Dissertation
Factors controlling organic pollution in Lake Kiba with shallow
and semi-closed environment

Graduate School of Natural Science and Technology
Kanazawa University

Major subject: Division of Material Chemistry
Course: Chemistry

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January 2017

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Abstract

Lakes play important roles in the carbon cycle through carbon sequestration in sediments and efflux of CO_2 to the atmosphere. Some lake environments in developing countries have been facing organic pollution over the last decade because of rapid economic development and an increase in the human population around watersheds. In Japan, results of water quality surveys of lakes and reservoirs in 2014 indicated that the compliance rate of environmental quality standards for living environmental items is 55.5% for chemical oxygen demand (COD) concentration. Another water quality problem is the slight increase in COD concentrations in lakes, though total nitrogen, phosphorus and biochemical oxygen demand (BOD) concentrations are constant or decrease with time. The increasing annual averages of COD appear to be caused by accumulation of refractory organic matter in the lakes. Therefore, the dynamics of organic matter are important to understand mechanism of organic pollution in lake systems.

Lake Kiba is located at Komatsu City, Ishikawa Prefecture, Japan and is a small, shallow and semi-closed lake environment. The chemical oxygen demand (COD) concentration was at a maximum, 11 mg l^{-1} in 1990, corresponding to the second worst in Japan. It has remained about double the national standard of this lake class (3 mg l^{-1}) during the last decade, though treatments for water quality improvement has been performed since 1991.The objective of this study are to understand present situation of organic pollution and its controlling factors in Lake Kiba.

To understand organic pollution in Lake Kiba over the last 100 years, we analyzed organic matter content and its characteristics recorded in the sediment core samples

collected in the central part of the lake. Organic matter flux increased from 1.1 to 2.3 and from 3.9 to 7.5 mgC cm^{-2} y^{-1}, during 1903–1974 and 1989–2012 respectively, although it was similar with the flux recorded for 1974–1989 following reclamation. The C/N ratio, δ^{13}C and δ^{15}N also changed during these time intervals. These results indicate that primary production is increasing with time and the recent contribution of phytoplankton to productivity has exceeded the level of past contributions.

During 2012–2016, a monitoring study was conducted for lake water environments. A strong positive correlation was found between the COD concentration and physicochemical parameters such as water temperature, pH, and chlorophyll-a concentrations. This indicates that the COD variation is controlled by phytoplankton activity in the lake. Particulate COD was 8–51% of total COD concentration, with an average value of 34 ± 11%. A positive correlation exists with particulate and dissolved COD concentrations. Results suggest that the input and output of particulate and dissolved COD in Lake Kiba are apparently similar year-round.

To understand more detailed variation mechanisms, we focused on the dynamics of particulate and dissolved organic matter in lake water throughout one year based on monthly observations during 2014–2016. The simultaneous use of Δ^{14}C and δ^{13}C values adds a second dimension to carbon cycling in surface aquatic environments. During the sampling period, we ascertained the basic physicochemical parameters, particulate organic carbon (POC) concentration and carbon isotopes. POC concentrations ranged from 0.44 to 5.01 mg l^{-1}. δ^{13}C and Δ^{14}C values were –30.3 to –22.8 ‰ and –156 to –33 ‰, respectively. The organic matter in suspended solid samples was consistently depleted for ^{14}C and an averaged Δ^{14}C value of –81 ± 37‰. The carbon isotopes

showed seasonal variation with higher concentrations in summer and positive correlations with POC content ($r = 0.73 - 0.82$, $p < 0.01$). The results suggest that the characteristics of POC are controlled by a mixture of two endmembers: organic matter produced by phytoplankton activity within the lake and watershed organic matter under shallow and semi-closed environments. Dissolved organic carbon (DOC) concentrations were higher in summer and had strongly relations with water temperature and water pH. Fulvic-like materials, which have refractory properties and are a major component of organic matter, were correlated well with DOC concentrations. However, maximum fluorescence peak position in water samples collected in spring-summer is shifted to shorter excitation wavelengths than that of autumn-winter. These results suggest that sources of fulvic-like materials are different from the spring-summer to autumn-winter seasons.

The results of this study provide basic and useful information of understanding organic pollutants in shallow lakes and lagoons.

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Chapter 1.

Introduction

1.1. Organic pollution in lake environments

Water quality is becoming increasingly important for water management of lakes. It is a basic factor that must be considered in environmental flows and environmental water allocation. Some lake environments have sustained organic pollution in recent years, such as Lake Biwa (largest lake in Japan), Lake Taihu, Lake Chaohu, and Lake Hulun in China. This severe issue is related to communities because of its harmful influences on aquatic ecosystem as well as human health. Therefore, it is important to elucidate organic matter behaviors and factors governing water quality in lake environments.

Organic matter, which is ubiquitous in waters and soils, can be viewed as the result of various stages of decomposition and mixing of various materials from plants, microbes, and animal products. In water environments, organic matter behavior has been supported by the metabolism of living things, ecological and geochemical functions, biogeochemical processes and photochemical reactions, transportation of inorganic and organic substrates and aggregation and photochemical reactivity (Xiaoying, 2001; Egeberg and Alberts, 2002; Maurice et al., 2002). Dissolved organic carbon is a parameter, defined as active chemical substances that can pass a 0.45 μm filter. The major DOC component is polymers of organic acids: humic substances. The DOC fraction accounts for about 90% of all organic carbon (TOC). Consequently, DOC is an important role in the carbon cycle in lake environments (Tranvik et al., 2009; IPCC, 2013). It has been commonly analyzed for elucidating organic polluted lakes. More aspects of organic matter have garnered concern, such as temporal and spatial variations in surfaces and sediments, as well as its original components. Because DOM

is the main fraction of organic matter, its characteristics are related to biogeochemical processes and water quality in aquatic environments. Variations in DOM composition can be presented via changes in DOM fluorescence from several autochthonous or allochthonous sources that are affected by physical, biological, and chemical processes occurring in the water column (McKnight et al., 2001; Stedmon et al., 2007; Singh et al., 2010). Chemical functions and physical parameters such as temperature and moisture are related to nutrient availability, amount of available free oxygen, and redox activity, and microbial functions with micro-floral succession patterns and availability of microorganisms (aerobic or anaerobic).

Higher organic matter concentrations are related to declining water quality and organic pollution in lake environments. Autochthonous and allochthonous products are two major sources of components and variations of organic pollution in lake environments. Autochthonous organic matter in natural waters and in sediment pore waters typically comprises phytoplankton or algal biomass, bacteria, coral, submerged aquatic vegetation, krill (shrimp-like marine crustaceans), marshes, and mangrove forests (McKnight et al., 1994, 2001; Wang et al., 2007; Henderson et al., 2008; Mostofa et al., 2009a, b; Zhang et al., 2009). Recently, phytoplankton, benthic algae, and aquatic macrophytes are emphasized as major autochthonous products (Henderson et al., 2008; Lapierre and Frenette, 2009; Zhang et al., 2009).

Autochthonous organic matter products in lakes and oceans generally occur in surface waters during the summer stratification period. The products of autochthonous lake environments are affected strongly by weather conditions because phytoplankton/algae growth and DOM products are affected by water temperatures, which in turn

affect photosynthesis activity and degradation. About 5–70% of photosynthetically derived organic matter is released to water ecosystems (Lancelot, 1979; Fogg, 1983). Therefore, it can be stated that photosynthetic activity plays a crucial role in understanding behaviors of organic matter in lake water because of the contribution of its products as autochthonous components. It also plays a role in the formation of organic matter (e.g. algae or cyanobacteria, phytoplankton), through light-stimulated inorganic carbon acquisition in surface waters (Mostofa et al., 2009a; Wu and Gao, 2009; Liu et al., 2010). Phytoplankton and bacteria attach to or live on suspended solids (Mulligan et al., 2009), whereas the POC value is determined for a suspension obtained from water samples after filtration through a filter having pore size of 0.45 μm. Additionally, algae or phytoplankton biomass and bacteria can release DOM into a water body in two steps. This process occurs in two ways including photoinduced respiration or assimilation of algae or phytoplankton biomass and bacteria (Biddanda and Benner, 1997; Mostofa et al., 2005a, 2009b, 2011; Aoki et al., 2008; Hulatt et al., 2009), and microbial respiration or assimilation of algae or phytoplankton and bacteria (McKnight et al., 1994, 2001; Mostofa et al., 2009a, b; Zhang et al., 2009). Therefore, POC and DOC fluctuation in lake waters is closely related to phytoplankton activity and is controlled by seasonal environmental conditions.

The first is the generation of numerous chemical species from DOM, which might proceed as follows: photoinduced degradation of DOM can produce many photoproducts such as H_2O_2, CO_2, DIC, CO, and low molecular weight DOM in upper surface waters (Mostofa and Sakugawa, 2009; Remington et al., 2011). Also, microbial degradation of DOM can produce similar compounds (Mostofa and Sakugawa, 2009).

These compounds can favor the occurrence of photosynthesis either directly or indirectly, and can engender fixation of organic matter from inorganic carbon in surface waters (Miller and Moran, 1997; Mostofa et al., 2009a; Wu and Gao, 2009; Liu et al., 2010). Secondly H_2O_2 and CO_2 are produced either by photoinduced or microbial degradation of DOM and POM, which can take part in photosynthesis to form new OM or carbohydrate-type compounds (Mostofa et al., 2009a, b). In the hypothesized process, H_2O_2 combines with CO_2 to release carbohydrates and oxygen. The oxygen formation occurs via H_2O_2 disproportionation, which is a common conversion reaction of H_2O_2 in water ecosystems and in the atmosphere (Liang et al., 2006; Buick, 2008). Some energy is produced during this activity.

According to Druon et al. (2010) the DOC production was mostly enhanced from phytoplankton exudation in the upper layer and the solubilization of POM deeper in the water column. Ortega-Retuerta et al. (2009) observed that the quantity and quality of DOM produced by bacteria can be influenced by the presence of photoproducts in aqueous media. Photosynthetically produced POM (algae or phytoplankton) and their photo- and microbial respirations are affected strongly by several factors such as chemical nature and contents of DOM (Tranvik and Hafle, 1987; Tranvik, 1989; Jones, 1992), high precipitation (Tranvik and Jasson, 2002; Zhang et al., 2010), land use changes that cause high transport of DOC from catchments to adjacent surface waters (Worrall et al., 2004; Raymond and Oh, 2007), nitrogen deposition (Pregitzer et al., 2004), sulfate (SO_4^{2-}) deposition (Zhang et al., 2010), drought and alteration of hydrologic pathways (Hongve et al., 2004;), and changes in overall solar UV radiation or an increase in temperature because of global warming (Freeman et al., 2001a; Sinha

et al., 2001; Sobek et al., 2007; Zhang et al., 2010).

A survey conducted by Aoki et al. (2008) showed that the increase of refractory organic matter in lake waters might be attributed to a change of the predominant phytoplankton. A study of three kinds of phytoplankton (collected from lake waters) demonstrated that fulvic acid-like and protein-like fluorescent components are released when they are controlled light/dark (12 h/ 12 h) cycle and water temperature at 20 °C. Some brown algae can produce considerably less DOM (e.g. *Pelvetia canaliculata*) compared to green and red species (Hulatt et al., 2009). Those results show that different phytoplankton types release different amounts of DOM in water environments. Subsurface DOM maxima are found below the plume during the highly stratified summer period but they are absent in the spring, which constitutes strong evidence of significant *in-situ* biological production of colored dissolved organic matter (CDOM) in natural waters (Chen and Gardner, 2004).

Suspended organic carbon consists of detached fauna and flora, and organic substances adsorbed onto mud and clay (Quyang, 2003). Therefore, degradation of POC can release new DOC into an aquatic environment. The POM production is closely coupled with DOM contents in natural waters. Actually, POM can produce new autochthonous DOM and nutrients under irradiation and microbial respiration/ assimilation (Mostofa et al., 2005a, 2009b; Yamashita and Jaffé, 2008; Zhang et al., 2009).

In contrast, DOM can support a marked amount of bacterial biomass growth, representing a further loss of algal assimilated carbon in water (Hulatt and Thomas, 2010). Dissolved combined amino acids, middle-reach peaks of particulate amino acids

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and non-protein amino acids are often decreased in downstream rivers, which is likely the result of photoinduced degradation of DOM and algae (Duan and Bianchi, 2007). The key processes of autochthonous DOM release by microbial respiration of algae or phytoplankton biomass in waters are presumably the extracellular release by living cells, cell death, and lysis, or herbivore grazing that might occur in the deeper waters of rivers, lakes, and oceans (Tanoue, 2000; Mostofa et al., 2009a; Tranvik et al., 2009). These key processes demonstrate that bacteria play a specific role in the subsequent processing of the DOM released by algae in natural water (Nelson et al., 1998, 2004). The DOC released by algae or phytoplankton and bacteria in waters is influenced by widely diverse factors such as the occurrence of the phytoplankton species and their contents, water quality, presence of nutrients, effect of UV and photosynthetic available radiation, water temperature, occurrence of microbes, and metabolic abilities or inabilities (Fogg, 1983; Norrman et al., 1995; Nelson et al., 1998, 2004).

Photosynthetic organisms can produce autochthonous DOM via photoinduced respiration (or photoinduced assimilation) and microbial respiration or assimilation in natural waters (Mostofa et al., 2009b; Zhang et al., 2009; Druon et al., 2010; Fu et al., 2010). A new hypothesis related to photosynthesis also includes consideration that H_2O_2 might be involved in the occurrence of oxygenic photosynthesis in both higher plants (Miller and Moran, 1997) and in natural water organisms (Mostofa et al., 2009a, b). Results of these studies have indicated that autochthonous DOM is produced from POM by several processes such as photoinduced and microbial respiration (or assimilation), zooplankton grazing, bacterial release and uptake, viral interactions, and complex microbial processes in sediment pore waters.

The variation of organic matter in lake water depends not only on autochthonous products but also on control by allochthonous input (Rossi et al., 2010). DOM including fulvic and humic acids (humic substances) originates from vascular plant material, root exudates and animal residues in terrestrial soil. The origin of allochthonous DOM from vascular plant materials or particulate detrital pools varies considerably among different regions (tropical, temperate, and boreal), according to the occurrence of three key factors: microbial, physical, and chemical functions (Wetzel, 1983, 1992; Mostofa et al., 2009a; Tu et al., 2011). Aerobic microorganisms can decompose organic matter faster than anaerobic ones can, depending on the availability of free oxygen. Compositional changes of DOM occur with soil depth, leading to a decrease of aromatic compounds and carbohydrates. Also, alkyl, methoxy, and carbonyl moieties increase with depth (Dai et al., 1996). The increase in alkyl and carboxylic C with depth are the respective results of forest litter biodegradation and lignin side chain oxidation (Kogel-Knabner et al., 1988). The origin of allochthonous DOM from microbial processes can be inferred from the stark variations in respired organic carbon in different soil environments. Experimental studies using $\delta^{13}C$ or $\Delta^{14}C$ to track sources and turnover of DOC indicate that DOM, which is transported over decimeters down into subsoil, mainly represents highly altered residues of organic matter processing (Schiff et al., 1997; Fröberg et al., 2007). It is noteworthy that allochthonous DOM is derived mostly in the surface to a few decimeters depth from the decomposition of plant materials by microbial processes in soils and shallow groundwater (IPCC, 1996; Uchida et al., 1998, 2000; Buckau et al., 2000; Fröberg et al., 2007). DOC leached from soil is partly retained in the vadose zone before reaching aquifers (Siemens and Kaupenjohann, 2003). For the range of

groundwater recharge of 95–652 mm yr^{-1}, a constant flux of DOC from soil into surface waters often takes place (Kindler et al., 2011). Therefore, allochthonous DOM is partly discharged through hydrological processes directly into streams or riverbeds or surrounding water bodies. The allochthonous DOM ultimately flows to lake or oceanic environments as a final water reservoir.

The quality of water is often evaluated using results of chemical and biological analysis, as well as weather conditions that alter water quality. Weather factors have been emphasized in aquatic studies in recent years because organic solubility and inorganic compounds depend on temperature, which affects the dissociation of dissolved compounds. The different concentrations of dissociated and un-dissociated compounds affect the pH and conductivity of water samples. Rain and melted snow water can affect organic matter concentrations in watersheds because of reduction of dissolved compounds. In parallel with such processes, rainwater dissolves different compounds from soil, thereby increasing the concentration of dissolved compounds because of infiltration into lake water. Heavy rains play a role in the transport of huge amounts of allochthonous organic matter (Park et al., 2009). Autochthonous organic matter appears to be predominant in the lake during the summer, although the relative contribution of organic matter of terrestrial origins increased after heavy rains in early autumn. Water input affects special fluctuation of organic matter concentration in lake water, the POC concentration increases because of increasing river water pollution (Barałkiewicz and Siepak, 1994a,b; Siepak, 1999). Suspended solids accumulate toxic components that eventually reach the bottom of the water. Phytoplankton and bacteria can live on or adhere to suspended solids (Mulligan et al., 2009). Therefore, the removal

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of suspended solids is necessary both for water clarity and for reduction of chemical oxygen.

Anthropogenic influences such as sewerage and domestic, agricultural, and industrial effluents contribute considerably to increased concentrations of organic matter in aquatic environments (Abril et al., 2002; Mostofa et al., 2005b, 2010; Fu et al., 2010). The occurrence of DOM derived from human activities is gradually increasing because of the increased widening and intensification of domestic, agricultural, and industrial activities.

Common nutrients released from decomposition processes of organic matter in lake environments include ammonium ion (NH_4^+), nitrate ion (NO_3^-), and phosphate ion (PO_4^{3-}). Nutrients are produced by degradation of DOM and POM. They typically derive from dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) (Bronk, 2002; Kim et al., 2006; Li et al., 2008). Nutrients are mostly released during the photoinduced and microbial respiration (or assimilation) of POM (algae or phytoplankton biomass), as shown by experiments conducted under light and dark incubations (Carrillo et al., 2002; Kim et al., 2006; Yamashita and Jaffé, 2008). Nitrated and nitrite ions are producible by oxidation of ammonia in nitrification and of DON in lake waters (Kopáček et al., 2004; Lehmann et al., 2004). Nutrients produced by organic matter can be used for new primary or secondary production in natural waters. Total concentrations of DOM in lake waters are responsible for variation of the trophic level, because of eutrophication/oligotrophication processes.

Various sources of organic matter in lake water typically point to a dominant source, which is important for formulating good solutions to improve water quality in lake

environments. From the study of organic matter sources, the DOM fraction is well known to be designated as either colored or chromophoric dissolved organic matter based on the absorption of ultraviolet (UV) and photosynthetic available radiation. DOM is generally controlled by downward irradiance flux through the water column of UV of 280–400 nm (UV-A of 320–400 nm and UV-B of 280–320 nm), and photosynthetically available UV wavelengths of 400–700 nm (Laurion et al., 2000; Markager and Vincent, 2000). DOM is associated with water color, water transparency, occurrence of euphotic zone and thermal stratification in the surface waters of lakes because of effects of solar radiation penetration (Laurion et al., 2000; Mostofa et al., 2005a).

Actually, DOM can strongly affect photosynthesis in natural waters, limit productivity (Jackson and Hecky, 1980; Carpenter et al., 1998), and affect epilimnetic (Hanson et al., 2003) and hypolimnetic respiration (Houser et al., 2003). Photoinduced and microbial oxidation of DOM is responsible for the simultaneous generation of H_2O_2, CO_2 and DIC (Palenik and Morel, 1988; Mostofa and Sakugawa, 2009c). Nutrients (PO_4^{3-} and NH_4^+) released by DOM and POM might also favor the occurrence of photosynthesis and consequently enhance phytoplankton blooms in natural waters (Lehmann et al., 2004; Kim et al., 2006; Li et al., 2008; Zhang et al., 2009). High chlorophyll *a* concentrations are often observed in waters with high contents of DOM; the reverse occurs in low-DOM waters (Meriläinen et al., 2001; Mostofa et al., 2005a, Satoh et al., 2006; Komatsu et al., 2007).

Three-dimensional excitation–emission matrix (EEM) spectroscopy has been a useful technique to discriminate humic substances of different types and sources in

dissolved fraction in natural waters. This method is characterized by identification of protein-like and humic-like fluorescence peaks based on detection of reactions to different excitation–emission wavelengths from water samples (Coble, 1996). However, an important shortcoming of this method is that traditional peak picking techniques might not evaluate the exact changes in fluorescence intensity of protein-like and humic-like because of different fluorescence peak overlaps (Maie et al., 2007).

Based on the similarities of the EEM spectra, the key component of autochthonous fluorescent DOM is defined as "autochthonous fulvic acid (C-like)" of algal or phytoplankton origin. Another component is defined as "autochthonous fulvic acid (M-like)" of algal or phytoplankton origin, based on similarities with the marine humic-like component (Coble, 1996, 2007). Fluorescence spectroscopy offers unique fingerprints for single compounds or a mixture of fluorescent components (Persson and Wedborg, 2001; Peuravuori et al., 2002; Her et al., 2003). Coble (1996) reported that a blue-shift, i.e. an emission shift to a shorter wavelength, is caused by a reduction in the π-electron system, such as a decrease in the number of aromatic rings or conjugated bonds in a chain structure, or the conversion of a linear ring system to a nonlinear one.

For shallow lakes, with conditions that favor development of submerged aquatic vegetation over large areas, the potential exists for large-scale reduction of nutrients and phytoplankton concentrations in the water column (Scheffer et al., 1994; Kufel, 2002; Bakker et al., 2013). This reduction occurs because submerged aquatic vegetation beds can stabilize sediments, sustain epiphytes that sequester nutrients, and engender physical and chemical conditions that elicit removal of both particulates and soluble nutrients from the water column (Jeppesen et al., 1998). High turbidity affects

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photosynthetic capacity, for example, primary production by phytoplankton becomes light-limited (Kromkamp et al., 1995; David et al., 2006); some planktonic organisms (copepods and mysids) reduce their food collecting abilities, egg production, and individual health (Bernát et al., 1994; Gasparini et al., 1999; David et al., 2005; Carrasco et al., 2007).

Stability of suspended solid concentrations with increasing turbidity implies either a change in sediment characteristics (density, grain size) or in the water color. Turbidity increases during rainfall events, so water color is also affected by dilution with event flow. It is not expected to interfere much with turbidity readings. Therefore, higher turbidity values more probably correlate with higher contents of fine particles (Tananaev and Debolskiy, 2014).

In addition, the lake type and position of a sampling site within a lake, in addition to the seasonal pattern of organic matter sedimentation might not only reflect its respective plankton succession (Bunn and Boon, 1993; Matthews and Mazumder, 2005; Taipale et al., 2007). It also might be more or less modified by loading of riverine organic matter. Consequently, a more or less pronounced spatial variation of organic matter sedimentation can be expected in addition to the well-known seasonal variation.

Lake sediments are generally rich in organic matter consisting of labile and refractory compounds, of which the relative importance changes as a function of a complex array of processes such as degradation, heterotrophic utilization, transformation, accumulation, and export (Zhao and Cheng, 2011). Sediment oxygen demand during the degradation of organic matter can induce hypoxia or anoxia in bottom waters. Oxygen demand and the quantities of regenerated nutrients are not a

simple function of the quantity of organic matter but also its quality (i.e. carbon and nitrogen ratio), which is affected by numerous biological and physical factors (Fiordelmondo and Pusceddu, 2004). POC/PN ratios were 6–10 at Lake Shiwa, Korea (Piirsoo et al., 2012), which indicated the contribution of phytoplankton-derived organic matter (Brzezinski, 1985; Montagnes et al., 1994), but higher values (>12) were of terrestrial origin (Faganeli et al., 1988; Thornton and McManus, 1994). Furthermore, algal carbon isotopic composition in freshwater shows depleted values compared with marine phytoplankton (Marty and Planas, 2008). These lower values might affect the depleted carbon isotope ratios of particulate matter in rural areas.

The study of lake sediments has been used as re-constructing depositional history, climatic changes, and elemental pollution attributable to natural and anthropogenic sources with time. Sedimentation in a lake is affected more strongly by regional geographic and climatic processes. In recent years, the role of sediments in the lake system dynamics is realized. Recycling of mineralized organic matter, especially the nutrients, in sediments by organic decay and pore fluid transfer processes are now recognized as fundamentally important components of models are designed to describe the nutrient dynamics of lake and reservoir systems (Lerman and Brunskill, 1971). Investigations of the mineralogical and chemical characteristics of sediment particles supplied to the lake by streams, shore erosion, atmospheric fall-out, and cultural sources can reveal important information about the bedrock and surficial geology of the drainage basin, weathering, the relative importance of various inputs, and quantitative estimates of cultural loading on the lake systems. Sediment contamination by heavy metals and other micro-pollutants might cause potential adverse effects on ecosystems

and also pose health risks to humans (e.g. Verweij et al., 2004; Wang et al., 2004). The main environmental risk is remobilization of the contaminants and their return to the hydrosphere either by sediment re-suspension or by infiltration into the groundwater (Eggleton and Thomas, 2004; Wildi et al., 2004). In addition, the influence of the external source of organic matter by bacterial activity is important, with internal organic matter supplies related to the lake's eutrophication (Thevenon et al., 2011). They reported that wastewater treatment plants affect lake trophic states and the time distribution of organic matter, bacterial abundance, and activity in freshwater lake sediments in Lake Geneva. Sediments near the wastewater treatment plant outlet exhibited extremely high organic matter concentrations after the sewage treatment plant installation in 1964 because of the local release of abundant organic products (Thevenon et al., 2011).

To identify the original source of OM in a lake environment, a common method is based on components of dissolved or particulate fractions. For a particulate fraction, C/N ratios are applicable to distinguish different origins of organic matter between terrestrial (soils, vascular plant debris) and aqueous (phytoplankton) sources in geochemical mixtures (Meyers, 1997). Typical C/N values for pure soil organic matter are greater than 10. Particularly, vascular plant debris that is greater than 20 can be regarded as systematically higher than those for freshwater phytoplankton, which are 4–9.

Stable carbon isotope analysis is a powerful tool to identify the origin of organic matter in aquatic ecosystems (e.g. Kendall et al., 2001; Lehmann et al., 2004a,b). The various ranges of stable isotopes are expected to reveal the origins of aquatic organic

components, which can be autochthonous sources such as algae/phytoplankton or allochthonous materials such as terrestrial sources from soil and leaf debris. Many studies have demonstrated that phytoplankton has response to change of inorganic carbon concentration such as increasing HCO_3^- concentrations and dissolved CO_2 limitation (Fogel et al., 1992; Popp et al., 1998; Matsuda et al., 2001; Rau et al., 2001; Raven, 2003). Eutrophic lakes generally have great potential to exhibit large spatial and temporal variations in $\delta^{13}C$ of phytoplankton because of differences in isotopic fractionation of ^{12}C and ^{13}C during uptake CO_2 into phytoplankton (Takahashi et al. 1990; Gu and Schelske, 2004; Xu et al., 2005a; Gu et al., 2006).

Water temperature (WT) is an important environmental factor affecting the variations of $\delta^{13}C$ value. According to one earlier report (Andreev and Klimanov, 2000), a temperature drop of 4°C might engender lower carbon isotope ratios. This temperature effect might have increased the CO_2 solubility in the water field and consequently caused an increased DIC pool and decreased ratios of $\delta^{13}C_{POC}$ and $\delta^{13}C_{TOC}$. Additionally, lower $\delta^{15}N_{TN}$ ratios are also caused by a decrease in water temperature.

Stable carbon isotopic compositions have fluctuated according to different organisms living in different environments. For instance, C3 plants such as *Leymus chinensis* (Trin.) Tzvel. and *Stipa grandis* P. Smirn. are the dominant species in Hulun Buir Steppe (Kiyokazu et al., 2008), which has average pasture $\delta^{13}C$ values of −26.0‰. Therefore, the $\delta^{13}C$ variations indicate different sources of organic components. For instance, the stable carbon isotopic compositions were from − 25.7‰ to − 25.5‰ (POM fraction) and from −25.6‰ to −25.4‰ (DOM fraction) in Lake Hulun, China, which suggests that it derived predominantly from terrigenous vegetation (Chen et al., 2012).

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In mid-summer, the $\delta^{13}C$ value of organic matter in lake water decreased rapidly, presumably because the oxic decomposition of organic compounds, mainly oxidation of CH_4, releases isotopically light DIC into the lake water, consuming O_2 and lowering the pH of pore and bottom waters (Liu et al., 1996; Leng and Marshall, 2004). In Lake Sarbsko, low ratios of C/N values (5.67–9.99) and $\delta^{13}C_{TOC}$ (−29.3‰ to −27.4‰) (Woszczyk et al., 2011) show a predominance of well-preserved autochthonous organic matter, with only a minor contribution of terrestrial organic compounds (Meyers, 1994).

1.2. Chemical oxygen demand (COD) and its relation with organic matter in lake environments

Chemical oxygen demand (COD) is a simple parameter denoting the amount of organic matter in a water environment. This method has been used widely in water research based on the determination on the amount of oxygen necessary to oxidize organic pollution in a water sample of given volume (Pisarevsky et al., 2005). The adequacy of decisions based on COD values is reliant upon the quality of the measurements. Organic matter in lake environments is often elucidated by the quantity of total carbon (TC) or total organic carbon (TOC), but TC and TOC values do not express the oxidized fraction of the organic matter responsible for eutrophication of the receptor medium. A COD determination method is most often estimated from their oxide-ability by potassium dichromate or potassium permanganate in specified concentrations, with particular catalytic, acidic and temperature conditions.

The COD concentration is characterized by temporal and spatial variations

throughout the year attributable to fluctuations of organic matter levels in lake water. For example, Lake Chaohu in China was found to have higher values of COD concentrations in summer than in other seasons, with no significant difference in spatial variation. Significantly higher COD concentrations in this lake are controlled by high phytoplankton biomass density (Jiang et al., 2014). The same circumstances were recorded at a polluted lake, Lake Tabacarie in Romania, with high COD concentration in July and lowest in November (Zagan and Enache, 2009). At Lake Taihu, the COD values were shifted from high COD concentration in the water river input to the lake (Wang et al., 2006, 2007a). However, variations of COD concentrations in Lake Taihu were generated mainly by autochthonous products: phytoplankton (Wang et al., 2007b). According to Lei et al. (2006) and Hu et al. (2010), the COD concentration decreased during macrophyte growth because they are able to uptake nutrients from the water in summer. However, during winter, the stems and leaves of these macrophytes wither and fall. Then they decompose. Zhou and Wang (2010) reported that controlled experiments assessing *Oenanthe javanica* growth and decay showed that the COD concentration declined in the purification phase, but then it increased markedly in the decay phase, leading to water quality deterioration. The concentration of COD in Lake Mogan, Turkey increased during winter because of increased household wastewater and abattoir waste discharge (Karakoç et al., 2003). COD was readily linked with the humic-like components in lake catchments (Zhang et al., 2011a).

Spring and summer produce the highest temperatures during any year, providing beneficial conditions for increasing autochthonous products because phytoplankton activity depends on air temperature. Phytoplankton species are also useful tools for

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elucidating water conditions because their biological functions (Abranthes et al., 2006; Bellinger et al., 2010) are affected by environmental factors. They have various cell organizations in water bodies such as lakes (Padisák et al., 2006). Algal photosynthetic capability increases concomitantly with increasing algal biomass, higher temperatures in summer, and improved summer photic conditions (Filstrup et al., 2009). Therefore, greater seasonal changes in temperature and the light regime exacerbate the seasonal isotopic variation in high-latitude eutrophic lakes dominated by phytoplankton. This variation contributes to increased organic matter concentrations.

POC is a dominant constituent of organic matter during phytoplankton blooms irrespective of the phytoplankton composition and size (Casareto et al., 2012). Kuimei et al. (2016) reported that in Poyang Lake, China high algal biomass growth in the water body occurred during late spring and summer at times of high water temperature, light conditions, and increased nutrients (concentrations of nitrogen and phosphorus). In the stage of phytoplankton bloom, the carbohydrate contents of both particulate and dissolved fractions were increased, accounting for 18–45% and 26–80% of TOC (Biddanda and Benner, 1997). Shifts in the phytoplankton composition affected not only the water quality variation, but also changes of physiochemical variables and biotic interactions (Jacoby et al., 2000). Krustok et al. (2015) demonstrated, from laboratory experiments conducted in a climate chamber, that pH declined in wastewater collected in December because the growth was particularly low, with low CO_2 assimilation, which suggests that pH increases during phytoplankton activity because of the rapid assimilation of CO_2.

1.3. Aim of this study

Lake Kiba, a small shallow eutrophic lake in central Komatsu city, Ishikawa Prefecture, Japan, has an area of 1.09 km^2 and a watershed area of 37.4 km^2. The land use of surrounding areas is 51% forest, 18% paddy field, and 21% urban. The highest and lowest water depths are, respectively, 3.5 m and 0.7 m. The water input is from the Hiyou River, with output to the Mae River. Lake Kiba has sustained organic pollution over two decades. The pollution has adversely affected resident activities around the lake. Concentrations of chemical oxygen demand and total nitrogen were twice as high as the national standard level of class A (COD<3 mg l^{-1}; TN<0.6 mg l^{-1}) in the last decade (Komatsu City Government, 2014). The suspended solid concentration was 12–21 mg l^{-1}. Total nitrogen was from 0.92 to 1.30 mg l^{-1}. The total phosphorous fluctuated within 0.066–0.11 mg l^{-1} during the surveyed period of 2000–2011 (Komatsu City Government, 2014). Other studies were conducted continually at Lake Kiba in 2013. Some studies of Lake Kiba have been reported, but information about behaviors as well as origins of organic pollution in the lake remains insufficient (Hasegawa et al., 2009; Komastu City Government, 2014). Consequently, this study was undertaken to elucidate factor-controlling variations of organic pollution in Lake Kiba. To achieve this objective, we (i) elucidated water quality based on variations of COD concentration, (ii) estimated seasonal and spatial variations of organic matter and its sources, and (iii) assessed organic matter sedimentation recorded in a sediment core.

Chapter 2.

COD variation in surface waters from a small, shallow and semi-closed lake, Lake Kiba during 2012-2016

2.1. Introduction

Chemical oxygen demand (COD) has been used as a simple indicator of pollution in lakes. In recent year, shallow lakes in China have been seriously polluted because of the rapid economic development and intensified human activities in watershed area (Yin et al., 2011, Jiang et al., 2014). Household and industry wastes discharged into lakes lead to severe organic contamination. Shallow lakes are also associated with a high growth rate of beneficial phytoplankton that is caused by sunlight transmission to the bottom and the continuous nutrient inflow. Therefore, much attention has been given to the eutrophication of the shallow lakes such as Lake Taihu and Lake Chaohu, which are key sources of drinking water (Yin et al., 2011; Jiang et al., 2014). Japanese shallow lakes such as Lake Inbanuma and Lake Teganuma are similar situation and one of worst lakes at last decade (Teganuma Aquatic Conservation Council, Inbanuma Aquatic Conservation Council). The lakes are shallow and completely reformed by the reclamation project for the flood control, rice field improvement and water resource development during 1963–1969 ((Teganuma Aquatic Conservation Council, Inbanuma Aquatic Conservation Council). Both lakes experienced and progressive eutrophication since 1970's when the population of human-being in the watershed increased rapidly (Teganuma Aquatic Conservation Council, Inbanuma Aquatic Conservation Council). In Japan, the results of water quality survey of lakes and reservoirs indicate that compliance rate of environmental quality standards for living environmental items is 55.5% for COD concentration in 2014 (Ministry of the Environment).

Lake Kiba (Kiba-gata), which is located at Komatsu city, Ishikawa Prefecture, Japan (Fig. 2-1), and has a mean water depth of 1.7 m, area of 1.14 km^2, and water volume of

1.7×10^4 m^3. The watershed area is 38 km^2. In 1932, the counter slice gate was constructed at the conjunction of the Kakehashi River to protect inflow of water from the river at flood events (Fig.2-1). Reclamation project, "Kaga three lagoons reclamation project" was planned to improve the lowland area drainage and to increase the productivity of surrounding farmland. The reclamation work was undertaken to open a new channel to divert floodwaters from the related basins into the sea and the reclamation of Lake Imae (Imae-gata) and 2/3 of Lake Shibayama (Shibayama-gata) during 1954–1969 (Hokuriku Regional Agricultural Administration Office, 1970). Lake Kiba was affected by changes in the drainage system and land consolidation around the lagoon. The Maekawa slice and drainage pump station was constructed at the Maekawa River to control water level of Lake Kiba. The organic matter flux recorded in the sediment core increased from 1.1 to 2.3 and from 3.9 to 7.5 mgC cm^{-2} y^{-1}, respectively, during 1903–1974 and 1989–2012, although it was similar with the flux recorded for 1974–1989 following reclamation (Nagao et al., 2016). The COD concentration was at a maximum, 11 mg l^{-1} in 1990, corresponding to the worst second in Japan and has remained about double the national standard of this lake class (3 mg l^{-1}) over the last decade (Komatsu City Government).

The objectives of this study are to explore the factors controlling COD concentration and its variation in Lake Kiba from monthly observation and relationship of water quality. We determined total COD concentration and existent forms of COD, dissolved and particulate COD, during the sampling period. The Lake Kiba is classified as lagoon, which is 146 lakes with higher lake area above 0.1 km^2 in Japan (Hayashi, 2015).

Therefore, the results of this study are basic and useful information of understanding organic pollution in shallow lakes and lagoon.

2.2. Materials and methods

Water sampling was carried out at a site of the central part of lake once in two-three months in May 2012–January 2013 and monthly during May 2013–March 2016. The surface water samples were collected using a bucket on the boat.

Water quality such as water temperature (WT), pH, chemical oxygen demand (COD), total nitrogen (T-N), and total phosphorous (T-P) in the surface water were determined by the procedures for Japan Industrial Standard (JIS) Method (JIS K 0102, 2010). The pH of lake water was determined by glass electrode method. COD (COD_{Mn}) concentration was measured by titration with acidic potassium permanganate before and after filtration with ADVANTEC GS-25 glass fiber filter. COD for the filtered sample is expressed as D-COD. Particulate COD (P-COD) was obtained as the difference between total COD (T-COD) and D-COD concentration. T-N and T-P concentrations were determined by ultraviolet absorption method and colorimetry, respectively, after heating with potassium peroxodisulfate. Suspended solids (SS) concentration was measured by filtration on a ADVANTEC GS-25 glass fiber filter (Ministry of the Environment). Chlorophyll-a concentration was photometry quantified by the trichromatic absorption method after the extraction of particles on a ADVANTEC 0.45μm membrane filter with 90% acetone (Ministry of Land, Infrastructure, Transport and Tourism)
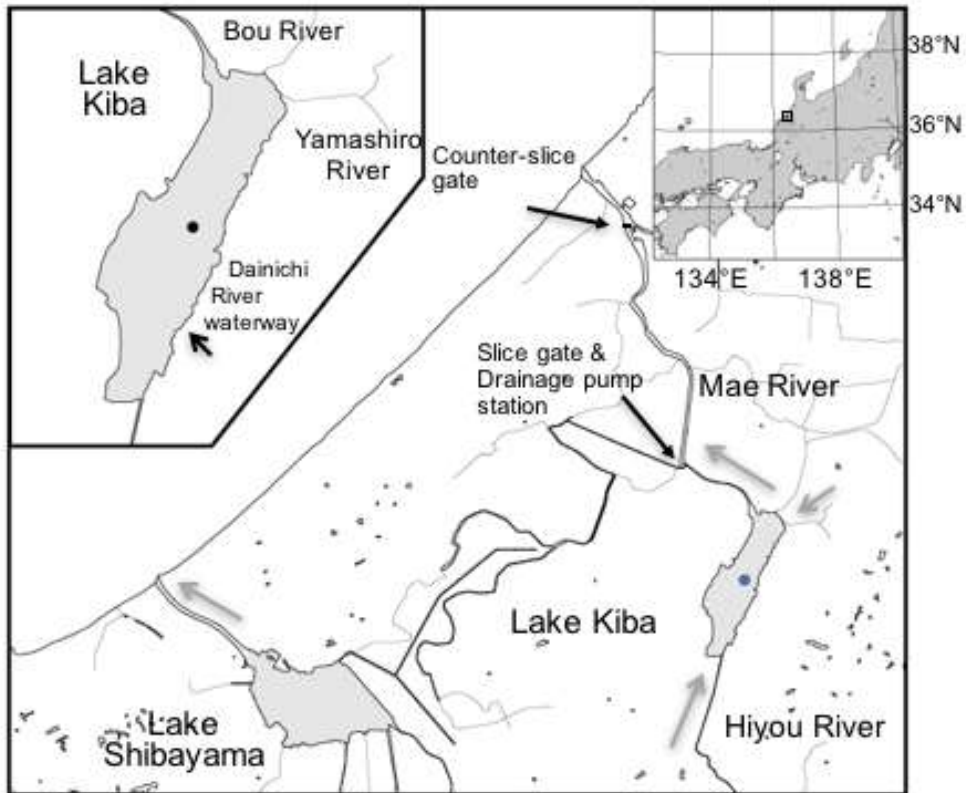
Figure 2-1. Sampling location. The closed circle indicates sampling site in Lake Kiba. Numerical map data are based on Fundamental Geospatial Data provided by the Geospatial Information Authority of Japan, and National Land Numerical Information provided by the Ministry of Land, Infrastructure, Transport and Tourism, Japan.

2.3. Results and discussion

2.3.1 Water quality

Water temperature and pH show seasonal variation with higher in summer. The pH on 31 July 2013 and 19 August 2014 is lower value before and after the month due to heavy rain events with precipitation of 199.5 mm (maximum 46.5 mm h^{-1}) on 29 July 2013 and 189.9 mm on 15–18 August 2014 at the observation site in Komatsu (Japan Meteorological Agency, Past weather data, Komatsu observatory data). Suspended solid (SS) concentration shows seasonal variation and varies with each year. T-N concentration was higher in summer (July–August) and winter season (October– November). T-P concentration ranged from 0.02 to 0.26 mg l^{-1}. The chlorophyll-a concentration has two peaks in April and August 2015.

2.3.2 COD concentration

T-COD and D-COD concentrations show seasonal variation with higher in summer season (Fig. 2-3). T-COD concentration ranged from 2.3 to 10.0 mg l^{-1} and maximum value is in the order of 2012 = 2013 < 2014 = 2015. T-COD concentration decreased significantly after the rain events on 29 July 2013 and 19 August 2014. The water sample collected on 15 September 2015 exhibited lower T-COD value with lower SS, total nitrogen and phosphorous concentration without any rain event. As shown in Fig. 2-2, pH of the lake water showed small variation. This result indicates that the inflow of Dainichi River via the Kaga three lagoons waterway, as shown in Fig. 2-1, may be reflected to lower values by the dilution of lake water.

The D-COD and P-COD concentrations are 1.8–6.5 mg l^{-1} and 0.2–5.3 mg l^{-1}, respectively. The percentage of P-COD to total COD is ranged from 8 to 57%. The

averaged percentage of P-COD is $34 \pm 11\%$ and lower than that of Lake Inbanuma and Lake Teganuma with higher T-COD concentration and SS concentration (Teganuma Aquatic Conservation Council, Inbanuma Aquatic Conservation Council). On the other hand, P-COD in the lakes with lower SS concentration are 20–30% for the Fuji five lakes (Yoshizawa, 2009), and 10% for the Akagi-Ohnuma and Lake Haruna (Ohtani , 2006). The lower percentage was observed in winter season in Lake Kiba, when the SS concentration decreased.

2.3.3 Relationship between COD and water quality

Figure 2-4 shows total COD concentration as a function of physicochemical parameters such as water temperature (WT), pH, suspended solids (SS) and chlorophyll-a concentration. There are good positive correlations (correlation factors of 0.72–0.83, $p<0.0001$) for water temperature, pH and chlorophyll-a concentration. Increase in pH is caused by utilization of CO_2 for phytoplankton activity. On the other hand, SS concentration has lower correlation factor of 0.47 ($p<0.01$) with COD concentration because of a mixture of freshly produced phytoplankton, re-suspension of surface bottom sediment and input of suspended solids from watershed.

To compare other lakes with higher COD concentration, we selected the lakes under the low concerning special measures for conservation of lake water quality by Ministry of Environment in Japan (e.g. Environmental Cooperation Office, Global Environmental Bureau, 2010). T-COD concentration in Lake Kojima, which is input of agricultural and drainage from watershed, ranged from 6 to 9 mg l^{-1} and showed higher
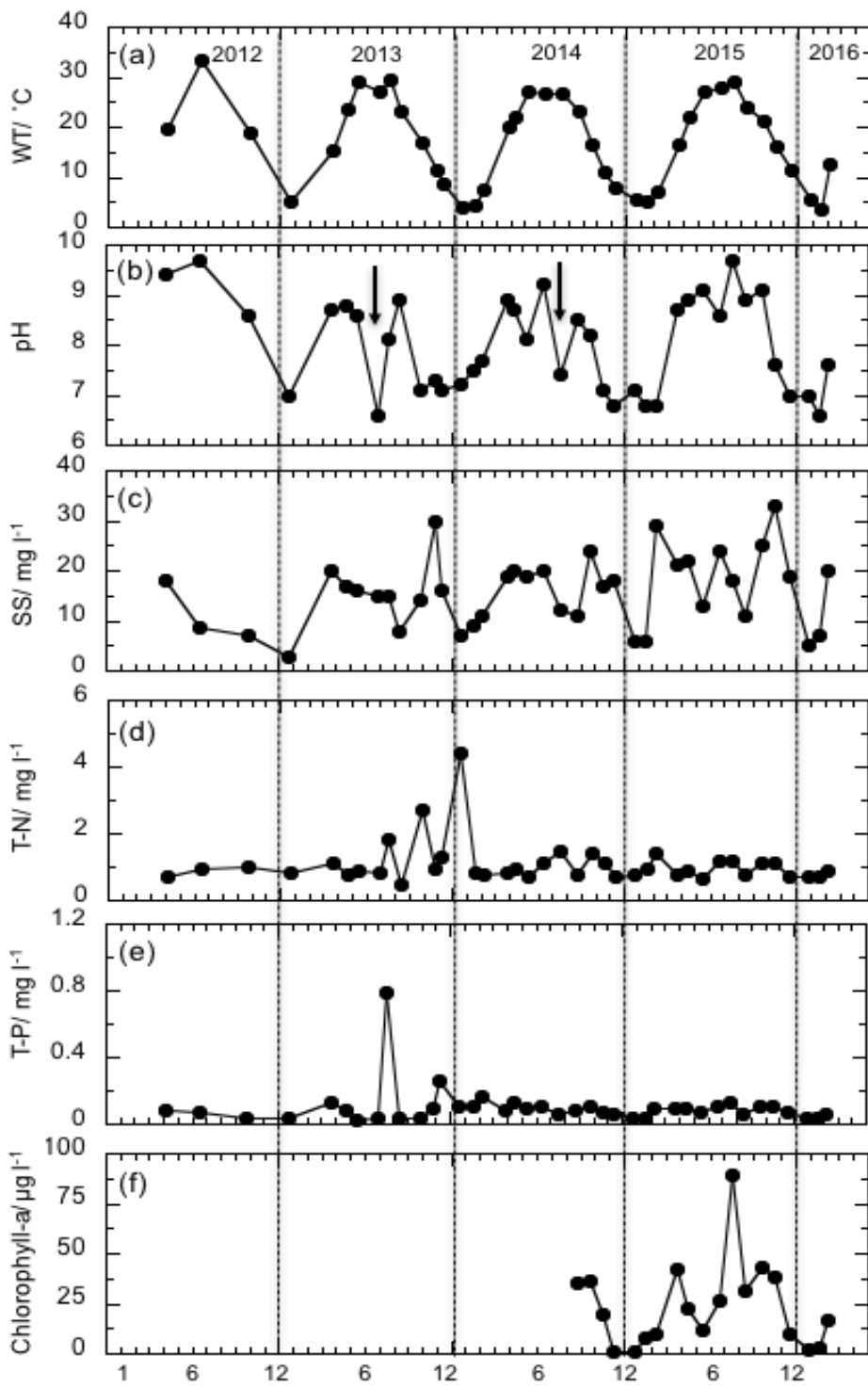
Figure 2-2. Variation of water temperature (WT), pH, suspended solids (SS), total nitrogen (T-N), total phosphorous (T-P) and chlorophyll-a concentration in surface water from Lake Kiba. The arrows indicate the samples affected by rain events

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in spring season (Takano, 2007). The T-COD value shows high correlation (r = 0.69) with chlorophyll-a concentration, but weak correlation with water temperature (r = 0.03) and pH (r = 0.38) (Takano, 2007). Lake Inbanuma and Lake Teganuma have clearly COD peaks in May and August in the observation of 2014 (Chiba Prefectural Government, List of public water quality, results of water quality). On the other hand, Lake Suwa indicates maximum of COD in September with higher percentage of P-COD (Nagano Prefectural Government, Water quality results, lakes). T-COD has a positive correlation with chlorophyll-a concentration for Lake Teganuma and Inbanuma (r = 0.63–0.73, p<0.0001) and Lake Suwa (r = 0.67, p<0.001) for monitoring data in April to March 2016 (Chiba Prefectural Government, List of public water quality, results of water quality, Nagano Prefectural Government, Water quality results, lakes). The water pH has correlation factor of 0.35 for Lake Inbanuma, 0.48 for Lake Suwa and 0.62 for the Teganuma (all data p<0.001) with T-COD concentration. Lake Kiba shows higher correlation factors, 0.72–0.83, as shown in Fig. 2-4. The variation was observed for each lake with the different in primary production, residence time of water mass, inflow from watershed and its social situation.
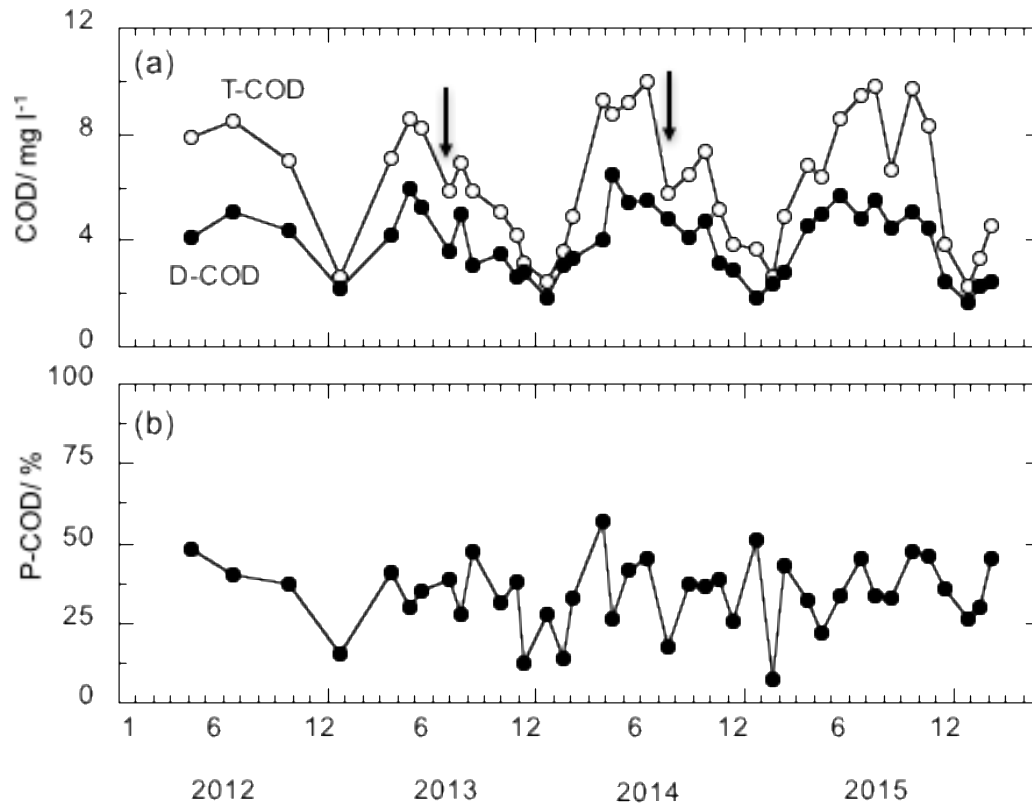
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Figure 2-3. Variation of total COD (T-COD: ○) and dissolved COD (D-COD: ●) concentration (a) and percentage of particulate COD (P-COD) in surface water from Lake Kiba (b) during May 2012–March 2016. The arrows indicate the samples affected by rain events.

2.3.4 Dissolved COD and Particulate COD concentration and their implication

Figure 2-5 shows the D-COD and P-COD concentrations versus water temperature, pH and chlorophyll-a concentration. Two phases of COD concentration are positive correlations for water temperature (correlation factors of 0.65–0.84, $p<0.0001$), pH (0.71–0.76, $p<0.0001$) and chlorophyll-a concentration (0.63–0.72, $p<0.0001$). The results indicate that both phases are related with phytoplankton activity during spring–summer season.

Figure 2-6 shows variation of D-COD and P-COD concentration in the five lakes with higher COD concentration ranging from 2.3 to 20 mg l^{-1}. Averaged percentage of P-COD to T-COD is 27 ± 8% for the Kasumigaura (e.g. Kasumigaura River Office) 34 ± 11% for the Kiba, 43 ± 11% for the Suwa (Nagano Prefectural Government) 52 ± 11% for the Teganuma (Chiba Prefectural Government), and 58 ± 9% for the Inbanuma Chiba Prefectural Government, List of public water quality, results of water quality). There is a positive correlation (r = 0.62–0.72, $p<0.0001$) with D-COD and P-COD concentration for Lake Kiba and Lake Suwa. Both lakes have semi-closed feature because of presence of the slice-gate and/or one outflow river (e.g. Environmental Cooperation Office, Global Environmental Bureau, 2010; Komatsu City Government). In these lakes, phytoplankton activity significantly reflects the abundance ratio of D-COD to P-COD. The input of COD from watershed and bottom sediment appears to affect variation in the abundance ratio. On the other hand, Lake Inbanuma, Teganuma and Kasumigaura indicate no correlation between D-COD and P-COD concentration. The lakes are classified into shallow lakes with average water depth of 0.86–4 m and have inflow from watershed via the rivers (Teganuma Aquatic Conservation Council,

Inbanuma Aquatic Conservation Council, Nagano Prefectural Government). The suspended solid concentration shows almost correlation with chlorophyll-a concentration for the Kasumigaura, Teganuma and Inbanuma in 2014–2016 ($r = 0.41$– 0.70, $p<0.01$) (Teganuma Aquatic Conservation Council, Inbanuma Aquatic Conservation Council, Nagano Prefectural Government), not shown in figure. This result indicates higher contribution of phytoplankton production in the lake. One possibility of the lower correlation between D-COD and P-COD is considered that the input ratio of D-COD to P-COD was variable through one year in comparison with that of Lake Kiba and Lake Suwa because of variation of input and output of D-COD and P-COD for the lake bottom sediment and watershed. For better understanding the phenomena, it is needed for the additional studies with relationship between COD value and organic matter concentration and its quality parameters such as carbon and nitrogen isotopes, biomarkers, fluorescence properties in the view point of their origin.
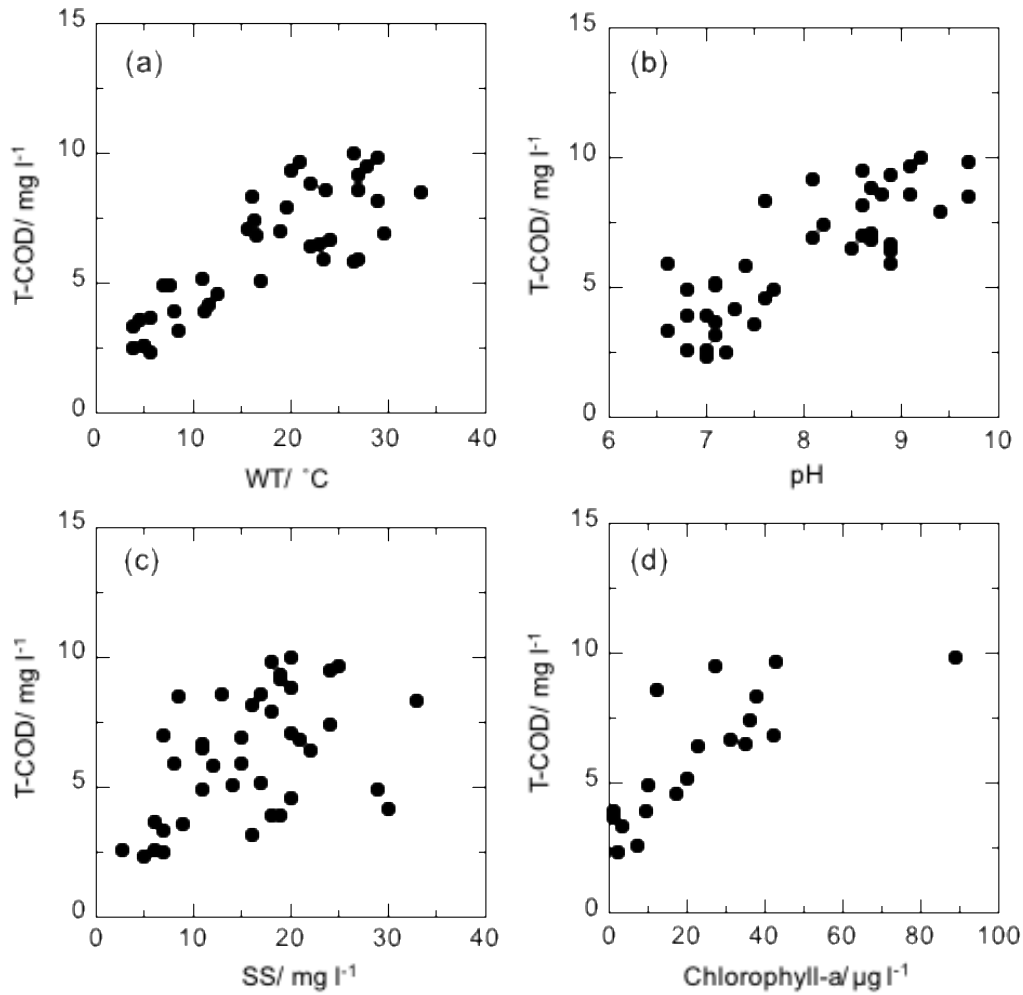
Figure 2-4. T-COD as a function of water temperature (a), pH (b) and chlorophyll-a concentration (c) in the Lake Kiba surface water. WT indicates water temperature.
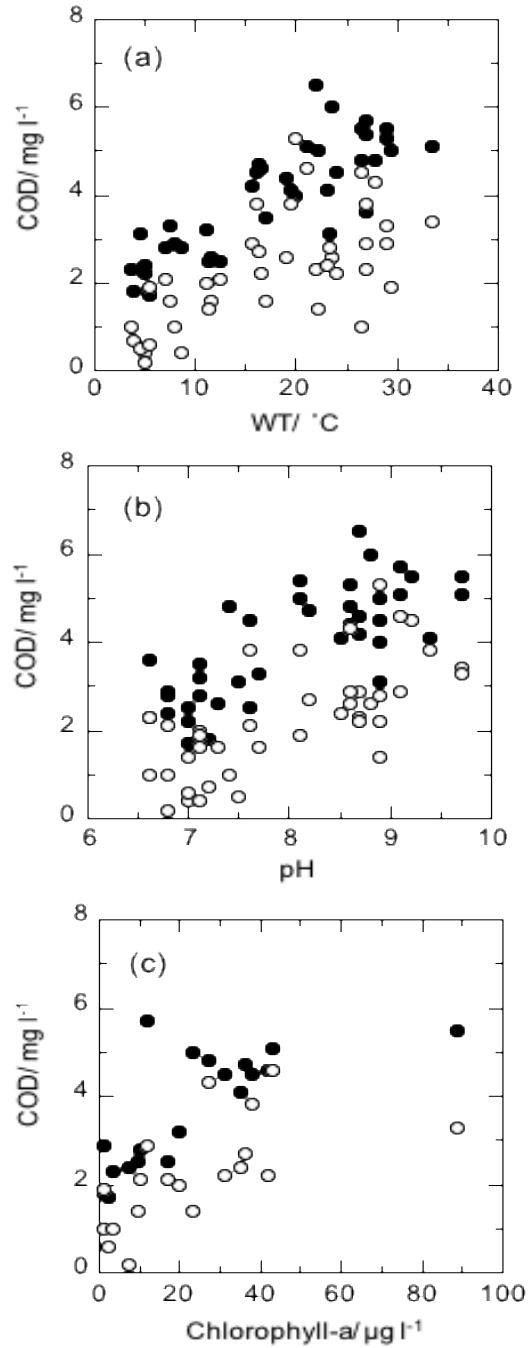
Figure 2-5. D-COD (●) and P-COD concentrations (○) as a function of water temperature (a), pH (b) and chlorophyll-a concentration (c) in the Lake Kiba surface water.
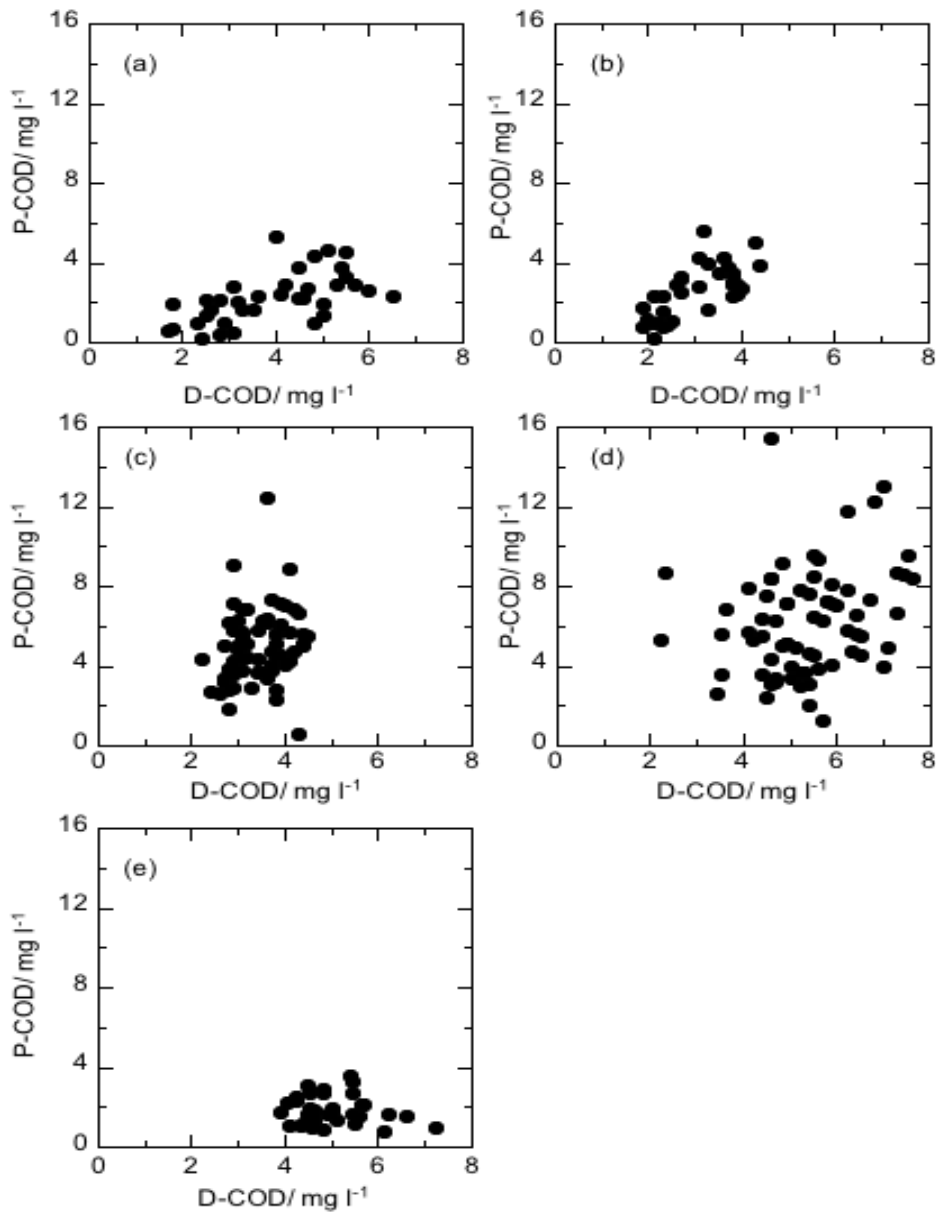
Figure 2-6. Relationship between D-COD and P-COD concentrations in surface water from Lake Kiba (a), Lake Suwa (b), Lake Teganuma (c), L. Inbanuma (d) and Lake Kasumigaura (e). Data was referenced from Nagano Prefectural Government (Lake Suwa) (Nagano Prefectural Government)and Chiba Prefectural Government (Lake Inbanuma and Lake Teganuma) (Chiba Prefectural Government), in April 2012–March 2016. Lake Kasumigaura was used from monitoring results during January 2012– December 2015 by the Kasumigaura River Office (e.g. Kasumigaura River Office, Kanto Regional Development Bureau). Lake Kiba is used for data as shown in Fig. 2-3.

2.4 Conclusions

Lake Kiba is a small, shallow and semi-closed lagoon and is facing to organic pollution. Averaged annual COD concentration is about two times higher than that of national regulation at least 30 years. This study focuses on identifying factors controlling COD concentration through one year. The field expedition was carried out at a site of central part of the lake once in two-three months in May 2012–January 2013 and monthly during May 2013–March 2016. The T-COD concentration ranged from 2.3 to 10.0 mg l^{-1} and showed seasonal variation with higher COD in summer. T-COD value was positively correlated with water temperature, pH and chlorophyll-a concentration. These results indicate that the increase in the COD concentration during spring–summer is caused by phytoplankton activity, though decrease in the COD concentration during autumn season is controlled by the dilution of water mass from the watershed. Lake Kiba exhibits a positive correlation between dissolved COD (D-COD) and particulate COD (P-COD) similar with Lake Suwa having shallow and semi-closed condition. The results suggest that the COD variation is controlled by the input and output of D-COD and P-COD in the water column in Lake Kiba and its ratio is almost constant through one year.

Chapter 3.

Temporal and spatial variations of organic pollution in Lake Kiba, Japan during 2014–2016

3.1 Particulate organic carbon

3.1.1 Introduction

Particulate organic carbon (POC) plays an important role in the global carbon cycle, functioning as a food source for heterotrophic organisms (Li and Minor, 2015), supporting transportation of organic matter produced in the eutrophic zone to the sediment (Wakeham et al., 1997; Hedges et al., 2000; Burdige, 2007), and ensuring turnover of organic metabolites (Llewellyn et al., 2015). In lake ecosystems, POC derives from two main natural sources: autochthonous production and allochthonous input. Autochthonous POC is originally produced within the lake by organisms such as aquatic plants, phytoplankton, algal, animal, and bacteria. The POC is an important source in terms of contributing to lake sediments, especially ponds with long resident time (Caraco and Cole, 2004; Moschen et al., 2009; Kumar et al., 2011). In contrast, allochthonous POC is transported from the catchment area, occurring as plant debris, leaves, grass, and humic substances (Aitkenhead and McDowell, 2000; Lozovik et al., 2007) or as the input of terrigenous materials from atmospheric deposition (Oseguera et al., 2011). The study of POC behavior in the lakes provides useful information to elucidate water properties.

In the last few decades, POC characteristics have become a matter of concern; almost all reports of the relevant literature describe studies of the many aspects of POC in oceans, river and lake sediments, and rivers. Dynamics of POC depend strongly on geochemical and environmental conditions such as lake shape, watershed condition, water pH, precipitation, and water temperature. The POC concentration is equal to or even greater than the dissolved organic carbon (DOC) value during intensive algae and

bacterial growth; it is quite lower in autumn (Wetzel, 2001a). The same pattern is observed in eutrophic Lake Taihu, China. The highest POC concentration was observed in summer, showing strong positive correlation with phytoplankton activity (Guangjia et al., 2015).

Knowledge of POC dynamics is a useful tool for elucidating organic pollution in lake environments and for elucidating POC characteristics under changes of environmental factors during the year. Stable isotopic components and the elemental ratio of C/N have been widely used to discuss organic matter sources (Andrews et al., 1998; Maksymowska et al., 2000; Gao et al., 2012). In fact, $\delta^{13}C$ and $\delta^{15}N$ are known as proxies for the isotopic component of POC sources in aquatic environments (Grey et al., 2001; Cloern et al., 2002). Consequently, these parameters were used for this study to identify the original contributors to organic pollution in Lake Kiba based on monthly observations.

Lake Kiba, located in the central Komatsu City, Ishikawa Prefecture, Japan, has sustained organic pollution for over 20 years, adversely affecting activities of residents around the lake. Some studies conducted at Lake Kiba have yielded only insufficient information about the dynamics of POC (Hasegawa et al., 2009; Komatsu City Government, 2014; Nagao et al., 2016). Consequently, this study was undertaken to find trends of variation in POC concentration and other characteristics of Lake Kiba throughout the year. Results from this study are expected to provide better understanding behaviors of POC in surface waters of the lake environment and to contribute to improvement of planning in support of better lake water quality.

3.1.2 *Materials and methods*

3.1.2.1. Sampling location

Lake Kiba is a small shallow eutrophic lake with area of 1.09 km^2 and 37.4 km^2 of watershed area. The surrounding land use is 51% forest, 18% paddy field, and 21% urban area. The highest and lowest water depths are, respectively, 3.5 m and 0.7 m. The water input is from the Hiyou River, with output to the Mae River (Fig. 1). Concentrations of chemical oxygen demand and total nitrogen were twice as high as the national standard level of class A (COD <3 mg l^{-1}, T-N: 0.6 mg l^{-1}) in the last decade (Komatsu City Government, 2014). The suspended solid concentration was 12–21 mg l^{-1}; total nitrogen was 0.92–1.3 mg l^{-1}. The total phosphorous shifted within 0.066–0.11 mg l^{-1} in the surveyed period of 2000–2011 (Komatsu City Government, 2014).
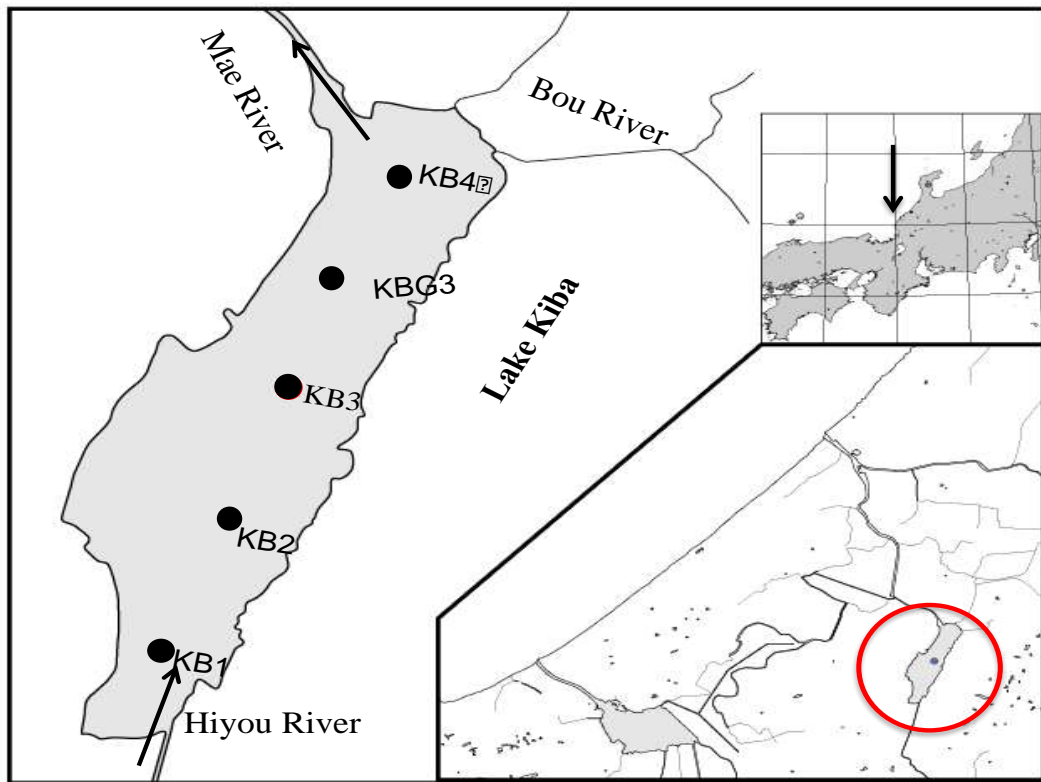
Figure 3.1-1. Sampling station (•) in Lake Kiba. Closed circles represent lake water sampling points.

3.1.2.2. Sampling and pretreatment

Water sampling was conducted monthly at a central site KB3 of the lake from February 2015 through March 2016. This report describes studies assessing winter (January–March), spring (April–June), summer (July–September), and autumn (October–December). In all, 60 liters of water samples were taken to assess suspended particles. After the samples were taken in collapsible water carriers, they were transported to the laboratory and were stored in a refrigerator. The suspended solids were collected by continuous flow centrifugation and were freeze-dried. Physicochemical parameters including water pH, water temperature (WT), dissolved oxygen (DO), conductivity, turbidity were measured directly in the field using a multi-parameter water quality meters WQC-24 (DKK- TOA corp.).

3.1.2.3. Analytical methods

A suspended solid sample was ground in an agate mortar. Then inorganic carbonates were removed with 1M HCl, rinsing with Milli-Q water, and drying again to analyze particulate organic carbon (POC), nitrogen (PN), and stable isotopic components (δ^{13}C and δ^{15}N). The POC and PN concentrations from suspended solids were found using an elemental analyzer (NA 2500; Thermo Fisher Scientific Inc., USA). Carbon and nitrogen stable isotopes were measured using a mass spectrometer (DELTA V Advantage; Thermo Scientific). The δ^{13}C and δ^{15}N values were expressed, respectively, in per mil units relative to Vienna PeeDee Belemnite (VPDB) and atmospheric N_2. The stable isotope compositions were the following.

$\delta X (‰) = (R_{sample}/ R_{standard} -1) \times 1000$

Therein, X = C (carbon) or N (nitrogen); $R_{sample}/ R_{standard}$ is the ratio of $^{13}C / ^{12}C$ or $^{15}N/$ ^{14}N. Standard materials were $\delta^{13}C_{VPDB}$= -26.39 ‰, $\delta^{15}N_{air}$= -4.52 ‰, L-Alanine ($\delta^{13}C_{VPDB}$= 19.6‰, $\delta^{15}N_{air}$= 1.6‰), ANU-sucrose ($\delta^{13}C_{VPDB}$= -10.80 ‰), IAEA-N1 ($\delta^{15}N_{air}$= 0.4 ‰), and IAEA-N2 ($\delta^{15}N_{air}$= 20.3 ‰).

3.1.3 Results

3.1.3.1 Seasonal variations in physicochemical parameters

Information related to the dynamics of environmental factors in surface water is important for greater understanding of POC behaviors. Figure 3.1-2 shows monitoring results for different physicochemical parameters such as WT, pH, suspended solids (SS), conductivity, and turbidity from February 2015 through March 2016. The figure shows that WT was high in spring (14.8–22.1°C) and summer (27.3–30.1°C), but lower and lower in autumn (7.8–17.0°C) and winter (4.6–11.1°C) (Table 3.1-1). Water pH extended within the weak alkaline region of 6.8–9.32 and showed similar variation to that of WT. The pH-value increased from 7.64 in April to 9.32 in September, corresponding to an increase in phytoplankton activity during phytoplankton season (April–September). The SS concentration was 5.0–30 mg l^{-1}, conductivity was 7.6– 12.25 mS m^{-1}, and turbidity was 7.5–30.2 NTU. Estimation of SS, conductivity, and turbidity concentrations can be done only to a slight degree because the data fluctuated greatly upward and downward throughout the year (Table 3.1- 1). However, both SS and turbidity concentrations were low in winter, showing improved values in spring and early autumn. Other physicochemical parameters were the following: SS concentration of 5.0–30.0 mg l^{-1}, conductivity of 7.6–12.3 mS m^{-1}, and turbidity of 7.5–30.2 NTU.
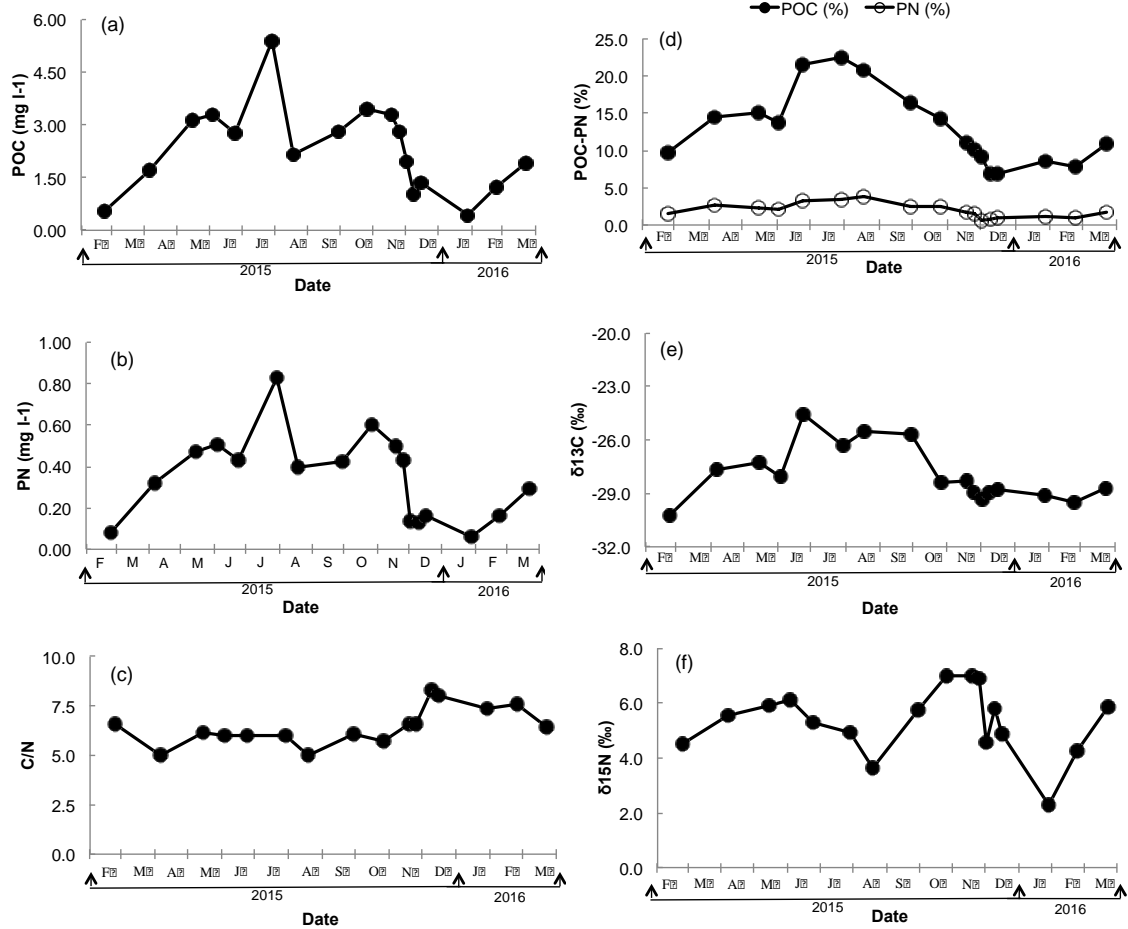
Figure 3.1-2 Concentrations of particulate organic carbon (a), and particulate nitrogen (b), C/N ratios (c), POC and PN content (d), $\delta^{13}C$ of POC (e), and $\delta^{15}N$ of T-N (f) from suspended solids in surface waters at the center of Lake Kiba (KB3) from February 2015 through March 2016.

3.1.3.2 Temporal variations of particulate organic carbon and other parameters

Organic carbon concentrations from suspended particulates fluctuated from 0.53 mg l^{-1} to 5.39 mg l^{-1} (Fig. 3.1-2a). The highest value was recorded in summer (July 2015). The POC concentration was lowest in winter (0.53 mg l^{-1} in February 2015), gradually increasing in April and May, and reaching the highest degree of concentration in July. The concentration increased again in September and October. November 2015 was about 0.28 times the value in December 2015. An increased trend was observed during February and March 2016. Variation of the particulate nitrogen (PN) concentration was similar to that of the POC concentration trend (Fig. 3.1-2b). The values were 0.47 mg l^{-1} to 0.83 mg l^{-1}. The PN concentration increased during spring and summer, with the highest value observed in July, and the lowest observed in January. The data increased gradually from winter to spring, and decreased late autumn.

Figure 3.1-2c shows the C/N ratio as 5.0–8.3. The ratio was almost constant around 6.0 from late spring to early summer. It fluctuated slightly from summer through autumn (August–December), reaching its highest level in December 2015.

Higher percentages of POC and PN were observed in summer 2015, with 13.7–22.6% for variation of POC and 2.1–3.9% of PN. The $\delta^{13}C$ of POC increased during summer and decreased during autumn–winter.

Regarding variation of the stable isotopic component, carbon isotopes rose in summer (February–September, 2015), and declined during autumn–winter. The values were -29.4‰ to -24.6‰, with higher values observed during June and September (around -25.5‰). The values decreased slightly from October 2015 through March

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2016 (Fig. 3.1-2e). The $\delta^{15}N$ values fluctuated between 4.0‰ and 7.0‰, except in August 2015 and January 2016 (Fig. 3.1-2f).

Table 3.1-1: Physicochemical parameters of Lake Kiba surface waters during February 2015 through March 2016

Parameters	pH	DO (mg/L)	Cond (mS/s)	Turb (NTU)	SS (mg/L)	WT (°C)
23. Feb.2015	6.87	ND	10.30	9.15	5.44	9.5
06. Apr. 2015	7.64	ND	11.45	13.30	11.84	14.8
15. May. 2015	8.50	ND	ND	ND	20.83	22.1
24. Jun. 2015	9.32	ND	10.30	10.70	12.89	27.3
29. Jul. 2015	9.18	ND	9.10	17.10	23.88	30.1
18. Aug. 2015	8.92	ND	10.10	18.20	10.39	28.5
29. Sep. 2015	8.93	ND	7.90	14.20	16.95	23.1
26. Oct. 2015	7.33	5.42	12.25	23.85	24.25	17.0
18. Nov. 2015	7.25	6.00	10.95	27.20	29.68	15.6
25. Nov. 2015	7.40	6.59	9.00	30.20	27.96	7.8
02. Dec. 2015	7.02	6.30	8.40	20.60	21.32	10.0
09. Dec. 2015	7.03	6.35	9.60	22.10	15.37	8.2
16. Dec. 2015	7.01	6.30	7.70	26.00	19.14	10.8
28. Jan. 2016	7.01	7.92	11.10	7.50	5.06	4.6
24. Feb. 2016	7.11	7.62	7.60	19.00	15.91	6.2
23. Mar. 2016	7.33	6.96	8.90	16.60	17.36	11.1

ND, not determined

3.1.3.3 Relations between POC and physicochemical parameters

To understand variations in POC concentration, we examined physicochemical parameters of the water in Lake Kiba. The POC concentration was found to be positively correlated with water pH: $r = 0.64$ (Fig. 3.1-3a). Seasonal variations of WT and pH were similar during the survey (Fig. 3.1-3a, b). A close relation between POC and WT (°C) was also found: $r = 0.72$. The correlation coefficient was 0.71 of POC and SS (Fig. 3.1-3c). Weak correlation to POC concentration was found for C/N ratios and isotope components: $r = 0.5$ (Fig. 3.1-3d, e and f).
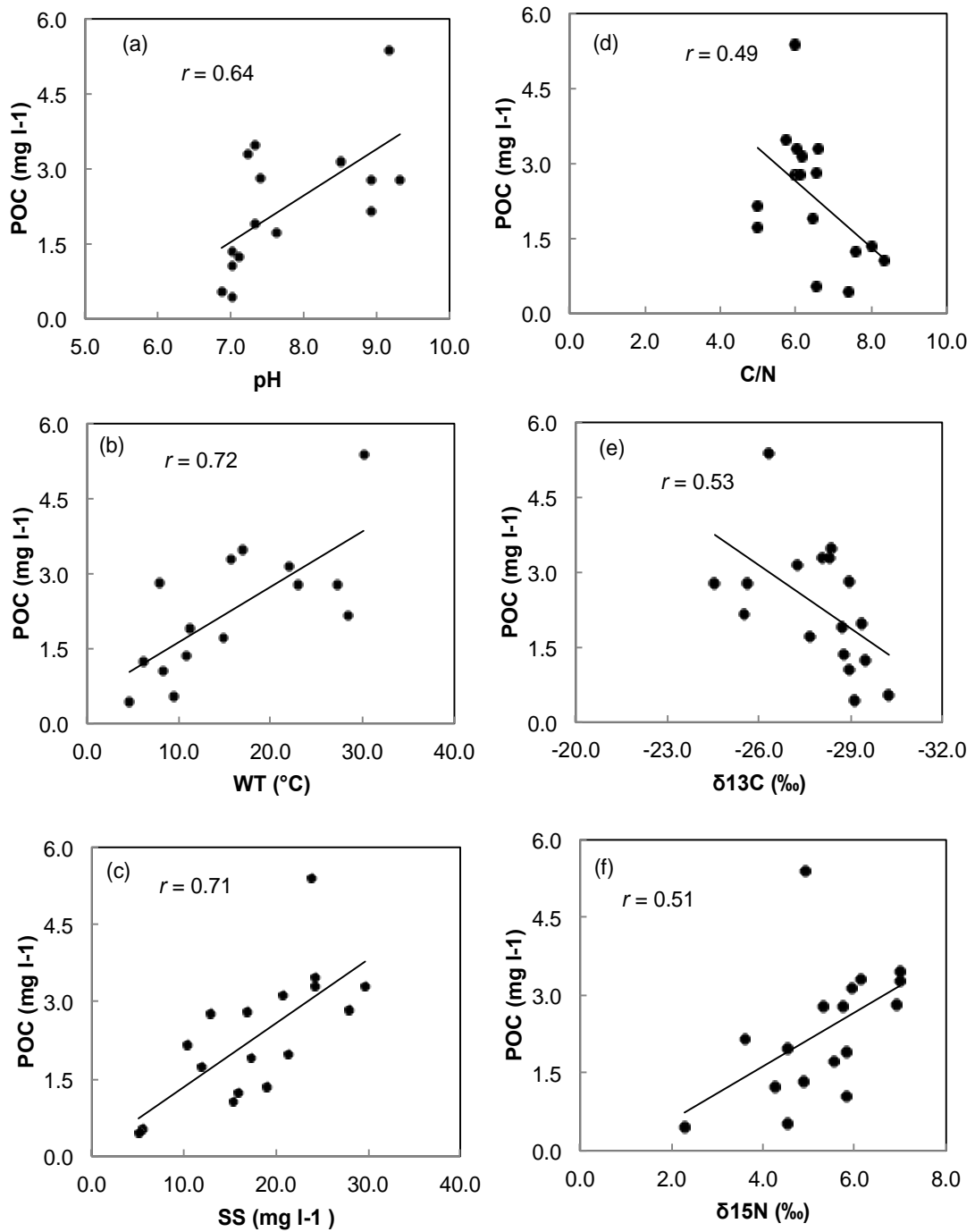
Figure 3.1-3 Particulate organic carbon (POC) concentration as a function of water pH (a), water temperature (WT) (b), suspended solids (SS) (c), C/N ratio (d), $\delta^{13}C$ of POC (e), and $\delta^{15}N$ of PN (f) in lake water suspended solids from February 2015 through March 2016.

3.1.4 Discussion

3.1.4.1. Effects of physicochemical parameters of POC concentration

Environmental factors of light intensity and light duration play crucially important roles in phytoplankton growth because they influence various weather conditions in different seasons (Jiang et al., 2014). Phytoplankton is regarded as the main autochthonous component in lake environments, contributing to POC concentration. Results show that changes of numerous environmental factors via the dynamics of phytoplankton in different seasons strongly affected the variation of POC concentration in Lake Kiba. Autochthonous products are organic carbon sources in many lakes (Watzel, 2001a). Phytoplankton, benthic algae, and aquatic macrophytes are the dominant contributors as autochthonous sources (Henderson et al., 2008; Lapierre and Frenette, 2009; Zhang et al., 2009). High positive correlation was found between WT, pH, SS, and POC concentrations (Fig. 3.1-3). These results indicate that the distribution of POC concentration is extremely sensitive to changes of environmental physicochemical factors over time, particularly for Lake Kiba. Also, water temperature (WT) is a key factor affecting phytoplankton activity in this lake environment (Nalewajko and Murphy, 2001). Phytoplankton communities use light for energy synthesis via photosynthesis activity. The pH value increases during photosynthesis because of carbon dioxide assimilation by phytoplankton (biochemical activity).

Physicochemical parameters such as WT, pH, and SS were lower values in winter, corresponding to the lower POC concentration. Actually, WT almost decreased in winter because of light weakness and the consequent reduction of aquatic phytoplankton

density because they directly use light energy and consume carbon dioxide during photosynthesis (Graham et al., 2009).

In spring and summer, WT increases and provides good conditions for phytoplankton bloom (Kosten et al., 2011). Jiang et al. (2014) found the highest number of algal cells in summer in Lake Chaohu, China. Higher POC concentrations were also observed in Lake Kiba in spring and summer. This result indicates that the phytoplankton activity might contribute to seasonal variations of POC concentration, corresponding to seasonal changes of WT and pH values. Furthermore, after 60 days of green algal cell decomposition, 50% of algal cell carbon remained in particulate form; 44% was transformed into particulate nitrogen (Wetzel, 2001b). In autumn, the POC value was reduced significantly in comparison to those of spring and summer. The energy source for photosynthesis is also restricted because WT gradually decreases during the season. Data show that POC concentrations increased because of biological production from photosynthesis activity. They decreased during decay and transformation to DOC or accumulation in sediment (Stramska and Stramski, 2005; Allison et al., 2010). Changes of POC concentrations in Lake Kiba surface waters were strongly affected by primary production, decomposition by bacteria, and settling as bottom sediment.

Although phytoplankton material dominates POC in Lake Kiba, the contributions of other factors might be considered. High correlation between suspended solids and POC concentration (Fig. 3c) might be associated with allochthonous sources such as soil erosion (Smith et al., 2005). During heavy rainfalls, soil organic matter is moved by raindrop impact energy, thereafter contributing to high POC concentrations (Gomez,

2003; Nearing et al., 2005; Neitsch et al., 2009). To clarify sources of organic pollution in the lake, we assessed isotopic components of POC fraction continuously.

3.1.4.2. Seasonal distributions of POC sources in the lake environment

The ratio of organic carbon/total nitrogen in suspended particles has often been applied to distinguish various sources of organic matter, typically from distinctive sources of terrestrial (soil, vascular plant debris) and aquatic components (phytoplankton) (Mayer, 1997; Perdue and Koprivnjak, 2007). $\delta^{13}C$ and $\delta^{15}N$ are major tissue components of plants. Therefore, they are affected to a great degree by local environment conditions, water availability, soil nutrients, and weather conditions. The C/N ratios were 5–8 (Redfield, 1958; LaZerte, 1983; Harris, 1986). The same inference was made for a plankton C/N ratio of around 6.6 (Redfield ratio). Cheng et al. (2012) reported some typical C/N for popular sources, such as approximately 4–9 for freshwater phytoplankton, greater than 10 for pure soil organic matter, and over 20 for vascular plant debris. In the present study, the C/N ratio was found to be 5.0–7.0, which does not conflict with earlier reports. Results show close relation to those reported for phytoplankton material. However, the ratios were quite different between the two periods, which suggests a difference in the POM components of spring–summer and autumn–winter. One possibility is the contribution of inorganic nitrogen.

Organic matter in Lake Kiba has been affected by human activities around the watershed, but variations of organic matter concentration and characteristics were derived from both autochthonous and allochthonous sources. In this study, the $\delta^{13}C$ was around -27.7‰ in spring, corresponding to that of terrestrial C3 plants (Boutton, 1991; Pancost and Boot, 2004). In summer, the $\delta^{13}C$ values increased slightly from -28.1‰ to

-25.5‰, with an average value of -26.0‰. The isotopic fractionation assimilation during photosynthesis depends on several environmental factors such as nutrient concentrations, light (Savoye, 2003), aqueous CO_2 concentration, diffusion rate, growth rate, and the degree of mixing (Fogel and Cifuentes, 1993; Laws et al., 1995). The isotopic fractionation of aquatic plants reflects the degree to which the different types of emergent and submerged plants use atmospheric CO_2 (which has a constant $\delta^{13}C$) versus DIC for photosynthesis (Kendall et al., 2011). Therefore, when photosynthesis activity usually occurs in spring and summer, a large amount of dissolved inorganic carbon (CO_2) and nitrogen (NH_4-N and NO_3-N) is used by phytoplankton. In that situation, $\delta^{13}C$ of POC and $\delta^{15}N$ of TN in suspended solids reach high values. In autumn, which is usually associated with the respiration stage and organic matter decomposition, much CO_2 is released to the aquatic environment (DIC concentration increases), which is a cause of $\delta^{13}C$ reduction. This process helps to explain the fluctuation of $\delta^{13}C$ in Lake Kiba during February 2015 through March 2016 (Fig. 3.1-2d). This result reflects the input of organic matter derived from phytoplankton activity.

In autumn and winter, $\delta^{13}C$ shifted by around -29.0‰, which is often related to terrestrial materials. Leaf litter generally contributes about 69–80% of allochthonous organic material entering deciduous forest streams (Wallace et al., 1995); most of this was imported during autumn when leaves fell (Benfield, 1997;; Abelho and Graç, 1998). Lake Kiba is bounded by about 51% of forest land-use. Higher suspended solid concentrations were found also in autumn (Table 3.1-1). Therefore, terrestrial materials might be related to the increase in $\delta^{13}C$ water.

The $\delta^{15}N$ of organic matter is mainly influenced by the isotopic composition of DIN in the lake water (Teranes and Bernasconi, 2000; Dolenec et al., 2005; Vander Zanden et al., 2005). Lake Kiba is an open and shallow lake. For that reason, it does not stratify; The lake water is usually well oxygenated (Table 3.1-1). The main component of DIN in Lake Kiba water is nitrate.

Variable mixtures of photosynthetic and non-photosynthetic organisms in addition to material can contaminate particulate nitrogen, presumably phytoplankton or algae (Fogel and Cifuentes, 1991). Moreover, the interpretation of the field data is hampered by the paucity of data related to $\delta^{15}N$ of ambient inorganic nitrogen. Because nitrogenous nutrients are generally present in low concentrations and are incorporated into algae, the isotopic composition of the residual substrate is often altered (Mariotti et al., 1982; Cifuentes et al., 1989). Therefore, the mutual correlations among $\delta^{13}C$, $\delta^{15}N$, C/N, and POC concentrations are weak, showing the correlation factor of $r = 0.5$. In aqueous environments, $\delta^{15}N$ of organic nitrogen derives from terrestrial sources, varying widely from - 6‰ to 18‰ as a result of complex nitrogen cycles that prevail in soil (Fogel and Cifuentes, 1991). Other studies have found a narrow range of 12–18‰ with $\delta^{15}N$ of particulate nitrogen deriving from fresh materials (Mariotti et al., 1984; Cifuentes et al., 1988,1989). In almost all cases of the present study, $\delta^{15}N$ fluctuated from 2.3‰ to 7.0‰, which shows good agreement with the results reported by McClelland et al. (1997). They reported that $\delta^{15}N$ of phytoplankton in natural waters with little contribution of anthropogenic disturbance often has a value of 2‰ to 8‰, reaching 10–20‰ in terms of water pollution. Actually, POM in rivers or lakes is

composed not only of phytoplankton material but also terrestrial organic matter (Wedchaparn et al., 2016).

In this study, higher concentrations of nitrogen isotopes were found in autumn, which apparently shows disagreement with results reported by Fogel and Cifuentes (1991), who concluded that the isotopic composition of the ammonium used by phytoplankton during growth was enriched in $\delta^{15}N$. Higher $\delta^{15}N$ concentrations were observed in October and November when heavy rainfall occurred, so precipitation might influence the higher values of $\delta^{15}N$ in autumn in Lake Kiba (Fig. 3.1-2f). The forest area around Lake Kiba might be the origin of terrestrial materials that easily enter the Lake with surface runoff, thereby contributing various isotopic components to POM.

In summary, the variations of $\delta^{13}C$, $\delta^{15}N$ and C/N from suspended particles indicated that POC shifts from phytoplankton in the spring–summer to forest soil in the autumn–winter. Lower $\delta^{13}C$ in the autumn–winter might be related to mixed sources between autochthonous and allochthonous organic matter.

3.1.5   *Conclusion*

Positive correlation between physicochemical parameters (WT, pH, SS, and POC) reflected the strong effect on seasonal POC in the Lake Kiba water. The POC and PN concentrations varied seasonally, exhibiting higher values in spring–summer, and lower values for autumn and winter data. The values of $\delta^{13}C$, $\delta^{15}N$, and C/N are associated with a mixed range of planktonic and soil materials in the particulate organic carbon component. Phytoplankton activity is a major factor increasing POC concentration in Lake Kiba during spring–summer.

3.2   **Dissolved organic carbon**

3.2.1 *Introduction*

Dissolved organic matter (DOM), which is organic material that can pass through a filter with 0.1–0.7 μm micropores, accounts for 90% of the organic matter in aquatic environments (Thurman, 1986; Kececioglu et al., 1997). DOM consists of complex mixtures of proteins and organic acids. Generally, DOM is derived from three main sources, including allochthonous (terrestrial material from soils), autochthonous (algae or phytoplankton), and synthetic organic substances of industrial or other anthropogenic sources. In freshwater and coastal seawater, DOM is dominated by humic substances (humic and fulvic acid) of terrestrial origin (Mostofa et al., 2009a), whereas autochthonous fulvic acids of algae or phytoplankton and bacteria are the main contributors to the DOM fraction (Coble, 1996, 2007; Parlanti et al., 2000; Amado et al. 2007; Mostofa et al., 2009a, b; Zhang et al., 2009). Humic acid and fulvic acid components are ubiquitous in natural waters, constituting approximately 40–60% of the dissolved organic carbon in water (Senesi, 1993). They play an influential role in physical, chemical, and biological functions in aqueous ecosystems. Usually, the DOM concentration is estimated via dissolved organic carbon (DOC) because organic carbon is a main component of the DOM formula. Therefore, identification of the original sources of DOC fraction is necessary to elucidate factors affecting variations of the amounts and characteristics of organic matter in Lake Kiba.

Widely diverse characterization tools are available for identifying DOC components such as preliminary characterization, size characterization, chemical identification and behavior, and spectral signatures. Fluorescence spectroscopy has been a powerful tool that is widely applied to distinguish different organic carbon sources in a dissolved

fraction (Coble, 1996; Coble, 2007; Yamashita and Jaffé, 2008; Zhang et al., 2011b). Fluorescence spectroscopy is a rapid, sensitive, non-invasive approach to studying fluorescent organic substances (Bro, 2005). Some salient advantages of this technique making it the most effective method for investigating the composition and source of DOM are its simplicity, sensitivity, and low cost (Fellman et al., 2010). Excitation–emission matrix (EEM) fluorescence spectroscopy has been used in marine environments since the early 1990s (Coble, 1990; Coble et al., 1993; Mopper and Schultz, 1993). Furthermore, this technique has been applied to elucidate organic matter characteristics via fluorescence properties in various aquatic environments such as marine ecosystems (Coble, 2007), freshwater areas (Yan et al., 2000; Nagao et al., 2003; Hudson et al., 2007; Fellman et al., 2010), water treatment systems (Henderson et al., 2009), urban watersheds (Holbrook et al., 2006), municipal wastewater (Saadi et al., 2006), landfill leachate (Baker and Curry, 2004), and industrial discharge (Baker, 2002). The fluorescence peak positions indicate the type of fluorescent substance. The intensity represents the concentration. The maximal peak position of excitation–emission (Ex/Em) can be detected for humic substances (fulvic acid or humic acid) depending on the nature and source in soil and nature water (Ghassemi and Christman, 1968; Levesque, 1972; Almgren et al., 1975; Brun and Milburn., 1977; Momzikoff et al., 1992). The maxima Ex/Em wavelength for fulvic acid is often present at shorter Ex/EM wavelengths than those of humic acid. In this study, EEM and fluorescence spectroscopy were applied to ascertain sources of the organic matter in Lake Kiba.

3.2.2 Materials and methods

3.2.2.1 Sampling location

Lake Kiba, characterized as a small shallow eutrophic lake, has an area of 1.09 km^2 and a watershed area of 37.4 km^2 (Fig. 3.1-1). The lake, which has sustained organic pollution for over two decades, is an open lake receiving water input from the Hiyou River, with output to the Mae River. Chemical oxygen demand and total nitrogen concentrations were over the national standard threshold, approximately twice as high as the standard level of class A (COD <3 mg l^{-1}, T-N: 0.6 mg l^{-1}) in the last decade (Komatsu City Government, 2014).

3.2.2.2 Sampling and pre-treatment

Water sampling was done monthly at a central lake from May 2014 through September 2016, spring (April–June), summer (July–September), autumn (October–December), and winter (January–March). Samples were gathered at six locations on the lake, including surface water at five sites and one site at the bottom of the central Lake. The total water volume collected at each site was approximately 1.1 liters, of which 1 liter was used for measuring DOC concentrations, DN, and the dissolved organic matter component, and relative fluorescence intensity. In addition, 100 ml was used for measuring mineral ions. The sampling was done using glass bottles, which were transported to the laboratory, where pretreatment was done in one day.

Physicochemical parameters, which included water pH, water temperature (WT), dissolved oxygen (DO), conductivity, turbidity, and water depth, were measured directly in the field using a multi-parameter water quality meter (WQC-24; TOA-DKK).

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3.2.2.3. Analytical methods

After transport to the laboratory, the water samples were filtrated using a Whatman GF/F glass microfiber filter. The samples were stored in a freezer at -20°C until analysis. DOC and DN concentrations were found using high-temperature combustion methods using a total organic carbon analyzer (TOC-V CSN; Shimadzu Corp.). The standard solution was made from potassium hydrogen phthalate, potassium nitrate, 1M hydrochloric acid, and Milli-Q water at 100 mgC l^{-1}.

Characteristics of aquatic organic substances were determined using three-dimensional excitation emission matrix spectra (3-DEEM). The EEM fluorescence was measured using a fluorescence spectrophotometer (Hitachi F-4500; Hitachi High-Technologies Corp., Tokyo, Japan) with a 700 V xenon lamp at 25 °C. The scanning ranges were 250–500 nm for excitation and 250–500 nm for emission. Data were collected at 5 nm intervals for excitation and emission wavelengths. The scanning speed was set to 2400 nm/min. Fluorescence intensity was normalized in quinine sulfate units (QSU), where 1 QSU is the maximum fluorescence intensity of 0.01 mg l^{-1} of quinine in 0.5M H_2SO_4 at the excitation wavelength (Ex; nm)/emission wavelength (Em; nm) of 350/455. Monitoring wavelengths of fulvic-like materials are at excitation (Ex) and emission (Em) af 320 nm and 430 nm (Spencer et al., 2007; Baker et al., 2009). Tryptophan materials are at Ex./Em: 280 nm/330 nm (Coble, 1996; Spencer et al., 2007; Baker et al., 2008; Hudson et al., 2008).
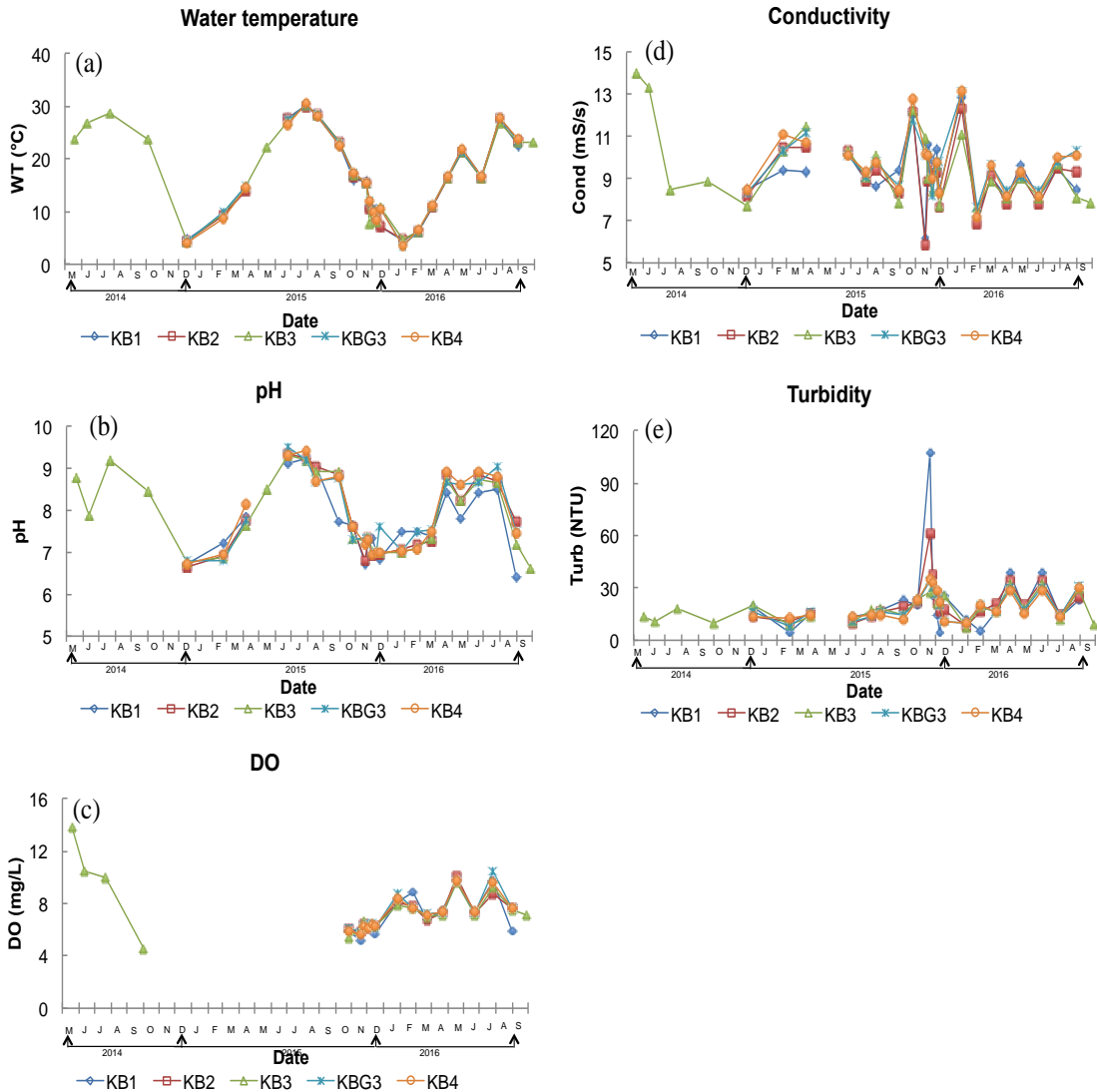
Figure 3.2-2. Variation of physicochemical parameters of surface waters at five stations in Lake Kiba during May 2014 through September 2016. The parameters are water temperature (WT) (a), pH (b), dissolved oxygen (DO) (c), conductivity (Cond) (d), and turbidity (Turb) (e).

3.2.3. Results

3.2.3.1 Seasonal variations in physicochemical factors

Elucidating the dynamics of seasonal environmental factors in surface water is necessary to examine behaviors of organic matter in a lake environment. Figure 3.2-2 shows different physicochemical parameters such as WT, pH, SS, conductivity, and turbidity from February 2015 through September 2016. No significant variation in temperature was found among the six sampling stations. The seasonal temperature variations at the five sampling positions showed a typical trend: highest values in summer and lowest values in winter. Water temperatures were highest in spring (14.8–22.1°C), except in June 2015, and summer (23.3–30.2°C), and were lower in autumn (4.3–16.9°C), except in October 2014 and winter (4.1–11.1°C), (Fig. 3.2-2a). The WT in October 2014 and June 2015 were recorded respectively as 23.8°C and 27.3°C, which is an abnormal WT in autumn and spring because the sample was collected early in the case of autumn (2 October, 2014) and late spring (24 June 2015).

Water pH was almost alkaline (6.8–9.32), exhibiting seasonal changes and showing similar variation, with WT higher in summer and lower in winter (Fig. 3.2-2b). The pH-value shifted from 7.64 to 9.32 during spring to summer (April–September), corresponding to the increased phytoplankton activity. The SS concentration was 5.0–30 mg l^{-1}. Conductivity was 7.6–12.25 mS m^{-1}. Turbidity was 7.5–107.2 NTU. Actually, SS, conductivity, and turbidity were difficult to estimate because the data fluctuated greatly throughout the year (Fig. 3.2-2c, d, e). However, both the SS concentration and turbidity were low in winter.

3.2.3.2 Temporal variations of dissolved organic carbon and its component

Variations of DOC concentrations in Lake Kiba were found, with significant difference between seasons (Fig. 3.2-3a, b). Higher concentrations were found from late spring through mid-autumn, with average values of 2.3–2.9 mg l^{-1} for data at different sampling positions (data from January 2015–September 2016), and altered from 1.8 to 3.29 for surface site of the central lake (data from May 2014–Sep 2016). The lower concentration shifted from 0.9 to 1.6 during late autumn and winter. The highest DOC concentration was observed at 3.6 mg l^{-1}at the bottom site of central Lake in June 2015. No significant change was found between sample collection at different sites throughout the lake, except for KB1 on 18 August 2015, 18 November 2015, and 23 March 2015, KB2 on 18 November 2015, and KBG3 on 24 June 2015.

Seasonal changes of dissolved organic nitrogen concentrations are shown in Fig. 3.2-3c, d. The values were characterized by great fluctuations between seasons. They fluctuated slightly between sampling positions with average values of 0.21–0.54 mg l^{-1}. The DN concentration was almost higher than 0.2 mg l^{-1}, or over international standard threshold (Japanese standard). Higher values were found in autumn and winter, except in July 2014 (0.43 mg l^{-1}on average) and August 2016 (0.54 mg l^{-1}on average). The highest concentration was 0.83 mg l^{-1} at the water input position (KB1) on 18 November 2015 and the lowest one at a surface central position (KB3) on 20 April 2016.

Determination of fluorescent peaks can provide useful information for us to ascertain the structure and properties of the dissolved fraction as well as determine its sources causing organic pollution in Lake Kiba. The wavelength of excitation and emission on

Fig. 3.2-4 was determined base on the highest value of the relative fluorescence intensity corresponding to the number of collected samples. The highest peak position indicated a dominant component in the samples. Fluorescent peaks were detected at Ex./Em: 305–310/ 420–430 nm for the spring–summer and Ex./Em: 320–335/430–435 nm for the autumn–winter samples (Fig. 3.2-4b). Although fluorescent wavelength was measured in autumn–winter that was greater, those couple of peaks in both seasons were related to fulvic materials. Differences in fluorescence peaks reflected the different sources in spring–summer and in autumn–winter. The values of both fulvic-like component and tryptophan material are presented in Fig. 3.2-4a. Both components show a similar trend and are characterized by high values from late spring through summer. Clear distinction can be made among values from season to season.
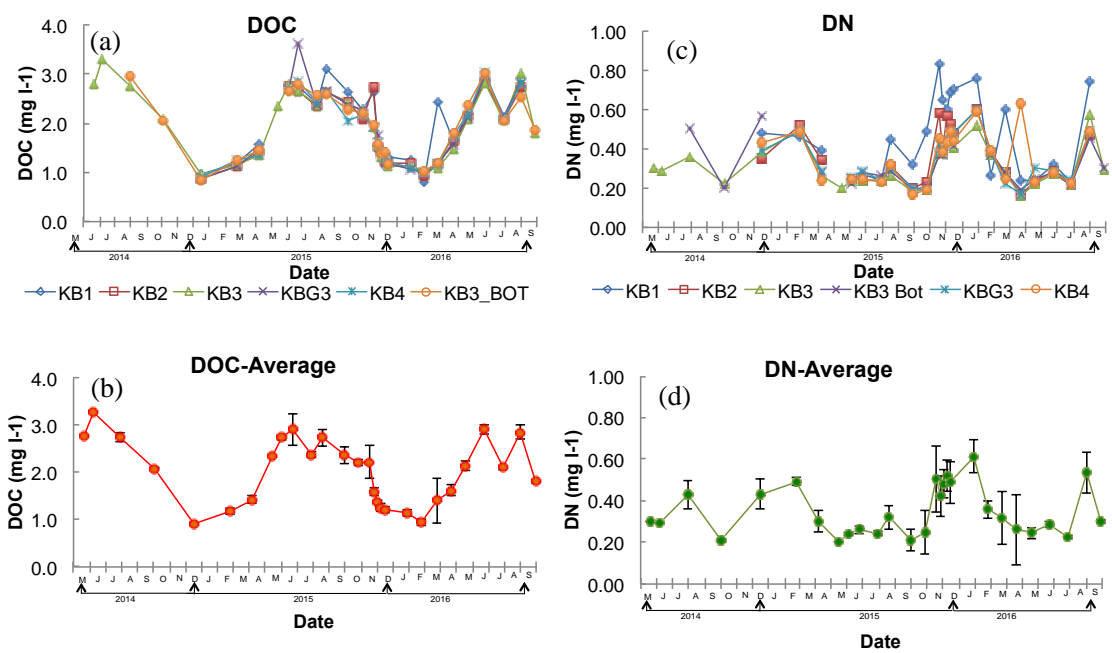
Figure 3.2-3. Variation of dissolved organic (a), nitrogen (b) at five monitoring stations and average values of DOC (c) and DN (d) at Lake Kiba from May 2014 through September 2016.

3.2.3.3 Relations between DOC and environmental factors

To access influences of environmental factors to variations of DOC in Lake Kiba, we discussed the relation between DOC concentration and physicochemical parameters. A correlation factor between COC concentration and pH was 0.67, indicating weak correlation (Fig. 3.2-5b). A good relation was observed between DOC concentration and WT at all sampling positions during May 2014 through September 2016: $r = 0.85$ (Fig. 3.2-5c). A weak relation was found between DOC concentration and DO: $r = 0.46$ (Fig. 3.2-5d). A strong relation was found between DOC concentration and RFI, with a correlation coefficient $r = 0.92$ (Fig. 3.2-6a) at monitoring wavelengths of Ex/Em = 320/430 nm, $r = 0.$ 84 at Ex/Em: 280/335 nm (Fig. 3.2-6b).
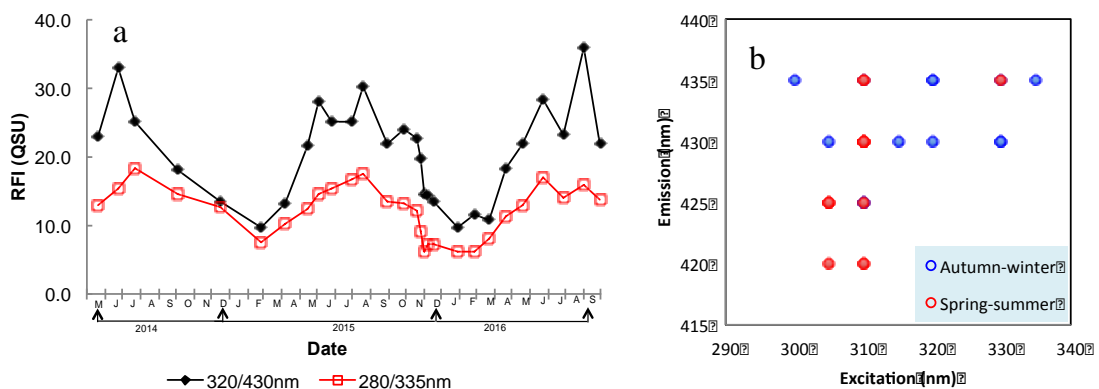
Figure 3.2-4. Seasonal fluctuations of the relative fluorescence intensity (RFI) of fulvic-like materials at excitation/ emission wavelength (Ex/Em) of 320/430 nm, with Tryptophan-like components at Ex/Em of 280/335 nm (a) and maximum fluorescent peak positions (b) in surface water at KB-3, a site in the middle of Lake Kiba during May 2014 through September 2016.

3.2.4 Discussion

3.2.4.1 Effects of environmental factors on DOC concentration variations

Organic matter in an aqueous environment comprises complex components deriving from soil and the water column, which are related to dead and living organic matter in the hydrological cycle (Egeberg and Alberts, 2002; Kitis et al., 2002). Results show that WT and pH play important roles in the variation of DOC concentrations, especially in aqueous environments affected by organic pollutants such as phytoplankton. In the case of Lake Kiba, DOC concentrations and WT showed the same trend, with higher values in spring and summer and lower ones in autumn and winter. Strong correlation ($r = 0.85$) was found as shown in Fig. 3.2-5c, which indicated that the DOC concentration fluctuation was influenced strongly by solar radiation and phytoplankton. Lancelot (1979) and Fogg (1983) pointed out that the contribution of extracellular release of photosynthetically-derived DOM varies from 5 to 70 % in natural waters. For the Arctic Ocean, the autochthonous production increased significantly with higher WT in comparison to those of lower WT (McKnight et al., 1994).

Previous studies proved the effect of WT on DOM fluctuation in aquatic ecosystems in which WT can produce photosynthetic efficiency as either enhanced or hindered (Fu et al., 2010). At temperatures lower than 12°C, related to low insolation of natural surface waters, engender low reactants such as CO_2, H_2O_2, and DIC, which are generated both photolytically and microbially from DOM and POM. The decrease of these reactants causes reduction of the aquatic microorganisms in natural waters. At moderate WT (12–25°C) usually with enhanced sunlight intensity, the key reactants are significantly increased. This effect might greatly enhance photosynthesis activity and

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primary production in waters. Results suggest that phytoplankton biomass in natural waters is significantly enhanced at optimum water temperatures. In spring–summer, autochthonous production and degradation occurred in parallel as a consequence of increasing DOC concentration at lake water column and surface bottom sediment.

In aquatic environments, water pH variations depend not only on phytoplankton activities (photosynthesis, respiration, and decomposition) but also on widely various factors such as organic detritus degradation, living organisms, and precipitation. In Lake Kiba, pH increased concomitantly with increasing WT during the summer period, which is able to link with photoinduced degradation of DOM and POM (Kopáček et al., 2003; Mostofa et al., 2005). The highest pH, 9.32, was measured in summer. Such high pH was believed to derive from phytoplankton activity. Phytoplankton activity is a crucially important factor for linking a positive relation between DOC concentration, WT, pH, and DOC. These results are consistent with those reported by Krustok (2015): water pH values increase because of rapid CO_2 assimilation when the algae started to grow, and vice versa.

The DO concentration is reduced by organic matter decomposition and respiration, but it increases because of O_2 released from photosynthesis. In this lake environment, the lowest DO was recorded in autumn, with somewhat higher values in spring, winter, and summer, which differed from the DOC trend. Higher DOC concentrations, WT, pH and lower concentrations of NH_4^+ and NO_3^- were found for spring–summer, which suggests that phytoplankton activity resulted from variations of these parameters.

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Phytoplankton engenders increased pH by CO_2 depletion and NH_4^+ and NO_3^- reduction by phytoplankton assimilation.

Turbidity is the most commonly applied parameter for elucidating water quality in a natural environment. Lower turbidity generally indicates high water quality. In this study, lower turbidity and high DOC were observed in summer, indicating that turbidity does not represent the status of pollution in this lake environment. The highest value of turbidity in November (107.2 NTU) occurred as a result of a heavy rain event, causing a huge amount of soil material runoff into the lake. Conductivity and turbidity varied throughout the year, indicating that at least a few factors influenced their fluctuation.
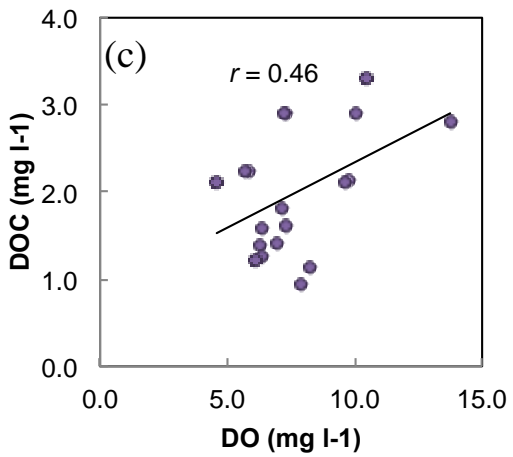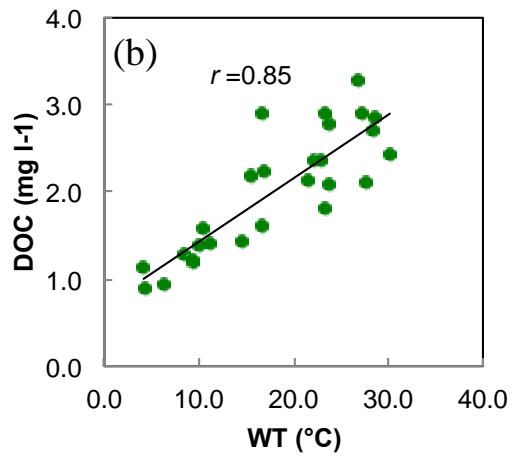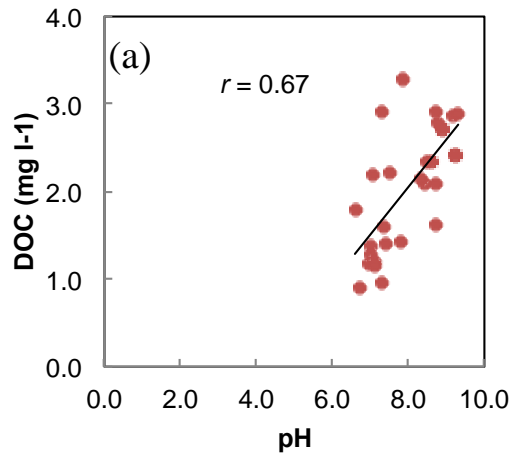
Figure 3.2-5. Dissolved organic carbon (DOC) concentration as a function of pH (a), water temperature (WT) (b), and dissolved oxygen (DO) (c).

3.2.4.2 Seasonal variations of DOC sources in the lake environment

Fluorescent peak positions for humic substances revealed their sources and nature (either fulvic acid or humic acid) in soil and natural waters (Ghassemi and Christman, 1968; Levesque, 1972; Almgren et al., 1975; Brun and Milburn, 1977; Gosh and Schnitzer, 1980; Momzikoff et al., 1992). The maximum fluorescence peak position for humic acid is often present at longer wavelengths than those of fulvic acid, and independently of the molecular weight. The fluorescent peaks are classified as peak C, peak M, peak A, peak T, and peak B, revealing characteristics and particular sources of DOM (Coble, 1996). Peaks C, M, and A are presented for humic-like substances while protein-like, tryptophan-like, and tyrosine-like materials are related to peak T and peak B. For this study, the fluorescence peak was calculated at an excitation/emission wavelength of 310/428 nm, on average, in the spring–summer and 318/432 nm in the autumn–winter. Those couple of peaks differed greatly from the peak A-region (215–280/380–550 nm), the peak T-region (260–285/290–380 nm), and were related with peak C (280–400/380–550 nm), which included fulvic acid and humic acid derived from terrestrial vascular plants (C-like and M-like). The result was also consistent with fulvic-like components observed for surface water from Lake Biwa, Japan (Ex/Em: 305–310/450–464 nm) (Mostofa et al., 2005b, 2010), implying dominance of fulvic-like materials in the DOM fraction.
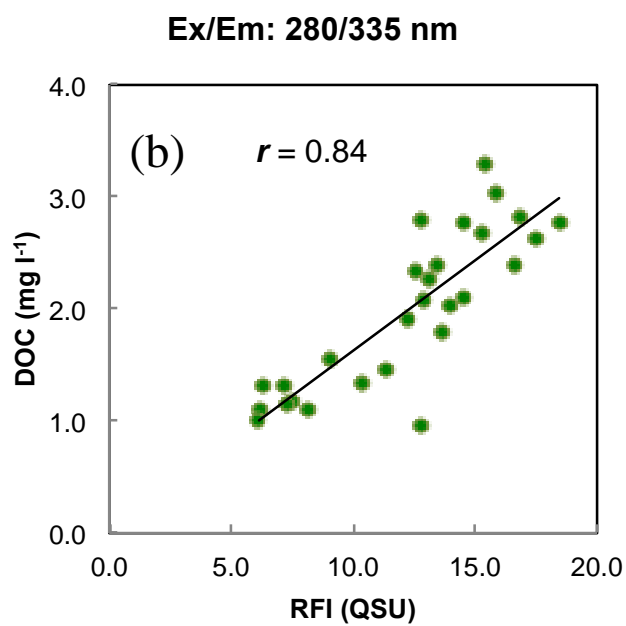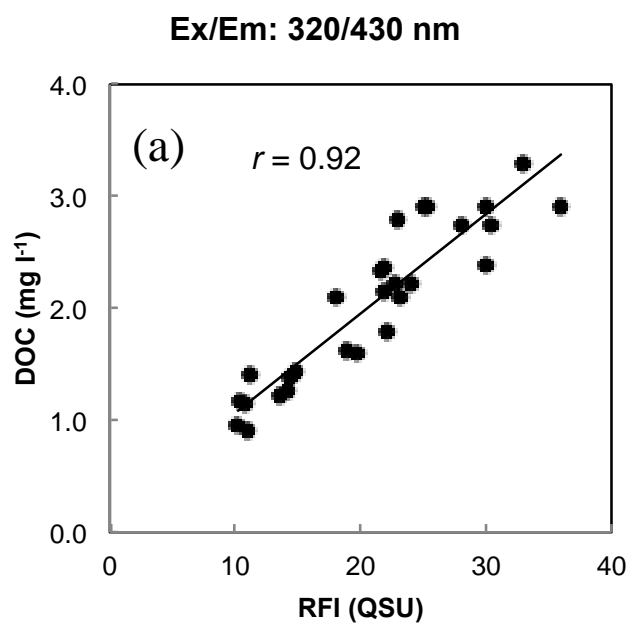
Ex/Em: 320/430 nm

Ex/Em: 280/335 nm

Figure 3.2-6 Relation between DOC concentration and the RFI of fulvic-like (a), tryptophan-like materials (b) at the central site of Lake Kiba from May 2014 to September 2016.

It is important to ascertain whether autochthonous or allochthonous fulvic-like materials are dominant in lake water. Therefore, we considered fluorescence characteristics of the Kiba Lake water based on EEM spectroscopy. The Ex/Em maxima of fluorescence for Lake Kiba waters are shifted from shorter wavelengths in the spring–summer to the longer wavelength region in autumn–winter, which absorbed from blue to red light, corresponding to the mineralization of fluorophores that are present in the molecular structure of fulvic acids (Moran et al., 2000; Mostofa et al., 2005a, 2007). Kirk (1976) reported that chloroplast pigments of cyanobacteria (algae) and aquatic higher plants absorbed bands in the blue region of the spectrum, whereas the red region was limited in absorption in the aqueous environment because the red light is rapidly attenuated by water. Autochthonous and allochthonous humic substances (fulvic and humic acids) absorbed light in the blue and ultraviolet range (Hutchinson, 1957; Kalle, 1966; Parlanti et al., 2000; Zhang et al., 2009). The maximum fluorescence peaks of all samples in spring–summer implied autochthonous fulvic-like materials derived from algal or phytoplankton origin. The fluorescent wavelengths detected from the dissolved fraction differed from spring–summer to autumn–winter, although both were related to the fulvic–like component. Results suggest that the dominant contributions to dissolved organic matter in Lake Kiba were not similar in spring–summer and autumn–winter.
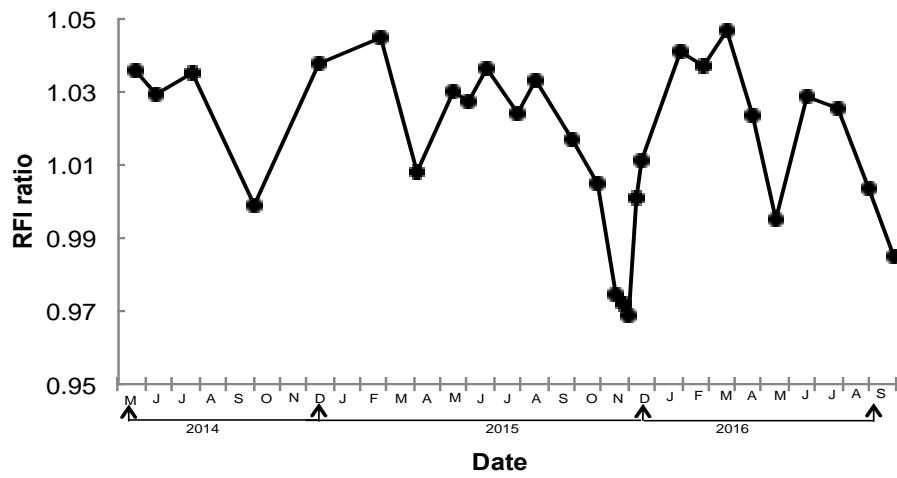
Figure 3.2-7 Variation of relative fluorescence intensity (RFI) at the average maximum peak position between spring–summer and autumn–winter from May 2014 through September 2016.

The RFI values were significant lower, 9.7–24.3 QSU (15.5 QSU on average) than those in spring–summer of 18.4–36.6 QSU, with a mean value of 26.4 QSU. The value of relative fluorescent intensity (RFI) for fulvic-like materials at an excitation /emission wavelength of 320/430 and DOC concentration showed a similar trend and strong positive correlation ($r = 0.95$), as depicted in Fig. 3.2-6(a). A high correlation factor was also observed between the DOC concentration and the RFI of tyrosine-like substances and maximum RFI of fulvic-like materials (Fig. 3.2-6b, c). That result suggests that autochthonous fulvic-like materials derived from phytoplankton or algae occupied a major fraction of DOM. The fulvic-like materials are dominant components of DOC.

Figure 3.2-7 shows the ratio of RFI at the average fluorescence peak position between spring–summer (Ex/Em of 310/428 nm) and autumn–winter (Ex/Em of 318/432 nm). The mixture of two types of fulvic-like materials is classified as three groups: 1) around 1.0 in spring–summer, 2) less than 1.0 in a change of season such as April and September, and 3) greater than 1.0 in autumn–winter. This classification shows that the contribution of phytoplankton has a decreasing trend in autumn–winter season. It augments the input of DOM from the lake watershed.

The longer wavelengths detected in winter (Fig. 3.2-8) are explainable by a combination of algae/phytoplankton degradation and terrestrial organic materials transported by water runoff. The lower pH, high DOC concentration, and brownish water were a consequence of heavy precipitation in early autumn. Therefore, the input of the terrestrial origin of humic substances increases during autumn–winter.
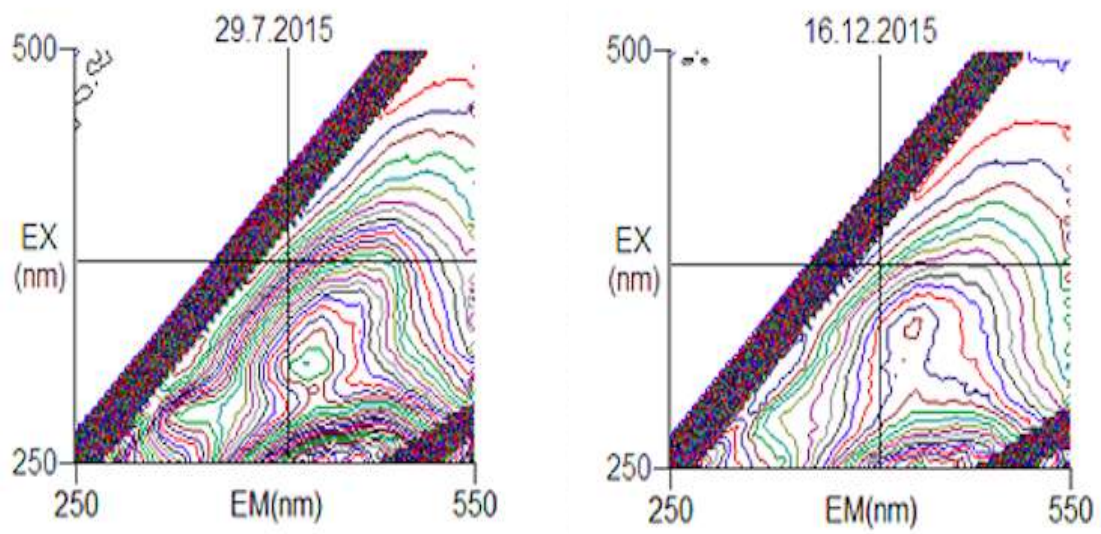
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Figure 3.2-8. Typical excitation–emission matrix spectra in water samples collected in summer and winter from Lake Kiba.

3.2.5 Conclusions

DOC concentrations were higher during the spring–summer and showed strong correlation with RFI of fulvic-like materials, water temperature, and water pH. The fluorescent organic matter, including fulvic-like materials, was characterized by shorter wavelengths of peak positions and higher RFI values in the spring–summer, although the fluorescent properties are opposite characteristics in the autumn–winter. The fluorescence intensity monitoring for the highest wavelength at Ex/Em: 320/430 nm of fulvic acid and 280/335 nm of tryptophan, respectively, showed similar variation to that of the DOC concentration. A range of the RFI ratio is evident for the spring–summer and the autumn–winter, with slightly higher values found during spring–summer. Those results suggest a shifted variation of organic matter in Lake Kiba from the spring–summer to the autumn–winter. Autochthonous fulvic acid derived from phytoplankton is the major contributor in increasing the DOC concentration. The lower value of DOC concentration and RFI along with high higher Ex/Em wavelength in the autumn–winter are expected to be contributed from terrestrial material because of surface water runoff.

Chapter 4.

Combined use of δ^{13}C and Δ^{14}C to analysis fate of organic matter in Lake Kiba

4.1 Introduction

Radiocarbon abundance has become an indicator of terrestrial versus marine sources because nuclear weapons testing in the 1950s and 1960s injected large quantities of ^{14}C into the atmosphere (Raymond, 2001; McNichol and Aluwihare, 2007). The $\Delta^{14}C$ values of organic matter in river suspended particles are –980 to +75‰, but plankton and particulate organic carbon in marine environments have enriched ^{14}C values of –45 to +110‰ (McNichol and Aluwihare, 2007 McNichol and Aluwihare, 2007; Hedges et al., 1986). Radiocarbon is also useful as a tracer of the dynamics of organic matter in river systems and lake environments (Masieelo, and M. Druffel, 2001; Raymond et al., 2004; Nagao et al., 2007). The paired $\Delta^{14}C$ versus $\delta^{13}C$ distributions vary among river systems. They can be divided into three groups: wetlands, forest-paddy fields, and permafrost watersheds (Nagao et al., 2010; Nagao et al., 2005; Guo et al., 2006). Riverine particulate organic matter (POM) from wetlands has lower $\delta^{13}C$ and higher $\Delta^{14}C$ than those of rivers in forests and fluvial plains, which indicates a greater contribution of apparently younger organic matter in wetland river systems. In lake environments, carbon isotopes have been applied to elucidate biogeochemical cycles and reservoir effect ranges and variations over time (Nagao et al., 2007; Abbott and Stafford, 1996; Nara et al., 2010). The phytoplankton $\Delta^{14}C$ reflects the $\Delta^{14}C$ of dissolved CO_2, which might be a mixture of aged and modern carbon (Zigah et al., 2012a; Albéric et al., 2013; Keaveney et al., 2015). The POC has a wide range of $\Delta^{14}C$ extending from –443 to +68‰ in these lakes. Their $\Delta^{14}C$ values have been useful in assessing the age, reactivity, and sources of carbon in lake systems. Oguri et al. (1996)

and Ueda et al. (2007) have demonstrated that radiocarbon behavior is influenced strongly by environmental factors in the Lake Obuchi and Lake Hamana ecosystems.

Lakes play important roles in the carbon cycle through carbon sequestration in sediments and efflux of CO_2 to the atmosphere (FaGupta et al., 2008; Heathcote et al., 2012). Some lake environments in economically developing countries have been sustaining organic pollution during the last decade because of rapid economic development and increased human populations around watersheds. In Japan, water quality survey results for lakes and reservoirs in 2014 indicated that the compliance rate of environmental quality standards for living environmental items is 55.5% for chemical oxygen demand (COD) concentrations (Ministry of Environmental Studies). Another water quality problem is the slight increase of COD concentrations in lakes, although total nitrogen, phosphorus, and biochemical oxygen (BOD) concentrations are constant or decreasing with time (National Institute for Environmental Studies, 1998, 2004; Hayakawa and Okamoto, 2012). The increasing annual measurements of COD appear to result from accumulation of refractory organic matter in the lakes. Therefore, the dynamics of organic matter are important to elucidate organic pollution mechanisms in lake systems.

Lake Kiba (Kiba-gata), located at Komatsu City, Ishikawa Prefecture, Japan (Fig. 4.1), has mean water depth of 1.7 m, area of 1.14 km^2, and water volume of 1.7×10^4 m^3. Its watershed area is 38 km^2. In 1932, a counter slice gate was constructed at the conjunction of the Kakehashi River to protect against inflow of water from the river during flood events. Lake Kiba was affected by changes in the drainage system and land consolidation around the lagoon during 1954–1969 (Hokuriku Regional Agricultural

Administration Office, 1970). The Maekawa slice and drainage pump station was constructed at the Maekawa River to control the Lake Kiba water level. The organic matter flux recorded in the sediment core increased from 1.1 to 2.3 and from 3.9 to 7.5 g cm^{-2} y^{-1}, respectively, during 1903–1974 and 1989–2012, although it was similar to the flux recorded for 1974–1989 following reclamation (Nagao et al., 2016). The COD concentration was at a maximum, 11 mg l^{-1} in 1990, corresponding to the second worst in Japan. It has remained about double the national standard of this lake class (3 mg l^{-1}) during the last decade (Komatsu City Government, Research of Natural Environment and Watershed Culture in and around Lake Kiba, 2016), although treatments for water quality improvement have been conducted since 1991.

The objectives of this study are to elucidate the dynamics of POM shallow and semi-closed Lake Kiba throughout a single year based on monthly observations obtained using carbon isotopes: $\delta^{13}C$ and $\Delta^{14}C$. The simultaneous use of $\Delta^{14}C$ and $\delta^{13}C$ values adds a second dimension to observations of carbon cycling in surface aquatic environments. During the sampling period, we ascertained the fundamental physicochemical parameters, POC concentration, and carbon isotopes. Results of this study are expected to provide basic and useful information to clarify organic pollutants affecting shallow lakes and lagoons.
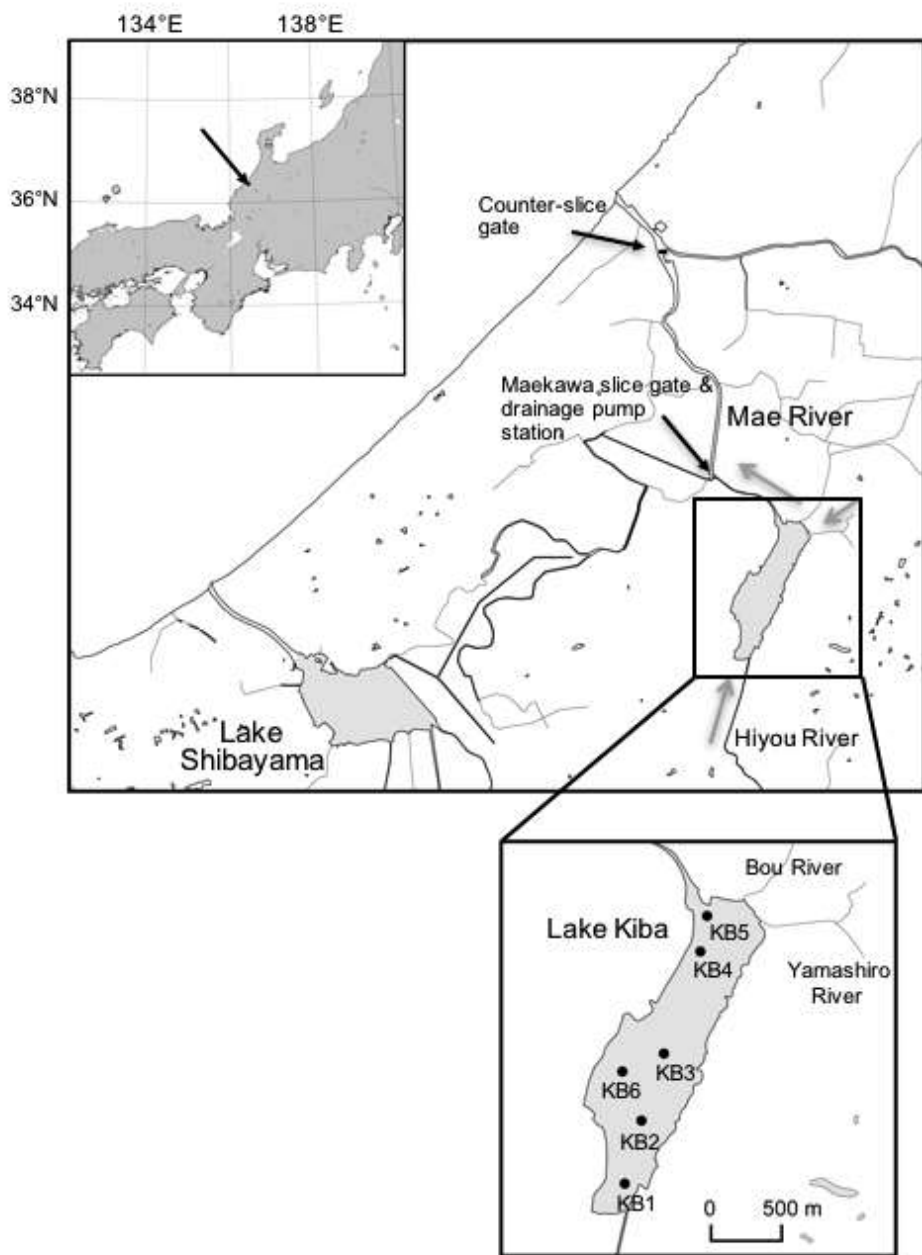
Figure 4.1: Sampling location. The closed circle denotes the sampling site at Lake Kiba. Numerical map data are based on Fundamental Geospatial Data provided by the Geospatial Information Authority of Japan, and National Land Numerical Information provided by the Ministry of Land, Infrastructure, Transport and Tourism, Japan.

4.2 Materials and methods

Water sampling was monthly conducted at site St. KB3 at the central part of the lake during April 2014 – March 2016 (Fig. 4.1). Surface water samples were collected using a bucket on a boat. During 18 November – 16 December 2015, sampling was also conducted weekly to elucidate changes in water quality during water quality improvement experiments using the Maekawa slice and drainage pump station, as presented in Fig. 4.1 (Komatsu City Government, Field demonstration for water quality improvement of Lake Kiba, 2016). Detailed results of those experiments will be reported elsewhere.

Water characteristics such as water temperature (WT), pH, conductivity, and turbidity in the surface water were measured using a water checker (WQC-24; DKK-TOA Corp.). Chlorophyll-a concentration was photometrically quantified using the trichromatic absorption method after extraction of particles using a 0.45 μm membrane filter (Advantec MFS Inc.) with 90% acetone (Ministry of the Environment, 2016). Samples of chlorophyll-a were collected at a similar position during monthly research conducted by the Komatsu City Government.

About 60 L of water was taken into polyethylene containers and was then transferred to the laboratory. Suspended particles in lake water samples were concentrated with a single-bowl continuous-flow centrifuge with a flow rate of 15 l h^{-1} (Nagao et al., 2010). The inside temperature was maintained at 10–20°C to avoid transformation of solids. Solid samples were dried at room temperature or freeze-dried. The suspended solids (SS) concentration was measured by weight of the suspended solids. Surface sediments were collected at six stations (Fig. 4.1) using an Ekman–Birge

grab sampler in 2012 and 2013. The sediment samples were freeze-dried and ground in an agate mortar after sieving with a 2 mm sieve.

Organic carbon contents were found using an elemental analyzer (NA2500, CE Instrument or Flash EA1112; Thermo Fisher Scientific Inc.). Before analysis of the suspended solids, carbonates were removed by adding 1 M HCl solution. The respective levels of precision of TOC and TN analyses were $\pm$ 0.009% and $\pm$0.003%. ^{14}C measurements were taken using accelerator mass spectrometry at the Beta Analytic Radiocarbon Dating Laboratory. For this study, Δ^{14}C is defined as the deviation in parts per thousand from the modern standard (NBS oxalic acid: SRM-4990C):

$$[F\ ^{14}C * e^{\lambda(1950-x)}-1]*1000$$

where x is the sampling date and F^{14}C is the ratio of the sample and standard ^{14}C/^{12}C (Stuiver, and Polach, 1977). A positive Δ^{14}C value reflects the presence of carbon released from atomic bomb tests in the 1950s and 1960s. Stable carbon isotopes were assessed for sub-samples of the CO_2 gas generated during graphite production using mass spectrometry, or were found using EA-IRMS analysis (Delta V or Delta V Advantage coupled to Flash EA1112; Thermo Fisher Scientific Inc.). The δ^{13}C value is expressed as follows.

$$\delta^{13}C = [(^{13}C/^{12}C)_{sample} /(^{13}C/^{12}C)_{standard} -1] \times 1000$$

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Therein, $(^{13}C/^{12}C)_{sample}$ is the abundance ratio of ^{13}C to ^{12}C of the sample. $(^{13}C/^{12}C)_{standard}$ is the ratio of VPDB: ANU-Sucrose ($\delta^{13}C = -10.80‰$) and L-Alanine ($\delta^{13}C = -19.6‰$).

4.3 Results and discussion

4.3.1 Water quality

Water temperature and pH show seasonal variation. They are higher in summer. Increased pH results from utilization of CO_2 for phytoplankton activity. Suspended solid (SS) concentration shows seasonal variation and varies among years. The particulate organic carbon (POC) concentration is higher in summer (July–August) and lower in winter (October–November). The chlorophyll-a concentration has two peaks in April and August, 2015. The POC concentration in the unit of mg l^{-1} is correlated with water temperature and pH ($r = 0.67$–0.70, $p<0.05$), but the POC content in % units, as portrayed in Fig. 4.4, shows a stronger positive correlation ($r = 0.87$, $p<0.0001$). This result suggests that the increase in POC is related to phytoplankton activity in the lake.
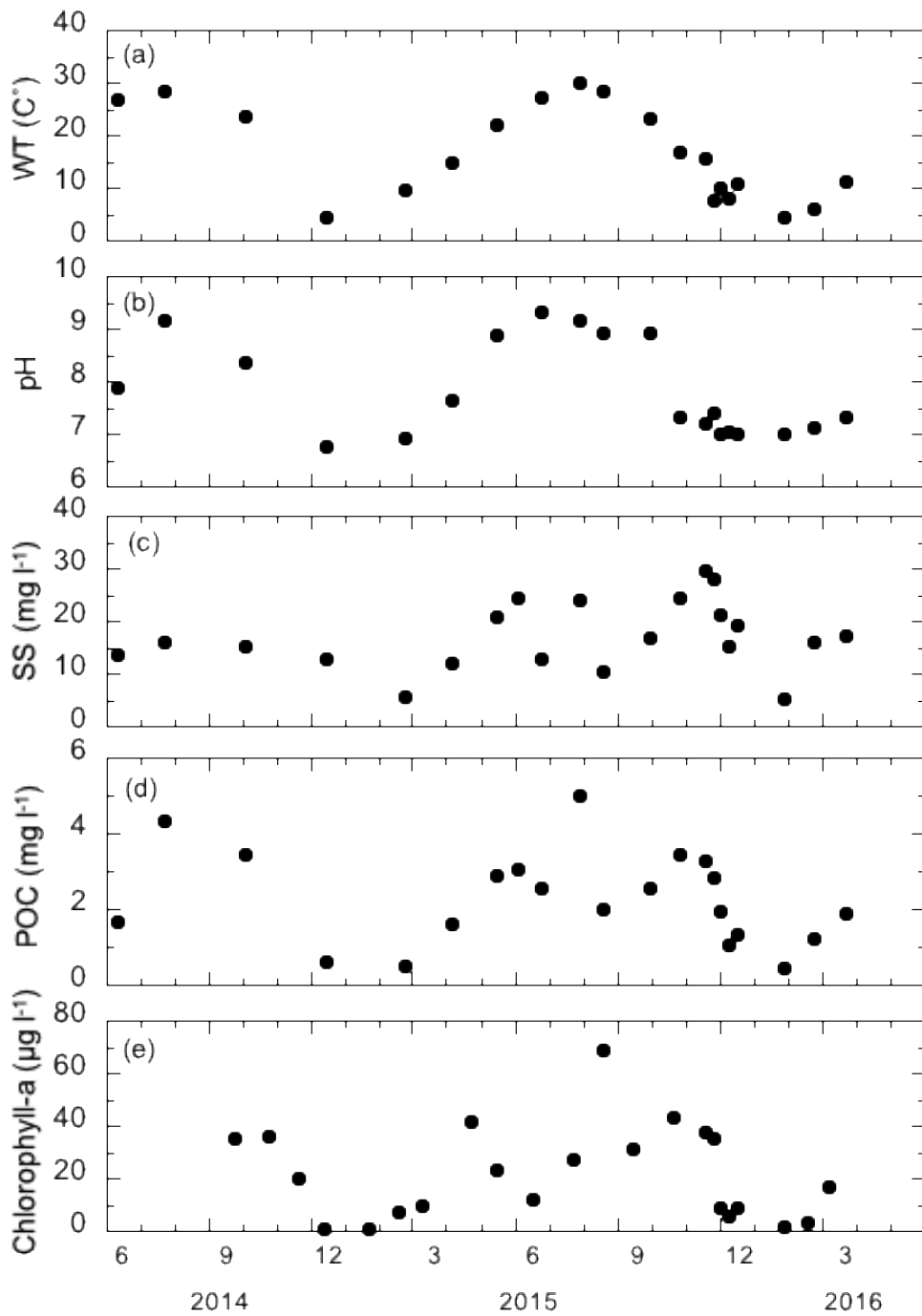
Figure 4.2: Variation of water temperature (WT), pH, suspended solids (SS), particulate

organic carbon (POC) and chlorophyll-a concentration in surface water from Lake Kiba

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4.3.2 Carbon isotopes of particulate organic matter

The POC contents were 4.9–27%, showing a maximum in July–September. The maximum value in 2014 is higher than that of 2015. The C/N ratio is varied, 5.0–9.8, except for the sample on 2 December 2015. The $\delta^{13}C$ value of organic matter in the suspended solids was –30.3 to –22.8‰. The maximum value in 2014 was higher than that of 2015. These values show similar variation along with POC contents ($r = 0.80$, $p< 0.0001$). The $\delta^{13}C$ values also correlated with pH of lake water ($r = 0.75$, $p< 0.0005$). Similar results were reported for the shallow lake environment (Yoshioka and Plankton, 1997; Doi et al., 2006). The $\delta^{13}C$ values of phytoplankton increase because of the reduced isotope fractionation during photosynthesis, when the phytoplankton biomass increases or the supply of dissolved inorganic carbon is limited (Yoshioka and Plankton, 1997).

The $\Delta^{14}C$ value of POC is more depleted than in the present atmospheric CO_2 (Beramendi-Orosco et al., 2015, exhibiting an average value of –81 ± 37‰. The lake water POC has lower $\Delta^{14}C$ than with inorganic carbon, plankton, and present biota in the river and lake watershed (Ueda et al., 2007; Nakamura et al., 1998), although the maximum $\Delta^{14}C$ value was observed in summer with higher pH, POC, and chlorophyll-a concentration. The bulk POC in a large lake, Lake Superior, had a mean $\Delta^{14}C$ value of +10 ± 29‰ ranging from –55 to +39‰. The $\Delta^{14}C$ of dissolved inorganic carbon (DIC) was +36 ± 62‰ (Zigah et al., 2012b). However, some lake water had lower $\Delta^{14}C$ values (–443 to –80‰) of POC together with lower DIC in lake waters (Albéric et al., 2013; Keaveney et al., 2015. Increases in $\delta^{13}C$ and $\Delta^{14}C$ values of dissolved organic carbon were observed in Lake Kasumigaura water during spring because of the primary

production of phytoplankton, although Δ^{14}C-DOC was more depleted than atmospheric CO_2 (Nara et al., 2007). Therefore, the depleted Δ^{14}C value of POC in Lake Kiba might be caused by lower Δ^{14}C inorganic compounds in lake water, which includes inputs from groundwater and wetland water in the watershed.
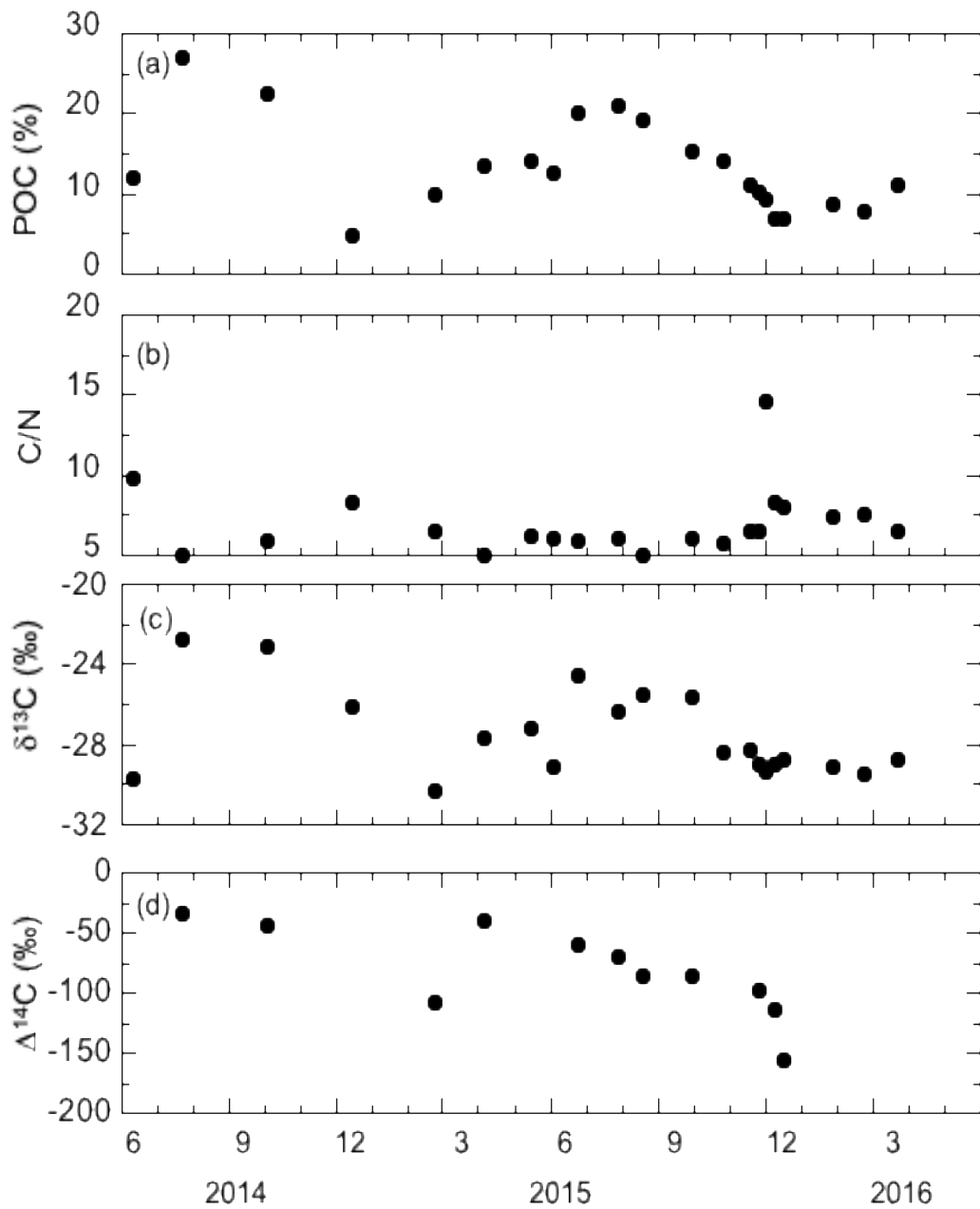
Figure 4.3: Variation of POC content, particulate organic carbon/ nitrogen (C/N), $\delta^{13}C$ and $\Delta^{14}C$ values of POC in surface water from Lake Kiba. Error bars correspond to 1σ uncertainty on $\Delta^{14}C$ measurements.
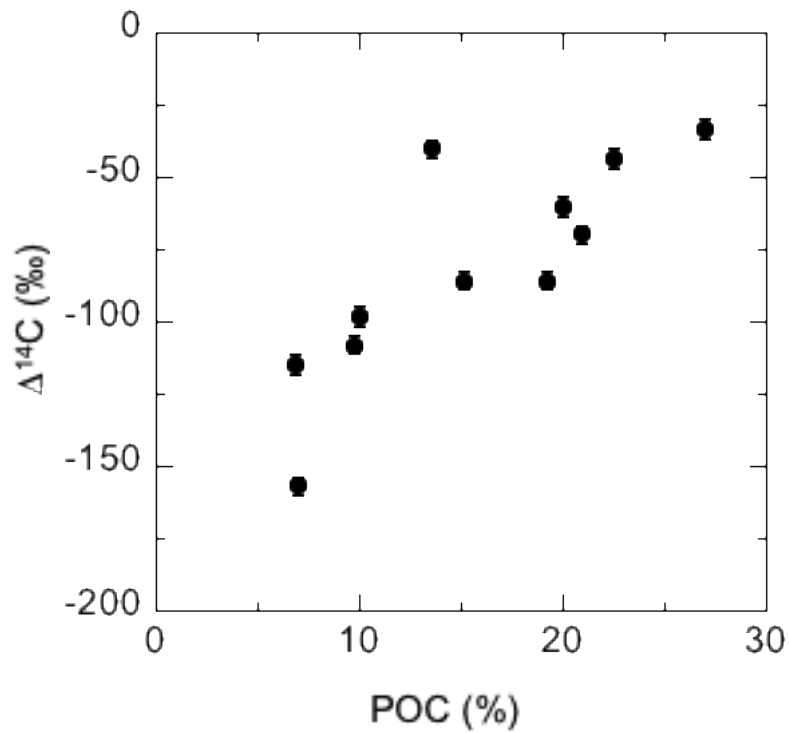
Figure 4.4: $\Delta^{14}C$ values of POC as a function of POC content in the Lake Kiba surface

water. Error bars correspond to 1σ uncertainty on $\Delta^{14}C$ measurements

4.3.3 Factors controlling characteristics of particulate organic matter

Radiocarbon of POC in lake water is derived from primary production within the lake system, re-suspension of sedimentary particulate matter, and inputs from the watershed. To elucidate the contribution of radiocarbon in Lake Kiba, relations between radiocarbon and characteristics of organic matter must be discussed. Figure 4.4 presents the relation between $\Delta^{14}C$ values of organic matter and its contents in suspended solids in Lake Kiba. With the increase of POC contents in the suspended solids, $\Delta^{14}C$ values increase (r = 0.82, $p<$ 0.005). Similar variation of chlorophyll-a concentration represents the contribution of phytoplankton activity within the lake.

Figure 4.5 presents $\Delta^{14}C$ values of organic matter in the lake suspended solids, shown as a function of the C/N ratio and $\delta^{13}C$ values. They have been used as a simple tracer to distinguish inputs of aquatic phytoplankton from soil organic matter (Finlay, and Kendall, 2007; Khan et al., 2015). A negative correlation was found between the C/N ratio and $\Delta^{14}C$ of POC (correlation coefficient of 0.82, $p<0.005$). Apparently, a younger signal results from the larger contribution of a newly produced one from phytoplankton activity. The $\Delta^{14}C$ of POC shows positive correlation with the $\delta^{13}C$ values (r = 0.73, $p<$ 0.01). Higher $\Delta^{14}C$ of POC and lower C/N ratio suggests an increase in signals of phytoplankton activity in the lake. This result is consistent with the POC content variation, as presented in Fig. 4.2.

Table 4.1 presents carbon isotope data for organic carbon in surface sediments at Lake Kiba. The $\delta^{13}C$ values are –26.1 to –27.0‰, with an average of –26.6 ± 0.3‰, and narrower and higher than the average value of surface water POC ($\delta^{13}C$ of –27.5 ± 2.1‰). The C/N ratios in surface sediment samples also have higher values (10.6–11.8)

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than the suspended POC in the lake water, as depicted in Fig. 4.3. A discrepancy exists in $\delta^{13}C$ and C/N ratio of organic matter between the suspended solids and surface sediments. Therefore, resuspension of sediment particles from the surface sediment exerts a weak effect on the increase in $\delta^{13}C$ and C/N ratio of POC during spring–summer. Newly produced particulate organic matter in the lake is decomposed and/or mixed with organic matter transported from the watershed forests and paddy fields.

Table 1 TOC content, C/N ratio and $\delta^{13}C$ of organic matter in surface sediments from Lake Kiba

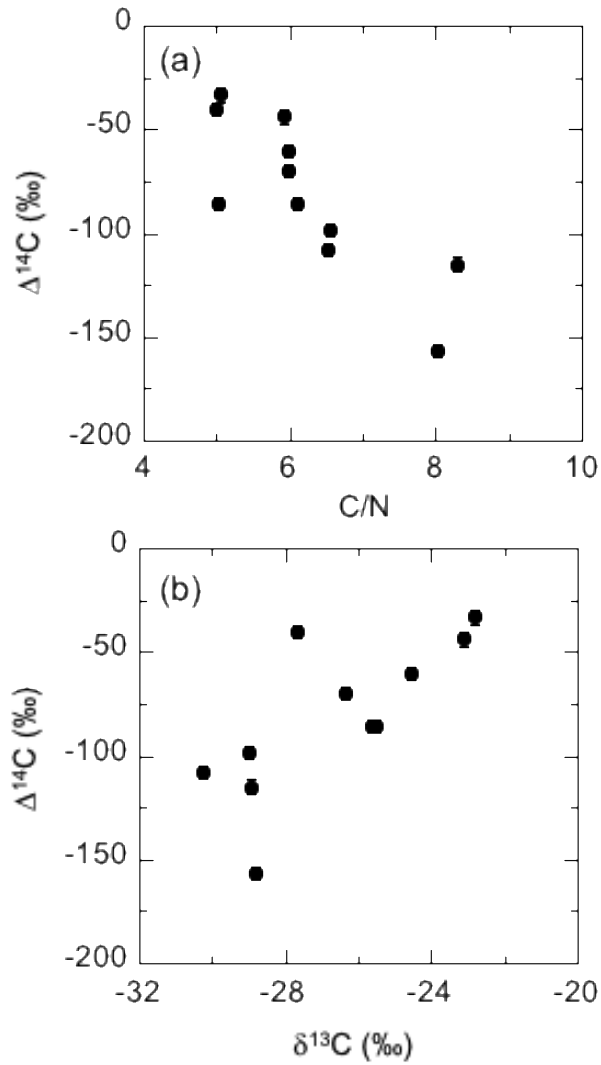|	Depth (cm)	TOC (%)	C/N	$\delta^{13}C$ (‰)
St. 1	0-2	2.86	10.6	-27.0
St. 2	0-2	5.61	11.2	-26.7
St. 3	0-2	7.24	11.5	-26.1
St. 4	0-2	5.27	10.6	-26.5
St. 5	0-2	4.77	11.1	-26.9
St. 6	0-1	7.32	11.8	-26.5

Figure 4.5: $\Delta^{14}C$ values of POC as a function of C/N ratio and $\delta^{13}C$ value for the POC in the Lake Kiba surface water. Error bars correspond to 1σ uncertainty on $\Delta^{14}C$ measurements.

4.4 Summary

Simultaneous use of $\Delta^{14}C$ and $\delta^{13}C$ values adds a second dimension to results of isotopic studies of carbon cycling in surface aquatic environments. This study applied the analysis of carbon isotopes to a lake environment from a shallow and semi-closed lake, Lake Kiba located at Komatsu City in Ishikawa Prefecture, Japan. The field research was conducted during June 2014 to March 2016. Suspended solids were collected from ca. 60 L of surface lake water at a monitoring station of the central area of Lake Kiba using continuous flow centrifugation. Particulate organic carbon (POC) concentration and its contents were, respectively, 0.44–5.01 mg l^{-1} and 4.9–27%. Strong positive correlations of POC content were found with its $\Delta^{14}C$ (–157 to –33‰) and $\delta^{13}C$ (–30.3 to –22.8‰), and negative correlation with the C/N ratio (5.0–14.7). These results indicate that organic matter in the surface water suspended solids consists mainly of a mixture of organic matter produced by phytoplankton within the lake and watershed organic matter, although the $\Delta^{14}C$ of POC is depleted to a greater degree than present atmospheric CO_2.

Chapter 5.

Reclamation and land consolidation effects on organic matter sedimentation in Lake Kiba-gata, Japan

5.1. Introduction

Lakes are globally important water resources for drinking water and for irrigation and hydroelectric power supply. Reclamation work, the process of creating new land from lakes, rivers, and coastal marine environments, is an important mode of human impact on aquatic environments such as landscape, earth surface processes and ecosystems. Land reclamation in and around lakes was prevalent in many parts of Japan during the 1950s–1970s (e.g., Hachiro-gata, Lake Nakaumi, Kahoku-gata) in order to facilitate increased food production, but there were negative consequences, including lake shrinkage, water quality deterioration and dramatic changes to lakeshore ecosystems (Saito, 1964). Closed and semi-closed lakes, which have no substantial surface or subsurface outflow, are particularly sensitive to human activities such as agricultural and industrial activities and reclamation projects. For better understanding the effects of reclamation on aquatic environment, it is important to study changes in sedimentation processes by using organic matter because the quantity and quality of organic matter in sediments reflect the variation of production and preservation rates in lakes.

The lowland around the three Kaga lagoons (Shibayama-gata, Imae-gata, and Kiba-gata) is located in the central part of Japan (Fig. 5-1). The lagoons were previously subject to frequent floods from counter-currents of the Kakehashi River, which was the only outlet for water from these three lagoons. However, the drainage capacity in lowland areas is rather poor. Most of the farmland was flooded frequently (Ishikawa Prefectural Government, 1986). Water in the lagoons flowed from Shibayama-gata and Kiba-gata into Imae-gata through the Mae River to the Kakehashi River. Imae-gata, a brackish lake, had chloride concentrations of 1–10 g l^{-1} (Mashiko, 1976) because of

backward flow from the Sea of Japan through the Kakehashi River. The frequent floods were occurred especially after subside of farmland by the Fukui earthquake in 1948. The local residents and communities have been strongly making an appeal for the consolidation and improvement of drainage around farmland (Hokuriku Regional Agricultural Administration Office, 1970).

A reclamation project, "Kaga three lagoons reclamation project" was planned to improve the lowland area drainage and to increase the productivity of surrounding farmland. The reclamation work was undertaken to open a new channel (Shinbori River, Fig. 5-1) to divert floodwaters from the related basins into the sea and the reclamation of Imae-gata and 2/3 of Shibayama-gata during 1954–1969 (Shigemi et al., 1966; Hokuriku Regional Agricultural Administration Office, 1970). Lake Kiba-gata was left untouched by reclamation because it plays an important role in irrigation and flood attenuation around the lowland area. However, the reclamation work was carried out in the marshy paddy field around Lake Kiba-gata. Farmland consolidation and the development of flow channels were also conducted. The drainage system was changed following reclamation. The Shibayama-gata water system was separated from the Imae-gata and Kiba-gata systems. The present water flow direction is presented in Fig. 5-1.

This study was conducted to assess reclamation effects such as drainage change on the watershed environment after reclamation in a small and semi-closed lagoon, Lake Kiba-gata. The sedimentation of organic matter in the lagoon was investigated using a sediment core sample collected from the central part of Kiba-gata in June 2012. Organic matter preserved in lake sediments can provide key information related to lacustrine nutrient dynamics as a function of the historical watershed scale land use change and

input of nutrients from the watershed (Meyers, 1994; Meyers and Teranes, 2001). The total organic carbon/ total nitrogen (TOC/TN) ratio, $\delta^{13}C$, and $\delta^{15}N$ are parameters that are useful to ascertain organic matter sources in lakes and lagoons (e.g., Yoshioka et al., 1988; Brenner et al., 1999; Lawson et al., 2004; Das et al., 2008). We measured these parameters to investigate the sedimentary organic matter sources and to assess its variation over time in Lake Kiba-gata.

The objectives of this study were to assess earth surface processes, especially erosion and transport of geo-materials and their effects on aquatic environment by reclamation and consolidation work. The changes in deposition of organic matter from watershed and lakes were identified from lake sediments because of high sensitivity and continuous records for the changes in aquatic environment (Meyers, 1994; Meyers and Teranes, 2001).
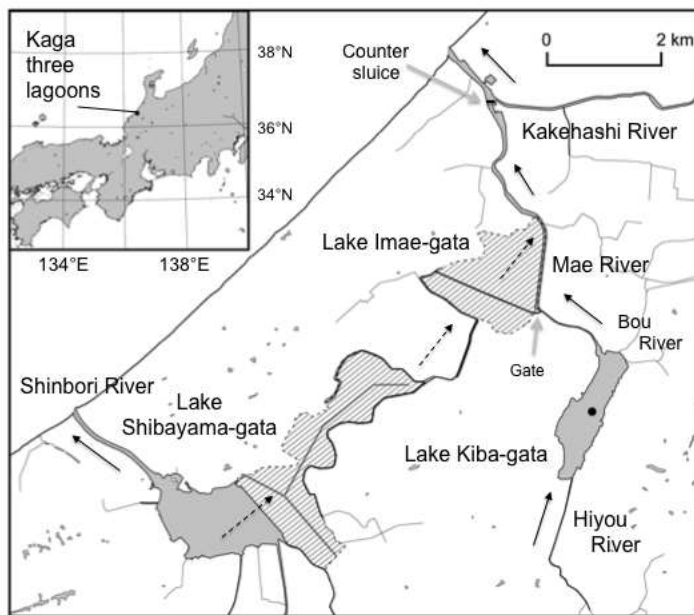
Figure 5-1. Sampling locations around Lagoon Kiba-gata. Reclaimed land is shown as shaded areas. The closed circle in Kiba-gata shows the sampling point of a core sample in this study. Dotted arrows indicate the past water flow direction before the reclamation. Numerical map data are based on Fundamental Geospatial Data provided by the Geospatial Information Authority of Japan, and National Land Numerical Information provided by the Ministry of Land, Infrastructure, Transport and Tourism, Japan.

5.2. Materials and methods

5.2.1. Sampling location

Lake Kiba-gata is located in the Kaga area of Ishikawa Prefecture in Japan (Fig. 5-1). Lake Kiba-gata has a mean water depth of 1.7 m, area of 1.14 km^2, and water volume of 1.7×10^4 m^3. The watershed area is 38 km^2. The chemical oxygen demand (COD) concentration was at a maximum, 11 mg l^{-1} in 1990, and has remained about double the national standard of this lake class (3 mg l^{-1}) over the last decade (Komatsu City Government, 2014). Suspended solid concentration was 12–21 mg l^{-1}, and total nitrogen and phosphorous were 0.92–1.3 mg l^{-1} and 0.066–0.11 mg l^{-1}, respectively in 2000–2011 (Komatsu City Government, 2014). Bottom sediments consist of silt, but the inflow area of Hiyou River and Bou River is sandy sediments (Sekito et al., 2006).

5.2.2. Sampling and pretreatment

A sediment core was obtained at the central part of the lagoon, to avoid the direct influence of river systems, with a gravity core sampler (HR-type; Rigo Co., Japan) on 11 June in 2012 (Fig. 5-1). The sediment core sample was sliced into 1 cm interval subsamples. To study the sources of lake sedimentary organic matter, we collected suspended solids in the surface waters in the central part of Lake Kiba-gata using a plankton net sampler (NXX17, mean mesh size of 0.072 mm) on 6 June 2013. We also collected the suspended solids using continuous flow centrifugation (Nagao et al., 2005) on 23 July and 2 October 2014. The sediment and suspended solid samples were freeze-dried and ground in an agate mortar.

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5.2.3. Analytical methods

Water content of the sediment samples was estimated from the loss of water after the freeze-drying operation. The grain size distribution was measured using a laser diffraction particle size analyzer (SALD-2200; Shimadzu Corp., Japan). The freeze-dried and ground samples were treated with 1M HCl to remove inorganic carbon for analyses of total organic carbon (TOC), total nitrogen (TN), and stable carbon and nitrogen isotope ratios. The TOC and TN contents were measured using the elemental analyzer (2400 Series II; PerkinElmer Inc., USA). The precision of TOC and TN analyses was, respectively, ± 0.009% and ± 0.003%. The stable carbon and nitrogen isotope ratios were analyzed with mass spectrometers of three types (IsoPrime EA, GV Instruments Ltd., UK; DLTA plus and DELTA V Advantage, Thermo Fisher Scientific Inc., USA). Stable carbon and nitrogen isotope ratios are shown as $\delta^{13}C$ values relative to VPDB and $\delta^{15}N$ relative to atmospheric N_2 as:

$$\delta^{13}C, \delta^{15}N = (R_{sample}/ R_{standard} - 1) * 1000$$

where R_{sample} and $R_{standard}$ respectively denote the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ atomic ratios of sample and international standard. The reference materials USGS40 ($\delta^{13}C_{VPDB} = -26.39‰$, $\delta^{15}N_{air} = -4.52‰$), L-Alanine ($\delta^{13}C_{VPDB} = -19.6‰$, $\delta^{15}N_{air} = 1.6‰$), ANU-sucrose ($\delta^{13}C_{VPDB} = -10.80‰$), IAEA-N1 ($\delta^{15}N_{air} = 0.4‰$), and IAEA-N2 ($\delta^{15}N_{air} = 20.3‰$) were used to calibrate the measurement results. The precision of $\delta^{13}C$ and $\delta^{15}N$ analyses was, respectively, ± 0.18‰ and ± 0.31‰.
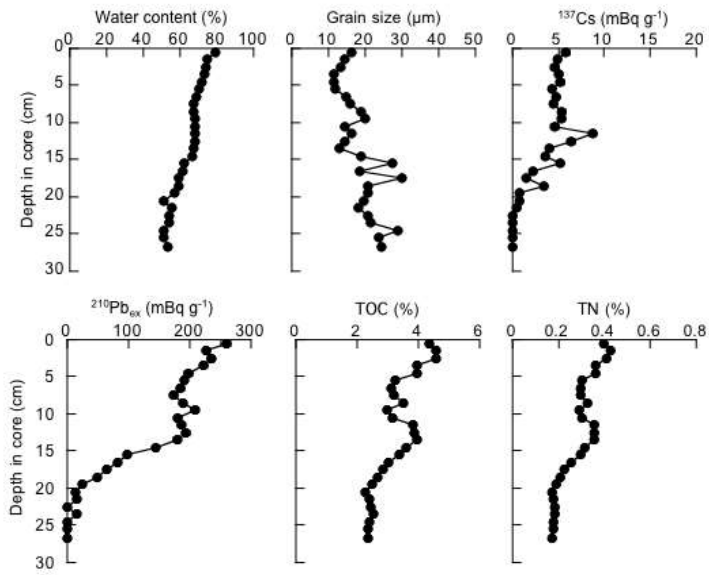
Figure 5-2. Water content, grain size, ^{137}Cs and excess ^{210}Pb radioactivity, total organic carbon (TOC) and total nitrogen (TN) contents of a sediment core sample from Kiba-gata.

The ^{210}Pb and ^{137}Cs radioactive concentrations were measured to estimate the sedimentation rate of the core. First, 10 g of powdered samples was pressed into discs (0.5 cm thickness, 5.0 cm diameter) using a hydraulic press and sealed in a plastic bag. After establishing the radioactive equilibrium between ^{222}Rn and ^{214}Pb (about one month), the activity concentrations of ^{210}Pb (46.5 keV), ^{214}Pb (352 keV), and ^{137}Cs (661.6 keV) were determined using gamma-ray spectrometry with a Ge detector (LO-AX-51370-20; Ortec, USA). The activity of excess ^{210}Pb (^{210}Pb$_{ex}$) was estimated by subtracting the activity of ^{214}Pb from that of ^{210}Pb. The sedimentation rate of the cores was then estimated based on the ^{210}Pb$_{ex}$ as a function of mass depth (Krishnaswamy et al., 1971; Appleby and Oldfield, 1978) and obtained by fitting results of the constant rate of supply (CRS) model (Kanai et al., 1995). The sediment layer dating was carried out from the estimated sedimentation rate.

5.3. Sedimentary physical properties and organic matter

Profiles of basic parameters are presented in Fig. 5-2. The water content decreases from 79% to 51% with depth in the core. Grain size increased with core depth from 11.5 to 24.5 μm, although four weak peaks are apparent. ^{137}Cs activity reaches a maximum at depth of 11–12 cm, but the radioactivity is almost constant with depth in the surface layer. This vertical profile is not a general trend and affected by changes in inflow flux of ^{137}Cs from the watershed. Therefore, we do not use ^{137}Cs profile to estimate the sedimentation rate. ^{210}Pb$_{ex}$ activity decreases concomitantly with increasing depth from 0 to 9 cm, constant at 9–12 cm depth and also decreases with depth interval of 12 to 22 cm. The sedimentation rate was estimated as 0.11–0.16 g cm^{-2} yr^{-1} (average 0.14 ± 0.02 g cm^{-2} yr^{-1}) at depths of 0–9 cm, 0.07–0.09 g cm^{-2} yr^{-1} (average 0.08 ± 0.01 g cm^{-2} yr^{-1})

at 9–12 cm and 0.04–0.06 g cm^{-2} yr^{-1} (average 0.05 ± 0.01 g cm^{-2} yr^{-1}) at depths of 12–22 cm by the CRC model. The sedimentation rate is changed at the three depth intervals. Total organic carbon (TOC) contents were 2.34–2.36% at depth of 25–27.4 cm and 4.37–4.59% in the surface layer of 0–3 cm. The profile of TOC content varies with depth and is similar variation pattern with ^{210}Pbex and total nitrogen (TN) content.

5.4. Accumulation of organic matter and its characteristics

The parameters of sedimentary organic matter are depicted in Fig. 5.3. The organic matter flux was estimated using the sedimentation rate and organic carbon content in the sediment core. The flux increased, respectively, from 1.13 to 2.26 mgC cm^{-2} yr^{-1} and from 2.66 to 7.46 mgC cm^{-2} yr^{-1} in two sedimentation steps during 1978–1989 and 1989–2012. The rate of increase at the present interval is three times higher than that in the past. These results suggest that eutrophication and organic sedimentation occurred after the reclamation. From the variation trend, the TOC flux is divisible into four time intervals: A, increase trend in 1989–present (2012, collection of the sediment core); B, constant during 1974–1984; C, increase trend in 1968–1903, D, almost constant from 1889 into the past.

The C/N ratio, δ^{13}C, and δ^{15}N values also vary among these sediment layer intervals. The C/N ratio almost constant (10.7 to 11.0) with depth during period A, but decreased from 12.7 to 10.9 during period C. During periods B and D, the C/N ratio was almost constant as 10.5 ± 0.2 in period B and 13.4 ± 0.2 in period D. This range of C/N ratio corresponds to the mid-range of values between those of algae and terrestrial plants (Meyers, 1994). The mixture of both sources varies with each time interval due to the

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changes in primary production of phytoplankton and the supply of terrestrial plants from the lake watershed.

Sedimentary organic matter in Lake Kiba-gata exhibited $\delta^{13}C$ values of -27.5‰ to -26.0‰. The $\delta^{13}C$ value increases slightly in magnitude from -26.4‰ to -26.0‰ and from -27.2‰ to -26.3‰ in periods A and C, respectively. In periods B and D, the $\delta^{13}C$ value is almost constant such as -26.3 ± 0.09‰ in period B and -27.2 ± 0.1‰ in period D. The $\delta^{13}C$ value was -27.5‰ for the TOC collected by the plankton net (7.65% of TOC and 9.1 of C/N ratio) on 6 June 2013, and was -22.8‰ to -23.5‰ for the TOC including phytoplankton (21.6–27.0% of TOC and 5.1–5.9 of C/N ratio) on 23 July and 2 October 2014, respectively, in Lake Kiba-gata. These values are more enriched than those generally reported (-30 to -25‰) for other lakes (Yoshioka et al., 1988; Meyers, 1994; Meyers and Lallier-Vergès, 1999; Vuorio et al., 2006). The $\delta^{13}C$ values of TOC shifted from -27.5‰ in June to -22.8‰ at the end of July in Lake Kiba-gata. Eutrophic lakes generally have great potential to exhibit large spatial and temporal variations in $\delta^{13}C$ of phytoplankton because of dense algae blooms (Mizutani and Wada, 1982; Goericke et al., 1994). The pH of Lake Kiba-gata surface water was 6.7–9.5 during the year and was maximal during spring–summer (Sawada et al., 1988). The vertical distribution of pH exhibits decreasing values with depth (Sawada et al., 1988). A similar trend was observed at the monitoring station in the center of Lake Kiba-gata in 2013 (Nagao, unpublished data). This fact reflects that the phytoplankton growth increases in the surface depth layer during spring–summer. Therefore, the shift of $\delta^{13}C$ values of POC in surface lake waters during spring–summer is considered to be the effect of growth of phytoplankton in the small lake, Kiba-gata. The upper Kakehashi River

exhibited $\delta^{13}C$ of -27.5‰ on 30 September 2014. Results indicate that the current organic matter characteristics in the Kiba-gata sediment shifted due to phytoplankton properties.

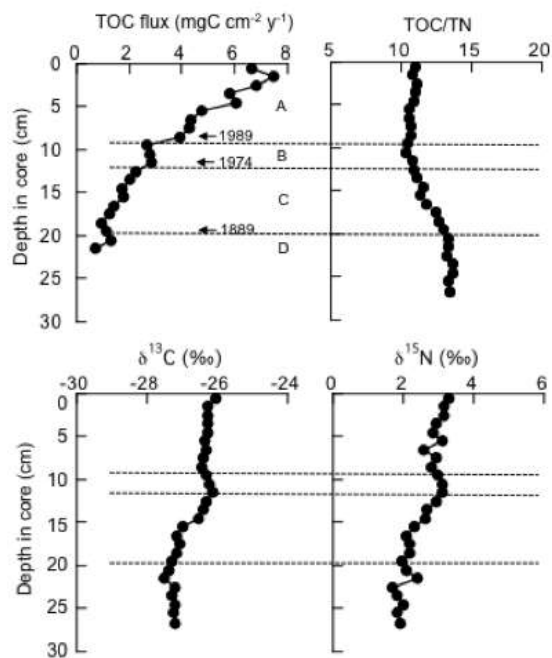**Figure 5-3.** Total organic carbon (TOC) flux, TOC/total nitrogen (TN) ratio, δ^{13}C of organic mater and δ^{15}N of total nitrogen as a function of core depth for a sediment core sample collected from the central part of Lake Kiba-gata.

The $\delta^{15}N$ value of total nitrogen in the Kiba-gata sediment whole core ranges from 1.82‰ to 3.30‰. The $\delta^{15}N$ value slightly increased from 2.81‰ to 3.30‰ and from 2.17‰ to 2.92‰, respectively, during periods A and C. In periods B and D, the $\delta^{13}C$ value remains almost constant (3.06 ± 0.07‰ in period B and 1.97 ± 0.23‰ in period D). The $\delta^{15}N$ value was 6.64‰ for the suspended solids collected using a plankton net on 6 June, 2013 and was 2.33‰ on 23 July 2014 and 5.43‰ on 23 July and 2 October 2014 for the suspended solids including phytoplankton. The trend resembles that of the $\delta^{13}C$ value of sedimentary organic matter. Despite the very real potential for digenetic biasing of the initial source character of organic matter, several parameters (C/N ratio, $\delta^{13}C$, and $\delta^{15}N$ values) that describe composition of bulk organic matter provide reliable evidence of its sources (Meyers, 1994; Meyers and Lallier-Vergès, 1999).

5.5. Effects of reclamation and land consolidation

The drastic changing point might be related to the reclamation and land consolidation that occurred in Lake Imae-gata and Shibayama-gata during 1954–1969. Hydrological conditions were changed because of land reclamation of Shibayama-gata and Imae-gata, paddy field arrangement around Lake Kiba-gata and the construction of the Mae River gate (Fig. 5-1). The Cl concentration in surface waters was 27–30 mg l^{-1} for Kiba-gata and 30 mg l^{-1} for Shibayama-gata in 1960 (Kanetsuna, 1973). However, in 1987, it was as slightly lower value such as 12–22 mg l^{-1} (Sawada et al., 1988) and 12–13 mg l^{-1} in July–December 2014 measured in this study. Rainfall is almost similar value in 1960 (2548 mm) and 2014 (2635 mm) (Japan Meteorological Agency, 2014). Therefore, dilution of lake waters by rain events is negligible. This reflects the decreased inflow of

brackish water from the Kakehashi River because of reclamation and the set up of counter slice at the junction of the Kakehashi River (Fig. 5-1). Increased organic carbon contents in present sediments commonly derive from human and industrial activities, reflecting the eutrophic status of a system (e.g. Meyers, 1994).

Aquatic environmental changes were also observed for other water properties. The level of transparency tended to drop from 4.8 m on average in October and November 1910 (Ishikawa Prefectural Fisheries Experimental Station, 1912), 1.3–2.4 m in 1930 (Kawa, 1969) to 0.5 m in 1987 (Sawada et al., 1988). Aquatic plants such as water caltrops *(Hydrilla verticllate, Potamogeton crispus*) and water snowflake (*Nymphoidas peltata, Trapa japonica*) in Lake Kiba-gata disappeared in 1980 (Editorial Committee of Kiba Town History, 2009). Also, the COD concentration reached a maximum value in 1990 (Komatsu City Government, 2014). The surface lagoon water pH was 6.6–7.8 in June 1974 and September 1976 (Sumita and Watanabe, 1979), but 6.7–9.5 on average 8.5 during 1987. The suspended solids in the upper of Kakehashi River water exhibited 12.8 for the C/N ratio, –27.5‰ for $\delta\,^{13}$C of organic matter, and 3.38‰ for $\delta\,^{15}$N. However, the suspended solids in the surface lake waters from Kiba-gata were 5.1–9.1 for the C/N ratio, –27.5‰ to –22.8‰ for $\delta\,^{13}$C of organic matter, and 2.33–6.64‰ for $\delta\,^{15}$N value. The C/N ratio, $\delta\,^{13}$C, and $\delta\,^{15}$N of the recent sediment samples have shifted to those of lake suspended solids including phytoplankton rather than those of terrestrial plants in the upper part of river. The results indicate that primary productivity in the lake is increasing over time and that the contribution of organic matter has shifted to phytoplankton. This inference is consistent with the variation of TOC flux and characteristics of organic matter recorded in the sediment core after "the Kaga three

lagoon reclamation project" and the land consolidation work around Lake Kiba-gata during 1954-1969.

5.6. Conclusions

Impacts of human activity on water quality, transport and deposition in aquatic environments are particularly strong in small, semi-closed, and closed lakes. This study specifically examined organic matter sedimentation in a lake during the last hundred years, before and after a reclamation project conducted during 1954–1969. Organic matter content and quality analysis provide information of the changes in erosion, deposition and water quality by reclamation and land consolidation. A sediment core was collected at the central part of Lake Kiba-gata, a semi-closed and small lake in June 2012. The organic matter flux increased during 1978–2012 in two sedimentation steps during 1978–1989 and 1989–2012. The flux in the later period increased to twice that of the former period. The C/N ratio, δ^{13}C, and δ^{15}N values show similar variation. The parameters in 1989–2012 are lower in C/N ratio and higher in δ^{13}C and δ^{15}N than those in 1978–1989. The inflexion point is related to the reclamation and land consolidation of Lake Imae-gata and Shibayama-gata during 1954–1969, as indicated by changes in hydrological conditions. These results indicate that deposition of organic matter supplied from forest and paddy filed increases by the increase in erosion. The primary productivity in the Lake Kiba-gata is also increasing and the organic matter contribution to the sediment has shifted to phytoplankton because of the increased residence time of water as a result of reclamation and land consolidation, though organic matter supplied from forest and paddy filed increases with increasing the erosion. The organic matter

fluxes recorded in the sediment core is continuous loading record in lake watershed and can use basic data set to access positive and negative consequences, that is, the reclamation and consolidation effects on earth surface processes and water quality deterioration in lake environment. These studies may be available to assess qualitatively the relationship between environmental loading effects and changes in watershed environment including local communities and occupation such as agriculture and forestry in some time intervals by using sediment core records.

Chapter 6.

Conclusions

Lake Kiba is located at Ishikawa Prefecture in Japan and is a small, shallow and semi-closed lake environment. The chemical oxygen demand (COD) concentration was at a maximum, 11 mg l-1 in 1990, corresponding to the second worst in Japan. It has remained about double the national standard of this lake class (3 mg l^{-1}) during a last few decades. Aim of this study is to understand past and present situation of organic pollution and its controlling factors. At last 100 years, we analyzed that organic matter flux increased from 1.1 to 2.3 and from 3.9 to 7.5 mgC cm^{-2} y^{-1}, respectively, during 1903–1974 and 1989–2012, although it was similar with the flux recorded for 1974–1989 following reclamation. The C/N ratio, δ^{13}C and δ^{15}N also changed during these time intervals. These results indicate that the primary production is increasing with time and the recent contribution of phytoplankton to productivity has exceeded the level of past contribution. During 2014–2016, monitoring study was conducted for lake water environments. Strong positive correlation was found between the COD concentration and physicochemical parameters (water temperature, pH, and chlorophyll-a concentration). Results indicate that the COD variation is controlled by phytoplankton activity within the lake. A positive correlation exists with particulate and dissolved COD concentrations. To understand more detail variation mechanisms, we focused on dynamics of particulate and dissolved organic matter in lake water. Particulate organic carbon (POC) concentration ranged from 0.44 to 5.01 mg l^{-1}. δ^{13}C and Δ^{14}C values were −30.3 to −22.8 ‰ and −156 to −33 ‰, respectively. The POC was consistently depleted for ^{14}C and an averaged Δ^{14}C value of −81 ± 37‰. The carbon isotopes showed seasonal variation with higher in summer and positive correlations with POC content. The results suggest that the variation in POC characteristics is controlled by a mixture

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of two endmembers, organic matter produced by phytoplankton activity within the lake and the watershed organic matter. Dissolved organic carbon (DOC) concentrations were also higher in summer and had strongly relations with water temperature and water pH. Fulvic-like materials, which is refractory properties and major component of organic matter, was a good correlation with DOC concentration. However, maximum fluorescence position in spring-summer shifted to shorter excitation wavelength rather than that of autumn-winter. The sources of fulvic-like materials are different from the spring-summer and autumn-winter seasons. These results of this study provide basic and useful information of understanding organic pollution in shallow lakes and lagoons.

Acknowledgements

References

Abbott, M. B., Stafford Jr, T. W., 1996. Radiocarbon of geochemistry of modern and ancient arctic lake systems, Baffin Island, Canada. Quaternary Research 45, 300-311.

Abelho, M., Graca M. A. S., 1998. Litter in a first-order stream of a temperate deciduous forest (Margaraca Forest, central Portugal). Hydrobiologia 386, 147–152.

Abranthes, N., Antunes, S.C., Pereira, M. J., 2006. Seasonal succession of cladocerans and phytoplankton and their interactions in a shallow eutrophic lake (Lake Vela, Portugal). Acta Oecologica 29, 54–64.

Abril, G., Nogueira, M., Etcheber, H., Cabeçadasm, G., Lemaire, E., Brogueira, M. J, 2002. Behaviour of organic carbon in nine contrasting European estuaries. Estuarine, Coastal and Shelf Science 54, 241–262.

Aitkenhead, J.A., McDowell, W. H., 2000. Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochemical Cycles 14, 127–38.

Albéric, P., Jézéquel, D., Bergonzin, L., Chapron, E., Viollier, E., Massault, M., Michard, G., 2013. Carbon cycling and organic radiocarbon reservoir effect in a meromictic crater lake (Lac Pavin, Puy-de-Dôme, France). Radiocarbon 55, 1029-1042.

Allison, D.B., Stramski, D., Mitchell, B. G., 2010. Seasonal and interannual variability of particulate organic carbon within the Southern Ocean from satellite ocean color observations. Journal of Geophysical Research 115, C06002. doi:10.1029/2009JC005347.

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Almgren, T., Josefsson, B., Nyquist, G., 1975. A fluorescence method for studies of spent sulfite liquor and humic substances in seawater. Analytica Chimica Acta 78, 411–422.

Amado, A. M., Cotner, J. B., Suhett, A.L., De Assis Esteves, F., Reinaldo Luiz Bozelli, R.L., Farjalla, V. F., 2007. Contrasting interactions mediate dissolved organic matter decomposition in tropical aquatic ecosystems. Aquatic Microbial Ecology 49, 25–34.

Andreev, A. A., Klimanov, V. A., 2000. Quantitative Holocene climatic reconstruction from Arctic Russia. Journal of Paleolimnology 24, 81–91.

Andrews, J. E., Greenaway, A. M., Dennis, P. F., 1998. Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. Estuarine, Coastal and Shelf Science 46, 743-756.

Aoki, S., Ohara, S., Kimura, K., Mizuguchi, H., Fuse, Y., Yamada, E., 2008. Characterization of fluorophores released from three kinds of lake phytoplankton using gel chromatography and fluorescence spectrophotometry. Analytical Science 24, 1461–1467.

Appleby, P. G., Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. Catena 5, 1–8.

Baker, A., 2002. Fluorescence excitation - emission matrix characterization of river waters impacted by a tissue mill effluent. Environmental Science and Technology 36, 1377-1382.

Baker, A., M. Curry., 2004. Fluorescence of leachates from three contrasting landfills. Water Research 38, 2605-2613.

Baker, A., Bolton, L., Newson, M., Spencer, R. G. M. 2008. Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment. Hydrological Processes 22, 2325-2336.

Bakker, E.S., Sarneel, J. M., Gulati, R. D., Liu, Z., Donk, E., 2013. Restoring macrophyte diversity in shallow temperate lakes: biotic versus abiotic constraints. Hydrobiologia 710, 23-37.

Barałkiewicz, D., Siepak, J., 1994a. Total organic carbon (TOC) – parameter of organic pollutants in natural waters. Materials of the Committee of Water Analysis of the Committee of Analytical Chemistry Pan, Warsaw (in Polish).

Barałkiewicz, D., Siepak, J. 1994b. The contents and variability of TOC, POC and DOC concentration natural waters. Polish Journal of Environmental Studies 2, 15-18.

Bellinger, E. G., Sigee, D. C., 2010. Freshwater Algae: Identification and Use as Bioindicators, John Wiley & Sons, Ltd, Chichester, UK. doi: 10.1002/9780470689554.fmatter.

Benfield, E. F., 1997. Comparison of litterfall input to streams. Journal of the North American Benthological Society 16, 104–108.

Beramendi-Orosco, L., Gonzalez-Hernandez, G., Martinez-Jurado, A., Martinez-Reyes, A., Garcia-Samano, A., Villanueva-Diaz, J., Santos-Arevalo, F. J., Gomez-Martinez, I., Amador-Muñoz, O., 2015. Temporal and spatial variations of atmospheric radiocarbon in the Mexico City metropolitan area. Radiocarbon 57, 363-375.

Bernát, N., Köpcke, B., Yasseri, S., Thiel, R., Wolfstein, K., 1994. Tidal variation in bacteria, phytoplankton, zooplankton, mysids, fish and suspended particulate matter in the turbidity zone of the Elbe estuary; interrelationships and causes. Netherlands Journal of Aquatic Ecology 28, 467–476.

Biddanda, B and Benner, R., 1997. Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton. Limnology and Oceanography 42, 506–518.

Boutton, T. W., 1991. Stable carbon isotope ratios of natural materials: II. Atmospheric, terrestrial, marine, and freshwater environments. In: Coleman, D.C., Fry, B. (eds.), Carbon Isotopes Techniques. Academic Press, San Diego, 173-185. http://dx.doi.org/10.1016/B978-0-12-179730-0.50016-3.

Brenner, M., Whitmore, T. J, Curtis, J. H., Hodell, D. A., Schelske, C. L., 1999. Stable isotope (δ^{13}C and δ^{15}N) signatures of sedimented organic matter as indicators of historic lake trophic state. Journal of Paleolimnology 22, 205–221.

Bronk, D. A., 2002. Dynamics of DON. In: Hansell, D. A., Carlson, C. A (eds.) Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, San Diego, 153–249.

Brun, G. L., Milburn, D. L. D., 1977. Automated fluorescence determination of humic substances in natural water. Analytical Letters 10, 1209–1219.

Brzezinski, M. A., 1985. The Si: C: N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. Journal of Phycology 21, 347–357.

Buckau, G., Antinger, R., Geyer, S., Wolf, M., Fritz, P., Kim, J. I., 2000. Groundwater

in situ generation of aquatic humic and fulvic acid and the mineralization of sedimentary organic carbon. Applied Geochemistry 15, 819–832.

Buick, R., 2008. When did oxygenic photosynthesis evolve? When did oxygenic photosynthesis evolve? Philosophical Transactions of Royal Society B, 363, 2731–2743.

Bunn, S., Boon, P., 1993. What sources of organic carbon drive food webs in Billabongs? A study based on stable-isotope analysis. Oecologia 96, 85–94.

Burdige, D. J., 2007. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chemical Reviews 107, 467–485.

Caraco, N., Cole, J., 2004. When terrestrial organic matter is sent down the river: importance of allochthonous C inputs to the metabolism in lakes and rivers. In: Polis, G.A., Power, M.E., Huxley, G.R. (eds.), Food Webs at the Landscape Level. University of Chicago Press, 301–316.

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

Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., Smith, V. H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, 559–568.

Carrasco, N. K., Perissinottoa, R., Miranda, N. A. F., 2007. Effects of silt loading on the feeding and mortality of the mysid Mesopodopsis africana in the St. Lucia Estuary, South Africa. Journal of Experimental Marine Biology and Ecology 352, 152–164.

Casareto, B. E., Niraula, M. P., Suzuki, Y., 2012. Dynamics of organic carbon under different inorganic nitrogen levels and phytoplankton composition. Estuarine, Coastal and Shelf Science 102-103, 84-94.

Chen, R. F., Gardner, G. B., 2004. High-resolution measurements of chromophoric dissolved organic matter in the Mississippi and Atchafalaya River plume regions. Marine Chemistry 89, 103–125.

Chen, X., Chuai, X., Yang, L., Zhao, H., 2012. Climatic warming and overgrazing induced the high concentration of organic matter in Lake Hulun, a large shallow eutrophic steppe lake in northern China. Science of the Total Environment 431, 332–338.

Chiba Prefectural Government, List of public water quality, results of water quality, http://www.pref.chiba.lg/jp/suiho/kasentou/koukyouyousui/data/ichiran-koshou.html (2016.12.1 accessed)

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

Cifuentes, L. A., Forgel, M. L., Pennock, J. R., Sharp, J. H., 1989. Seasonal variations in the stable nitrogen isotope ratio of ammonium in the Delaware Estuary. Geochimica Cosmochimica Acta 53, 2713-2721.

Cloern, J. E., Canuel, E. A., Harris, D., 2002. Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. Limnology and Oceanography 47, 713–729.

Coble, P. G., 1990. Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy. Nature 348, 432-435.

Coble, P. G., Schultz, C. A., Mopper, K., 1993. Fluorescence contouring analysis of DOC intercalibration experiment samples: a comparison of techniques. Marine Chemistry 41, 173-178.

Coble, P. G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. Marine Chemistry 51, 325-346.

Coble, P. G., 2007. Marine optical biogeochemistry: the chem- istry of ocean color. Chemical Reviews 107: 402–418.

Dai, K.O., David, M., Vance, G., 1996. Characterization of solid and dissolved carbon in a spruce-fir Spodosol. Biogeochemistry 35, 339–365 .

Das, B., Nordin, R., Mazumder A., 2008. An alternative approach to reconstructing organic matter accumulation with contrasting watershed disturbance histories from lake sediments. Environmental Pollution 155, 117–124.

David, V., Sautour, B., Chardy, P., Leconte, M., 2005. Long-term changes of the zooplankton variability in a turbid environment: The Gironde Estuary (France). Estuarine, Coastal and Shelf Science 64, 171–184.

David, V., Sautour, B., Galois, R., Chardy, P., 2006. The paradox high zooplankton biomass-low vegetal particulate organic matter in high turbidity zones: what way for energy transfer? Journal of Experimental Marine Biology and Ecology 333, 202–218.

Doi, H., Zuykova, E. I., Kikuchi, E., Shikano, S., Kanou, K., Yurlova, N., Yadrenkina, E., 2006. Spatial changes in carbon and nitrogen stable isotopes of the plankton food web in a saline lake ecosystem. Hydrobiologia 571, 395-400.

Dolenec, T., Vokal, B., Dolenec, M., 2005. Nitrogen-15 signals of anthropogenic nutrient loading in Anemonia sulcata as a possible indicator of human sewage impacts on marine coastal ecosystems: a case study of Pirovac Bay and the Murter Sea (Central Adriatic). Croatica Chemica Acta 78, 593-600.

Druon, J. N., Mannino, A., Signorini, S., McClain, C., Friedrichs, M., Wilkin, J., Fennel, K., 2010. Modeling the dynamics and export of dissolved organic matter in the Northeastern US continental shelf. Estuarine, Coastal and Shelf Science 88, 488–507 .

Duan, S., Bianchi, T. S., 2007. Particulate and dissolved amino acids in the lower Mississippi and Pearl Rivers (USA). Marine Chemistry 107, 214–229.

Editorial Committee of Kiba Town History (ed.), 2009. Kiba Choshi: Shouwa 34 nenn~ (Kiba Town History: 1959~). Kiba Town Community Center.

Egeberg, P. K., Alberts, J. J., 2002. Determination of hydrophobicity of NOM by RP-HPLC, and the effect of pH and ionic strength. Water Research 36, 4997-5004.

Eggleton, J., Thomas, K.V., 2004. A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environment International 30, 973–980.

Environmental Cooperation Office, Global Environmental Bureau, Ministry of the Environment, Manual of measures against Lake Eutrophication (2010) https://www.env.go.jp/earth/coop/coop/document/mie2_e/contents.html

(2016.11.14 accessed).

Faganeli, J., Malej, A., Pezdic, J., Malacic, V., 1988. C: N: P ratios and stable C-isotopic ratios as indicators of sources of organic-matter in the Gulf of Trieste (northern Adriatic). Oceanologica Acta 11, 377–382.

Fellman, J.B., Hood, E., Spencer, R.G.M., 2010. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: a review. Limnology Oceanography 55, 2452–2462.

Filstrup, C. T, Scott, J. T., Lind, O. T., 2009. Allochthonous organic matter supplements and sediment transport in a polymictic reservoir determined using elemental and isotopic ratios. Biogeochemistry 96, 87-100.

Finlay, J. C., Kendall, C., 2007. Stable isotope tracing of temporal and spatial variability in organic matter sources to freshwater ecosystems. In: Michener, R., Lajtha, K. (eds.), Stable Isotopes in Ecology and Environmental Science, 2nd edition. Blackwell, Oxford, 283-333.

Fiordelmondo, C., Pusceddu, A., 2004. Short-term response of benthic bacteria and nanoflagellates to sediment resuspension: an experimental study. Chemistry and Ecology 20, 107–121.

Fogel. M. L., Cifuentes, L. A.1991. Isotopefractionation during primary production. In (M. H. Engel& S.A. Macko, Eds) Organic Geochemistry. New York, Plenum Press. doi: 10.4319/lo.1994.39.6.1500.

Fogel, M. L., Cifuentes, L. A., Velinsky, D. J., Sharp, J. H., 1992. Relationship of carbon availability in estuarine phytoplankton to isotopic composition. Marine

Ecology Progress Series 82, 291–300.

Fogel, M. L., Cifuentes, L. A., 1993. Isotope fractionation during primary production. In: Engel, M.H., Macko, S.A. (eds.), Organic Geochemistry. Plenum Press, New York 73–98.

Fogg, G. E., 1983. The ecological significance of extracellular products of phytoplankton photosynthesis. Botanica Maria 26, 3–14.

Förstner, U., Wittmann, G. T. W., 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin. 486. doi: 10.1002/jobm.19810210712.

Fröberg, M., Berggren, K. D., Hagedorn, F., 2007. The contribution of fresh litter to dissolved carbon leaching from a coniferous forest floor. European Journal of Soil Science 58, 108–114.

Fry, B., Sherr, E. B., 1984. $\delta^{13}C$ measurements as indicators or carbon flow in marine and freshwater ecosystems. Contributions to Marine Science 27, 13–47.

Fry, B., 1996. $^{13}C/^{12}C$ fractionation by marine diatoms. Marine Ecology Progress Series 134, 283-294.

Fu, P., Mostofa, K.M.G., Wu, F.C., Liu, C.Q, Li, W., Liao, H., Wang, L., Wang, J., Mei, Y., 2010 Excitation- emission matrix characterization of dissolved organic matter sources in two eutrophic lakes (Southwestern China Plateau). Geochemical Journal 44, 99–112 .

Gao, X., Yang, Y., Wang. C., 2012. 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.

Gasparini, S., Castel, J., Irigoien, X., 1999. Impact of suspended particulate matter on

egg production of the estuarine copepod, Eurytemora affinis. Journal of Marine Systems 22, 195–205.

Ghassemi, M., Christman, R. F., 1968. Properties of the yellow organic acids of natural waters. Limnology and Oceanography 13, 583–597.

Goericke, P., Montoya, J. P., Fry, B., 1994. Physiology of isotopic fractionation in algae and cyanobacteria. In: Lajth, K.M., Michener, R.H. (eds.), Stable Isotopes in Ecology and Environmental Science. Blackwell, Oxford, 187–221.

Gomez, B., Trustrum, N. A., Hicks, D.M., Rogers, K.M., Tate, K.R., 2003. Production, storage, and output of particulate organic carbon: Waipaoa River basin, New Zealand. Water Resources Research 39, doi:10.1029/ 2002WR001619.

Gosh, K., Schnitzer, M., 1980. Fluorescence excitation spectra of humic substances. Canadian Journal of Soil Science 60, 373–379.

Graham, L., Graham, J., Wilcox, L., 2009. Algae, 2nd ed., Benjamin Cumming (Pearson), San Francisco, CA.

Grey., Jonathan., Jones, R.I., Sleep, D., 2001. Seasonal changes in the importance of the source of organic matter to the diet of zooplankton in Loch Ness, as indicated by stable isotope analysis. Limnology and Oceanography 46, 505–513.

Gu, B., Schelske, C. L., 2004. Extreme ^{13}C enrichments in a shallow hypereutrophic lake: implications for carbon cycling. Limnology and Oceanography 49, 1152–1159.

Gu, B., Chapman, A. D., Schelske, C. L., 2006. Factors controlling seasonal variations in stable isotope composition of particulate organic matter in a soft water eutrophic lake. Limnology and Oceanography 51, 2837–2848.

Guangjia, J., Ronghua, M., Steven, A. L., Hongtao, D., Wen. S., Weixu, C., Chuguang, H., Jie, Y., Wei, Y., 2015. Remote sensing of particulate organic carbon dynamics in a eutrophic lake (Taihu Lake, China). Science of the Total Environment 532, 245–254.

Guo, L., Macdonald, R. W., 2006. Source and transport of terriginous organic matter in the upper Yukon River: evidence from isotope (δ^{13}C, Δ^{14}C and δ^{15}N) composition of dissolved, colloidal, and particulate phases. Global Biogeochemical Cycles 20, GB2011, doi: 10.1029/2005GB002593.

Gupta, G., Sarma, V., Robin, R., Raman, A., Kumar, M. J., Rakesh, M., Subramanian, B., 2008. Influence of net ecosystem metabolism in transferring riverine organic carbon to atmospheric CO_2 in a tropical coastal lagoon (Chilka Lake, India). Biogeochemistry 87, 265-285.

Hansell, D.A. 2002. DOC in the global ocean carbon cycle. In: Hansell, D.A., Carlson, C.A. (eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, San Diego, 685-715.

Hanson, P.C., Bade, D.L, Carpenter, S.R, Kratz, T.K., 2003. Lake metabolism: relationships with dissolved organic carbon and phosphorus. Limnology Oceanography 48, 1112–1119 .

Harris, G. P., 1986. Phytoplankton Ecology: Structure, function and fluctuation, Chapman and Hall, London, 329-372.

Hasegawa, H., Rahman, M. A., Mastuda, T., Kitahara, T., Maki, T., Ueda, K., 2009. Effect of eutrophication on the distribution of arsenic species in eutrophic and mesotrophic lakes. Science of the Total Environment 407, 1418-1425.

Hayakawa, K., Okamoto, T., 2012. New issue- COD increase in the water of Lake Biwa. In Kawanabe, H., Nishino M., Maehata, M. (eds.), Interactions between Nature and People, Springer, Tokyo, 441-446.

Hayashi, M., 2015. Geomorphological seawater of Japanese lagoons with special reference to the Nakaumi-Shinjiko Lakes. Gakujyutsu no Doukou 20, 76-82.

Heathcote, A. J., Downing, J. A., 2012. Impacts of eutrophication on carbon burial in freshwater lakes in an intensively agricultural landscape. Ecosystems 15, 60-70.

Hedges, J. I., Ertel, J. R., Quay, P. D., Grootes, P. M., Richey, J. E., Devol, A. H., Farwell, G. W., Schmitdt, F. W., Salati, E., 1986. Organic carbon-14 in the Amazon River system. Science 231, 1129−1131.

Hedges, J. I., Eglinton, G., Hatcher, P., Kirchman, D. L., Arnosti, C., Derenne, S., Evershed, R. P., Kogel-Knabner, I., de Leeuw, J.W., Littke, R., Michaelis, W., Rullkötter, J., 2000. The molecularly uncharacterized component of nonliving organic matter in natural environments. Organic Geochemistry 31, 945–958.

Henderson, R. K., Baker, A., Parsons, S. A., Jefferson, B., 2008. Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. Water Research 42, 3435–3445.

Henderson, R. K., Baker, A., Murphy, K., Hambly, A., Stuetz, R. M., Khan, S. J., 2009. Fluorescence as a potential monitoring tool for recycled water systems: a review. Water Research 43, 863-881.

Her, N., Amy, G., McKnight, D., Sohn, J., Yoon, Y., 2003. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. Water Research 37, 4295–4303.

Hokuriku Regional Agricultural Administration Office (1970) Report of Reclamation and Construction Work for Kaga Sanko. Kaga Sanko Reclamation Work Office of Hokuriku Regional Agricultural Administration Office. Meiji Publishing Company, Kanazawa.

Holbrook, R. D., Yen J. H., Grizzard, T. J., 2006. Characterizing natural organic material from the Occoquan Watershed (Northern Virginia, US) using fluorescence spectroscopy and PARAFAC. Science of the Total Environment 361, 249-266.

Hongve, D., Riise, G., Kristiansen, J. F., 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water—a result of increased precipitation? Aquatic Science 66, 231–238.

Houser, J. N., Bade, D. L, Cole, J. J., Pace, M. L., 2003. The dual influences of dissolved organic carbon on hypolimnetic metabolism: organic substrate and photosynthetic reduction. Biogeochemistry 64, 247–269.

Hu, L., Hu, W., Zhai, S., Wu, H., 2010. Effects on water quality following water transfer in Lake Taihu, China. Ecological Engineering 36, 471–481.

Hudson, N., Baker, A., Reynolds, D., 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters-a review. River Research and Applications 23, 631-649.

Hudson, N., Baker, A., Ward, D., Reynlds, D. M., Brunsdon, C., Carliell-Marquet, C., Browning, S., 2008. Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An

example from South West England. Science of the Total Environment 391, 149-158.

Hulatt, C.J., Thomas, D.N., Bowers, D.G., Norman, L., Zhang, C., 2009. Exudation and decomposition of chromophoric dissolved organic matter (CDOM) from some temperate macroalgae. Estuarine, Coastal and Shelf Science 84, 147–153.

Hulatt, C. J and Thomas D. N., 2010. Dissolved organic matter (DOM) in microalgal photobioreactors: a potential loss in solar energy conversion? Bioresource Technology 101, 8690–8697.

Hutchinson, G., 1957. A treatise on limnology, 1. Wiley eutrophication of the St Lawrence Great Lakes. Journal of Fisheries Research Board of Canada 29, 1451–1462.

Inbanuma Aquatic Conservation Council, http://www.insuikyo.jp/environment/ (2016.11.30 accessed)

IPCC, 1996. In: Houghton, J.T., Filho, L.G.M., Calander, B.A., Harris, N., Kattenberg, A., Maskell, K. (eds.), Climate Change 1995: The Science of Climate Change. Cambridge University Press, New York.

IPCC, 2013. Climate Change 2013: The physical Science Basis. In: Stocker, T.F., Qin, Plattner, G.K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (eds.). Cambridge University Press, New York.

Ishikawa Prefectural Fisheries Experimental Station, 1912. Report for Water Surface Use Research in Lakes, Lagoons and Bay in Ishikawa Prefecture, Japan. Vol. 1 (Imae-gata and Kiba-gata), Kanazawa.

Ishikawa Prefectural Government, 1986. History of land Improvement in Ishikawa Prefecture, Cultivated Land Construction Division, Department of Agriculture, Forestry and Fisheries of Ishikawa Prefectural Government.

Jackson, T. A., Hecky, R. E., 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. Journal of Fisheries Research Board of Canada 37, 2300–2317 .

Jacoby, J. M., Collier, D. C., Welch, E. B., Hardy, F. J., Crayton, M., 2000. Environmental factors associated with a toxic bloom of Microcystis aeruginosa. Journal of Fisheries Research Board of Canada 57, 231–240.

Japan Meteorological Agency, 2014. http://www.data.jma.go.jp/obd/stats/etrn/index.php. Accessed 17 July 2015

Japan Meteorological Agency, Past weather data, Komatsu observatory data, http://www.data.jma.go.jp/obd/stats/etrn/index.php?prec_no=56&block_no=1324 &year=2015&month=&day=&view=. (2016.11.28 accessed)

Jiang, Y. J., He, W., Liu, W. X., Quin, N., Ouyang, H. L., Wang, Q. M., Kong, X. Z., He, Q. S., Yang, C., Yang, B., Xu, F. L., 2014. The seasonal and spatial variations of phytoplankton community and their correlation with environmental factors in a large eutrophic Chinese lake (Lake Chaohu). Ecological Indicators 40, 58–67.

JIS K 0102, 2010. Japanese Industrial Standard, Testing Methods for Industrial Wastewater. Japanese Standard Association, Tokyo.

Jones, R. I., 1992. The influence of humic substances on lacustrine planktonic food chains. Hydrobiologia 229, 73–91.

Kalle, K., 1966. The problem of the gelbstoff in the sea. Oceanography Marine Biology 4, 91–104.

Kanai, Y., Inouchi, Y., Katayama, H., Saito, Y., 1995. Estimation of sedimentation rate at the lake Suwa in Nagano Prefecture determined by Pb-210 and Cs-137 radioactivities. Bull. Geology Survey of Japan 46, 225–238.

Kanetsu, Y., 1973. On the relation between the plankton and the salinity of the waters in the Hokuriku district, Japan. Japanese Journal of Limnology 34, 24–34.

Karakoç, G., Erkoç, F. Ü., Katırcıoğlu, H., 2003. Water quality and impacts of pollution sources for Eymir and Mogan Lakes (Turkey). Environment International 29, 21–27.

Kasumigaura River Office, Kanto Regional Development Bureau, Ministry of Land, Infrastructure, Transport and Tourism, Water quality data for Kasumigaura, http://www.ktr.mlit.go.jp/kasumi/kasumi00145.html (2016.12.3 accessed).

Kawa, Y., 1969. Imaegata to Imaegatacho no Rekishi (History of Imae-gata and Imae town). Imae Public Hall, Komatsu.

Keaveney, E. M., Reimer, P. J., Foy, R. H., 2015. Young, old, and weathered carbon—part 1: using radiocarbon and stable isotopes to identify carbon sources in an alkaline, humic lake. Radiocarbon 57, 407-423.

Kececioglu, J., Ming, L., Tromp, J., Benner, R., Biddanda, B., Black, B., McCarthy, M., 1997. Abundance, size distribution, and stable carbon and nitrogen isotopic compositions of marine organic matter isolated by tangential-flow ultrafiltration. Marine Chemistry 57, 243–263.

Kendall, C., Silva, S. R., Kelly, V. J., 2001. Carbon and nitrogen isotopic compositions

of particulate organic matter in four large river systems across the United States. Hydrological Processes 15, 1301– 1346.

Khan, N. S., Vane, C. H., Horton, B. P. 2015. Stable carbon isotope and C/N geochemistry of coastal wetland sediments as a sea-level indicator. In: Shennan., Long, A. J., Horton, B. P. (eds.), Handbook of Sea-level Research. John Wiley & Sons Ltd., New York, 295-311.

Kim, C., Nishimura, Y., Nagata, T., 2006. Role of dissolved organic matter in hypolimnetic mineralization of carbon and nitrogen in a large, monomictic lake. Limnology and Oceanography 51, 70–78.

Kim, H. C., Yu, M. J., Han, I., 2006. Multi-method study of the characteristic chemical nature of aquatic humic substances isolated from the Han River, Korea. Applied Geochemistry 21, 1226–1239.

Kindler, R., Siemens, J.A.N., Kaiser, K., et al., 2011. Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. Global Change Biology 17:1167–1185.

Kirk, J., 1976. Yellow substance (Gelbstoff) and its contribution to the attenuation of photosynthetically active radiation in some inland and coastal south-eastern Australian waters. Marine and Freshwater Research 27, 61–71.

Kitis, M., Karanfil, T., Wigton, A., Kilduff, J. E., 2002. Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. Water Research 36, 3834-3848.

Kiyokazu, K., Kurosu, M., Cheng, Y., Tsendeekhuu, T., Wu, Y., Nakamura, T., 2008.

Floristic composition, grazing effects and above-ground plant biomass in the Hulunbeier Grasslands of Inner Mongolia, China. Journal of Ecology and Field Biology 31, 297–307.

Kögel-Knabner, I., Zech, W., Hatcher, P. G., 1988. Chemical composition of the organic matter in forest soils: III the humus layer. Zeitschrift für Pflanzenernährung und Bodenkunde 151, 331–340.

Komatsu City Government, 2014. http://www.city.komatsu.lg.jp/secure/5448/h24kiba_deta.pdf. Assessed 30 August 2014.

Komatsu City Government, Field demonstration for water quality improvement of Lake Kiba by use of the Maekawa slice gate, http://www.city.komatsu.lg.jp/12055.htm (accessed 30 November 2016).

Komatsu City Government, Kibagata, http://www.city.komatsu.lg.jp/3613.html (2016.12.1 accessed).

Komatsu City Government, Research of natural environment and waterside culture in and around Lake Kiba, http://www.city.komatsu.lg.jp/secure/15650/kiba_lake_report.pdf (accessed 30 November 2016).

Komatsu, E., Fukushima, T., Harasawa, H., 2007. A modeling approach to forecast the effect of long-term climate change on lake water quality. Ecology Model 209, 351–366 .

Kopáček, J., Hejzlar, J., Kana, J., Porcal, P., Klementová, S., 2003. Photochemical, chemical, and biological transformations of dissolved organic carbon and its

effect on alkalinity production in acidified lakes. Limnology and Oceanography 48, 106–117.

Kopáček, J., Brzáková, M., Hejzlar, J., Nedoma, J., Porcal, P., Vrba. J., 2004. Nutrient cycling in a strongly acidified mesotrophic lake. Limnology and Oceanography 49, 1202–1213.

Kosten, S., Jeppesen, E., Huszar, V. L. M., Mazzeo, N., van Nes, E. H., Peeters, E. T. H. M., Scheffer, M., 2011. Ambiguous climate impacts on competition between submerged macrophytes and phytoplankton in shallow lakes. Freshwater Biology 56, 1540–1553.

Krishnaswamy, S., Lal, D., Martin, J. M., Meybeck, M., 1971. Geochronology of lake sediments. Earth and Planetary Science Letters 11, 407–414.

Kromkamp, J., Peene, J., Rijswijk, P., Sandee, A., Goosen, N., 1995. Nutrients, light and primary production by phytoplankton and microphytobenthos in the eutrophic, turbid Water Schelde estuary (The Netherlands). Hydrobiologia 311, 9–19.

Krustok, I., Odlare, M., Shabiimam, M.A., Truu, J., Truu, M., Ligi, T., Nehrenheim, E., 2015. Characterization of algal and microbial community growth in a wastewater treating batch photo-bioreactor inoculated with lake water. Algal Research 11, 421-427.

Kufel, L., Kufel, I., 2002. Chara beds acting as nutrient sinks in shallow lakes-a review. Aquatic Botany 72, 249-260.

Kuimei, Q., Xia, L., Yuwei, C., 2016. Effects of water level fluctuation on phytoplankton succession in Poyang Lake, China – A five year study. Ecohydrology and Hydrobiology 16, 175–184.

Kumar, S., Finlay, J., Sterner, R., 2011. Isotopic composition of nitrogen in suspended particulate matter of Lake Superior: implications for nutrient cycling and organic matter transformation. Biogeochemistry 103, 1–14.

Lancelot, C., 1979. Gross excretion rates of natural marine phytoplankton and heterotrophic uptake of excreted products in the southern North Sea, as determined by short-term experiments. Marine Ecology Progress Series 1, 179–186.

Lapierre, J. F., Frenette, J. J., 2009. Effects of macrophytes and terrestrial inputs on fluorescent dissolved organic matter in a large river system. Aquatic Science 71, 15–24.

Laurion, I., Ventura, M., Catalan, J., Psenner, R., Sommarruga, R., 2000. Attenuation of ultraviolet radiation in mountain lakes: factors controlling the among- and within-lake variability. Limnology and Oceanography 45, 1274–1288.

Laws, E. A., Popp, B. N., Bidigare, R. R., Kennicutt, M. C., Macko, S. A., 1995. Dependence of phytoplankton isotopic composition on growth rate and $[CO_2]_{aq}$: theoretical considerations and experimental results. Geochimica Cosmochimica Acta 59, 1131–1138.

Lawson, J., Doran, P. T., Kenig, F., Des Marais, D. J., Priscu, J. C., 2004. Stable carbon and nitrogen isotopic composition of benthic and pelagic organic matter in lakes of the McMurdo Dry Valleys, Antarctica. Aquatic Geochemistry 10, 269–301.

Lazerte, B. D., 1983. Stable carbon isotope ratios: implications for the source sediment carbon and for phytoplankton carbon assimilation in Lake Memphremagog, Quebec. Canadian Journal of Fishery and Aquatic Science 40, 1658–1666.

Lehmann, M. F., Bernasconi, S. M., Barbieri, A., Simona, M., McKenzie, J. A., 2004a. Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: a long-term sediment trap study. Limnology and Oceanography 49, 839–849.

Lehmann, M. F., Bernasconi, S. M., Mckenzie, J. A., Barbieri, A., Simona, M., Veronesi, M., 2004b. Seasonal variation of the $\delta^{13}C$ and $\delta^{15}N$ of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake. Limnology and Oceanography 49, 415–429.

Lei, Y., Yin, C., Li, C., 2006. Differences in some morphological, physiological, and biochemical responses to drought stress in two contrasting populations of Populus przewalskii. Physiologia Plantarum 127, 182–191.

Leng, M. J., Marshall, J. D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. Quaternary Science Reviews 23, 811– 831.

Lerman, A., Brunskill, G. J., 1971. Migration of major constituents from lake sediments into lake water and its bearing on lake water composition. Limnology and Oceanography 16, 880-890.

Levesque, M., 1972. Fluorescence and gel filtration of humic compounds. Soil Science 113, 346–353.

Li, H., Minoe, E. C., 2015. Biological characteristics of settling particulate organic matter in Lake Superior: A seasonal comparison. Limnology and Oceanography 85, 76-88.

Li, W., Wu, F. C., Liu, C. Q., Fu, P. Q., Wang, J., Mei, Y., Wang, L., Guo, J., 2008. Temporal and spatial distributions of dissolved organic carbon and nitrogen in two small lakes on the Southwestern China. Limnology 9, 163–171.

Liu, X. S., Kim, C. N., Pohl, J., Wang, X., 1996. Purification and characterization of an interleukin-1β converting enzyme family of protease that activates cysteine protease P32 (CPP32). Journal of Biological Chemistry 271, 13371–13376.

Liu, Y. M., Wang, C, Fung, C., Li X. F., 2010. Quantification of Viable but Nonculturable *Escherichia coli* O157:H7 by Targeting the *rpoS* mRNA. Analytical Chemistry 82, 2612–2615.

Llewellyn, C. A., Sommer, U., Dupont, C. L., Allen, A. E., Viant, M. R., 2015. Using community metabolomics as a new approach to discriminate marine microbial particulate organic matter in the western English Channel. Progress in Oceanography 137, 421-433.

Lozovik, P. A., Morozov, A. K., Zobkov, M. B., Dukhovicheva, T. A., Osipova, L. A., 2007. Allochthonous and autochthonous organic matter in surface waters in Karelia. Water Resources Research 34, 204–216.

Maie, N., Scully, N. M., Pisani, O., Jaffeí, R., 2007. Composition of a protein-like fluorophore of dissolved organic matter in coastal wetland and estuarine ecosystems. Water Research 41, 563–570.

Maksymowska, D., Richard, P., Piekarek-Jankowska, H., Riera, P., 2000. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdansk (Southern Baltic Sea). Estuarine, Coastal and Shelf Science 51, 585-598.

Mariotti, A., Mariotti, F., Champigny, M. L., Amarger, N., Moyse., 1982. Nitrogen isotope fractionaton associated with nitrate reductase activity and uptake of NO_3^- by pearl millet. Plant Physiology 69, 880-884.

Mariotti, A., Lancelot, C., Billen, G., 1984. Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. Geochimica Cosmochimica Acta 48, 549-555.

Markager, S., Vincent, W. F., 2000. Spectral light attenuation and the absorption of UV and blue light in natural waters. Limnology and Oceanography 45, 642–650.

Marty, J., Planas, D., 2008. Comparison of methods to determine algal $\delta^{13}C$ in freshwater. Limnology and Oceanography: Methods 6, 51–63.

Mashiko, K., 1976. Effects of reclamation of Kaga Sanko. The Japanese Society of Irrigation, Drainage and Rural Engineering 44, 835–838.

Masieelo, C. A., Druffel, E. R. M., 2001. Carbon isotope geochemistry of the Santa Clara River. Global Biogeochemistry Cycles 15, 407- 416.

Matsuda, Y., Hara, T., Coleman, B., 2001. Regulation of the induction of bicarbonate uptake by dissolved CO_2 in the marine diatom, Phaeodactylum tricornutum. Plant Cell Environment 24, 611–620.

Matthews, B., Mazumder, A., 2005. Temporal variation in body composition (C: N) helps explain seasonal patterns of zooplankton $\delta^{13}C$. Freshwater Biology 50, 502–515.

Maurice, P. A., Pullin, M. J., Cabaniss, S. E., Zhou, Q. H., Namjesnik-dejanovic, K., Aiken, G. R., 2002. A comparison of surface water natural organic matter in raw

filtered water samples, XAD, and reverse osmosis isolates. Water Research, 36**,** 2357-2371.

McClelland, J. W., Valiela, I., Michener, R. H., 1997. Nitrogen-stable isotope signatures in estuarine food web: a record of increasing urbanization in coastal watersheds. Limnology and Oceanography 42, 930-937.

McKnight, D. M., Andrews, E. D., Spaulding, S.A., Aiken, G.R., 1994. Aquatic fulvic acids in algal-rich Antarctic ponds. Limnology and Oceanography 39,1972–1979.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P.T., Kulbe, T., Andersen, D. T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnology and Oceanography 46, 38–48.

McNichol, A. P., Aluwihare, L. I., 2007. The power of radiocarbon in biochemical studies of marine carbon cycle: insights from studies of dissolved and particulate carbon (DOC and POC). Chemical Reviews 107, 443-466.

Meriläinen, J. J., Hynynen, J., Palomäki, A., Veijola, H., Witick, A., Mäntykoski, K., Granberg, K., Lehtinen, K., 2001. Pulp and paper mill pollution and subsequent ecosystem recovery of a large boreal lake in Finland: a palaeolimnological analysis. Journal of Paleolimnology 26, 11–35.

Meyers, P. A., Eadie, B. J., 1993. Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. Organic Geochemistry 20, 47–56.

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

Meyers, P. A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry 27, 213–250.

Meyers, P. A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. Journal of Paleolimnology 21, 345–372.

Meyers, P. A., Teranes, J. L., 2001. Sediment organic matter. In: Last, W.M., Smol, J.P. (eds.), Tracking Environmental Change using Lake Sediments Volume 2. Physical and Geochemical Methods. Kluwer Academic Publishers, Netherlands, 239–269.

Miller, W. L., Moran, M. A., 1997. 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.

Ministry of Environmental Studies, Water quality data for public waters, http://www.env.go.jp/water/suiiki/h26/h26-1.pdf. (accessed 30 November 2016).

Ministry of Land, Infrastructure, Transport and Tourism, River water quality test method, http://www.milt.go.jp/river/shishin_guidline/kasen/suishitsu/houhou.html (2016.12.1 accessed).

Ministry of the Environment, Analytical method for suspended solids concentration, http://www.env.go.jp/kijun/wt_a09.html (accessed 1 December 2016).

Ministry of the Environment, Analytical method for suspended solids concentration, http://www.env.go.jp/kijun/wt_a09.html (2016.12.1 accessed).

Ministry of the Environment, Water quality data for public waters, http://www.env.go.jp/water/suiiki/h26/h26-1.pdf (201611.30 accessed).

Mizutani, M and Wada, H., 1982. Effect of high atmospheric CO_2 concentrations on $\delta^{13}C$ of algae. Origin of Life and Evolution of Biospheres 12, 377–390.

Momzikoff, A., Dallot, S., Pizay, M. D., 1992. Blue and yellow fluorescence of filtered seawater in a frontal zone (Ligurian Sea, northwest Mediterranean Sea). Deep-Sea Research 39, 1481–1498.

Montagnes, D. J., Berges, J. A., Harrison, P. J., Taylor, F. J. R., 1994. Estimating carbon, nitrogen, protein, and chlorophyll a from volume in marine phytoplankton. Limnology and Oceanography 39, 1044–1060.

Mopper, K., Schultz, C. A., 1993. Fluorescence as a possible tool for studying the nature and water column distribution of DOC components. Marine Chemistry 41, 229-238.

Moran, M. A., Sheldon Jr, W. M., Zepp, R. G., 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnology and Oceanography 45, 1254–1264.

Moschen, R., Lücke, A., Parplies, J., Schleser, G., 2009. Controls on the seasonal and interannual dynamics of organic matter stable carbon isotopes in mesotrophic Lake Holzmaar, Germany. Limnology and Oceanography 54, 194–209.

Mostofa, K. M. G., Honda, Y., Sakugawa, H., 2005a. Dynamics and optical nature of fluorescent dissolved organic matter in river waters in Hiroshima prefecture, Japan. Geochemical Journal 39, 257–271.

Mostofa, K. M. G., Yoshioka, T., Konohira, E., Tanoue, E., Hayakawa, K., Takahashi, M., 2005b. Three-dimensional fluorescence as a tool for investigating the dynamics of dissolved organic matter in the Lake Biwa watershed. Limnology 6, 101–115.

Mostofa, K. M. G., Yoshioka, T., Konohira, E., Tanoue, E., 2007. Photodegradation of fluorescent dissolved organic matters in river waters. Geochemical Journal 41, 323–331.

Mostofa, K. M. G., Sakugawa, H., 2009. Spatial and temporal variations and factors controlling the concentrations of hydrogen peroxide and organic peroxides in rivers. Environmental Chemistry 6, 524–534.

Mostofa, K. M. G., Liu C. Q., Wu, F. C., Fu, P. Q., Ying, W. L., Yuan, J., 2009a. Overview of key biogeochemical functions in lake ecosystem: impacts of organic matter pollution and global warming. In: Keynote Speech, Proceedings of the 13th World Lake Conference, 1–5 November 2009. Wuhan, China, 59–60.

Mostofa, K. M. G., Wu, F. C., Yoshioka, T., Sakugawa, H., Tanoue, E., 2009b. Dissolved organic matter in the aquatic environments. In: Wu, F.C., Xing, B. (eds.) Natural Organic Matter and its Significance in the Environment. Science Press, Beijing, 3–66.

Mostofa, K. M. G., Wu, F. C., Liu, C. Q., Fang, W. L., Yuan, J., Ying, W. L., Wen, L., Yi, M., 2010. Characterization of Nanming River (Southwestern China) impacted by sewerage pollution using excitation- emission matrix and PARAFAC. Limnology 11, 217–231.

Mulligan, C. N., Davarpanah, N., Fukue, M., Inoue T., 2009. Filtration of contaminated suspended solids for the treatment of surface water. Chemosphere 74, 779–786.

Mulligan, C. N., Davarpanah, N., Fukue, M., Inoue, T., 2009. Filtration of contaminated suspended solids for the treatment of surface water. Chemosphere 74, 779–786.

Nagano Prefectural Government, Water quality results, lakes, http://www.pref.nagano.lg.jp/,izutaiki/sjozen/suishitsu/documents/koshou.pdf (2016.11.14 accessed).

Nagao, S., Matsunaga, T., Suzuki, Y., Ueno, T., Amano, H., 2003. Characteristics of humic substances in the Kuji River waters as determined by high-performance size exclusion chromatography with fluorescence detection. Water Research 37, 4159–4170.

Nagao, S., Usui, T., Yamamoto, M., Minagawa, M., Iwatsuki, T., Noda, A., 2005. Combined use of $\Delta^{14}C$ and $\delta^{13}C$ values to trace transportation and deposition processes of terrestrial particulate organic matter in coastal marine environments. Chemical Geology 218, 63–72.

Nagao, S., Kodama, H., Aramaki, T., Fujitake, N., Yonebayashi, K., 2007. Variations in $\Delta^{14}C$ of humic substances in the Lake Biwa waters. Nuclear Instrument and Methods in Physics Research Section B 259, 552-557.

Nagao, S., Aramaki, T., Seki, O., Uchida, M., Shibata, Y., 2010. Carbon isotopes and ligin composition of POC in a small river in Bekanbueshi Moor, northern Japan. Nuclear Instrument and Methods in Physics Research Section B 268, 1098-1101.

Nagao, S., Bui, H. T., Kawano, Y., Suzuki, T., Ochiai, S., Yonebayashi, K., Okazaki, M., Goto, A., Hasegawa, T. Yamamoto, M., 2016 Reclamation and land consolidation effects on organic matter sedimentation in Lake Kiba-gata, Japan. In: Meadows, M. E., Lin, J. C. (eds.), Geomorphology and Society. Springer, Tokyo, 181-192.

Nakamura, T., Kojima, S., Ohta, T., Oda, H., Ikeda, A., Okuno, M., Yokota, K., Mizutani, Y., Kretschner, W., 1998. Isotopic analysis and cycling of dissolved inorganic carbon at Lake Biwa, central Japan. Radiocarbon 40, 933-944.

Nalewajko, C., Murphy, T. P., 2001. Effects of temperature and availability of nitrogen and phosphorus on the abundance of Anabaena and Microcystis in Lake Biwa, Japan: an experimental approach. Limnology 2, 45–48.

Nara, F., Imai, A., Yoneda, M., Matsushige, K., Komura, K., Nagai, T., Shiha, Y., Watanabe, T., 2007. Seasonal variation in sources of dissolved organic carbon in a lacustrine environment revealed by paired isotopic measurements (Δ^{14}C and δ^{13}C). Radiocarbon 49, 767-773.

Nara, F. W., Imai, A., Uchida, M., Matsushige, K., Komatsu, K., Kawai, N., Shibata, Y., Amano, K., Mikami, H., Hanaishi, R., 2010. High contribution of recalcitrant organic matter to DOC in a Japanese oligotrophic lake revealed by Δ^{14}C measurement. Radiocarbon 52, 1078-1083.

National Institute for Environmental Studies (1998) Ecosystem Management Studies in Lake Towada. Report of Special Research R-146-'99 (National Institute for Environmental Studies, Japan, Tsukuba), 218.

National Institute for Environmental Studies (2004), Studies on Mass Balance of Dissolved Organic Matter in Lake and its Functions and Effects on Lacustrine Ecosystems and Water Quality Report of Special Research SR-62 (National Institute for Environmental Studies, Japan, Tsukuba), 59.

Nearing, M. A., Jetten, V., Baffaut, C., Cerdan, O., Couturier, A., Hernandez, M., Le Bissonnais, Y., Nichols, M. H., Nunes, J. P., Renschler, C. S., Souchère, V., van Oost, K., 2005. Modeling response of soil erosion and runoff to changes in precipitation and cover. Catena 61, 131–154.

Neitsch, S. L., Arnold, J. G., Kiniry, J. L. R., Willianms, J. R., 2009. Soil and Water Assessment Tool Theoretical Documentation, Version 2009. Texas A&M University System, College Station, Texas.

Nelson, N. B., Siegel, D. A., Michaels, A. F., 1998. Seasonal dynamics of colored dissolved material in the Sargasso Sea. Deep-Sea Research 45, 931–957.

Nelson, N. B., Carlson, C. A., Steinberg, D. K., 2004. Production of chromophoric dissolved organic matter by Sargasso Sea microbes. Marine Chemistry 89, 273–287 .

Norrman, B., Zweifel, U. L., Hopkinson, C. S., Fry, B., 1995. Production and utilization of dissolved organic carbon during an experimental diatom bloom. Limnology and Oceanography 40, 898-907.

O'Leary, M., 1981. Carbon isotope fractionation in plants. Phytochemistry 28, 553–567.

Oguri, K., Matsumoto, E., Hino, A., Kurokura, H., Okamoto, K., 1996. A study on particulate organic matter in the Lake Haman: An approach from carbon isotopes.

the In Summaries of Researches Using AMS at Nagoya University (VII) (Dating and Materials Research Center, Nagoya University, 184-192.

Ohtani, Y., Yamaguchi, T., Horikoshi, S., Shimada Y., 2006. Annual Report of Gunma Prefectural Institute of Public Health and Environmental Sciences 38, 31.

Ortega-Retuerta, E., Frazer, T.K., Duarte, C.M., Ruiz-Halpern, S., Tovar-Sánchez, A., Arrieta, J. M., Reche I., 2009. Biogeneration of chromophoric dissolved organic matter by bacteria and krill in the Southern Ocean. Limnology and Oceanography 54, 1941–1950.

Oseguera, L. A., Alcocer, J., Vilaclara, G., 2011. Relative importance of dust inputs and aquatic biological production as sources of lake sediments in an oligotrophic lake in a semi- arid area. Earth Surface Processes and Landforms 36, 419–426.

Padisák, J., Grigorszky, I., Borics, G., Soróczki-Pintér, E., 2006. Use of phytoplankton assemblages for monitoring ecological status of lakes within the Water Framework Directive: The assemblage index. Hydrobiologia 553, 1–14.

Palenik, B., Morel, F. M. M., 1988. Dark production of H_2O_2 in the Sargasso Sea. Limnology and Oceanography 33, 1606–1611.

Pancost, R. D., Boot, C. S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. Marine Chemistry 92, 239-261.

Park, H. K., Byeon, M. S., Shin, Y. N., Jung, D. I., 2009. Sources and spatial and temporal characteristics of organic carbon in two large reservoirs with contrasting hydrologic characteristics. Water Resource Research 45, W11418. doi: 10.1029/2009WR008043.

Parlanti, E., Wörz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. Organic Geochemistry 31, 1765–1781.

Perdue, E. M., Koprivnjak, J. F., 2007. Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments. Estuarine, Coastal and Shelf Science 73, 65–72.

Persson, T., Wedborg, M., 2001. Multivariate evaluation of the fluorescence of aquatic organic matter. Analytica Chimica Acta 434, 179–192.

Peuravuori, J., Koivikko, R., Pihlaja, K., 2002. Characterization, differentiation and classification of aquatic humic matter separated with different sorbents: synchronous scanning fluorescence spectroscopy. Water Research 36, 4552–4562.

Piirsoo, K., Viik, M., Kõiv, T., Käiro, K., Laas, A., Nõges T., Pall, P., Selberg A., Toomsalu, L., Vilbaste S. 2012. Characteristics of dissolved organic matter in the inflows and in the outflow of Lake Võrtsjärv, Estonia. Journal of Hydrology 475, 306–313.

Pisarevsky, A.M., Polozova, I.P., Hockridge, P.M., 2005. Chemical oxygen demand. Russian Journal of Applied Chemistry 78, 101–107.

Popp, B. N., Laws, E. A., Bidigare, R. R., Dore, J. E., Hanson, K. L., Wakeham, S. G., 1998. Effect of phytoplankton cell geometry on carbon isotopic fractionation. Geochimica Cosmochimica Acta 62, 66– 77.

Pregitzer, K., Zak, D. R., Burton, A. J., Ashby, J. A., MacDonald, N. W., 2004. Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry 68, 179–197.

Quyang. Y., 2003. Simulating dynamic load of naturally occurring TOC from watershed into a river. Water Research 37, 823.

Rau, G. H., Takahashi, T., Des Marais, D. J., 1989. Latitudinal variations in plankton [13]C: implication for CO_2 and productivity in past oceans. Nature 341, 516–518.

Rau, G. H., Chavez, F. P., Friederich, G.E., 2001. Plankton $^{13}C/^{12}C$ variations in Monterey Bay, California: evidence of non-diffusive inorganic carbon uptake by phytoplankton in an upwelling environment. Deep-Sea Research 48, 79–94.

Raven, J. A., 2003. Inorganic carbon concentrating mechanisms in relation to the biology of algae. Photosynthesis Research 77, 155–171.

Raymond, P. A., Bauer J. E., 2001. Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: A review and synthesis. Organic Geochemistry 32, 469-485.

Raymond, P. A., Bauer, J. E., Caraco, N. F., Cole, J. J., Longworth, B., Petsch S. T., 2004. Control on variability of organic matter and dissolved organic ages in northeast US rivers. Marine Chemistry 92, 353-366.

Raymond, P. A., Oh, N. H., 2007. An empirical study of climatic controls on riverine C export from three major US watersheds. Global Biogeochemical Cycles 21:GB2022. doi: 10.1029/2006GB002783.

Redfield, A. C., 1958. The biological control of chemical factors in the environment. American Scientist 46, 205–221.

Remington, S., Krusche, A., Richey, J., 2011. Effects of DOM photochemistry on bacterial metabolism and CO_2 evasion during falling water in a humic and a whitewater river in the Brazilian Amazon. Biogeochemistry 105, 185–200.

Rossi, L., Costantini, M. L., Carlino, P., Di Lascio, A., Rossi, D., 2010. Autochthonous and allochthonous plant contributions to coastal benthic detritus deposits: a dual-stable isotope study in a volcanic lake. Aquatic Science 72, 227–36.

Saadi, I., Borisover, M., Armon, R., Laor, Y., 2006. Monitoring of effluent DOM biodegradation using fluorescence, UV and DOC measurements. Chemosphere 63, 530-539.

Saito, A., 1964. A fragment history of lake reclamation in Japan II. Studies and Essay by the Faculty of Law and Literature, Kanazawa University 12, 45–62.

Satoh, Y., Katano, T., Satoh, T., Mitamura, O., Anbutsu, K., Nakano, S. I., Ueno, H., Kihira, M., Drucker, V., Tanaka, Y., Mimura, T., Watanabe, Y., Sugiyama, M., 2006. Nutrient limitation of the primary production of phytoplankton in Lake Baikal. Limnology 7, 225–229.

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

Sawada, M., Yashiki, M., Kitano, K., Higashi, K., Hori, S., Yoshida, M., Ishida, Y., Honda, K., Nishi, T., 1988. Water quality and algal growth in Lake Kibagata. Annual Report of Ishikawa Research Laboratory for Public Health and Environment 25, 232–254.

Scheffer, M., Van den Berg, M., Breukelaar, A., Breukers, C., Coops, H., Doef, R., Meijer, M.L., 1994. Vegetated areas with clear water in turbid shallow lakes. Aquatic Botany 49, 193-196.

Sekito, S., Nakagawa, N., Tsuchida, J., Hino, T., Nagano, M., 2006. Bottom sediments in Kiba-gata. Memoirs of the Komatsu City Museum 46, 26–30.

Senesi, N., 1993. Nature of interactions between organic chemicals and dissolved humic substances and the influence of environmental factors. In Jones, K. C., Hayes, M. H. B., Mingelgrin, U., Beck, A. J. (eds.), Organic Substances in Soil and Water: Natural Constituents and their Influences on Contaminant Behaviour. Royal Society of Chemistry, Cambridge, 73-101.

Shigemi, T., Amano, K., Mizuno, K., Takada, T., 1966. Execution of training dikes at the outlet of a diversion channel on the coast of the Japan Sea. In: Proceedings of Tenth Conference on Coastal Engineering, Tokyo, Japan, American Society of Civil Engineers, 1201–1211.

Siemens, J., Kaupenjohann, M., 2003. Dissolved organic matter induced denitrification in subsoils and aquifers? Geoderma 113, 253–271.

Siepak, J., 1999. Total organic carbon (TOC) as a sum parameter of water pollution in selected Polish rivers (Vistula, Odra, and Warta). Acta Hydrochimica et Hydrobiologica 27, 282-285.

Singh, S., D'Sa, E. J., Swenson, E. M., 2010. Chromophoric dissolved organic matter (CDOM) variability in Barataria Basin using excitation–emission matrix (EEM) fluorescence and parallel factor analysis (PARAFAC). Science of the Total Environment 408, 3211–3222.

Sinha, R., Klisch, M., Gröniger, A., Häder, D. P., 2001. Responses of aquatic algae and cyanobacteria to solar UV-B. Plant Ecology 154, 219–236.

Smith, S.V., Sleezer, R. O., Renwick, W. H., Buddemeier, R. W., 2005. Fates of eroded soil organic carbon: Mississippi Basin case study. Ecological Applications 15, 1929–1940.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., Cole, J. J., 2007. Patterns and regulation of dissolved organic carbon: an analysis of 7,500 widely distributed lakes. Limnology and Oceanography 52, 1208–1219.

Spencer, R. G. M., Baker, A., Ahad, J. M. E., Cowie, G. L., Ganeshram, R., Upstill-Goddard, R. C., Uher, G., 2007. Discriminatory classification of natural and anthropogenic waters in two UK estuaries. Science of the Total Environment 373, 305-323.

Stedmon, C. A., Thomas, D. N., Granskog, M., Kaartokallio, H., Papadimitriou, S., Kuosa, H., 2007. Characteristics of dissolved organic matter in Baltic coastal sea ice: allochthonous or autochthonous origins? Environmental Science and Technology 41, 7273–7279.

Stramska, M., Stramski, D., 2005. Variability of particulate organic carbon concentration in the north polar Atlantic based on ocean color observations with Sea-viewing Wide Field-of-view Sensor (SeaWiFS). Journal of Geophysical Research 110, C10018. http://dx.doi.org/10. 1029/2004JC002762.

Stuiver, M., Polach, H. A., 1977. Discussion: reporting of ^{14}C data. Radiocarbon 19, 1127-1151.

Sumita, M., Watanabe, T., 1979. The limnological characters of Lake Kiba-gata in Ishikawa Prefecture from point view of diatom communities. Japanese Journal of Water Treatment Biology 15, 11–18.

Taipale, S., Kankaala, P., Jones, R., 2007. Contributions of different organic carbon sources to Daphnia in the pelagic foodweb of a small polyhumic lake: results from Mesocosm DI^{13}C-additions. Ecosystems 10, 757–772.

Takahashi, K., Yoshioka, T., Wada, E., Sakamoto, M., 1990. Temporal variations in carbon isotope ratio of phytoplankton in a eutrophic lake. Journal of Plankton Research 12, 799–808.

Takano, H., Yamamoto, J., Saitou M., Nakagawa, S., 2007. Annual Report of Okayama Prefectural Institute for Environmental Science and Public Health 31, 33-40.

Tananaev, N. I., Debolskiy, M. V., 2014. Turbidity observations in sediment flux studies: Examples from Russian rivers in cold environments. Geomorphology 218, 63–71.

Tanoue, E., 2000. Proteins in the sea-synthesis. In: Handa, N., Tanoue, E., Hama, T. (eds.) Dynamics and Characterization of Marine Organic Matter. TERRAPUB/Kluwer, Tokyo, 383–463.

Teganuma Aquatic Conservation Council, http://www.tesuikyo.jp/environment/ (2016.11.30 accessed).

Teranes, J. L., Bernasconi, S. M., 2000. The record of nitrate utilization and productivity limitation provided by δ^{15}N values in lake organic matter: a study of sediment trap and core sediments from Baldeggersee, Switzerland. Limnology and Oceanography 45, 801-813.

Thevenon, F., Graham, N. D., Herbez, A., Wildi, W., Poté, J., 2011. Spatio-temporal distribution of organic and inorganic pollutants from Lake Geneva (Switzerland)

reveals strong interacting effects of sewage treatment plant and eutrophication on microbial abundance. Chemosphere 84, 609–617.

Thornton, S. F., McManus, J., 1994. 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.

Thurman, E. M., 1986. Organic Geochemistry of Natural Waters, 2nd ed. Martinus Nijhoff/Dr W Junk Publishers, The Netherlands.

Tranvik, L. J., Hafle, M. G., 1987. Bacterial growth in mixed cultures on dissolved organic carbon from humic and clear waters. Apply Environmental Microbiology 53, 482–488.

Tranvik, L. J., 1989. Bacterioplankton growth, grazing mortality and quantitative relationship to primary production in a humic and a clearwater lake. Journal of Plankton Research 11, 985–1000.

Tranvik, L. J., Jasson, M., 2002. Climate change—terrestrial export of organic carbon. Nature 415, 861–862.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., et al., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnology and Oceanography 54, 2298–2314.

Tu, C. L, Liu, C. Q., Lu, X. H., Yuan, J., Lang, Y. C., 2011. Sources of dissolved organic carbon in forest soils: evidences from the differences of organic carbon concentration and isotope composition studies. Environmental Earth Sciences 63,

723–730.

Uchida, M., Nakatsubo, T., Horikoshi, T., Nakane, K., 1998. Contribution of microorganisms to the carbon dynamics in black spruce (Picea mariana) forest soil in Canada. Ecology Research 13, 17–26.

Uchida, M., Nakatsubo, T., Kasai, Y., Nakane, K., Horikoshi, T., 2000. Altitude differences in organic matter mass loss and fungal biomass in a subalpine coniferous forest, Mt. Fuji, Japan. Arctic, Antarctic, and Alpine Research 32, 262–269.

Ueda, S., Kondo, K., Inaba, J. 2007. Background concentration of ^{14}C in aquatic samples from brackish lake Obuchi, Rokkasho, Japan, adjacent to nuclear fuel reprocessing facilities. Radiocarbon 49, 161-171.

Vander Zanden, M. J., Vadeboncoeur, Y., Diebel, M. W., Jeppesen, E., 2005. Primary consumer stable nitrogen isotopes as indicators of nutrient source. Environmental Science and Technology 39, 7509-7515.

Verweij, F., Booij, K., Satumalay, K., Molen, N., Oost, R., 2004. Assessment of bioavailable PAH, PCB and OCP concentrations in water, using semipermeable membrane devices (SPMDs), sediments and caged carp. Chemosphere 54, 1675–1689.

Vuorio, K., Meili, M., Sarvala, J., 2006. Taxon-specific variation in the stable isotopic signatures (δ^{13}C and δ^{15}N) of lake phytoplankton. Freshwater Biolology 51, 807–822.

Wakeham, S.G., Lee, C., Hedges, J. I., Hernes, P. J., Peterson, M. L., 1997. Molecular indicators of diagenetic status in marine organic matter. Geochimica Cosmochimica Acta 61, 5363–5369.

Wallace, J. B., Whiles, M. R., Eggert, S., Cuffney, T. F., Lugthart, G. H., Chung, K., 1995. Long-term dynamics of coarse particulate organic-matter in three Appalachian Mountain streams. Journal of the North American Benthological Society 14, 217–232.

Wang, Q., Kim, D., Dionysiou, D. D., Sorial, G. A., Timberlake, D., 2004. Sources and remediation for mercury contamination in aquatic systems—a literature review. Environmental Pollution 131, 323–336.

Wang, Q. G., Gu, G., Higano, Y., 2006. Toward integrated environmental management for challenges in water envi- ronmental protection of Lake Taihu Basin in China. Environmental Management 37, 579–588.

Wang,X .L., Lu, Y.L., He, G.Z., Han, J.Y., Wang, T.Y., 2007a. Multivariate analysis of interactions between phytoplankton biomass and environment variables in Taihu Lake, China. Environmental Monitoring and Assessment 133, 243–253.

Wang, X.L., Lu, Y.L., He, G.Z., Han, J.Y., Wang, T.Y., 2007b. Exploration of relationships between phytoplank- ton biomass and related environmental variables using multivariate statistic analysis in a eutrophic shallow lake: a 5-year study. Journal of Environmental Sciences 19, 920–927.

Wedchaparn, O., Zhao, L, Fan, Y., et al., 2016. Comparison of the trophic niches between two planktivorous fishes in two large lakes using stable isotope analysis.
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Biochemical Systematics and Ecology 68, 148-155.

Wetzel, R. G., 1983. Limnology, 2nd ed., Saunders College Publishing, Philadelphia, 860.

Wetzel, R. G., 1990. Land-water interfaces: metabolic and limnological regulators Edgardo Baldi Memorial Lecture. Verhandlungen Internationale Vereinigung für therorische und angwandte Limnology 24, 6–24 .

Wetzel, R. G., 1992. Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiologia 229, 181–198.

Wetzel, R., 2001a. Limnology. Lake and River Ecosystems, 3rd ed. Academic Press, San Diego, 755-756.

Wetzel, R., 2001b. Limnology. Lake and River Ecosystems, 3rd ed. Academic Press, San Diego, 513-414.

Wildi, W., Dominik, J., Loizeau, J. L., et al., 2004. River, reservoir and lake sediment contamination by heavy metals downstream from urban areas of Switzerland. Lakes Reservoir: Research Management 9, 75–87.

Worrall, F., Harriman, R., Evans, C. R., Watts, C. D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P., 2004. Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70, 369–402.

Woszczyk, M., Bechtel, A., Gratzer, R., Kotarba, M. J., Kokocínski, M., Fiebig, J., Ciéslínski, R., 2011. Composition and origin of organic matter in surface

sediments of Lake Sarbsko: A highly eutrophic and shallow coastal lake (northern Poland). Organic Geochemistry 42, 1025–1038.

Wu, H and Gao, K., 2009. Ultraviolet radiation-stimulated activity of extracellular carbonic anhydrase in the marine diatom *Skeletonema costatum* Functional Plant Biology 36, 137–143.

Xiaoying, Y., 2001. Humic acids from endemic arsenicosis areas in Inner Mongolia and from the Blackfoot-disease areas in Taiwan: A comparative study. Environmental Geochemistry and Health 23, 27-42.

Xu, J., Xie, P., Zhang, M., Yang, H., 2005a. Variation in stable isotope signatures of seston and a zooplanktivorous fish in a eutrophic Chinese lake. Hydrobiologia 541, 215–220.

Yamashita, Y., Jaffe′, R., 2008. Characterizing the interactions between trace metals and dissolved organic matter using excitation emission matrix and parallel factor analysis. Environmental Science and Technology 42, 7374-7379.

Yan, Y., Li, H., Myrick, M. L., 2000. Fluorescence fingerprint of waters: Excitation-emission matrix spectroscopy as a tracking tool. Applied Spectroscopy 54, 1539-1542.

Yin, Y., Zhang, Y., Liu, X., Zhu, G., Qin, B., Shi, Z., Feng, L., 2011. Hydrobiologia 665, 129-141.

Yoshioka, T., Wada, E., Saijo, Y., 1988. Isotopic characterization of Lake Kizaki and Lake Suwa. Japanese Journal of Limnology 49, 119–128.

Yoshioka, T., 1997. Phytoplanktonic carbon isotope fractionation: equations accounting for CO_2-concentrating mechanisms. Journal of Plankton Research 19, 1455-1476.

Yoshizawa, K., 2009. Annual Report of the Yamanashi Institute for Public Health, 53, 61.

Zagan, S., Enache, I., 2009. Pollution degree of Tabacarie Lake in 2009. Proceedings of the 3rd International Conference on Environmental and Geological Science and Engineering, 132-136.

Zhang, Y., Van Dijk, M. A., Liu, M., Zhu, G., Qin, B., 2009. The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: field and experimental evidence. Water Research 43, 4685–4697.

Zhang, Y., Zhang, E., Yin, Y., Van Dijk, M. A., Feng, L., Shi, Z., 2010. Characteristics and sources of chromophoric dissolved organic matter in lakes of the Yungui Plateau, China, differing in trophic state and altitude. Limnology and Oceanography 55, 2645–2659.

Zhang, Y. L., Lee, X. Q., Cao, F., 2011a. Chemical characteristics and sources of organic acids in precipitation at a semi-urban site in Southwest China. Atmospheric Environment 45, 413–419 .

Zhang, Y. L., Yin, Y., Zhang, E. L., Zhu, G.W., Liu, M. L., Feng, L.Q., Qin, B.Q., Liu, X.H., 2011b. Spectral attenuation of ultraviolet and visible radiation in lakes in the Yunnan Plateau, and the middle and lower reaches of the Yangtze River, China. Photochemical and Photobiological Sciences 10, 469-482.

Zhao, X., Cheng, J., 2011. Organic matter composition in sediments of the Baiyangdian Lake in China. Procedia Environmental Sciences 10, 1768-1773.

Zhou, X. H., Wang, G. X., 2010. Nutrient concentration variations during Ocean the javanica growth and decay in the ecological floating bed system. Journal of Environmental Sciences 22, 1710–1717.

Zigah, P. K., Minor, E. C., Werne, J. P., 2012a. Radiocarbon and stable-isotope geochemistry of organic and inorganic carbon in Lake Superior Global Biogeochemistry Cycles 26, GB1023. doi:10.1029/2011GB004132.

Zigah, P. K., Minor, E. C., Werne, J. P., McCallister, S. L., 2012b. An isotopic (Δ^{14}C, δ^{13}C, and δ^{15}N) investigation of the composition of particulate organic matter and zooplankton food sources in Lake Superior and across a size-gradient of aquatic systems. Biogeoscience 9, 3663-3678.