Short-term variation in behavior of allochthonous particulate organic matter accompanying changes of river discharge in Ise Bay, Japan

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Abstract

The composition and behavior of allochthonous particulate organic matter (POM) in the northern part of Ise Bay, Japan were investigated to elucidate the short-term variation in POM accompanying changes in river discharge. The behavior of POM was significantly regulated by hydrographic conditions, but behavior was different in the upper layer versus the middle and lower layers. The former showed simple dynamics controlled by the river plume, while the latter showed complex dynamics because of changes in river discharge and subsequent variation in estuarine circulation. During normal discharge, the contribution of riverine materials to POC in the surface water within the bay was negligible because most riverine organic matter is deposited before flowing into the bay. During high discharge, on the other hand, the contribution of riverine organic matter to total POM increased to 50% at ~10 km from the river mouth. Though riverine organic matter loads increased, the total amount of POC decreased around the river mouth due to flushing of phytoplankton. After river discharge, the contribution decreased rapidly.

The behavior of POM in the middle and lower layers differed from that in the surface layer. At normal discharge, the influence of riverine organic matter was weak. During high discharge, high flooding temporarily weakened the bottom inflow, resulting in heavier riverine organic matter distributed from the river mouth to mid regions within the bay in the lower layer. The maximum contribution of riverine organic matter to total POM was estimated to be ~60% around 25 km from the river mouth. After high discharge, riverine POM in the lower layer was pushed to the bay head by enhanced estuarine circulation and was uplifted to the middle layer. The behavior of riverine POM dynamically changed in relation to river discharge, and exerted a significant influence on bottom water conditions in the bay.

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1. Introduction

Estuaries serve important functions in the global carbon cycle, acting both as sites of organic matter production and recycling and conduits through which materials are exchanged between the terrestrial and oceanic reservoirs (Canuel, 2001). Moreover, estuaries receive inputs from multiple sources of POM, including allochthonous terrestrial materials exported from land by rivers, allochthonous marine materials brought in through tidal action from the open ocean and autochthonous production of algae and intertidal vegetation. Each of the organic matter sources may contribute substantially to the total input, although the relative importance of these sources may vary spatially and temporally within individual estuaries (Jassby et al., 1993).

The origin and behavior of POM have been investigated in many estuaries. One way to distinguish among sources of organic materials that contribute to POM in estuarine waters is by direct measurement of stable carbon isotopes (δ13C) in
chlorophyll. A study showed that Ise Bay exhibits short-term variations in the ecosystem in estuaries. The reasons for the uncertainties remain regarding the sources, fate and role of organic carbon in the ecosystem in estuaries. The reasons for the uncertainties include the complex interactions among the various physical, geological and biological factors. In particular, physical processes influencing the transport and delivery of particles can vary over time scales from as short as minutes and days (e.g., Hedges et al., 1986; Bianchi et al., 2002) and lipid compounds (e.g., Canuel and Zimmerman, 1999; Canuel, 2001). In spite of these valuable studies, questions still remain regarding the sources, fate and role of organic carbon in the ecosystem in estuaries. The reasons for the uncertainties include the complex interactions among the various physical, geological and biological factors. In particular, physical processes influencing the transport and delivery of particles can vary over time scales from as short as minutes and days (e.g., in response to tidal, wind and river resuspension of advection events) to time scales on the order of seasons and years (Canuel and Zimmerman, 1999; Kasai et al., 2004a). Variation in river discharge has a large effect on the behavior and subsequent flux of POM in estuaries. In the Mississippi River estuary, river discharge and horizontal mixing played important roles in the distribution and transport of terrestrial organic carbon offshore (Wong et al., 2004). The contribution of terrestrial organic matter changes due to seasonal variation in river discharge in several estuaries, with particularly strong contributions during high river discharge seasons (Riera and Richard, 1997; Eddins, 2001). However, few studies have ever tried to clarify the detailed dynamics of POM accompanying short-term variation in river discharge.

Our region of study, Ise Bay, is one of the most eutrophic gulf-type estuaries in Japan. In the 1970s water was highly polluted and eutrophication became a serious problem. In the following decades, a great deal of effort was made to reduce the pollutant load from the rivers. However, red tides are often still observed and the bottom water becomes hypoxic in summer. It is therefore desirable to clarify the roles of allochthonous and autochthonous materials in water pollution in the estuary. Despite extensive knowledge of physical processes in Ise Bay (e.g., Fujiiwara et al., 1996; Kasai et al., 2002), dynamics of POM is poorly known. In this research, detailed observations were conducted in the northern part of Ise Bay, and the composition and behavior of POM associated with short-term variations in river discharge were investigated. Part of the data on the surface water obtained from this survey has already been presented by Sugimoto et al. (2004). Their study showed that Ise Bay exhibits short-term variations in chlorophyll a concentrations associated with changes in river discharge. Although chlorophyll a concentrations decreased by physical processes such as advection and diffusion during the flood, they recovered promptly to previous levels because of the blooming of phytoplankton, especially Skeletonema costatum, which used the plentiful nutrient supply from the rivers after the flood.

In this paper, we pay particular attention to the behavior of allochthonous organic matter supplied by the river to the bay. The river plume flows out in the surface layer of the bay, while the pressure gradient between the bay mouth and the bay head caused by the river discharge drives estuarine circulation: outflow in the upper layer and inflow in the lower layer. It is well known that the volume flux of estuarine circulation is considerably larger than that of river discharge in Ise Bay (Fujiiwara et al., 1997; Kasai, 2003). This indicates that estuarine circulation should have important effects on water quality and ecosystem in the bay. Allochthonous organic matter can be scavenged by suspended sediment particles and may become trapped in the estuary, either as part of the estuarine circulation or as deposits on the estuarine bed. Therefore, both river discharge and estuarine circulation could have large effects on the behavior of allochthonous organic matter from rivers. Based on these concepts, we present a detailed picture of the short time variations in riverine POM in associate with river discharge and estuarine circulation.

2. Materials and methods

2.1. Study area

Fig. 1 shows the topography of Ise Bay and the sampling locations. The bay has a surface area of 1738 km², a volume of 33.9 km³, and a mean depth of 19.5 m with the deepest longitudinal depression of over 35 m depth in the middle. The tide in Ise Bay is dominated by semi-diurnal constituents. Typical amplitude of tidal currents is 0.1 m s⁻¹ in the bay, while tidal flow converges to Irago Strait, where its speed exceeds 0.8 m s⁻¹ during spring tides (Fujiiwara et al., 2002). Three major rivers (Kiso, Nagara and Ibi River), known collectively as the Kiso Rivers, flow into the head of the bay in the north. A weir across 5 km upstream from the river mouth controls the water flux of Nagara River. Fig. 2 shows a time series of river discharge of the Kiso Rivers from 1990 to 2001. It contributes ~85% of the total freshwater discharge into the bay (Fujiiwara et al., 1996). The discharge of the Kiso Rivers shows a seasonal variation, which is large in summer and small in winter, with an annual mean of ~350 m³ s⁻¹. The mode flow is ~210 m³ s⁻¹ in winter and ~400 m³ s⁻¹ in summer. In addition, the river discharge of the Kiso Rivers shows short time variations because of the mountainous topography in their catchment basin. The large discharge over 1000 m³ s⁻¹ is often observed in summer, and rarely in winter.

The density structure is dominated by salinity in the upper layer, whereas it is controlled by both temperature and salinity in the lower layer (Fujiiwara et al., 2002). From the stratification—circulation diagram of Hansen and Rattray (1966), the water column in the central bay can be classified as being in
the strongly stratified regime from April to October and in the weakly stratified regime during the rest of the year (Fujiwara et al., 1996). During strongly stratified periods, estuarine circulation prevails in the bay and accounts for more than 99% of the longitudinal transport (Fujiwara et al., 1996). However, it is worth noticing that the strength of the estuarine circulation changes with variation in the river discharge: the circulation is temporarily weakened by an increase of river discharge but it is intensified after a large discharge (Yamao et al., 2002).

2.2. Observations

Detailed observations were conducted in the northern part of Ise Bay by two vessels on three separate occasions (Fig. 1). In the figure, closed circles (sites A) indicate main observational points of temperature, salinity and turbidity. The data were corrected every 0.1 m depth with a Clorotec (Alec Electronics, ACL1150-DK) on 20 June, 28 June and 4 July, 2000. Water samples for determining $\delta^{13}$C, chlorophyll $a$ (Chl $a$) concentration,
particulate organic carbon (POC), particulate organic nitrogen (PON) and phosphate (PO₄-P), were taken from between three and five layers at every station. Open circles (sites B) indicate minor observational points of temperature, salinity and current fields. Temperature and salinity were measured every 0.1 m depth with a CTD (Alec Electronics, AST-200), and current fields were measured by a ship-board acoustic Doppler current profiler (ADCP, Furuno Electronics, CI-60G) on 20 June, 27 June and 4 July, 2000. Unfortunately, the second sampling was conducted over two days (sites A on 28 June and sites B on 27 June) because of bad weather on 27 June.

To elucidate the composition of riverine organic matter, surface water samples were taken near the center of the stream at ~15 km upstream from the river mouth in Kiso River, Nagara River and Ibi River on 20 June, 28 June and 4 July, 2000, respectively.

2.3. Analytical methods

Water samples were filtered through precombusted (at 450 °C for 2 h) Whatman GF/F filters. POM is defined as the particles collected on filters. The filter samples were put in a desiccator with an HCl fume for the first 24 h, to eliminate CaCO₃, and with NaOH for the next 24 h, to neutralize the acid (Kasai et al., 2004b). δ¹³C were measured using a mass spectrometer (Finnigan Mat, delta S) coupled with an elemental analyzer (Carlo Erba, EA1108). δ¹³C is expressed as per-mil (‰) deviation from the standard as defined by the following equation:

$$\delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 10^3,$$

where R is ¹³C/¹²C. The standard is Pee Dee Belemnite limestone that has been assigned a value of 0.0‰. The precisions of δ¹³C determination were less than 0.2‰. POC and PON concentrations were determined using a TCD detector attached to the elemental analyzer.

For Chl a and pheophytin concentrations, POM samples were extracted in the dark for 12 h by 90% acetone, and their concentrations were measured by the fluorometric method (Japan Meteorological Agency, 1970), using a calibrated Turner Designs TD700 fluorometer. In this study, chlorophyll (Chl) was determined as the total pigment including pheophytin. PO₄-P was extracted filtrate by the ascorbic acid–Mo blue method (Strickland and Parsons, 1965), using a Technicon Auto Analyzer.

3. Results

3.1. Variations in river discharge and riverine POM composition

River discharge of the Kiso Rivers changed considerably during the observation period (Fig. 3). Discharge was low (<500 m³ s⁻¹) until 22 June, and suddenly increased on 24 June (the first flood, ~2000 m³ s⁻¹), reaching a peak flood on 28 June (the second flood, ~3000 m³ s⁻¹). After that, it decreased rapidly and settled back to the previous level on 4 July. The three corresponding observational dates of 20 June, 28 June and 4 July are therefore termed ‘normal discharge’, ‘high discharge’ and ‘after discharge’, respectively.

Table 1 shows a summary of physical and chemical conditions in the Kiso Rivers. During high discharge, POC concentrations in the Kiso River and the Ibi River were higher than during normal discharge. However, the concentration in the Nagara River at high discharge was the same level as that at normal discharge. After discharge, POC concentrations decreased in all rivers. δ¹³C of POM in the Kiso River and the Nagara River varied from −27.3‰ to −23.1‰ and from −29.7‰ to −25.9‰, respectively. On the other hand, δ¹³C of POM in the Ibi River remained fairly constant (ca. −30‰). The C/N ratios varied from 7.8 to 22.3 and reached the highest values during high discharge in all rivers.

<table>
<thead>
<tr>
<th>Date</th>
<th>Discharge (m³ s⁻¹)</th>
<th>POC (mg l⁻¹)</th>
<th>PON (mg l⁻¹)</th>
<th>δ¹³C (‰)</th>
<th>C/N (mol ratio)</th>
</tr>
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<tr>
<td>Kiso River</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>20 June</td>
<td>155</td>
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<td>0.06</td>
<td>−27.3</td>
<td>12.6</td>
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<tr>
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<td>0.09</td>
<td>−25.5</td>
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</tr>
<tr>
<td>4 July</td>
<td>269</td>
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<td>0.03</td>
<td>−23.1</td>
<td>12.5</td>
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<tr>
<td>Nagara River</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>20 June</td>
<td>63</td>
<td>2.28</td>
<td>0.34</td>
<td>−27.7</td>
<td>7.8</td>
</tr>
<tr>
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<tr>
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<td>0.44</td>
<td>0.06</td>
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<td>Ibi River</td>
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<tr>
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<tr>
<td>4 July</td>
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<td>0.60</td>
<td>0.10</td>
<td>−29.0</td>
<td>7.9</td>
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</table>
3.2. Hydrographic condition and POM dynamics in the surface water

Surface distributions of salinity, POC, δ\(^{13}\)C and C/N ratio changed both spatially and temporally accompanying changes in the river discharge (Fig. 4). During normal discharge, low salinity water (15–25) was distributed at the head of the bay and the river plume extended southward along the western side of the bay. High concentrations of POC (> 1 mg l\(^{-1}\)) were observed at the head of the bay and along the western coastline, corresponding to the river plume. The extremely high concentrations were observed at the eastern part of the bay head, showing a maximum concentration of 2.52 mg l\(^{-1}\) in the vicinity of the Nagoya port (Sta. A3). δ\(^{13}\)C values ranged from −17.3\(^{\%}\)o to −21.7\(^{\%}\)o and C/N ratios from 5.8 to 8.2 during normal discharge. These values agree with typical marine phytoplankton values. Moreover, POC concentrations are significantly correlated with Chl concentrations \((r^2 = 0.96)\), indicating the evidence of the predominance of marine phytoplankton.

During high discharge, on the other hand, brackish water (< 15) occupied the head of the bay, and thus low salinity water, which was distributed at the head of the bay on 20 June, was pushed toward the center of the bay. POC distributions were characterized by low concentrations less than 1.5 mg l\(^{-1}\) over almost the whole area. δ\(^{13}\)C values ranged from −17.6\(^{\%}\)o to −26.5\(^{\%}\)o and C/N ratios from 7.7 to 15.0. POM with low δ\(^{13}\)C (< −21\(^{\%}\)o), high C/N ratios (> 10) and high C/Chl \(a\) ratios (> 200) observed at the head of the bay indicates a strong influence of riverine materials from the Kiso Rivers during high discharge.

Low salinity water was distributed over the whole observational area after discharge. Latitudinal gradients show that low

Fig. 4. Horizontal distributions of salinity, POC, δ\(^{13}\)C and C/N ratio in the surface water in the northern part of Ise Bay on 20 June, 28 June and 4 July, 2000.
salinity water flowed southwest because of the Coriolis force. The concentrations of POC were the highest of the three observational dates, showing a maximum (3.63 mg l\(^{-1}\)) at Sta. A3. High POC concentrations were distributed extensively at the northern part of the bay with the exception of the vicinity of the western river mouth, corresponding with the brackish water region (\(s < 15\)). Outside the strong salinity gradient at the center of the bay, POC concentrations were low. \(\delta^{13}C\) values ranged from \(-14.3\%_{oo}\) to \(-21.0\%_{oo}\) and C/N ratios from 5.5 to 7.3. These values and the high correlation \((r^2 = 0.93)\) between POC and Chl indicate that POM was dominated by phytoplankton as in normal discharge. Recovered high POC concentrations and \(\delta^{13}C\) values resulted from the blooming of phytoplankton (Sugimoto et al., 2004).

3.3. Hydrographic conditions and POM dynamics in water column

Fig. 5 shows vertical distributions of temperature, salinity and PO\(_4\)-P along the longitudinal section. The water is strongly stratified and a well-defined pycnocline separates upper and lower layers in each observation. Water masses can be divided into two groups; the upper layer water was fresher and warmer, while the middle and lower layer water was saltier and colder. During normal discharge, the influence of freshwater was moderate, and thus low temperature (<20 °C) and high salinity water (>31) occurred at depths shallower than 10 m. During high discharge, however, low salinity water (<25) occupied the upper layer and high salinity water retreated below 10 m (Fig. 5). Temperature in the upper layer became vertically homogeneous. After discharge, the water was strongly re-stratified in the upper layer, and the high salinity water was restored to shallower depths.

During normal and after discharge, high concentrations of PO\(_4\)-P (>1 μM) were distributed widely in the lower layer and a part of it was supplied to the upper layer at the head of the bay (Sta. A1) by estuarine circulation. The highest concentration of PO\(_4\)-P (>3 μM) was observed after the discharge (Sta. A11). However, this nutrient pool was pressed to the bottom and pushed southward during high discharge. The distributions of PO\(_4\)-P indicate the flood weakened the estuarine circulation temporarily, but the circulation recovered after the discharge.

Vertical distributions of POC, \(\delta^{13}C\), C/N ratio and turbidity along the longitudinal sections in the bay are shown in Fig. 6. The POC concentrations in the upper layer greatly changed with river discharge, whereas those in the middle and lower layers remained at a low level (<0.2 mg l\(^{-1}\)). On the other hand, the distributions of \(\delta^{13}C\) and C/N ratios indicate that the composition of POM in the middle and lower layers changed more than that in the upper layer. Furthermore, turbidity distributions separated clearly two nepheloid layers at the surface and bottom (>2 ppm). The surface nepheloid layer was always detected, whereas the bottom nepheloid layer was observed only during high and after discharge. In particular, the turbidity maximum (>10 ppm) was prominent at the head of the bay after discharge.

Fig. 5. Longitudinal distributions of temperature, salinity and PO\(_4\)-P on 20 June, 28 June and 4 July, 2000.
During normal discharge, high POC concentrations (> 1 mg l^-1) were observed in the upper layer, showing a decreasing trend offshore. High δ¹³C (> -21%) and low C/N ratios (<10) were also observed in the upper layer, with the exception of the maximum C/N ratio (11.5) near the river mouth. During high discharge, POC concentrations decreased significantly in the upper layer. POC with higher δ¹³C was pushed toward the central region by the flood and vertical variation of δ¹³C decreased along with the weakened pycnocline. C/N ratios were slightly higher than those during normal discharge in the surface layer. After discharge, the POC concentrations recovered rapidly because of phytoplankton blooming (Sugimoto et al., 2004), and thus POM with high δ¹³C and low C/N ratios were observed in the upper layer.

Dynamics of POM in the middle and lower layers was considerably different from that in the upper layer. During normal discharge, low C/N ratio (<10) and low δ¹³C (< -21%) were observed in the middle layer, with the minimum δ¹³C value (-23.2%) near the river mouth. During high discharge, on the other hand, the C/N ratios were high (>10) and δ¹³C was low (< 21%) in the lower layer, indicating that terrestrial material dominated to at least 20 km from the river mouth. Correspondingly, the nutrient pool was pressed to the bottom and pushed southward (Fig. 5). After discharge, low δ¹³C and high C/N ratios were observed in the middle layer near the head of the bay. POM with higher δ¹³C and lower C/N ratios apparently intruded from the offshore side in the lower layer (Fig. 6). This feature is clearly displayed in a temperature–δ¹³C diagram at high and after discharge at the head of the bay where POM moved dynamically (Fig. 7). During high discharge, the data can be divided into two groups: an upper layer group that has higher temperature (>22 °C) and higher δ¹³C (> -22%), and a middle and lower layer group that has lower temperature (<22 °C) and lower δ¹³C (< -20%). After discharge, on the other hand, the data can be divided into three groups: an upper layer group that has significantly high temperature (>24 °C) and high δ¹³C (> -22%), a middle layer group that has low temperature (<20 °C) and low δ¹³C (< -20%), and a lower layer group that has low temperature (<20 °C) and significantly high δ¹³C (> -18%) value, which is entirely different from the other groups. The after-discharge middle layer group must
be the relic of the high-discharge middle and lower layer group, because they are plotted in the same area on the diagram. Vertical profiles of deviation of observed current (Sta. B2), density (Sta. B2) and $\delta^{13}C$ for POM (Sta. A5) also support that POM in the lower layer at high discharge and the middle layer after discharge were the same material (Fig. 8). The observed currents were measured from 2 m to 18 m by the ADCP during ebb tide. Positive and negative velocity in the figure indicates down-estuary outflow and up-estuary inflow, respectively. The steep shear in the middle layer (~12 m) indicates the strong inflow in the lower layer. This intruding bottom water (<13 m) had an almost constant density ($\sigma_z \approx 23.5$) and was distinguishable from the water in the middle layer as discontinuity of density at 11 and 14 m. The $\delta^{13}C$ for POM in the outflow was lower ($-21.8\%$) than those in upper and bottom waters ($> -18.5\%$). Apparently, riverine POM loaded in the middle and lower layers at high discharge was pushed to the head of the bay and uplifted to the middle layer after discharge.

3.4. Estimates of the riverine fraction of POC in the bay

In order to assess the riverine contribution into the bay, we have applied a mixing model based on bulk composition of POM. To calculate contribution of riverine organic matter to POM in the bay, it is assumed that the isotopic composition of POC in the bay resulted from mixing of riverine and marine end-members with distinct carbon isotopic compositions. The isotopic composition of each end-member was assumed to be constant at each observational date and unaffected by end-member tissue decomposition (Gearing et al., 1984). The ratio of terrestrial organic carbon ($f$) was calculated using the following two-source formula (Sweeny and Kaplan, 1980; Eddins, 2001):

$$f(\%) = \frac{(\delta^{13}C_M - \delta^{13}C_S)}{(\delta^{13}C_M - \delta^{13}C_R)} \times 100,$$

where $\delta^{13}C_M$, $\delta^{13}C_S$, and $\delta^{13}C_R$ are the values of $\delta^{13}C$ for the marine end-member, the suspended POM samples and the riverine end-member, respectively. In order to estimate the contribution of riverine organic carbon using the two-source formula, we have to estimate the values of $\delta^{13}C_M$ and $\delta^{13}C_R$. The isotopic composition of the riverine end-member ($\delta^{13}C_R$) was calculated as follows:

$$\delta^{13}C_R = a\delta^{13}C_K + b\delta^{13}C_N + c\delta^{13}C_I$$

$$a = R_K / (R_K + R_N + R_I)$$

$$b = R_N / (R_K + R_N + R_I)$$

$$c = R_I / (R_K + R_N + R_I)$$

where $\delta^{13}C_K, \delta^{13}C_N, \delta^{13}C_I$ and $R_I$ are isotopic composition and river discharge of the Kiso, Nagara and Ibi Rivers, respectively. Using the values listed in Table 1, $\delta^{13}C_R$ is calculated as $-27.7\%$ on 20 June, $-26.5\%$ on 28 June and $-25.7\%$ on 4 July. The isotopic composition of the marine end-member was taken as the generally accepted value ($\delta^{13}C_M = -20\%$). We assume no fraction ($f = 0\%$) of terrestrial materials if $f$ is calculated as a negative value.
Fig. 9 shows the horizontal and vertical distributions of the contribution of riverine organic matter to POM in the surface water and in the water column along a longitudinal section, respectively. During normal and after discharge, the contribution of riverine organic matter to the surface water was less than 15%, while it increased to more than 50% within 10 km from the river mouth during high discharge (Fig. 9a). The distribution of high riverine fractions corresponded with that of brackish water (Figs. 4 and 9a). The contribution in the water column was significantly different from that in the surface water. The contribution was less than 30% in the middle layer at normal discharge. On the other hand, at high discharge, the contribution was highest in the bottom layer, with a maximum of 60% around 25 km from the river mouth. After discharge, the maximum contribution (>20%) was not located in the bottom, but rather in the middle layer.

The calculated contribution might be underestimated because the marine end-member was taken as $-20^\circ_\text{o}$. If the marine end-member was taken as the observed maximum values in each observation, the contribution in the surface water would slightly increase during high discharge ($\delta^{13}\text{C}_\text{M} = -17.6^\circ_\text{o}$), while that after discharge would significantly increase to $\sim$50% near the river mouth ($\delta^{13}\text{C}_\text{M} = -14.5^\circ_\text{o}$). In the water column, on the other hand, the contribution would become $\sim$80% in the bottom layer during high discharge ($\delta^{13}\text{C}_\text{M} = -17.6^\circ_\text{o}$) and $\sim$40% in the middle layer after discharge ($\delta^{13}\text{C}_\text{M} = -14.5^\circ_\text{o}$). Even in this case, however, the uplift of riverine organic matter still appears after discharge.

4. Discussion

4.1. Spatial and temporal variation in POM compositions

There were two peak discharges within a week (Fig. 3). The observation was conducted on the second peak. The first discharge possibly flushed riverine POM and thus the influence of terrestrial materials could be underestimated in our analyses. However, the significant increase in POC concentrations and C/N ratios of POM in the river during high discharge (Table 1) ensure that we grasp the gist of POM behavior following large river discharge.

Composition and concentration of POM in the Kiso Rivers were significantly changed by the variation in river discharge (Table 1). Phytoplankton production in Japanese rivers is usually small because the catchment basin is mountainous and thus water retention time is short (Murakami et al., 1994). During high discharge, POC concentrations in the Kiso River and the Ibi River increased rapidly, presumably as a result of riverbed sediments and large terrestrial loads. Sediments deposited on the riverbed during low discharge are usually resuspended during high discharge (Meade et al., 1985; Bianchi et al., 2002). However, POC concentrations in the Nagara River stay approximately constant over the first two dates and the initial PON is different from those found in the other rivers. These differences lead to C/N ratios varying similarly on all three rivers but clearly the Nagara River is different. After the estuarine weir began operating in the Nagara River in 1994, the blooming of freshwater phytoplankton, mainly composed of diatoms, was frequently found upstream of the weir (Murakami et al., 1998). This indicates high POC and PON concentrations in the Nagara River during normal discharge may be due to freshwater phytoplankton. The lower C/N ratio in the Nagara River than those in the other rivers supports the predominance of phytoplankton. The composition of the riverine POM that intruded into the bay thus varies temporally with river discharge.

POC to Chl a ratio (C/Chl a ratio) indicates the relative amount of phytoplankton in total POM, and reflects its photosynthetic ability (Parsons, 1975). C/Chl a ratios lower than 100 indicate a dominance of fresh phytoplankton, while that of non-phytoplanktonic material shows a remarkably higher
value (Zeitzschel, 1970; Cifuentes et al., 1988; Maksymowska et al., 2000). Fig. 10 displays the relationships between C/Chl \( a \) ratio and C/N ratios and \( \delta^{13}C \) in the bay on 20 June, 28 June and 4 July, 2000. During normal discharge, POM with low C/Chl \( a \) ratio in the upper layer showed high \( \delta^{13}C \) and low C/N ratio, and thus POM would consist mainly of marine phytoplankton. In the middle layer, however, higher C/Chl \( a \) ratios (>100) were obtained, and \( \delta^{13}C \) and C/N ratios were mostly low and high, respectively. Yamada et al. (1998) reported that \( \delta^{13}C \) of POM occupied by freshwater diatoms (−30 to −28‰) is lower than that of marine phytoplankton. In rivers and lakes, the production of CO\(_2\) during the decomposition processes is sufficient to provide dissolved inorganic carbon (DIC) with low values of \( \delta^{13}C \). Phytoplankton that takes up recycled DIC with low \( \delta^{13}C \) produces POM with low \( \delta^{13}C \) (Ogawa and Ogura, 1997; Hellings et al., 1999). Moreover, C/N ratios in the middle layer were slightly high compared to other layers (Figs. 6 and 10). Degradation of POM increases C/N ratios, while \( \delta^{13}C \) changes little (Andrews et al., 1998). It is suggested, therefore, that riverine algae and their detritus, not marine phytoplankton or terrestrial organic matter, might dominate POM in the middle layer during normal discharge.

The contribution of terrestrial materials to POM significantly increased in the bay during high discharge (Fig. 9). Though most of POM in the upper layer has low C/Chl \( a \) ratios (<100), the values of \( \delta^{13}C \) and C/N ratio during high discharge were clearly lower and higher than those during normal discharge \( (p < 0.05, \text{respectively}) \). On the other hand, C/Chl \( a \) ratios (>100) were high in the middle and lower layers, where the contribution of riverine POM was strong (Fig. 9b). The heavier terrestrial POM, which was loaded from the Kiso Rivers, would be transported into the water column and accumulated in the bottom layer.

After discharge, riverine contribution was estimated to be less than 20% in the upper layer, but 20–40% in the middle layer (Fig. 9). Most of POM showed low C/Chl \( a \) ratios, high \( \delta^{13}C \) and low C/N ratios (Fig. 10), and thus POM in the upper layer would originate from marine phytoplankton. On the other hand, C/Chl \( a \) ratios in the middle and lower layers were significantly different from those in the upper layer. Most of POM with high C/Chl \( a \) ratios (>100) in the middle layer had low \( \delta^{13}C \) and high C/N ratios, and thus the POM would be composed of terrestrial POM. Degradation of organic matter can elevate C/Chl \( a \) ratios if Chl \( a \) decomposes at a greater rate than total organic carbon (Cifuentes et al., 1988). Thus, POM in the lower layer with high \( \delta^{13}C \) and high C/Chl \( a \) ratio could be degraded marine phytoplankton, which had bloomed in the surface water. POM in the middle and lower layers were a complicated admixture of several materials (terrestrial materials, freshwater and marine algae) compared to that in the upper layer, and the admixture greatly changed temporally and spatially.

4.2. Influence of terrestrial POM on the bay

Terrestrial organic carbon must undergo rapid removal and decomposition during estuarine mixing processes (Hedges et al., 1997). In slow-flowing river, they deposit and accumulate by flocculation in oligohaline zones (Matson and Brinson, 1990; Thill et al., 2001). Turbidity maximum is formed at the edge of the intrusion of salt water, or null point. In Chesapeake Bay, sedimentation is the ultimate fate of most terrigenous material delivered to the estuary turbidity maximum (Sanford et al., 2001). Salt water intrudes into the Kiso Rivers, except for the upstream side of the weir in the Nagara River. Most terrestrial organic carbon is deposited in the oligohaline zone before reaching the river mouth at normal and after discharge, and thus the fraction of riverine POC was small in the surface water (Fig. 9a). During high discharge, however, POC concentrations in the Kiso Rivers clearly increased. The extension of the salt wedge is mainly controlled by river discharge, with the salt wedge being pushed seaward during high discharge (Thill

![Fig. 10. Scatter diagram of C/N ratios (upper) and \( \delta^{13}C \) (lower), and C/Chl \( a \) ratios on 20 June, 28 June and 4 July, 2000. Pluses, triangles and circles indicate the data in the upper (<5 m), middle (6–20 m) and lower (>21 m) layers, respectively.](image-url)
et al., 2001). In addition to high concentrations of riverine materials, disturbance and seaward movement of the salt wedge would lead to high contributions of riverine materials in both surface waters and water column during high discharge.

Though the amount of riverine organic matter load increased at high discharge, the total amount of POC in the upper layer decreased around the river mouth (Figs. 4 and 9a). The strong relationship ($r^2 = 0.97$, $p < 0.01$) between Chl $a$ concentrations and salinity in the surface water indicates that the decrease of POC concentrations was mainly due to rapid changes of physical processes with flushing (Sugimoto et al., 2004). It was also suggested that the aggregation of algal cells in a bay and clay particles loaded from rivers and sedimentation may occur at the head of the bay (Avnimelech et al., 1982). Naudin et al. (1997) reported that the decrease in salinity induced by the spreading of freshwater into the marine environment interrupted primary production, and prevented its restarting as long as the riverine influence was dominant. After discharge, on the other hand, phytoplankton bloomed using nutrients that were loaded from the rivers during high discharge, and the highest POC concentrations and the highest $\delta^{13}C$ were recorded among the three observational periods (Sugimoto et al., 2004). These results suggest that the behavior of phytoplankton is more important than riverine material in determining the surface concentration and distribution of POM in the bay.

The highest POC concentration was detected near the Nagoya port (Fig. 4), suggesting that the port might be one of sources of POM. The port is highly polluted region that receives a large amount of anthropogenic materials from Nagoya. Moreover, Chl concentrations near the port (Sta. A3) were higher than that in the bay (not shown here). During high discharge, the concentration of pheophytin was drastically decreased near the port but increased in the bay, indicating that the large amount of POM pooled in the port was flushed out by the discharge (Sugimoto et al., 2004).

4.3. Behavior of POM and estuarine circulation

The longitudinal estuarine circulation is most important for water and material exchanges, although the flow structure is essentially three-dimensional in Ise Bay (Fujiwara et al., 1997; Fujiwara et al., 2002; Kasai et al., 2002). Oceanic water intruding into the bay goes through the deepest depression in the northern part (Fujiwara et al., 1997; Kasai et al., 2000). In this survey, water of highest density was observed in the bottom layer along the depression (not shown here), supporting the previous studies. Therefore, the longitudinal section was mainly highlighted in this paper.

Suspended matter from the rivers is exported to the coastal zone along the two major pathways in the surface and the bottom layer (Naudin et al., 1997; Thill et al., 2001). The latter was significantly affected by estuarine circulation. Dynamic movement of POM observed near the head of the bay after discharge (Fig. 6). Terrestrial POM in the bottom layer was pushed to the head of the bay by the enhanced estuarine circulation and was uplifted to the middle layer. This behavior of terrestrial organic matter is similar to the formation of middle layer hypoxia in Ise Bay. The sudden intrusion of oceanic water uplifted hypoxia, which had been situated in the bottom (Kasai et al., 2004a). Moreover, in our case, the turbidity maximum was formed at the head of the bay after discharge (Fig. 6). The estuarine circulation in Chesapeake Bay enhances flood currents below the salt front and causes resuspension of sediments during full flood (Sanford et al., 2001). The formation of this turbidity maximum supported our idea that the return flow in the bottom layer plays an important role in material transport and to the subsequent distributions. On the other hand, POM with significantly high $\delta^{13}C$ was brought into the lower layer after discharge. In Winyah Bay, the enhanced landward flow of marine water brought marine POC into the estuary and the isotopic composition of POC became significantly higher (Eddins, 2001). In our case, phytoplankton grown at the bay head was transported to the bay mouth by the surface current, and then came back to the bay head through the lower layer by strong mixing at the Irago Strait (bay mouth) and the bottom return flow.

Mishima et al. (1999) reported from analysis of sedimentary organic matter that most terrestrial organic matter is deposited within 10 km from the river mouth in Osaka Bay. In the bay, riverine POM would also be deposited before reaching the river mouth as in the Kiso Rivers during low discharge. $\delta^{13}C$ for sedimentary organic matter usually represents integrated values resulting from various processes (e.g. flood and resuspension). $\delta^{13}C$ for sedimentary organic matter in Osaka Bay may not reflect the steady state, but rather the large amount of riverine POM loads during high discharge.

A pulse discharge of over 1000 m$^3$ s$^{-1}$ from the Kiso Rivers is often observed, especially in summer (Fig. 2). Therefore, the response reported in this study would frequently occur in Ise Bay. Furthermore, it is well known that hypoxia develops extensively in summer. The deposition of terrestrial POM is one of the major causes of hypoxia. To clarify the fate of allochthonous materials moving in the water column is thus important for future management of Ise Bay.

5. Conclusions

The data presented in this paper provide a series of hydrographic conditions and POM dynamics accompanying changes of river discharge in the major gulf-type estuary of Japan. The conclusions of this study are schematically illustrated in Fig. 11. The behavior of riverine POM was significantly regulated by the hydrographic conditions and was divided into two groups; the upper layer and the middle and lower layers. The former showed simple dynamics accompanying changes in the river plume. The contribution of riverine POM significantly increased to 50% at ~10 km from the river mouth during high discharge, while it was negligible during normal and after discharge. On the other hand, the latter showed complex dynamics because of the changes in both river discharge and estuarine circulation. Before the flood, the contribution of terrestrial POM was negligible. Terrestrial POM was loaded into
the bottom layer by high discharge. It was then pushed to the head of the bay by the enhanced estuarine circulation and uplifted to the middle layer after discharge.

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