Shelf humic substances as carriers for basin-scale iron transport in the North Pacific

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Iron is one of the key elements controlling phytoplankton growth in large areas of the global ocean. Aeolian dust has traditionally been considered the major external source of iron in the North Pacific. Recent studies have indicated that sedimentary iron from the shelf region of the Sea of Okhotsk has a strong impact on the iron distribution in the North Pacific, while the mechanism supporting its long-distance transport remains poorly understood. Here, we report that refractory shelf humic substances, which complex and carry dissolved iron, are transported conservatively at least 4000 km from the shallow sediments of the Sea of Okhotsk to the subtropical North Pacific with the circulation of intermediate water. This result indicates that shelf humic substances are probably one of the key factors shaping the distribution of dissolved iron in the ocean interior.

Iron (Fe) is one of the essential elements for marine life and has low solubility in oxic seawater1,2; therefore, external inputs of Fe influence ocean primary productivity3,4. Aeolian dust, shelf sediments, and hydrothermal vents are major external sources of dissolved Fe (Fe3d), and the mechanisms that make Fe soluble and contribute to long-distance transport are vital to connecting external sources with primary productivity in remote ocean areas5,6. Although aeolian dust has traditionally been considered the major external source of Fe to the ocean6,7, shelf sediments have been noted to be much more important than aeolian dust or hydrothermal vents in terms of the percentage of the Fe3d inventory in the ocean and its role in fueling the biological carbon pump6. The chemical species of Fe3d contributing to long-distance transport from sediments are thus critical information to understand not only marine Fe cycle but also global carbon cycle.

Organic ligands increase the capacity of Fe to dissolve in seawater by complexing with Fe and possibly contribute to long-distance transport through protecting Fe3d from being scavenged1–4. Siderophores, saccharides, and humic substances have been considered probable Fe-binding organic ligands in marine environments4,8. Among these substances, refractory humic substances are probably the most important Fe3d carriers in the subsurface ocean because siderophores and saccharides are microbiologically labile10,11. Humic substances, which are complex and heterogeneous mixtures of organic molecules that form during the decay and transformation of biogenic remains, are highly functionalized and are generally characterized by their color due to their ultraviolet-visible (UV-Vis) absorbance12. As a consequence of their absorbance characteristics, humic substances exhibit fluorescence properties commonly referred to as humic-like fluorescent dissolved organic matter (FDOMH)13,14. It is well established that FDOMH is universally distributed over the Earth’s surface, namely, from streams to deep oceans15,16. Fe-binding ligands17 and FDOMH18–20 have been reported to be released during the microbial degradation of sinking particles, and a linear relationship was found between FDOMH and Fe(III) solubility (dissolution capacity of Fe) in subsurface waters21–24; thus, FDOMH is very likely a major Fe-binding organic ligand in the dark ocean. A global ocean Fe biogeochemical model also successfully applied autochthonous FDOMH as the main organic ligand to reproduce the Fe3d distribution in the ocean25. However, oceanographic linkage between Fe3d and FDOMH has not been explored with the basin-scale.

Here, we present the distribution of Fe3d together with FDOMH along a section in the western North Pacific (Fig. 1a) where basin-scale transport of sedimentary Fe3d from the shelf region of the Sea of Okhotsk has been reported26,27. We hypothesize that sedimentary Fe3d complexed with FDOMH is stable and contributes to long-distance transport with the circulation of intermediate water. Therefore, we separate the allochthonous (shelf-derived) fraction of FDOMH from the autochthonous fraction, which was determined by the relationship
with apparent oxygen utilization (AOU)\(^{18-20}\), and identify the relative contribution of allochthonous FDOM\(_H\) as a carrier of Fed in the intermediate water of the western North Pacific.

**Results**

**Transport of allochthonous FDOM\(_H\) by intermediate water.** Analogous to previous studies\(^{26,27}\), this study found the highest concentrations of Fed evident in the shelf region of the Sea of Okhotsk, and high concentrations of Fed were measured in intermediate to deep waters around the Bussol’ Strait due to strong diapycnal tidal mixing (Fig. 1b). The diapycnal tidal mixing at the deep sill of the Bussol’ Strait (2200 m) is known to be important to determine the physical and chemical properties of the intermediate water\(^{28-30}\). The levels of Fed in the North Pacific Intermediate Water (NPIW; 26.6–27.5\(\sigma_\theta\))\(^{31}\), which is characterized by a salinity minimum in subtropical regions (Supplementary Fig. 1a), were higher than those in the upper/deeper water masses. It has been suggested that the Fed derived from shelf sediments in the Sea of Okhotsk is transported to the basin region by the Okhotsk Sea Intermediate Water (OSIW; 26.6–27.0\(\sigma_\theta\))\(^{32}\) and then spreads through the circulation of intermediate water, including the NPIW, in the North Pacific\(^{26,27}\).

The lowest level of FDOM\(_H\) was observed in surface waters, which was likely due to the photobleaching of FDOM\(_H\)\(^{33-35}\), except in the shelf region of the Sea of Okhotsk (Fig. 1c). The levels along the transect generally increased with depth in the mesopelagic layer (200–1000 m) and then slightly decreased with depth in the deep layer (>1000 m). The distribution pattern of FDOM\(_H\) was almost identical to that of AOU (Supplementary Fig. 1b), as previously reported\(^{18-20,36,37}\).

Interestingly, however, the FDOM\(_H\)-AOU relationships in the mesopelagic layer and the deep layer were different (Fig. 2a). The FDOM\(_H\) levels in the mesopelagic layer were higher than those in the deep layer, thus showing deviations from the linear regression line obtained for the deep layer. Similar but smaller deviations in mesopelagic FDOM\(_H\) from the deep linear regression line have also been observed in the central North Pacific\(^{18}\). Because AOU represents the amount of oxygen consumed by respiration after the subduction of a water mass, the deep linear regression line has been attributed to the *in situ* FDOM\(_H\) produced by microbes during the oxidation of organic matter\(^{18-20}\). Thus, the autochthonous fraction of FDOM\(_H\) in the mesopelagic layer corresponds to the linear portion of the regression between AOU and FDOM\(_H\) (determined for the deep layer); then, the contribution of allochthonous FDOM\(_H\), which is defined here as FDOM\(_H^*\), can be estimated quantitatively (see Methods).

The distribution pattern of FDOM\(_H^*\) was distinctly different from that of FDOM\(_H\) (Fig. 1c,d). The highest level was observed in the shelf region of the Sea of Okhotsk. The levels of FDOM\(_H^*\) in the OSIW and the upper intermediate water (26.6–27.0\(\sigma_\theta\))\(^{31}\) were higher than those in the upper/deeper water masses from the Sea of Okhotsk to the south as far as 20°N in the subtropical North Pacific gyre, corresponding to the southernmost region of the NPIW distribution\(^{31}\). FDOM\(_H^*\) accounted for 37 ± 7% (\(n = 4\)) and 12 ± 4% (\(n = 9\)) of the bulk FDOM\(_H\) in the OSIW and the upper NPIW at 20–30°N, respectively (Supplementary Fig. 2). A negative linear relationship was evident between FDOM\(_H^*\) and salinity in the intermediate water (adjusted \(R^2 = 0.78\), Fig. 2b), even though FDOM\(_H\) was not linearly related to salinity in the intermediate water (adjusted \(R^2 = 0.003\).
the OSIW, which is influenced by the dense shelf water that forms in the coastal polynya through sea-ice formation involving the interaction with sediments\textsuperscript{32}, greatly contributes to the formation of the upper intermediate water\textsuperscript{31}, its negative relationship with salinity indicates that FDOM\textsubscript{H}\textsuperscript{*} from the shelf sediments of the Sea of Okhotsk is conservatively transported across the North Pacific through the formation and circulation of the intermediate water. The residence time of the OSIW in the Sea of Okhotsk was estimated to be 1.4–7 years\textsuperscript{38,39}. The apparent ages of intermediate water, including the NPIW, from the western subarctic to the subtropical North Pacific gyre were suggested to be ~25 years\textsuperscript{40}. Such timescales of the circulation of the intermediate water indicate that FDOM\textsubscript{H}\textsuperscript{*} is not removed nor transformed in the dark ocean for at least several decades.

Role of FDOM\textsubscript{H} in the chemical speciation of Fe\textsubscript{a}.

The Fe(III) solubility has been found to be controlled by organic complexation\textsuperscript{12}; thus, Fe(III) solubility is not simply related to FDOM\textsubscript{H} level in surface waters where siderophores and saccharides in addition to FDOM\textsubscript{H} are possibly key organic ligands of Fe\textsubscript{a}\textsuperscript{21,23,41,42}. However, it has been reported that the FDOM\textsubscript{H} level is linearly related to the Fe(III) solubility throughout the water column, except in the surface water\textsuperscript{21–23}. The linear relationship did not differ between the deep layer and the mesopelagic layer in the Sea of Okhotsk and the western subarctic Pacific\textsuperscript{21}, where autochthonous FDOM\textsubscript{H} is dominant and where FDOM\textsubscript{H}\textsuperscript{*} co-occurs with autochthonous FDOM\textsubscript{H}. Such a relationship indicates that Fe(III) solubility represented by the FDOM\textsubscript{H} level is the same between allochthonous and autochthonous fractions in the region. Therefore, we can estimate the Fe(III) solubility of bulk FDOM\textsubscript{H}, as well as FDOM\textsubscript{H}\textsuperscript{*}, based on a linear relationship between Fe(III) solubility and FDOM\textsubscript{H} level (see Methods).

The Fe(III) solubility of FDOM\textsubscript{H}\textsuperscript{*} (Fe(III) solubility\textsuperscript{*}) was lower than the corresponding Fe\textsubscript{a} concentration in the upper intermediate water and the lower intermediate water (27.0–27.5σ\textsubscript{θ}) (Fig. 3a). The majority of the flux of Fe\textsubscript{e} from sediments to the water column has been considered to be dominated by organic-Fe(III) complexes\textsuperscript{43,44}. Thus, the relationship (Fig. 3a) indicates that a specific fraction of Fe\textsubscript{e} from shelf sediments occurs as Fe\textsubscript{e} complexed with FDOM\textsubscript{H}\textsuperscript{*} and is transported across the North Pacific with the conservative spread of FDOM\textsubscript{H}\textsuperscript{*}. This

![Figure 2. Allochthonous FDOM\textsubscript{H} (FDOM\textsubscript{H}\textsuperscript{*}) in the intermediate water. (a) Relationship between AOU and FDOM\textsubscript{H} in the deep layer (>1000 m) of the 160°E transect (red circles) and in the mesopelagic layer (200–1000 m) from the basin of the Sea of Okhotsk to the subtropical North Pacific (blue circles). The red line represents the linear regression of the deep layer. (b) Relationship between salinity and FDOM\textsubscript{H}\textsuperscript{*} in the intermediate water. The samples in the water masses with a density range of 26.6–27.5σ\textsubscript{θ} and depths of greater than 200 m from the basin of the Sea of Okhotsk to the subtropical North Pacific (20°N) are plotted.](https://www.nature.com/scientificreports/)
mechanism is effective for the long-distance transport of Fe₄, particularly in the mesopelagic and deep layers where FDOM₄ is not degraded by sunlight.

The other fractions of Fe₄, namely, excess Fe₄ compared with corresponding Fe(III) solubility* (Fig. 3a), are not complexed with FDOM₄*. The Fe₄ concentration also exceeded the Fe(III) solubility of bulk FDOM₄, particularly in the OSIW, as well as in the lower intermediate water in the Sea of Okhotsk and the western subarctic Pacific gyre (~40°N) (Figs. 1b and 3b), suggesting that some fractions of Fe₄ are complexed with neither FDOM₄* nor autochthonous FDOM₄. Similar to our observations, excess Fe₄ concentrations compared with its bulk solubility have been reported in the mesopelagic and deep layers of the western subarctic Pacific23. The Fe(III) solubility was obtained by measuring Fe in the soluble fraction (<0.025 μm)21–23. Because the molecular weight of FDOM₄ is reported to be less than 1.8 kDa35, quite smaller than 0.025 μm, soluble Fe can form complexes with humic substances, as indicated by FDOM₄. These pieces of evidence indicate that excess Fe₄ compared with the solubility derived from bulk FDOM₄ can occur as colloidal Fe (0.025–0.22 μm), which is not complexed with FDOM₄. Although the size fractionation was not determined in this study, the substantial occurrence of colloidal Fe has been observed in the intermediate water of the western subarctic Pacific45, which is the same water mass observed in this study.

Discussion

FDOM₄*, namely, allochthonous FDOM₄, is most likely supplied from sediments as stable complexes with Fe₄ since major forms of sediment-derived Fe₄ are organic complexes43,44. Assuming that the other Fe₄ preferentially forms complexes with autochthonous FDOM₄ in the intermediate and deep waters, the spatial distribution of Fe₄ concentrations (Fig. 1b) can be separated into three groups (Fig. 4 and Supplementary Fig. 3). High concentrations of allochthonous FDOM₄-Fe complexes and colloidal Fe occur in the shelf region of the Sea of Okhotsk and spread to the western North Pacific through circulation of intermediate water, including the NPIW. The allochthonous FDOM₄-Fe complexes and colloidal Fe are mainly distributed in the upper and lower intermediate waters, respectively, implying that the allochthonous FDOM₄-Fe complexes can make more important contributions to primary production in remote areas due to intrusion into the upper layer. Interestingly, a shift in

Figure 3. Relationships between Fe₄ concentration and Fe(III) solubility. (a) Fe₄ concentration versus Fe(III) solubility* estimated from FDOM₄*. (b) Fe₄ concentration versus Fe(III) solubility estimated from FDOM₄. The samples in the upper intermediate water (26.6–27.0σθ, orange circles) and lower intermediate water (27.0–27.5σθ, blue circles) from the basin of the Sea of Okhotsk to the subtropical North Pacific (20°N) are plotted. Solid lines and dotted lines indicate the 1:1 line of Fe₄ concentration versus its solubility and standard deviation of the 1:1 line, respectively.
dominant groups of sedimentary Fe\textsubscript{a} from colloidal Fe to allochthonous FDOM\textsubscript{H}-Fe complexes involving a dramatic decrease in Fe\textsubscript{a} concentration was evident during transport by the circulation of upper and lower intermediate waters. The values of 0–2 km are stretched out on the y-axes. The solid white lines in (a) and dotted black lines in (b) represent the 26.6\(\sigma\theta\text{km}\), 27.0\(\sigma\theta\text{km}\), and 27.5\(\sigma\theta\text{km}\) contours, and 26.6–27.0\(\sigma\theta\text{km}\) and 27.0–27.5\(\sigma\theta\text{km}\) correspond to upper and lower intermediate water, respectively. Pie diagrams in (b) show the average relative contributions of allochthonous FDOM\textsubscript{H}-Fe complexes and colloidal Fe. Concentric circles represent average concentrations of allochthonous FDOM\textsubscript{H}-Fe complexes + colloidal Fe (warm colors) and autochthonous FDOM\textsubscript{H}-Fe complexes (cold colors). Note that the two circles for upper and lower intermediate waters located at 47.3–46.6°N are illustrated non-concentrically because the concentrations of the two fractions are almost the same. The concentrations described near the circles represent the average Fe\textsubscript{a} concentrations.

Figure 4. Basin-scale transport of sedimentary Fe\textsubscript{a} by the complexation with allochthonous FDOM\textsubscript{H}. (a) Distribution of allochthonous FDOM\textsubscript{H}-Fe complexes from the northernmost station on the shelf of the Sea of Okhotsk to the subtropical North Pacific (20°N). (b) Illustration of the chemical forms of Fe\textsubscript{a} during transport by the circulation of upper and lower intermediate waters. The values of 0–2 km are stretched out on the y-axes. The solid white lines in (a) and dotted black lines in (b) represent the 26.6\(\sigma\theta\text{km}\), 27.0\(\sigma\theta\text{km}\), and 27.5\(\sigma\theta\text{km}\) contours, and 26.6–27.0\(\sigma\theta\text{km}\) and 27.0–27.5\(\sigma\theta\text{km}\) correspond to upper and lower intermediate water, respectively. Pie diagrams in (b) show the average relative contributions of allochthonous FDOM\textsubscript{H}-Fe complexes and colloidal Fe. Concentric circles represent average concentrations of allochthonous FDOM\textsubscript{H}-Fe complexes + colloidal Fe (warm colors) and autochthonous FDOM\textsubscript{H}-Fe complexes (cold colors). Note that the two circles for upper and lower intermediate waters located at 47.3–46.6°N are illustrated non-concentrically because the concentrations of the two fractions are almost the same. The concentrations described near the circles represent the average Fe\textsubscript{a} concentrations.

Relatively high concentrations of colloidal Fe and autochthonous FDOM\textsubscript{H}-Fe complexes were observed in and below the lower intermediate water in the subarctic gyre (Supplementary Fig. 3). Such high concentrations may be explained by scavenged sedimentary Fe\textsubscript{a} occurring as a result of reversible Fe exchange processes, including stabilization by organic ligands in the dissolved phase, aggregation and disaggregation of nanoparticles, and sinking of aggregated nanoparticles\textsuperscript{47,48}. The colloidal Fe was greater than allochthonous FDOM\textsubscript{H}-Fe in the lower intermediate water from the source region to 30°N (~3500 km of transport distance) but was completely replaced with allochthonous FDOM\textsubscript{H}-Fe complexes in the lower NPIW at 25–20°N. These results suggest that reversible Fe exchange processes are effective for long-distance transport of sedimentary Fe\textsubscript{a}, similar to hydrothermal plumes\textsuperscript{47}, but they are not as effective as complexation with allochthonous FDOM\textsubscript{H}. Although dissolved organic matter (DOM) complexation with soluble Fe\textsubscript{a} has not yet been understood for hydrothermal plumes\textsuperscript{47}, this study clarifies that the conservative behavior of allochthonous FDOM\textsubscript{H} can contribute to the long-distance transport of sedimentary Fe\textsubscript{a} in the subsurface ocean.
The transport mechanism of sedimentary Fe₄ reported in this study can be applied to the western Arctic Ocean, where high levels of Fe₄ and FDOM₄ are evident in dense shelf water. It has been documented that hypoxic shallow sediments are an important source of Fe₄ and labile particulate Fe through the supply of Fe(II) from the sediments, oxidation to Fe(III), and chelation of Fe(III) with organic ligands or formation of inorganic Fe(III) to labile particles. It has also been reported that FDOM₄ is produced in marine sediments even under anoxic conditions. Therefore, it can be concluded that FDOM₄ is a primary organic ligand contributing to the long-distance transport of sedimentary Fe for the whole ocean, although stable transport is limited to the deep ocean where photodegradation of FDOM₄ is inhibited. An application of the method used in this study to other intermediate water systems will clarify the generality regarding with the relationship between Fe(III) solubility and FDOM₄ as well as the role of FDOM₄ as a carrier of sedimentary Fe.

Apart from macronutrients, the chemical framework of the Fe cycle in the ocean has not been well established because Fe has extremely low solubility in modern seawater. The chemical properties of Fe control input from external sources and its residence time, which shape the Fe distribution in the ocean. Although organic ligands have been considered a major factor increasing Fe solubility, the exact role of organic complexation in the Fe cycle, and in fact the very nature of the ligands that stabilize soluble Fe, have been incompletely characterized. This study clearly indicates that FDOM₄ is a factor that controls the residence time of Fe₄, at least sedimentary Fe₄. Although aeolian dust has traditionally been considered a major source of Fe for phytoplankton growth in the western North Pacific, the episodic inputs of aeolian dust may not be sufficient to sustain primary productivity in the region. The stable transport of sedimentary Fe₄ complexed with allogeneous FDOM₄ by intermediate water possibly influence primary productivity in a wide area of the western North Pacific. Thus, FDOM₄ can be a crucial factor controlling the Fe cycle in the ocean.

Allochthonous and autochthonous FDOM₄ as ligands of Fe₄ are able to be determined by salinity and AOU in the western North Pacific (Fig. 2). A global ocean Fe biogeochemical model successfully parameterized autochthonous FDOM₄ as the main ligand. A parameterization of allochthonous and autochthonous FDOM₄ in the biogeochemical models may result in the accurate reproduction of the modern ocean Fe cycle and consequently ocean ecosystems and carbon cycling, which will have implications for the appropriate estimation of how climate change will affect ocean productivity.

### Methods

**Oceanographic observations.** Observations in the western North Pacific were conducted along the 160°E transect in July 2012 as part of the R/V Hakuho Maru cruise (KH-12-3). Observations from the basin of the Sea of Okhotsk to the western subarctic Pacific gyre through the Bussol’ Strait and the shelf region of the Sea of Okhotsk were conducted in June 2014 by the R/V Professor Multanovskiy and in August 2006 by the R/V Professor Khromov, respectively. Salinity and temperature were measured using a conductivity-temperature-depth (CTD) sensor, and dissolved oxygen (DO) concentrations were measured using an oxygen sensor connected to a CTD. The DO concentrations were also measured on board by the Winkler titration method, and the DO concentrations measured by the sensor were calibrated using the concentrations determined by the Winkler method. The oxygen solubility was calculated using the function of Weiss (1970), and apparent oxygen utilization (AOU) was then calculated as the difference between the solubility and the measured DO concentration. Seawater from the surface to bottom layers (16–29 depths) was collected with acid-cleaned Teflon-coated 10- or 12-L Niskin-X bottles and seawater from the two stations (C3 and B5) located in the shelf region of the Sea of Okhotsk during the R/V Professor Khromov cruise has been described elsewhere.

**Dissolved iron.** Concentrations of dissolved iron (Fe₄) in the shelf region of the Sea of Okhotsk measured during the R/V Professor Khromov cruise were derived from previously reported data. To collect a subsample from the Niskin-X sampler during the R/V Hakuho Maru (KH-12-3) cruise, the sampler was transported in a clean air bubble (filled with air that had been passed through a high-efficiency particulate air filter) and a 0.2-μm Acropak filter (Pall Corporation) was connected to the Niskin-X spigot; the filtrate was then collected in acid-cleaned 125-mL low density polyethylene (LDPE) bottles (Nalgene Co., Ltd). To collect a subsample from the Niskin-X sampler during the R/V Professor Multanovskiy cruise, the sampler was placed in a clean tent and a 0.22-μm Millipak filter (Millipore Corporation) was connected to the Niskin-X spigot; the filtrate was then collected in acid-cleaned 125-mL LDPE bottles (Nalgene Co., Ltd). We confirmed that there were no significant differences between the Fe₄ concentrations measured using the Acropak filter and the Millipak filter.

The filtrate (<0.22 μm) was adjusted to pH <2 by the addition of ultrapure HCl (Tamapure AA-10, final HCl concentration of the sample was 0.024 M) and then allowed for one to three months at room temperature on the onboard clean room. Each sample was then adjusted to pH 3.2 just before its measurements by the addition of ammonium solution and a formic acid (10 M)–ammonium (2.4 M) buffer. Fe₄, defined as the leachable Fe in the filtrate at pH <2, was then analyzed in the onshore laboratory using a flow injection analysis (FIA) chemiluminescence detection system. All sample treatments were performed under laminar flow in the onboard or onshore clean air laboratory.

The Fe₄ measurements and reference seawater analyses in this study were quality controlled using SAFe (Sampling and Analysis of Iron) cruise reference standard seawater (obtained from the University of California Santa Cruz for an inter-comparison study). We measured a SAFe reference sample during every sample measurement run of the FIA instrument performed in the onboard and onshore laboratories. The consensus values for Fe(III) in the SAFe reference standard seawater are 0.993 ± 0.008 nM (S) and 0.933 ± 0.023 nM (D2) (May 2013, www.geotraces.org), and we obtained values of 0.986 ± 0.010 nM (n = 12) (S) and 0.976 ± 0.010 nM (n = 10) (D2) using our method. This good agreement demonstrates that our data quality was high and that our data are comparable with the global GEOTRACES dataset. The detection limit (three times the standard deviation of the Fe(III)
concentration of purified seawater (0.036 nM) that had been passed through an 8-quinolinol resin column three times to remove Fe was 0.020 nM.

Humic-like fluorescent dissolved organic matter. To determine the level of humic-like fluorescent dissolved organic matter (FDOMH) in the samples obtained during the R/V Hakuho Maru and R/V Professor Maltanovskiy cruises, the seawater samples from the Niskin-X sampler were poured directly into pre-combusted, triple-rinsed glass vials with Teflon-lined caps. The glass vials were thoroughly washed with Milli-Q water for their next use on board the ship. Just after sampling, the seawater was allowed to stand until reaching room temperature without undergoing any filtration procedure, and fluorescence measurements were performed with a spectrophotometer (RF-1500, Shimadzu) with a 1-cm quartz cell. The fluorescence intensity of the FDOMH was determined at excitation and emission wavelengths of 320 nm and 420 nm, respectively, according to Yamashita et al. It was reported that the observed differences in FDOMH levels with and without filtration using GF/F glass fiber filters were negligible for the open ocean samples.

Seawater samples collected at two stations located in the shelf region of the Sea of Okhotsk during the R/V Professor Khromov cruise were filtered with a 0.22-μm Millipak filter (Millipore Corporation) connected to the Niskin-X spigot and poured into acid-cleaned fluorinated high-density polyethylene (HDPE) bottles (Nalgene Co., Ltd). The filtrate was stored frozen in the dark until analysis. The frozen samples were thawed and allowed to stand until reaching room temperature; fluorescence measurements were then conducted as described above.

After the analysis, the fluorescence intensities were corrected to the area under the water Raman peak of Milli-Q water (excitation = 320 nm), which was analyzed daily with freshly prepared Milli-Q water and calibrated to Raman Units (RU; fluorescence intensity in quinine sulfate units (QSU) was determined for the deep waters (>1000 m). The conversion factor from RU320 to commonly used Raman Units (RU; fluorescence intensity corrected by peak area of Raman scatter at 350 nm) was 1.87.

Allochthonous humic-like fluorescent dissolved organic matter. A general linear relationship between FDOMH and AOU in intermediate and deep layers, which is indicative of the in situ production of FDOMH during the microbial degradation of organic matter, has been observed throughout the open ocean.

In this study, the linear relationship between FDOMH and AOU was also evident in the deep layer (>1000 m) along the 160 °E transect (FDOMH = 1.54 × 10⁻⁵ × AOU + 2.17 × 10⁻³, n = 46, adjusted R² = 0.93, p < 0.01). However, many samples in the mesopelagic layer (200–1000 m) did not follow the linear relationship observed in the deep layer but exhibited deviations from this linear relationship at high levels of FDOMH. This deviation from the linear relationship signifies the lack of involvement of the in situ process and corresponds to allochthonous FDOMH. Thus, in this study, allochthonous FDOMH is defined as FDOMH * and is estimated using FDOMH, AOU, and the linear regression equation observed in the deep layer as follows:

\[ \text{FDOM}_{\text{H}}^* = \text{FDOM}_{\text{H}} - (1.54 \times 10^{-5} \times \text{AOU} + 2.17 \times 10^{-3}) \]

Iron solubility. It has been reported that Fe(III) solubility is linearly related to the FDOMH fluorescence intensity in intermediate and deep waters but not in surface waters. Such differences in these relationships are likely due to the occurrence of organic ligands (e.g., siderophores and saccharides) other than FDOMH in surface waters. Thus, using a previously published dataset, the linear regression between Fe(III) solubility and FDOMH fluorescence intensity in quinine sulfate units (QSU) was determined for the deep waters (>1000 m) of the western subarctic Pacific gyre and the basin of the Sea of Okhotsk collected in 2000 during the R/V Mirai cruise (Supplementary Fig. 4). Because the instrument-specific response of the spectrophotometer used in the previous study was not corrected, the regression equation in Supplementary Fig. 4 could not be directly applied to this study.

Therefore, to determine the calibration factor between the two fluorescence units, namely, the previously reported QSU and the RU320, used in this study, we compared the FDOMH fluorescence in QSU and RU320 using samples in the deep layer. For this comparison, two stations located in the western subarctic Pacific gyre and in the basin of the Sea of Okhotsk were selected from each cruise (Supplementary Fig. 5a). Although the observations in this study (MU14) were conducted 14 years after those of the previous study (MR00), the vertical profiles of AOU in the deep layer were almost identical between the two observations (Supplementary Fig. 5b,c). Additionally, the linear relationship between the AOU values in the deep layer of the two cruises is evident, with a slope of almost one (Supplementary Fig. 5d), indicating that the water mass was observed to have the same biogeochemical characteristics in both cruises, thus allowing one to make a calibration factor between RU320 and QSU using the relationship between the FDOMH values of the deep layer observed in both cruises (Supplementary Fig. 6).

The conversion factor from FDOMH to Fe(III) solubility with units of nM was achieved using the slope (± standard deviation) of two relationships, namely, FDOMH [RU320] versus FDOMH [QSU] (Supplementary Fig. 6) and Fe(III) solubility [nM] versus FDOMH [QSU] (Supplementary Fig. 4), as follows:

\[ \text{Fe(III) solubility} = 200(\pm 11) \times 0.481(\pm 0.041) \times \text{FDOM}_{\text{H}}\text{[RU320]} \]

The estimated value (96.2 ± 9.7) was applied as the conversion factor from FDOMH [RU320] to Fe(III) solubility [nM] in this study. The bulk Fe(III) solubility and allochthonous Fe(III) solubility (Fe(III) solubility*) were estimated using the conversion factor with the fluorescence intensity of bulk FDOMH and FDOMH * respectively.
Ocean data view parameters. Ocean Data View (ODV; http://odv.awi.de)\(^5^9\) was used to produce the basin-scale distributions of each parameter in Figs. 1 and 4 and Supplementary Figs. 1–3. Although high levels of Fe\(_2\)O\(_3\), FDOM\(_{OH}\), and FDOM\(_{HF}\) were observed in the shelf region of the Sea of Okhotsk (0.1 nM, 0.020 RU\(_{320}\), and 0.018 RU\(_{320}\), respectively), the highest ends of the color scales were set to 5 nM for the Fe\(_2\)O\(_3\) concentration (Fig. 1b) and to 0.01 RU\(_{320}\) for FDOM\(_{OH}\) (Fig. 1c) and FDOM\(_{HF}\) (Fig. 1d) for better visualization. The lowest end of the color scale was set to 0 for FDOM\(_{HF}\) (Fig. 1d) even though negative values were evident, particularly in surface waters. While high concentrations of colloidal Fe and allochthonous FDOM\(_{HF}\) complexes were also observed in the shelf region of the Sea of Okhotsk (up to 8.4 nM and 1.8 nM, respectively), as shown in Fig. 4 and Supplementary Fig. 3; the highest end of the color scale was set to 0.7 nM for both species in the figures.

Data availability

The datasets presented in the current study are available from the corresponding authors upon reasonable request.

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**Author contributions**

All authors contributed to the design of the research. Y.Y. and J.N. performed fluorescence and iron analyses, respectively. Y.Y. analysed the results and prepared the manuscript with inputs from J.N., H.Ob., and H.Og.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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