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Determination of the freshwater origin of Coastal Oyashio Water using humic-like fluorescence in dissolved organic matter

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Abstract
Coastal Oyashio Water (COW), defined as a water mass with a temperature lower than 2 °C and a salinity lower than 33.0, is distributed in the North Pacific Ocean off southeastern Hokkaido, Japan, from winter to spring. COW is rich in macronutrients and dissolved iron and is thus considered to affect the spring phytoplankton blooms in the Oyashio region. Although river water and sea-ice melt water have been considered freshwater end-members of COW, the contributions of these freshwater sources to COW have not been well described. In this study, the humic-like components in dissolved organic matter were first applied as a parameter to evaluate the freshwater end-members of COW in March 2015. Linear regressions with negative slopes were determined between the humic-like components and the salinity of COW. The intercepts of the regressions against the humic-like components were within the ranges of those observed for the local rivers of Hokkaido but were very different from those of sea ice. These findings suggest that river water contributed to the COW observed here as a freshwater end-member, although the contribution of sea-ice melt water to COW could not be evaluated. This novel approach also highlighted two different less-saline water masses in COW. The first was characterized by a lower temperature and relatively high levels of humic-like components, while the second was higher in temperature and had higher levels of humic-like components. It is suggested that these different characteristics are due to the contributions of water from different rivers and/or different effects of sea-ice melt water.

Keywords Coastal Oyashio Water · Freshwater end-member · River water · Sea-ice melt water · Dissolved organic matter · Humic fluorescence

1 Introduction
Riverine humic substances can be considered one of the major components of dissolved organic matter (DOM) in coastal environments because linear negative correlations between the salinity and dissolved organic carbon (DOC) concentration as well as the fluorescence derived from terrestrial humic substances have often been observed (Fellman et al. 2010; Yamashita et al. 2011; 2015a; Cao et al. 2016). These negative correlations also suggest that the fluorescence intensity of terrestrial humic substances (in other words, the levels of terrestrial humic fluorophores) can be used as a tracer of river water, similar to the oxygen isotopes of water or alkalinity (e.g., Yamamoto-Kawai et al. 2009). However, it should be noted that marine organisms, in particular bacteria, produce humic-like fluorophores (e.g., Romera-Castillo et al. 2011; Goto et al. 2017; Arai et al. 2018), sunlight degrades humic-like fluorophores
environments in coastal regions, such as a region where sev-
traced using humic-like fluorophores in combination with
ies imply that freshwater end-members can be specified and
sudera 1986), is widely distributed (Isoda et al. 2003; Kono
salinity lower than 33.0 (Ohtani 1971; Hanawa and Mit-
as a water mass with a temperature lower than 2 °C and a
winter to spring, the Coastal Oyashio Water (COW), defined
from various rivers in Hokkaido, estuarine water from the
Amur River, and sea ice from the Sea of Okhotsk were used
as freshwater end-members. Negative correlations between
salinity and humic-like fluorophores are usually observed in
costal environments, as mentioned above, indicating that
the levels of humic-like fluorophores in riverine end-mem-
bers are higher than those in marine end-members in coastal
environments. It is well established that levels of humic-
like fluorophores in sea-ice melt water are low compared to
seawater due to drainage with brine rejection during sea-ice
formation (Stedmon et al. 2007, 2011; Müller et al. 2013).
Therefore, to evaluate the major freshwater end-members
of COW, it is important to assess the relationship between
salinity and humic-like fluorophores.

2 Materials and methods

2.1 Observations and sample collection in COW
and the Oyashio region

Observations of the Oyashio region, covering the COW,
were carried out in March 2015 during a cruise on the R/V
Hakuho Maru KH-15-1 (Fig. 1). An observation transect
was followed along the “A-line” from off Akkeshi to south-
east Hokkaido, Japan. Station A1 was observed 7 times from
the 9th to the 20th (JST) during the cruise. The sampling
dates for the other stations were as follows: 8th (station A0),
9th (station A2), 14th (station A3), 15th (station A4), 16th
(stations A11 and A8), 17th (station A6), and 18th (station
A5). In addition to the A-line, observations were carried out
at eight stations in the region.

Seawater samples were generally collected from the surface
to the bottom or 250 m using a
conductivity-temperature-depth (CTD)-carousel multiple sampling (CMS) system (SBE-911plus and SBE-32 water samplers, Sea Bird Electronics, Inc.) equipped with acid-cleaned Niskin-X bottles. Samples were collected from the surface to ~ 5000 m at some stations. An acid-cleaned 0.22 μm Durapore filter (Millipak, Millipore) was attached directly to the spigot of the Niskin bottles, and seawater was gravity filtered into a precombusted glass vial with an acid-cleaned Teflon-lined cap after triple rinsing. The samples were then stored frozen in the dark until analysis (4–16 months). The temperature and salinity used in this study were collected by the CTD sensors. Chlorophyll a concentrations were determined with the fluorometric method of Welschmeyer (1994).

The current velocity data at station A1 were obtained by a vessel-mounted acoustic Doppler current profiler (ADCP) at 10-min intervals (Teledyne RD Instruments, broadband 76.8 kHz). After correcting the misalignment of the ADCP (Joyce 1989) and removing erroneous data whose percent good derived from the ADCP data was less than 80 as well as those obtained when the ship was accelerating, we obtained a velocity profile of each cast by temporally averaging the data during the cast.

2.2 Collection of sea-ice samples

Four sea-ice blocks were collected with a basket suspended from the ship’s crane over the ice surface in the southern Sea of Okhotsk (Fig. 1) during cruises aboard the icebreaker P/V Soya in February 2012, February 2013, and February 2014, according to Kanna et al. (2014). The sea-ice blocks were placed in double plastic bags and then stored frozen in the dark. In the onshore laboratory, a sea-ice block was broken into small pieces with an icepick and a ceramic knife, and small pieces were placed into an acid-cleaned Teflon beaker and melted in the dark at room temperature. Immediately after melting, the sea-ice melt water was filtered through a 0.22 μm filter (Durapore, Millipore) under a gentle vacuum, collected in precombusted glass vials with acid-cleaned, Teflon-lined caps after triple rinsing, and then stored at − 20 °C for 2 days until analysis. The salinity of the sea-ice samples was measured by an automatic salt/chloride analyzer (model SAT-210, Towa Electronic Industry) with a conversion factor for salinity, according to Kanna et al. (2014).

2.3 Collection of a sample in the estuary of the Amur River

One estuarine sample was collected at a station in the vicinity of the mouth of the Amur River (53.45°E, 142.00°N) on 8 September 2006 by the R/V Professor Khromov (Far Eastern Hydrometeorological Research Institute; FERHRI). The sampling procedure is described here only briefly, but is described in detail elsewhere (Nishioka et al. 2014). Surface water (2 m) was collected by the CTD-CMS system equipped with acid-cleaned Niskin-X bottles, filtered through a 0.22 μm Durapore filter (Millipak, Millipore), collected in an acid-cleaned FLPE bottle, and then stored frozen in the dark until analysis. The temperature and salinity used in this study were collected by the CTD sensors.

2.4 Collection of river water samples in Hokkaido, Japan

Observations of 33 rivers located in the southern and eastern parts of Hokkaido, Japan, were carried out on 18–20 September 2011. The hydrographs of the rivers during sampling could be characterized as base flow. The rivers consisted of small streams to the middle and lower reaches of relatively large rivers, such as the Tokachi, Kushiro, and Abashiri rivers. The upper reaches of the relatively large rivers are generally covered with forests (Woli et al. 2008; Muneoka et al. 2012). The middle reaches of the Tokachi and Abashiri rivers are covered with agricultural areas (Woli et al. 2008; Muneoka et al. 2012). The lower reaches of the Kushiro River flow through the Kushiro Mire (Ahn et al. 2008). Thus, the rivers observed in this study cover various types of watersheds: forests, agricultural areas, and wetlands. It is well established that the quantity and quality of DOM in river water are dependent on the watershed environment (e.g., Stedmon et al. 2003; Williams et al. 2010). As such, it can be expected that the riverine DOM observed in this study will show wide variability in quantity and quality due to the range of watershed environments.

River water samples were collected from the center of a bridge using a bucket that had been rinsed three times. The
Parallel factor analysis (PARAFAC) statistically decomposes EEMs into several fluorescent components and residues. PARAFAC modeling of EEMs has already been described in detail elsewhere (Stedmon et al. 2003; Stedmon and Bro 2008). PARAFAC analysis was conducted using MATLAB (MathWorks, Natick, MA, USA) with the DOM-Fluo toolbox (Stedmon and Bro 2008). The wavelength range used for PARAFAC was 250–455 and 290–520 nm for excitation and emission, respectively. Two river water samples were identified as outliers through the PARAFAC procedure, and the three-component model was validated by split-half validation and random initialization (Stedmon and Bro 2008).

3 Results

3.1 Hydrographic conditions during the observations

The spatial distributions of the temperature, salinity, and chlorophyll a concentration in the upper 250 m layer of the A-line are shown in Fig. 2. The lowest temperature (−0.2 °C) and salinity (32.2) were observed at station A0, and the temperatures at depths shallower than 75 m gradually increased towards the offshore. COW, namely, the water mass characterized by a temperature lower than 2 °C and a salinity lower than 33.0, was observed at the surface layer at stations A0 to A6 along the transect. The temperature and salinity at depths deeper than 75 m at onshore stations were generally low compared with those at offshore stations, while a water mass characterized by relatively high temperature and salinity was distributed between 75 and 200 m at station A3.

Figure 3 shows the temporal changes in the current velocity at 27 m, the temperature, and the salinity during consecutive observations at station A1. A water mass characterized by low temperature (<0 °C) and relatively high salinity (approximately 32.5) was distributed throughout the water column on 9 March. From 14 to 18 March, a water mass featuring a slightly higher temperature (~1 °C) and a lower salinity (<32.4) was distributed in the surface layer. A water mass other than the COW was distributed in the water column deeper than 16 m on 14 March. The temperature and salinity were relatively uniform throughout the water column from 19 to 20 March (0.8–1.2 and 32.7–32.9 °C, respectively). The current direction did not change much during consecutive observations and was generally comparable to the climatological mean seasonal flow for the coastal region of south Hokkaido (Rosa et al. 2007). However, a low-pressure system developed during the cruise and passed over Hokkaido from south to north from 10 to 11 March 2015; thus, the low-pressure system may have led to significant changes in temperature and salinity at station A01 between 9 and 14 March.

The discharge from local rivers in eastern Hokkaido during winter (January–February) 2015 seemed typical, while the discharge during the first half of March 2015 appeared to be relatively high compared with that in other years. For example, at an observational station along the lower reaches of the Tokachi River (Moiwa), the average discharge in February 2015 (100 ± 3 m³ s⁻¹) was comparable to the range
observed in the 10 years preceding 2015 (104 ± 10 m³ s⁻¹ in 2005, 101 ± 17 m³ s⁻¹ in 2006, 109 ± 13 m³ s⁻¹ in 2007, 95 ± 6 m³ s⁻¹ in 2008, 80 ± 7 m³ s⁻¹ in 2009, 104 ± 12 m³ s⁻¹ in 2010, 124 ± 13 m³ s⁻¹ in 2011, 114 ± 10 m³ s⁻¹ in 2012, 137 ± 22 m³ s⁻¹ in 2013, and 124 ± 11 m³ s⁻¹ in 2014). However, the average discharge from 1 to 15 March 2015 (143 ± 54 m³ s⁻¹) at the Moiwa station was higher than that during the same period in 2005–2014 (from 93 ± 7 m³ s⁻¹ in 2005 to 119 ± 5 m³ s⁻¹ in 2013).

Figure 4 shows a temperature–salinity (T–S) diagram for the seawater samples collected from the upper 250 m at all stations. Approximately 60% of the samples collected were characterized as COW. According to Nakayama et al. (2010), samples corresponding to a relatively high temperature and salinity could be characterized as modified Kuroshio Water (MKW), which detaches from the Kuroshio Extension (Yasuda et al. 1992). Other samples could be categorized as Oyashio Water (OYW).

The chlorophyll a concentration ranged from 0.01 to 4.01 mg m⁻³ in this study. Levels of chlorophyll a along the A-line were generally high in the surface layer and decreased with depth (Fig. 2). Higher levels (1.0–1.5 mg m⁻³) of chlorophyll a along the A-line were observed at onshore stations (i.e., A0 and A1), and the highest levels seen in this study (3.4–4.0 mg m⁻³) were observed at station I located at 145.29°E, 42.93°N. The chlorophyll a concentration observed in this study generally corresponded to prebloom periods because a long-term observation carried out from 1990 to 1998 found that the chlorophyll a concentration in the spring bloom of the Oyashio region ranged from 2.2 to 12.8 mg m⁻³, with a mean ± 1 standard error of 5.67 ± 3.6 mg m⁻³ (Saito et al. 2002).

### 3.2 EEM-PARAFAC

A three-component model was validated based on the PARAFAC modeling of four EEMs of sea-ice melt water, 31 EEMs of river water in Hokkaido, one EEM of estuary water from the Amur River, and 290 EEMs of seawater (Fig. 5), implying that the EEM of the dataset exhibited relatively
small variations. Component 1 (C1) produced peaks at an emission wavelength of 480 nm from excitation wavelengths of < 250 and 350 nm. This component could be categorized as a humic-like fluorophore that is traditionally defined as terrestrial (Coble 1996). Component 2 (C2) could also be designated a humic-like fluorophore that is traditionally defined as marine because this component produced peaks at an emission wavelength of 398 nm from excitation wavelengths of < 250 and 315 nm (Coble 1996). In contrast, a peak produced at an emission wavelength of 334 nm from an excitation wavelength of 280 nm by component 3 (C3) represented a protein-like fluorophore, in particular a tryptophan molecule (Coble 1996; Yamashita and Tanoue 2003).

### 3.3 PARAFAC components in COW and the Oyashio region

The spatial distributions of the fluorescence intensities of individual PARAFAC components along the A-line are shown in Fig. 6. The distribution pattern of humic-like C1 is similar to that of humic-like C2. High levels of these humic-like components were generally found in the upper layer at onshore stations (A0 and A1) and in the water column deeper than 200 m. Low levels of humic-like components corresponded to water masses characterized by high temperatures (Figs. 2, 6).

The spatial distribution of protein-like C3 was somewhat different from those of humic-like C1 and C2 (Fig. 6). The levels of protein-like C3 were generally high in the surface layers and decreased with depth, irrespective of the differences in the stations. In the surface layers, particularly high levels were evident at the onshore stations (A0 and A1).
This distribution pattern of the protein-like component was similar to that of the chlorophyll \( a \) concentration (Figs. 2, 6).

Scatter plots between each PARAFAC component and salinity as well as the chlorophyll \( a \) concentration, with temperature on the \( z \)-axis, were determined for the COW observed in this study (Fig. 7). Negative linear relationships were evident between three PARAFAC components and salinity: 

\[
[C1] = -0.0072 \pm 0.0006 \times [\text{salinity}] + 0.25 \pm 0.02, \quad R^2 = 0.49, \quad n = 144, \quad p < 0.001; \\
[C2] = -0.0091 \pm 0.0009 \times [\text{salinity}] + 0.31 \pm 0.03, \quad R^2 = 0.42, \quad n = 144, \quad p < 0.001; \quad \text{and} \\
[C3] = -0.0064 \pm 0.0006 \times [\text{salinity}] + 0.22 \pm 0.02, \quad R^2 = 0.45, \quad n = 144, \quad p < 0.001.
\]

The chlorophyll \( a \) concentrations were exceptionally high (3.4–4.0 mg m\(^{-3}\)) for four samples obtained from 0–20 m at station I (Figs. 1, 7). Except for these samples, the correlation of the chlorophyll \( a \) concentration with protein-like C3 \( (r=0.58, n=140, p<0.001) \) was better than those with humic-like C1 \( (r=0.29, n=140, p<0.001) \) and C2 \( (r=0.21, n=140, p<0.001) \).

### 3.4 PARAFAC components in possible freshwater end-members of COW

The fluorescence intensity of humic-like C1 ranged from 0.038 to 0.471 for river water, from 0.002 to 0.011 for sea-ice melt water, and was 0.457 for the Amur River estuarine water. The fluorescence intensity of humic-like C2 ranged from 0.037 to 0.500 for river water, from 0.003 to 0.012 for sea-ice melt water, and was 0.555 for the Amur River estuarine water. Among the river water sources, the highest levels of humic-like C1 and C2 were derived from the lower reaches of the Kushiro River, which flows through the Kushiro Mire. The fluorescence intensity of protein-like C3 ranged from 0.006 to 0.093 for river water, from 0.007 to 0.024 for sea-ice melt water, and was 0.124 for the Amur River estuarine water. Thus, if one compares these end-member levels with the levels found in COW (Fig. 7), the abundance of humic-like C1 and C2 was highest for river water samples (including the estuarine water sample), followed by COW, and then the sea-ice melt water samples. The levels of protein-like C3 were similar in some of the river water samples, sea-ice melt water samples, and COW, even though the estuarine water and other river water samples contained levels that were one order of magnitude higher than those in COW.

### 4 Discussion

COW was evident in the coastal region of southeastern Hokkaido during this study (Figs. 2, 3), which is typical for this region (Kusaka et al. 2009). Higher concentrations of dissolved iron were evident, corresponding to less-saline water during the A-line observations in January (Nishioka et al. 2011). Thus, the freshwater origin of COW is crucial to understanding the mechanism of iron supply and thus to clarifying the mechanisms of the induction and maintenance of spring phytoplankton blooms (in other words, the factors shaping the spatiotemporal distribution of spring phytoplankton blooms) in the Oyashio region. Two different freshwater sources, namely, river water and sea-ice melt water, have been considered the end-members of COW (Ohtani 1971, 1989; Oguma et al. 2007, 2008; Kusaka et al. 2009). Mizuta et al. (2003) indicated that the surface water of the East Sakhalin Current is characterized by less-saline East Sakhalin Current Water due to the contribution of Amur River water. It was also suggested that the local rivers of eastern Hokkaido supply freshwater to COW (Oguma et al. 2007, 2008).
Negative linear relationships between the humic-like and protein-like components derived from EEM-PARAFAC and salinity were observed for COW (Fig. 7), implying that the major factor controlling the abundance of these PARAFAC components in COW was the mixing of low (and/or moderate)-salinity water with high-salinity water. More importantly, the relationships imply that these components can be useful for evaluating the freshwater end-member(s) of COW. However, it has often been observed that the abundance of protein-like PARAFAC components, in particular tryptophan-like PARAFAC components, is highest in intermediate-salinity water in some coastal environments due to the contribution of autochthonous DOM (Yamashita et al. 2008; Fellman et al. 2010, 2011). In this study, the ranges of the abundance of the protein-like component were similar among some river water samples, sea-ice melt water samples, and COW, implying that the protein-like component is produced in terrestrial aquatic environments, in sea ice, and possibly in coastal environments.

It has recently been well documented that both the traditionally defined terrestrial and marine humic-like fluorophores are produced by marine microbes (e.g., Yamashita et al. 2010; Catalá et al. 2015; Goto et al. 2017; Zhao et al. 2017; Tada et al. 2017), implying that it is difficult to determine the origin of humic-like fluorophores from their spectral characteristics. However, the levels of humic-like fluorophores, including traditionally defined terrestrial and marine humic-like PARAFAC components, in river water are usually high enough to trace these species in coastal environments (e.g., Dorsch and Bidleman 1982; Hayase et al. 1987; Del Castillo et al. 1999; Yamashita et al. 2008). In addition, the levels of humic-like components in sea-ice melt water are generally low due to brine rejection during sea-ice formation (Stedmon et al. 2007, 2011; Müller et al. 2013). Such characteristics of humic-like components indicate that the freshwater end-member(s) of COW can be evaluated using the relationships between humic-like components and salinity.
Figure 8 shows the relationships between the humic-like components and salinity for river water, the Amur River estuarine water, and sea-ice melt water in addition to COW. A linear regression line between the individual humic-like components and salinity determined using the COW samples (Fig. 7a, c) was extrapolated to a salinity of 0 in Fig. 8a, b, respectively. The intercepts of the regressions against fluorescence intensity (0.25 ± 0.02 and 0.31 ± 0.03 for C1 and C2, respectively) were within the range of fluorescence intensities of humic-like C1 and C2 observed for the river
water samples. The plots of the sea-ice melt water samples were very different from the regression lines for both humic-like C1 and C2. Furthermore, the levels of humic-like C1 and C2 in the sea-ice melt water samples were lower than those in COW. These results suggest minimal contributions from sea-ice melt water to COW at the time of sampling.

The relatively low $R^2$ values for the regression between humic-like components and salinity (Fig. 7) imply that the freshwater from various rivers possibly contributed to the COW observed in this study. Otherwise, the local rivers connected to the North Pacific may affect the COW only locally. Further studies are necessary to clarify the river(s) contributing to freshwater end-member(s) of COW.

It is interesting to note that two distinct water masses seemed to contribute less-saline water (<32.5) to COW (Fig. 7a, c). The first water mass featured a lower temperature (<0 °C) and relatively high levels of humic-like components. This water mass plotted near the regression line between humic-like components and salinity and seemed to mainly control the intercept with the humic-like components axis (Fig. 8). Temperatures below 0 °C and relatively high levels of humic-like components indicated that the river water was mixed with seawater and then cooled in a coastal environment to produce the features of this water mass. The other possible way to form the first water mass is through the influence of sea-ice melt water. A minor contribution from sea-ice melt water in addition to a major contribution from river water can produce moderate-salinity water. Subsequent mixing of moderate- and high-salinity water could form the first water mass.

The second water mass was characterized by a relatively high temperature (>0.8 °C; Fig. 7a, c). This water mass was observed in the surface layer at station A1 just after the passage of the low-pressure system (14–15 March; Fig. 3). The levels of humic-like components in this water mass were highest, and the plots of this water mass deviated slightly from the regression lines between humic-like components (in particular humic-like C1) and salinity. The deviations from the general regression lines imply that different rivers possibly contributed freshwater to the first and second water masses of the COW, respectively, and/or the sea-ice melt water contributions to the first and second water masses of the COW differed.

![Fig. 8a–b Scatter plots of humic-like C1 (a) and humic-like C2 (b) against salinity for the Coastal Oyashio Water (COW) and its possible end-members (river water, the Amur River estuarine water, and sea-ice melt water). The line in each panel is the linear regression between the humic-like component and salinity determined using the COW samples.](image-url)
5 Conclusions and implications

This study is the first to apply the relationship between salinity and humic-like fluorescence to evaluate the distribution of two distinct freshwater end-members in a coastal environment. The novel approach used in this study clarified that river water is the major freshwater end-member of the COW observed in this study. However, the approach could not be used to evaluate the contribution from sea-ice melt water to COW. Because the major freshwater end-member(s) of COW possibly change spatially and temporally, a comprehensive evaluation of the temperature, salinity, and humic-like fluorescence from winter to spring over a wider area (including the Sea of Okhotsk) is necessary. Moreover, the addition of different parameters that can evaluate freshwater end-members, e.g., δ18O of water (Oguma et al. 2007, 2008), would enable better evaluation of the spatiotemporal variations in the contributions of river water and sea-ice melt water to COW. In addition, a thorough investigation of the humic-like fluorescence in local rivers in Hokkaido, the Amur River and other rivers in Sakhalin should be carried out to identify the major river(s) that serve as the freshwater end-members of COW.

Two humic-like PARAFAC components, i.e., terrestrial humic-like C1 and marine humic-like C2 according to the traditional definitions, seemed to be useful for evaluating the freshwater end-members of COW. Both humic-like components are also produced in the open ocean by marine microbes (e.g., Yamashita et al. 2010; Catalá et al. 2015). Different behaviors of humic-like components (i.e., conservative and nonconservative behavior for terrestrial and marine humic-like components, respectively) were also observed in coastal environments (Yamashita et al. 2008; Cawley et al. 2014). Thus, in future studies, it would be better to use terrestrial humic-like components rather than marine humic-like components to evaluate the freshwater end-members of COW. An in situ fluorescence sensor that has excitation and emission wavelengths close to the peak of the terrestrial humic-like component (e.g., Yamashita et al. 2015b) would also be applicable to such future COW studies.

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