Y., Ye, F., Motegi, M., Nojiri, K., Hosono, S., Suzuki, T., Kosugi, Y., Yaguchi, K., and Masunaga, S.: Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo Bay basin of Japan, Environmental Science and Technology, 45, 2887-2893, 2011.

Appendix

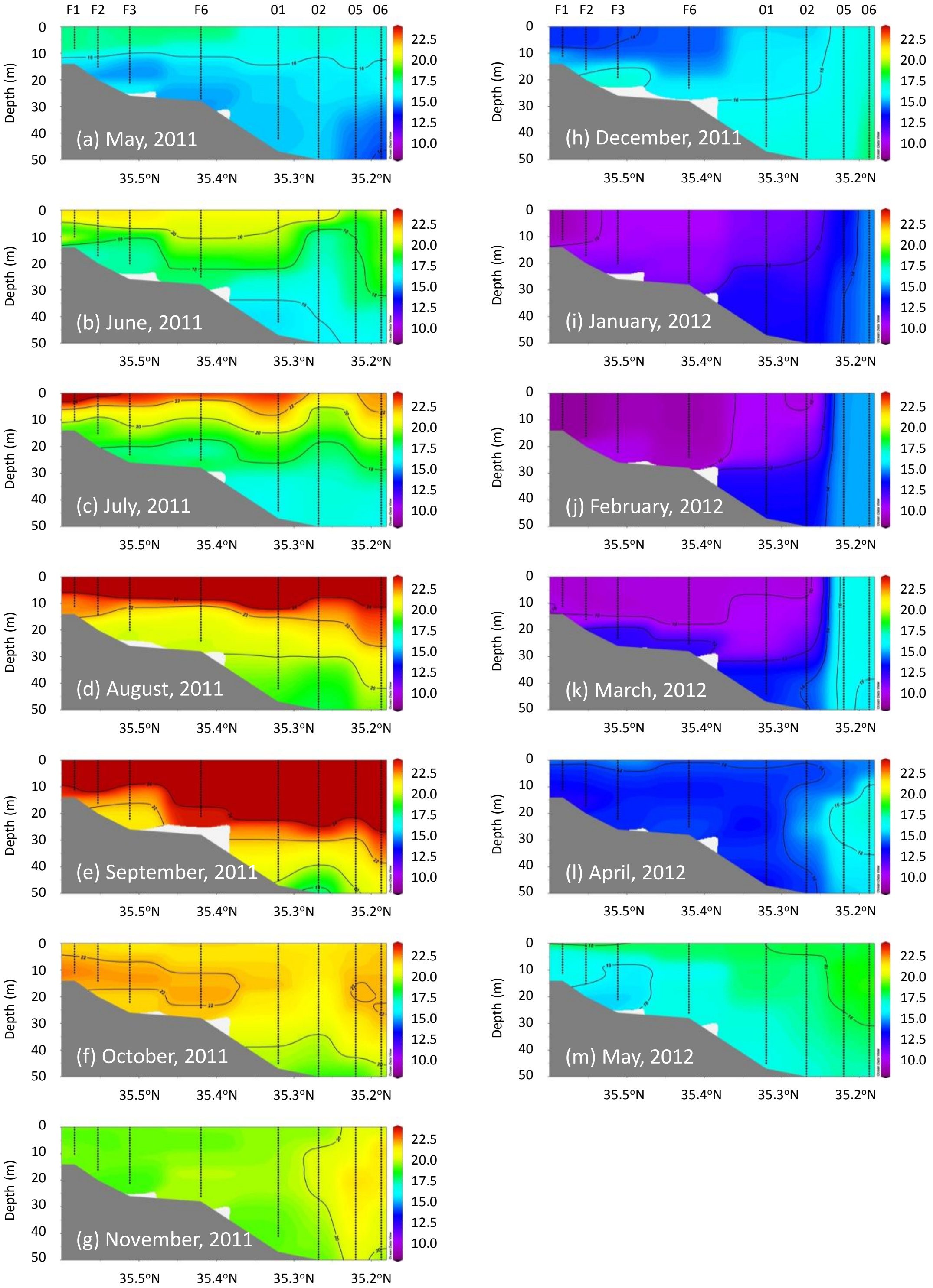

Figure A1-1 Spatial distribution of temperature (°C) in the upper 50 m of water.

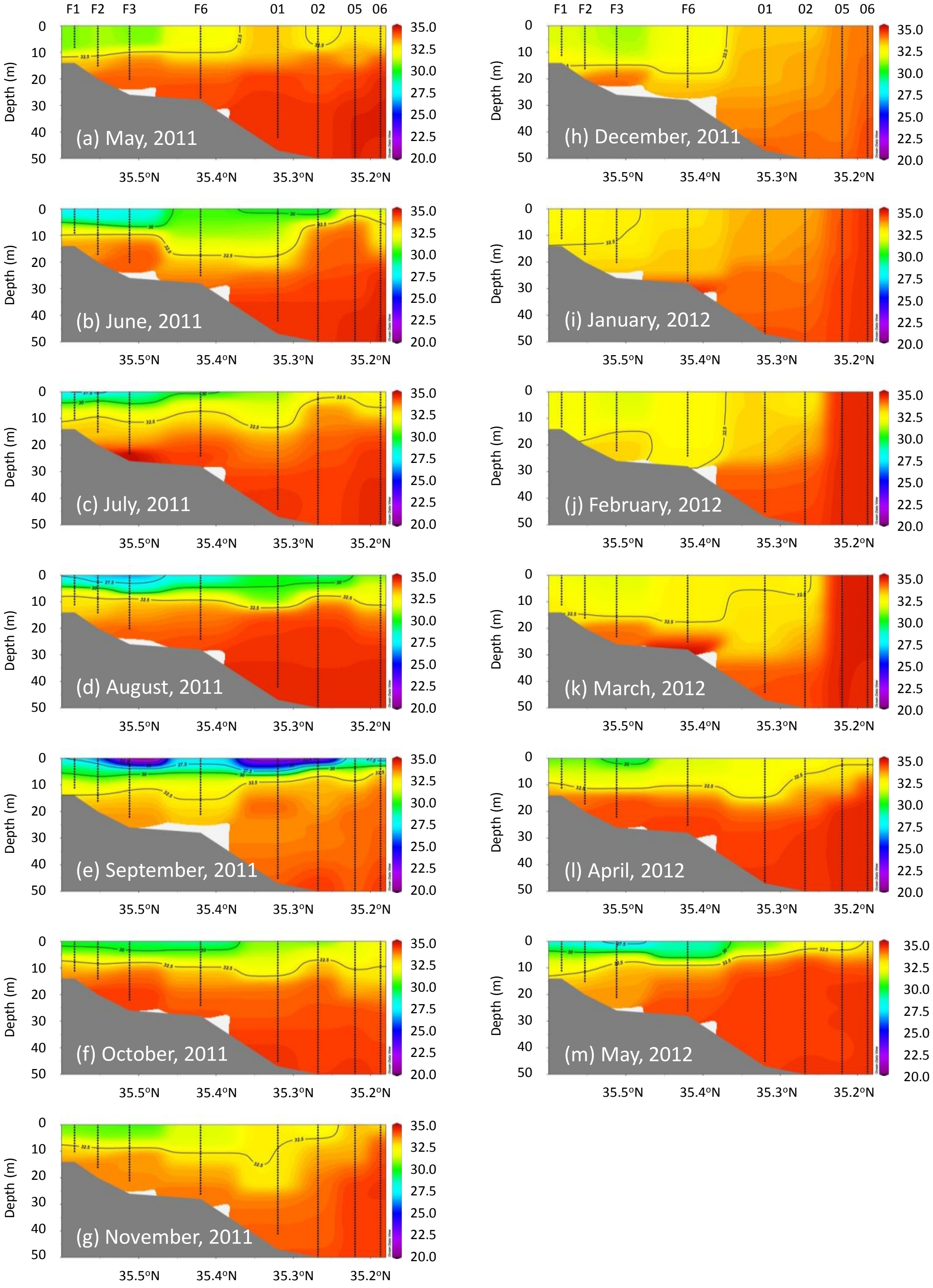

Figure A1-2 Spatial distribution of salinity in the upper 50 m of water.

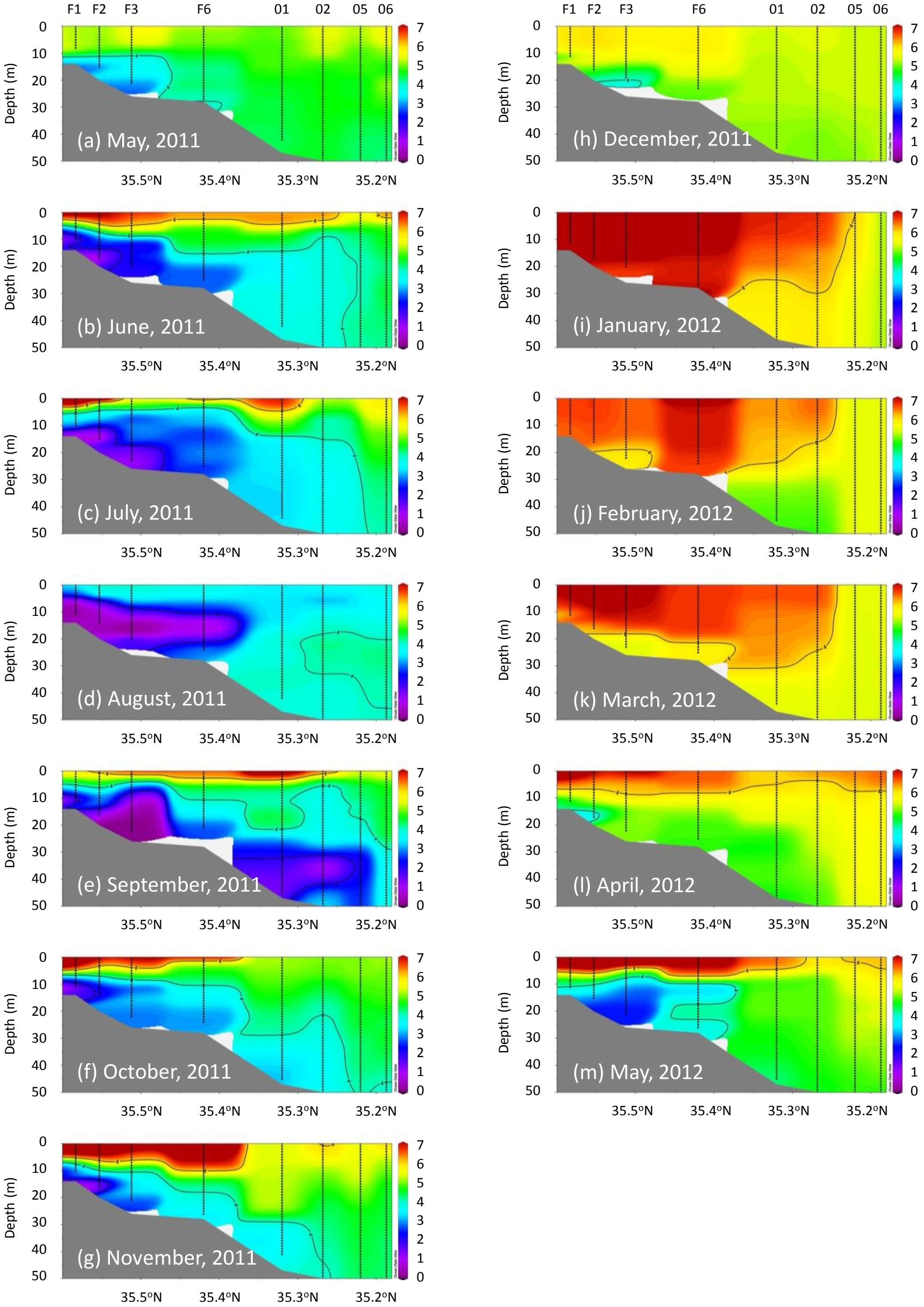

Figure A1-3 Spatial distribution of DO (mL L^{-1}) in the upper 50 m of water.

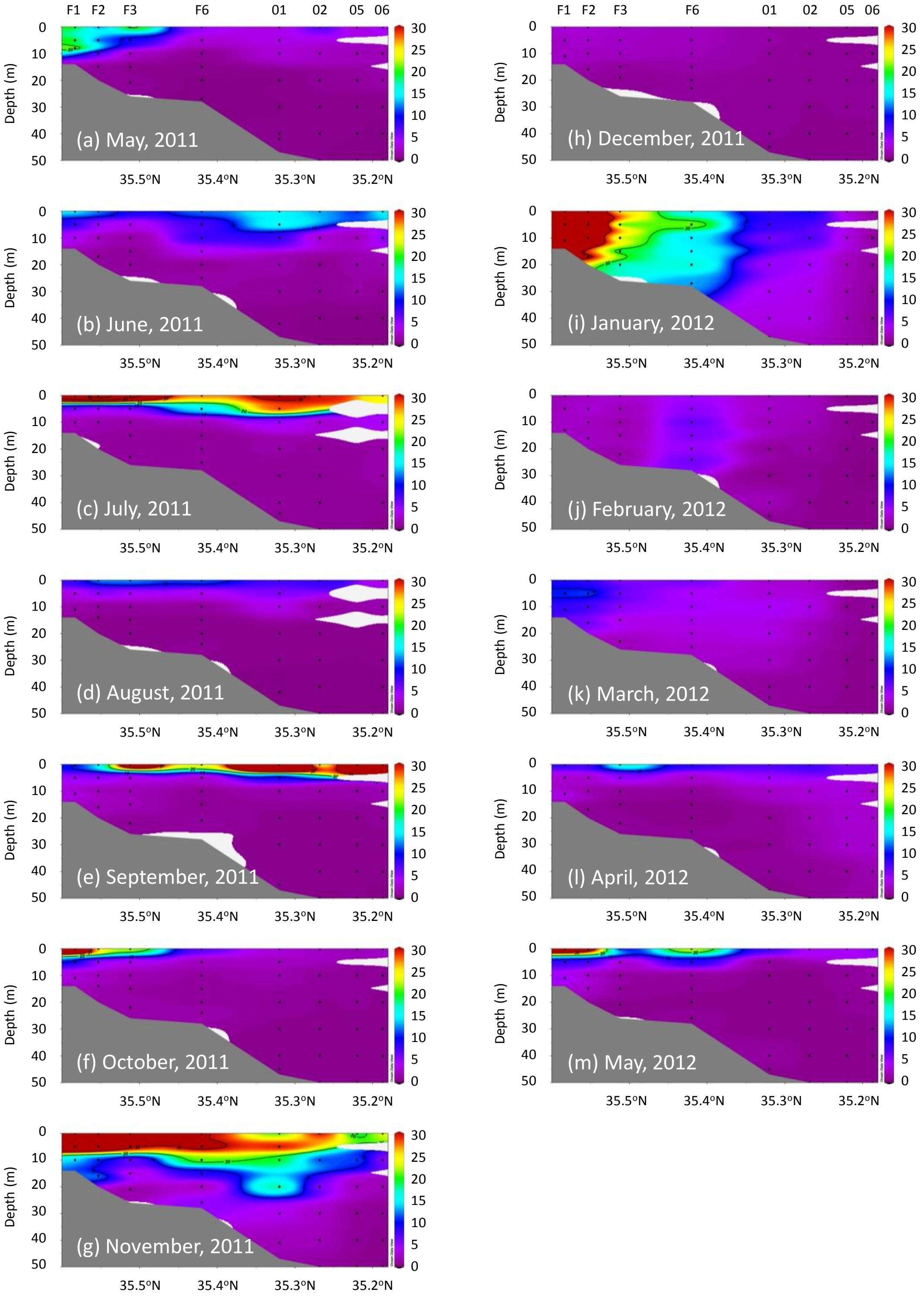

Figure A1-4 Spatial distribution of Chl *a* (μg L^{-1}) in the upper 50 m of water.

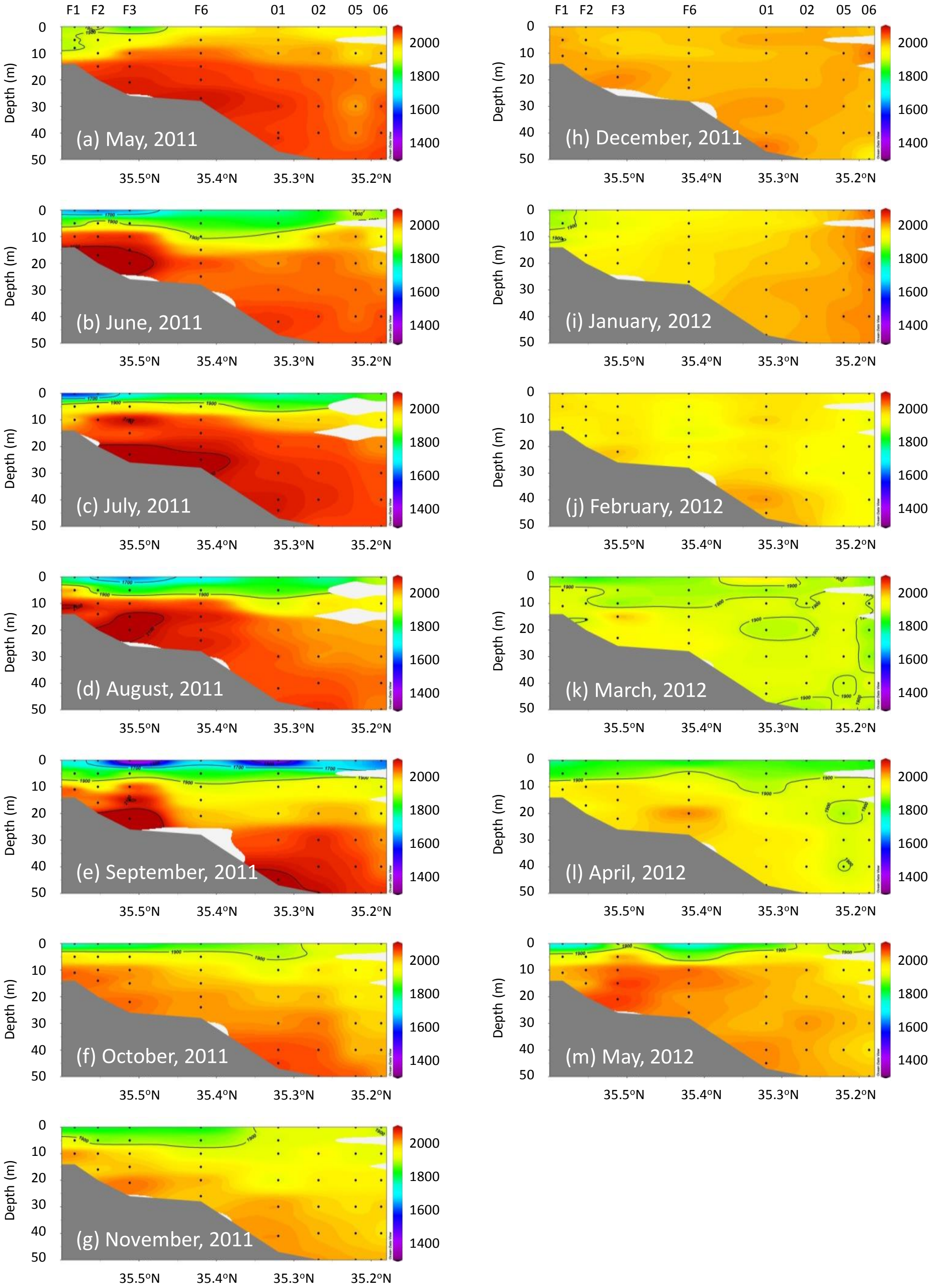

Figure A1-5 Spatial distribution of DIC (μmol L^{-1}) in the upper 50 m of water.

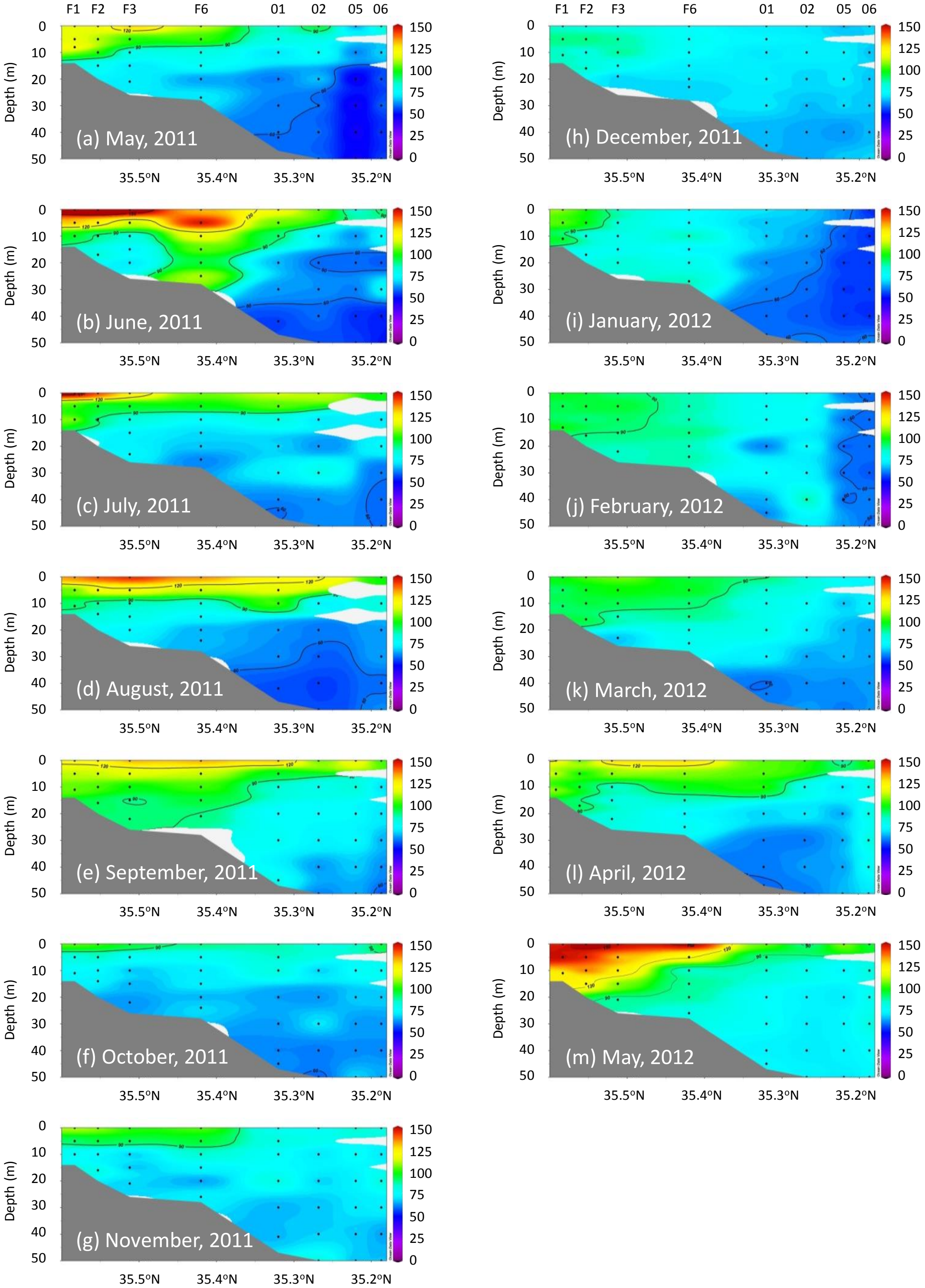

Figure A1-6 Spatial distribution of DOC (μmol L^{-1}) in the upper 50 m of water.

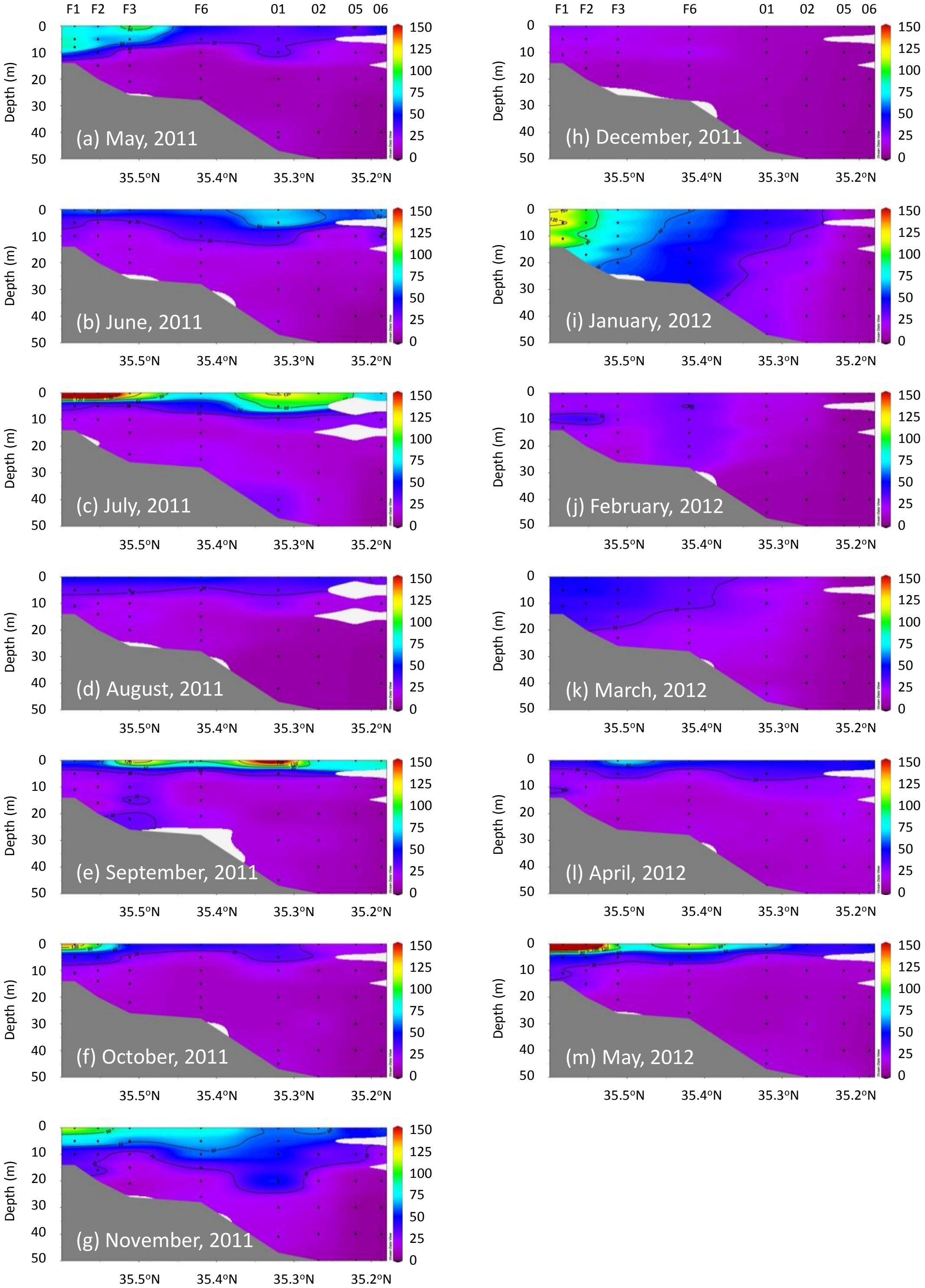

Figure A1-7 Spatial distribution of POC (μmol L^{-1}) in the upper 50 m of water.

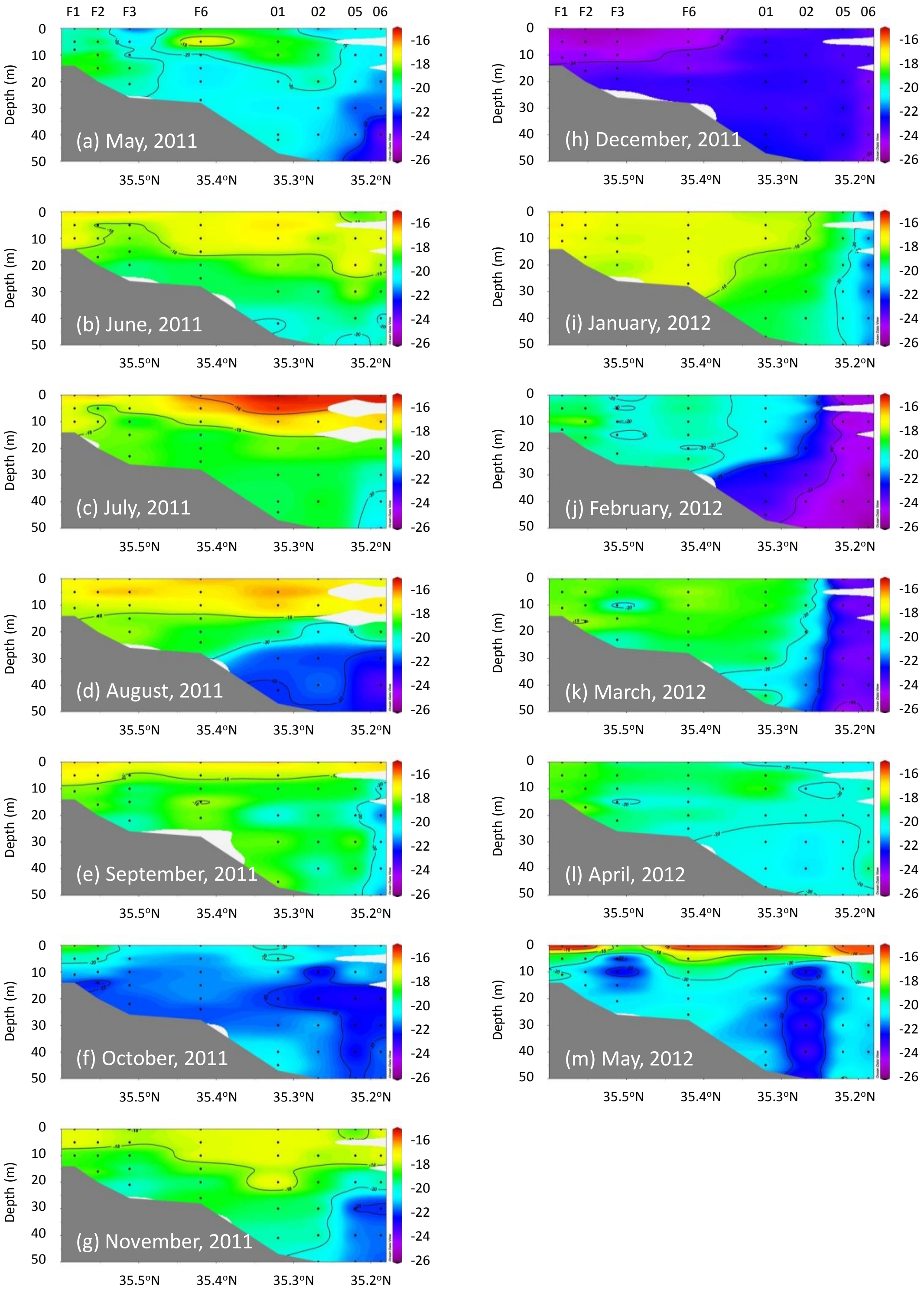

Figure A1-8 Spatial distribution of $\delta^{13}C_{POM}$ (‰) in the upper 50 m of water.