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First Quantification of the Controlling Role of Humic Substances in the Transport of Iron Across the Surface of the Arctic Ocean

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Supporting Information

ABSTRACT: One of the main reasons behind our current lack of understanding of iron cycling in the oceans is our inability to characterize the ligands that control iron solubility, photosensitivity, reactivity, and bioavailability. We currently lack consensus about the nature and origin of these ligands. Here, we present the first field application of a new methodological development that allows the selective quantification of the fraction of Fe complexed to humic substances (HS). In the HS-rich surface Arctic waters, including the Fe-rich Transpolar Drift (TPD), we found that HS iron binding groups were largely occupied by iron (49%). The overall contribution of Fe–HS complexes to DFe concentrations was substantial at 80% without significant differences between TPD and non-TPD waters. Stabilization and transport of large concentrations of DFe across the surface of the Arctic Ocean are due to the formation of high concentrations of Fe–HS complexes. Competition of Arctic Fe–HS complexes with desferrioxamine and EDTA indicated that their stability constants are considerably higher than the stability constants previously found for riverine HS in temperate estuaries and HS standard material. This is the first case of identification of the ligand-dominating iron speciation over a specific region of the global ocean.

INTRODUCTION

Iron is the most relevant micronutrient in ocean waters because of its limiting role in primary productivity and CO₂ uptake over vast areas of the global ocean.^{1,2} Iron concentrations are constrained by the extremely low solubility ($\sim 10^{-11}$ M) of the thermodynamically stable species Fe(III).³ Complexation with organic ligands naturally present in seawater increases iron solubility by two to three orders of magnitude up to the nanomolar level.⁴ The concentration and chemical characteristics of these ligands also modulate other processes such as bioavailability, aggregation, precipitation, and changes in redox speciation.⁴

Because there is no analytical method available to measure the concentration of iron bound to a specific ligand or type of ligands in natural waters, the study of iron organic complexation is currently based on the independent determinations of the concentrations of dissolved iron (DFe) and of its natural ligands.

The overall concentration of ligands ($[L]_T$) is routinely determined by competing ligand equilibrium against a commercial-added ligand (AL) and detection of the ferric complex formed (Fe–AL) by adsorptive cathodic stripping voltammetry (CLE-AdCSV) at different iron concentrations.⁵ In addition to $[L]_T$, CLE-AdCSV provides the conditional stability constant of FeL complexes ($K'_{Fe'-L}$). $K'_{Fe'-L}$ is compared to the conditional stability constants of model iron ligands obtained by CLE-AdCSV in dissolved organic matter (DOM) free seawater.⁵ Because $K'_{Fe'-L}$ is a weighted average of the conditional stability constants of the iron complexes formed with the different individual ligands present in the sample, this approach is clearly insufficient for ligand

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characterization purposes. Several types of natural ligands have been selected by different authors as candidates to represent the bulk of iron ligands in ocean waters: siderophores and their degradation products,⁶ humic substances (HS),⁷ cellular organics released by exudation or cell lysis⁸ and polysaccharides.⁹ HS are the physical and chemical heterogeneous mixtures of hydrophobic organics resulting from biological and chemical transformations of dead plants and microbes and are ubiquitous in natural waters. HS are operationally divided in humic acids (HA) and fulvic acids (FA) depending on whether they are soluble (FA) or not (HA) in acidic solution.

Characterization of natural ligands in seawater is a challenging task due to their heterogeneity, low overall concentrations (0.1–10 nM) and the difficulties associated with their extraction from a complex matrix at high ionic strength. Only recently have advances in separation science and mass spectroscopy (MS) permitted the quantification of many siderophores and ligands with the heme group at natural oceanic ligand concentrations by liquid chromatography–MS (LC–MS). Siderophores found in different oceanic areas were in the range of zero to a few tens of pM, which accounts for only a minor fraction of both DFe and $[L]_T$.^{10–12} The authors also reported the concentration of Fe bound to individual ligands, although LC equipment is not free of risk of contamination at the natural trace concentrations of iron. Interestingly, LC–MS reanalysis of ocean waters after addition of excess iron revealed that these siderophores were not fully saturated with iron.^{10,13} This is the evidence that there are ligands of different natures that effectively compete with siderophores for iron sequestration.

The heterogeneous, complex, and multifunctional nature of HS complicates their quantification in water with chromatographic techniques¹⁴ and in a matrix such as seawater, other analytical approaches are required. Bulk HS concentrations in seawater are usually measured by direct fluorescence or voltammetry. Voltammetric methods are based on the saturation of HS with a selected metal (Fe, Cu, and Mo), the accumulation of the complex onto the electrode, and the reduction of the metal during a cathodic potential scan.^{15–17} Signals are converted to mass of HS per volume units after internal calibration with a commercial HS, usually Suwannee River FA (SRFA), from the International HSs Society (IHSS).

The paradigm for decades was that HS were not a significant contributor to iron binding in ocean waters.¹⁸ Nearly all iron bound to riverine HS would coprecipitate completely during estuarine transition.¹⁹ Moreover, K'_{FeHS} of iron complexes with SRFA and SRHA was found at about 1–2 orders of magnitude lower than those of siderophores and porphyrins.^{7,20} However, the body of evidence accumulated during the last decade undermines this hypothesis.²¹ Time series experiments using estuarine waters and ligand-free seawater spiked with commercial HS (from IHSS) proved that iron and HS coprecipitation stopped when Fe–HS concentrations decreased to the nanomolar range.^{7,22} Work in high latitude transition waters have shown small DFe and DOM losses during estuarine mixing,²³ suggesting that there are different Fe and HS coprecipitation efficiencies as a function of the physicochemical conditions. The correlation between DFe and HS-like FDOM (fluorescent DOM) is high in different oceanic and coastal waters.^{24,25} In the few voltammetric studies available in estuarine, coastal, and open seawater, [DFe] showed high correlation to [HS].^{7,26–28} However, high

correlations are not definitive proof of the natural formation of Fe–HS complexes.

There has not been success in identifying the major component of the ligand pool that control iron complexation in any particular region of the global ocean. Furthermore, there is a lack of consensus about the nature of these ligands.^{6,7,9} Shedding light on iron speciation requires a shift from the current independent measurement of ligand and iron concentrations, to the development of specific methods to determine the concentration of iron complexed with a particular ligand or type of ligands. In response, we have recently extended the protocol of our voltammetric method based on the reduction of Fe–HS complexes in the presence of bromate (Fe/BrO₃ method hereafter). Details can be found in the methods section and elsewhere.²⁹ With the extended Fe/BrO₃ method, we still determine the bulk concentration of HS ([HS], in mg SRFA L^{−1}) and the iron binding capacity of HS (BC_{HS}, in nM). Additionally, we determine the percentage of HS iron binding sites bound to iron in natural conditions (HS saturation index, in %), the concentration of Fe–HS complexes ([Fe–HS], in nM), and the percentage of DFe present as Fe–HS complexes (humic iron index, in %). Both indexes are conditional to the matrix composition (just as log K'_{FeL}).

For the first application of the upgraded Fe/BrO₃ method, we selected the surface waters of the Arctic Ocean. This is an oceanic region of paramount scientific interest because of the dramatic changes that the sea-ice coverage suffered over the past decade and the catastrophic projections for future scenarios. Here, lignin phenol analysis has revealed that terrigenous DOM is an important component of DOM.³⁰ Prior work in the Arctic Ocean found high correlations of [DFe] with terrigenous DOM, $[L]_T$ and [HS].^{31–33} We determined the concentration of Fe–HS complexes to explore their contribution to DFe and $[L]_T$. We also carried out ligand exchange experiments to assess whether K'_{FeHS} of surface Arctic HS were in agreement with values obtained by standard CLE-AdCSV methods.²⁸

■ EXPERIMENTAL SECTION

Sampling and Non Voltammetric Analyses. Samples were collected during the PS94 TransArcII cruise (summer 2015) onboard FS Polarstern (Figure 1) with an ultraclean sampling system.³⁴ The dissolved fraction was collected after filtration through a 0.2 μ m filter cartridge (Sartoban P, Sartorius). FDOM and DFe were analyzed onboard by fluorescence and chemiluminescence, respectively. Samples for voltammetric measurements were immediately frozen at −20 °C until analysis. The sampling protocol, equipment, and the analytical methods used to determine DFe and FDOM have been published elsewhere.^{28,35}

Voltammetric Measurements. A detailed account of the equipment and methodology used for the Fe/BrO₃ method has been published elsewhere.²⁹ Briefly, direct voltammetric measurement of Fe–HS complexes was carried out by catalytic CSV in the presence of 20 mM KBrO₃ (catalytic reagent) and 5 mM POPSO buffer as in.²⁹ The selectivity of the method against iron complexes with siderophores, heme ligands, polysaccharides, and iron oxyhydroxides was established previously.^{16,29}

The analysis is comprised of the following steps. After careful equilibration of the cell at the sample matrix, we ran a CSV scan to quantify Fe–HS complexes at the natural iron

Figure 1. Map of the area studied during the PS 94 cruise. Stations are indicated by blue dots. Red lines indicate Sections 1–3. The broad arrow indicates the approximate flow path of the TPD, with boundaries based on the concentration of FDOM as in Slagter et al. (2017). The main sources of HS in the region are indicated with light blue arrows.

concentration. The scan is repeated after addition of excess iron to saturate the iron binding sites of HS and cell precipitation of the uncomplexed iron. The signal ratio is a direct measurement of the percentage of HS iron binding sites occupied by iron in natural conditions (HS saturation index). The bulk [HS] is quantified from the iron-saturated CSV signal after calibration with iron-saturated SRFA (mg SRFA L⁻¹ units). The iron binding capacity of HS (BC_{HS}, in nM) is estimated according to

$$BC_{HS} = [HS] \cdot BC_{SRFA} \quad (1)$$

where BC_{SRFA} is the iron binding capacity of the SRFA standard determined after titration with iron in DOM-free seawater [14.6 ± 0.7 nmol Fe (mg SRFA)⁻¹].²⁹ The implications of the use of a single conversion factor for the whole area of study are discussed in the [Supporting Information](#) file.

Fe–HS concentrations are estimated according to

$$[Fe-HS] = (BC_{HS}) \cdot (HS \text{ saturation index}) \quad (2)$$

The percentage of DFe present as Fe–HS complexes (humic iron index) is determined from the [Fe–HS]/[DFe] ratio.

In order to facilitate comparison among stations and sections, we calculated DFe, Fe–HS, and BC_{HS} standing stocks down to 150 m deep. Humic iron indexes were also integrated down to 150 m deep. All these vertical integrations are shown in [Table 2](#).

RESULTS AND DISCUSSION

Study Area. Seawater of the central basins of the Arctic Ocean and the Barents Sea was collected from the upper 150–200 m of the water column at 14 stations distributed in three

transects, two across the TPD, a low salinity surface current (upper 100 m) that flows across the Arctic central basins toward the Greenland Sea via the Fram Strait^{35,36} (Sections 1 and 2), and one N–S transect on the western end of the Barents Sea (Section 3) ([Figures 1](#) and [2](#)). At three stations, we collected a few samples below 200 m for an initial assessment of the concentration of Fe–HS complexes in deep Arctic waters.

Water Mass Characterization. In the TPD, we sampled salinities as low as 27 psu as a result of the combination of the lateral input of estuarine waters from Siberian rivers and local ice melting ([Figure 2](#)). Estuarine inputs can be traced by high concentrations of FDOM. Variable sea ice melting inputs³⁷ required us to use an operational definition of TPD waters not based on salinities but on a threshold FDOM concentration. Here, waters have been labeled as TPD if FDOM >0.5 in arbitrary units.³¹ According to this threshold, we collected TPD waters at all stations in Sections 1 and 2 except for station 117 that was bordering and stations 69 and 134 that were clearly outside of the TPD influence ([Figures 1](#) and [2](#)). In the upper 150 m of the water column, there was a transition from TPD waters to the warmer and more saline Arctic Atlantic water ([Figure 2](#)). Salinities at 200 m depth or below were >34.3 at all stations. Across Section 3, there were no signals of freshwater inputs ([Figure 2](#)).

The riverine origin of surface DOM in the area is corroborated by the high negative correlation between salinity and FDOM ($r = 0.84$, $p < 0.001$, [Table 1](#)). Ice melting is behind the loss of linearity found at salinities <30 ([Figure S1A](#)).

Iron and Humic Distributions. DFe concentrations were in a ~50 fold range (0.09–4.4 nM) with significantly higher concentrations in TPD waters (0.7–4.4 nM range versus 0.1–1.8 nM range in non TPD waters) ([Figure 3](#), box plot in [Figure S2](#) and values in [Table S1](#)). In TPD stations, DFe profiles showed an exponential decrease down to 100–150 m and were low and flat in the remainder.³¹ The correlation of DFe with salinity and FDOM was very high at $r = -0.83$ and 0.83 , respectively ($p < 0.001$). Here, there was no general loss of linearity, indicating that both riverine and ice melt waters supplied DFe ([Figure S2B](#)). The exception was a subsurface high [DFe] of 3.2 nM at station 4/50 m (Barents Sea) coincident with high trace metal concentrations (Mn, Zn, Pb, and Cu, data not published). We concur with prior reports that suggested that iron from the shelf of the nearby Svalbard Island is resuspended.³⁵

HS concentrations were in a ~30-fold range from 16 to 446 μg SRFA L⁻¹ ([Figure 2](#)) with higher values in TPD waters (ranges 93–446 μg SRFA L⁻¹ vs 16–170 μg SRFA L⁻¹, respectively; box plot in [Figure S2](#)). Correlations to salinity, FDOM, and DFe were high ($r = 0.80$, 0.71 , and 0.80 , respectively, all $p < 0.001$, [Table 1](#)), indicating that most HS and DFe had a common origin.³¹

At station 4/50 m, we also found a remarkably high HS concentration ([Figure 2](#)). This is in line with the off-shelf spreading of HS-like FDOM observed in the Chukchi Sea.³⁸

Iron and Humic Interaction. BC_{HS} ranged from 0.24 to 6.5 nM and was on average three times higher in TPD waters. However, HS had the capacity to bind DFe throughout our area of study because BC_{HS} was consistently higher than or similar to DFe concentrations in nearly all samples ([Figure 3](#)).

HS saturation indexes are shown in [Table S1](#). In two samples, station 153/28 m and station 161/150 m, the index could not be determined because there were no apparent

Figure 2. Vertical profiles of salinity, FDOM (in arbitrary units), and HS during the PS 94 cruise. Vertical red lines mark the TPD threshold of $\text{FDOM} \geq 0.5$ a.u. Profiles are separated in sections according to Figure 1.

Table 1. Pearson Product Moment Correlation Coefficients for Salinity, FDOM, the Concentration of HSs (from CSV Analysis), Dissolved Iron and Iron–HSs Complexes and the Percentage of Saturation with Iron of the HSs Binding Groups in All Samples from the Upper 200 m Combined^b

	FDOM	[HS]	[DFe]	[Fe–HS]	HS saturation index	humic iron index ^a
Salinity	−0.832 ($n = 77$)	−0.796 ($n = 94$)	−0.834 ($n = 94$)	−0.698 ($n = 94$)	−0.206 ($p = 0.049$; $n = 92$)	0.099 ($p = 0.350$; $n = 91$)
FDOM		0.714 ($n = 77$)	0.776 ($n = 77$)	0.706 ($n = 77$)	0.186 ($p = 0.105$; $n = 77$)	−0.033 ($p = 0.778$; $n = 77$)
[HS]			0.799 ($n = 103$)	0.758 ($n = 105$)	0.148 ($p = 0.137$; $n = 101$)	0.060 ($p = 0.554$; $n = 100$)
[DFe]				0.828 ($n = 103$)	0.383 ($n = 101$)	−0.130 ($p = 0.199$; $n = 100$)
[Fe–HS]					0.653 ($n = 103$)	0.308 ($p = 0.002$; $n = 100$)
HS sat. index						0.518 ($n = 100$)

^aThe value at station 154, 14 m deep is considered an outlier. ^bIf not stated, $p < 0.001$.

voltammetric peaks before iron saturation. Overall, the HS saturation index was considerable at $49 \pm 27\%$, with a small although significant (Figure 4A) higher saturation in TPD waters (average $58 \pm 25\%$) with respect to non-TPD waters (average $44 \pm 27\%$). The overall undersaturation of the humic

iron binding groups does not imply that approximately half of the HS iron binding groups were free and completely available to possible iron inputs. At a constant [HS], the HS saturation index increases with the DFe concentration but decreases with the salinity and the concentrations of other trace ele-

Figure 3. Vertical distribution of the concentrations of dissolved iron (from Slagter et al. 2017), iron–HSs complexes, and iron binding capacities of HSs (BC_{HS}) in the upper 200 m of the water column during the PS 94 cruise. Blue-shaded areas and TPD labels have been assigned to stations where surface water fulfilled the criterion $FDOM > 0.5$ (as in Slagter et al. 2017). Note that the X-axis scale for TPD stations is 0–8 and 0–4 nM for non-TPD stations.

ments^{7,39,40} and competing nonhumic ligands. HS saturation indexes correlated poorly with salinity, $[HS]$, and $[DFe]$ (r always < 0.4 , Table 1 and Figures S1C and S1D) and showed no overall pattern related to depth (Figure S3). Lack of correlation with other variables could be caused by ligands of a nonhumic nature playing a role in modulating HS saturation indexes.

The power of our analytical approach was demonstrated by examining HS saturation index profiles over the area of study. We observed that HS saturation index profiles were coherently low down to 200 m at some specific locations: the Barents Sea (stations 153 and 161 with the exception of station 4 were the water column was possibly altered by resuspension of the shelf material), in the southern end of Section 2 (station 69 in the Nansen Basin), and at the eastern end of Section 1 (stations 125, 130, and 134). Meanwhile, in the rest of stations (western half of Section 1, Section 2 with the exception of station 69, and station 4), HS saturation index profiles were coherently high (box plots in Figure 4B and depth trends in Figure S3). This regionalization will be the key to interpret the spatial distribution of the percentage of DFe found as Fe–HS complexes.

Fe–HS concentrations (eq 2) ranged from below the LOD to 3.7 nM (Table S1 and Figure 3) and were highly correlated to salinity, $FDOM$ and $[HS]$ ($r = -0.69$, 0.71 , and 0.76 , respectively, all $p < 0.001$, Table 1). As expected, TPD waters showed significantly (Figure S2) higher Fe–HS concentrations

(range 0.2–3.7 nM) than in the rest of samples (from $< LOD$ to 1.3 nM). The overall correlation of DFe and Fe–HS was remarkable at $r = 0.83$ ($p < 0.001$) and remained high if the data were split in sections (Figure S4). Depth profiles of $[DFe]$ and $[Fe-HS]$ were spatially coherent; at most locations, both profiles were close (example station 121, Figure 3) and in a few, they were considerably separated (stations 69, 125, and 130, Figure 3). Furthermore, $[DFe]$ and $[Fe-HS]$ vertical profiles showed the same main features at all stations (Figure 3).

The sample from station 4/50 m also showed a high Fe–HS concentration (2.7 nM), suggesting that the DFe resuspension from the Svalbard shelf was also in the form of Fe–HS complexes as suggested for the Chukchi Plateau.³²

Contribution of Fe–HS Complexes to DFe Speciation.

The humic iron index was overall high at $80 \pm 51\%$ although spread in a very wide range (range 28–>100%) ($n = 99$) (Table 2). The wide range and standard deviation is the result of dividing many low and similar concentrations determined in subsamples with two independent methods. In 28 cases out of 99, analytical uncertainties resulted in $[Fe-HS] > [DFe]$ data pairs (Table S1). Because the humic iron index is directly related to the HS saturation index (eqs 1 and 2), its correlation with salinity and DFe, HS, and Fe–HS concentrations was low (Table 1). The humic iron index was statistically (Mann–Whitney Rank Sum test, $n = 35/69$, $U = 1171$; $P = 0.804$) the same in TPD waters at $79 \pm 46\%$ and non-TPD waters at $84 \pm$

Figure 4. (A,B): Box plots of the percentage of HS binding groups that are saturated at the natural iron concentration (HS saturation index) in all samples collected in the upper 200 m of the water column. Stations are divided as a function of (A) whether they are inside or outside the TPD and (B) station location where samples from stations 125–161 are separated from the rest (exception station 69). Box design: the same as described in the [Supporting Information](#) file. In both cases, Mann–Whitney Rank Sum Tests yielded statistically significant differences: (A) $n = 37/65$, $U = 820$, $P = 0.008$; (B) $n = 39/62$, $U = 221.5$, $P < 0.001$; (C): the decrease in the normalized peak area of the Fe–HS signal as a function of the addition of desferrioxamine for samples collected at stations 91 and 99 at a depth of 17 m. (D): The decrease in the normalized peak area of the Fe–HS signal as a function of the addition of EDTA for solutions of 1 mg L^{−1} of SRFA and SRHA in UV digested seawater and the sample collected at station 99 depth 17 m.

Table 2. Standing Stocks of Dissolved Iron (DFe), Binding Capacities of HSs (BC_{HS}), and Iron–HSs Complexes (Fe–HS)^a

stations	inventory (0–150 m) ($\mu\text{mol m}^{-2}$)			inventory humic iron index
	DFe	BC _{HS}	Fe–HS	Fe–HS/DFe
Section 1				
St 117	123	173	99	81%
St 121	187	202	163	87%
St 125	184	255	94	51%
St 130	159	366	50	31%
St 134	63	129	41	65%
Section 2				
St 69	88	142	28	32%
St 81	162	179	101	62%
St 87	178	358	182	102%
St 91	203	385	228	112%
St 96	205	330	175	86%
St 99	234	322	214	92%
Section 3				
St 4	139	180	147	106%
St 153	31	55	n.c.	n.c.
St 161	34	55	11	32%

^aValues were integrated for the upper 150 m of the water column. The humic iron index is the fraction of DFe standing stocks found as Fe–HS complexes. Stations located in the TPD are underlined. Although all parameters were measured at station 153, the presence of one < LOD and one possible outlier prevented the accurate estimation of the Fe–HS standing stock (n.c.: not calculated).

60% confirming that humic complexation regulates iron solubility throughout our area of study. Accordingly, the humic iron index correlated strongly with the HS saturation

index at $r = 0.52$ ($p < 0.001$, [Table 1](#)) and followed the same regionalization described above. At the stations characterized by low HS saturation indexes (station 69 in the Nansen Basin, stations 153 and 161 in the Barents Sea and the eastern end of Section 1, stations 125 to 134), humic iron indexes were low in the range of 31–65% ([Figure 4B](#)). At the rest of stations characterized by high HS saturation indexes (station 4, border station 117, and all the TPD stations not located at the eastern end of Section 1), DFe was mostly, and in many cases entirely, in the form of HS complexes. In that area, integrated humic iron indexes were in the range of 62–106% ([Table 2](#)).

Deep Samples. In the seven samples collected below 200 m at stations 99, 134, and 161 ([Table S1](#)), DFe and HS showed low concentrations (DFe from 0.12 to 0.34 nM and HS from 18 to 123 $\mu\text{g SRFA L}^{-1}$) and common features (station 134 in [Figure S5](#)). In two samples, [Fe–HS] was below LOD. At a LOD of 0.01 nM, HS saturation indexes in these two samples were below 5%. In the other five samples, we found low HS saturation indexes in a narrow range (15–28%) and humic iron indexes in a wider range (16–79%). Although the low number of deep samples does not allow us to reach a definitive conclusion on the contribution of Fe–HS complexes to DFe speciation in the deep Arctic, we suspect that it is important but less than 50%.

Performance of the FeBrO₃ Method. Our method to determine Fe–HS complexes is direct (no separation steps), specific to the rest of proposed natural iron ligands and works at the representative pH and ionic strength of seawater preserving the original organic speciation of iron. The LOD of Fe–HS complexes at 0.10 nM is excellent and allows direct analysis in seawater except for iron-depleted open ocean waters (~ 0.1 nM DFe). This is the first study where it is identified by the ligand controlling most of iron speciation in a specific region of the global ocean. Analytical methods targeting bulk

HS concentrations, and specifically voltammetric methods, present specific sources of uncertainty that have been discussed before at length.^{29,41} The relevance for the determination of Fe–HS complexes is detailed in the [Supporting Information](#) file.

Because of its performance, we strongly recommend the use of the extended Fe/BrO₃ method to complement iron speciation studies by CLE-AdCSV and/or LC–MS.

Competing Ligand Equilibrium against Desferrioxamine and EDTA. The stability of Fe–HS complexes can be studied from the decrease in the Fe–HS voltammetric peak as a response to additions of a competing iron ligand as in ref 7. We selected for this purpose two TPD samples, station 91/17 m deep and station 99/17 m deep, characterized by DFe concentrations above and below BC_{HS}. Ligand exchange was forced by the addition of two ligands described in previous works as much stronger (desferrioxamine, DFO) and weaker ethylenediaminetetraacetic acid (EDTA) than HS if used at similar concentrations.⁴ The addition to sample 91/17 m (420 μg SRFA L⁻¹ and 3.8 nM DFe of which 97% nM were Fe–HS complexes) of 6 nM DFO, a concentration approximately equal to BC_{HS} (6.1 nM, approximately double that of DFe), decreased the Fe–HS signal considerably to 54% of its initial value (Figure 4C). However, a further increase in the DFO concentration to 20 nM barely dissociated more Fe–HS complexes (52% of the initial value). This can be interpreted as approximately half of HS having a considerably lower $K'_{\text{Fe}'-\text{HS}}$ (the complexes that were easily dissociated by the initial DFO spike) than the other half (not dissociated by a DFO concentration 3-fold BC_{HS}). In the case of sample 99/17 m (177 μg SRFA L⁻¹ and 3.7 nM DFe of which 57% were Fe–HS complexes), the addition of 4 nM DFO (BC_{HS} of 2.6 nM, 70% of DFe) decreased the Fe–HS signal substantially to 23% of its initial value. In this case, a DFO concentration of 20 nM reduced [Fe–HS] further to 8% of its initial value. It is remarkable that, in both cases, DFO/BC_{HS} ratios up to 7.7 provoked only a partial dissociation of Fe–HS complexes.

We also equilibrated sample 99/17 m with increasing concentrations of EDTA. The concentration of EDTA that reduced the initial Fe–HS signal in half was 0.32 mM (Figure 4D). This is substantially more than the concentration previously shown to halve the voltammetric signals of 1000 μg L⁻¹ of Fe–SRFA and Fe–SRHA complexes in DOM-free seawater.⁷ Although EDTA competition with non-HS ligands interferes with the accurate determination of $K'_{\text{Fe}'-\text{HS}}$, it is possible to obtain a close estimate using $K'_{\text{Fe}'-\text{EDTA}}$ as in ref 7. The log $K'_{\text{Fe}'-\text{HS}}$ of a ligand at a concentration of 2.6 nM that matches the complexing strength of 0.32 mM EDTA is 12.8. This log $K'_{\text{Fe}'-\text{HS}}$ is about 1–2 log units higher than the log $K'_{\text{Fe}'-\text{SRHS}}$ reported for IHSS standards by CLE-AdCSV in DOM-free seawater (~10.6 for SRFA and ~11.1–11.6 for SRHA)^{7,42} and log $K'_{\text{Fe}'-\text{HS}}$ found in estuarine waters from temperate latitudes (10.6–12.4).^{7,43,44} Therefore, the natural HS iron ligands of the surface Arctic Ocean, or at least a fraction of them, belong to the group of strong ligands ubiquitous in surface ocean waters.⁴

HS saturation and humic iron indexes below 100% may be the consequence of the presence of nonhumic iron ligands sequestering a minor fraction of DFe. The ability of HS to outcompete other ligands is modulated by a variable affinity of HS binding groups to iron (heterogeneity of $K'_{\text{Fe}'-\text{HS}}$) and/or by the concentration and stability constants of competing nonhumic iron ligands. Our experiments proved that, at least

in surface Arctic waters, there are Fe–HS complexes characterized by $K'_{\text{Fe}'-\text{HS}}$ much higher than those reported previously. Unfortunately, we do not have any knowledge on the chemical characteristics of Arctic HS that would set them apart from other HS. The markedly different extent of iron sequestration by DFO shown in different samples (Figure 4C) supports the hypothesis that $K'_{\text{Fe}'-\text{HS}}$ could vary substantially over the area of study. Spatial variations of the binding strength of HS iron ligands could explain the wide spread of the humic iron index referred above. Competing non-HS ligands must be of biological origin of local and/or riverine origin. The ice coverage in Sections 1 and 2 is permanent and chlorophyll concentrations in the TPD and surrounding waters were very low during the cruise.³⁵ Higher chlorophyll concentrations and cytometry counts in Section 3³⁵ were not coupled to a clear decrease in the contribution of Fe–HS to DFe. The presence of riverine humic and nonhumic ligands (sharing common spread and dilution patterns) could explain the similarity of HS saturation and humic iron indexes in TPD and non TPD waters. We lack sufficient insights into regional biogeochemical processes to be able to estimate their contribution to DFe speciation.

Implications for CLE-AdCSV Studies. CLE-AdCSV analysis of SRFA and SRHA standards in DOM-free seawater seemed to indicate that $K'_{\text{Fe}'-\text{HS}}$ were too low to concede that HS contributed to the pool of strong natural ligands found in seawater with the exception of estuaries.⁴ We have provided evidence that the natural HS iron ligands of the surface Arctic Ocean, or at least a fraction of them, belong to the group of strong ligands ubiquitous in surface ocean waters.

There are also analytical uncertainties to consider. CLE-AdCSV of IHSS standards showed that at least two well-established methods, using as competing ligands TAC (2-(2-thiazolylazo)-*p*-cresol) and DHN (dihydroxynaphthalene) in the presence of bromate, do not detect most HS iron complexation.⁴⁵ On the contrary, the methods using DHN (with no bromate) and SA (salicylaldoxime) as competing ligands have successfully included the contribution of HS to [L]_T.^{42,45} In a previous work, we tried to shed light on this method disparity using the TAC and SA methods in a number of aliquots of the samples used here.²⁸ According to the previous findings, the SA method gave higher [L]_T than [L]_T obtained by the TAC method in all samples. Often, TAC [L]_T was below BC_{HS} and occasionally even below DFe. Despite the high [L]_T versus [HS] correlation obtained with both methods, we determined that, according to the traditional understanding of iron–HS complexation, log $K'_{\text{Fe}'-\text{L}}$ was high enough (12.0 ± 0.4 and 11.8 ± 0.4 in TPD waters for TAC and SA, respectively) to cast doubts about the humic nature of the ligands found. Here, we prove that in surface Arctic waters, most DFe is complexed by HS; [L]_T is therefore mainly constituted by HS and that $K'_{\text{Fe}'-\text{HS}}$ of at least a fraction of Arctic HS is considerably higher than that of IHSS standards and similar to those obtained by CLE-AdCSV in the area of study.²⁸ We also confirm our prior hypothesis that the contribution of a fraction of HS to [L]_T is not accounted for with the TAC method.

Oceanographic Importance. DFe concentrations in the TPD are orders of magnitude over the solubility of iron in seawater. Overall, these could only be justified by complexation with high concentrations of HS. High-surface DFe concentrations in the Arctic are thus stabilized over several years, the period in which the TPD completes its transition

from the Eurasian coast to the Fram Strait.⁴⁶ Our method revealed a regionalization of the humic influence on iron speciation. With our limited knowledge of Arctic biogeochemistry, it is difficult to hypothesize the processes that could lead to this regionalization. The eastern end of Section 1 is farther from the influence of Siberian Rivers and closer to the Canadian Basins. The cross-section inventories of DFe, HS, and Fe–HS obtained across Section 2 were higher than those obtained across Section 1 (Table 2), suggesting additional lateral inputs of humic iron from the Siberian coast as the southbound TPD moved toward the Fram Strait and therefore reducing any influence from the other side of the Arctic Ocean. Prior work found iron limitation in the Nansen Basin and potentially in the Barents Sea.³⁵ Selective biological consumption of the humic fraction of iron⁴⁷ may have decreased the saturation of HS and their contribution to iron speciation.

Arctic terrigenous DOM (mostly HS) is an important component of the DOM found in the prolongation of the TPD beyond the Fram Strait, the East Greenland Current. As a result, 4.4–6.6 Tg of terrigenous NOM are exported annually to the North Atlantic.³⁰ If Arctic iron completes its transit through the Greenland Sea into the Iceland Basin by remaining bound to HS, it could contribute substantially to sustain the annual North Atlantic spring bloom⁴⁸ that brings North Atlantic surface waters into iron limitation.⁴⁹

Arctic NOM was also found deep in sites of formation of North Atlantic Deep Water (NADW), the major driver of the global ocean conveyor belt.³⁰ We hypothesize here that non-saturated Arctic HS may explain the stabilization of a fraction of hydrothermal DFe observed at 60° N in deep North Atlantic waters.⁵⁰ Moreover, a substantial export of refractory Arctic Fe–HS complexes via the NADW current during the formation of the conveyor belt could contribute significantly to the high deep DFe concentrations found at depth in all oceanic basins.

Relevance in the Context of a Warming Arctic. Our data corroborate the recent hypothesis that in many high latitude estuaries, HS and DFe coprecipitation is less effective,⁵¹ and the export of Fe–HS complexes is substantial.^{21,52} Understanding iron complexation and estuarine transition in Arctic waters is important in the context of a warming planet. Permafrost thawing will bring a substantial change in the geochemistry of the Eurasian rivers' watershed soils,⁵³ increasing estuarine discharge⁵⁴ and thus the export of HS and iron into Arctic waters. This could lead to local increments of primary productivity, for example, the iron-limited Nansen basin,³⁵ to an increase in the DFe (as Fe–HS) transport into the Fram Strait and the stabilization of a fraction of the increasing iron flux from Greenland meltwater. Possible implications include the alleviation of the iron limitation observed after postspring blooms in the Iceland Basin.⁴⁹ In the near future, the ice sheet may not cover portions of Sections 1 and 2 during summer increasing the biological requirement of iron and exposing Fe–HS complexes to photoreactions.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b04240.

All iron, humic, and Fe–humic complexes data, FDOM and DFe data, the HS saturation index plotted against the salinity and HS concentrations; box plots of all

relevant data split between TPD and non TPD waters; depth profiles of all data combined split according to the magnitude of the HS saturation index; all Fe–HS versus DFe data pairs separated in sections and DFe, Fe–HS, and BC_{HS} profiles down to 3000 m deep at station 134, and a section discussing the sources of uncertainty of the method (PDF)

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Notes

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All the data used in this research are available in Table S2 of the Supporting Information File.

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■ REFERENCES

- (1) Martin, J. H.; Fitzwater, S. E. Iron deficiency limits phytoplankton growth in the north-east pacific subarctic. *Nature* **1988**, *331*, 341–343.
- (2) de Baar, H.; Buma, A.; Nolting, R.; Cadée, G.; Jacques, G.; Treguer, P. On iron limitation of the Southern Ocean: experimental observations in the Weddell and Scotia seas. *Mar. Ecol. Prog. Ser.* **1990**, *65*, 105–122.
- (3) Liu, X.; Millero, F. J. The solubility of iron in seawater. *Mar. Chem.* **2002**, *77*, 43–54.
- (4) Gledhill, M.; Buck, K. N. The organic complexation of iron in the marine environment: a review. *Front. Microbiol.* **2012**, *3*, 69.
- (5) Gerringa, L. J. A.; Rijkenberg, M. J. A.; Thuróczy, C.-E.; Maas, L. R. M. A critical look at the calculation of the binding characteristics and concentration of iron complexing ligands in seawater with suggested improvements. *Environ. Chem.* **2014**, *11*, 114–136.
- (6) Hunter, K. A.; Boyd, P. W. Iron-binding ligands and their role in the ocean biogeochemistry of iron. *Environ. Chem.* **2007**, *4*, 221–232.
- (7) Laglera, L. M.; van den Berg, C. M. G. Evidence for geochemical control of iron by humic substances in seawater. *Limnol. Oceanogr.* **2009**, *54*, 610–619.
- (8) Gledhill, M.; Achterberg, E. P.; Honey, D. J.; Nielsdottir, M. C.; Rijkenberg, M. J. A. Distributions of particulate Heme b in the Atlantic and Southern Oceans—Implications for electron transport in phytoplankton. *Global Biogeochem. Cycles* **2013**, *27*, 1072–1082.

- (9) Hassler, C. S.; Schoemann, V.; Nichols, C. M.; Butler, E. C. V.; Boyd, P. W. Saccharides enhance iron bioavailability to southern ocean phytoplankton. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 1076–1081.
- (10) Boiteau, R. M.; Mende, D. R.; Hawco, N. J.; McIlvin, M. R.; Fitzsimmons, J. N.; Saito, M. A.; Sedwick, P. N.; DeLong, E. F.; Repeta, D. J. Siderophore-based microbial adaptations to iron scarcity across the eastern Pacific Ocean. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 14237–14242.
- (11) Mawji, E.; Gledhill, M.; Milton, J. A.; Zubkov, M. V.; Thompson, A.; Wolff, G. A.; Achterberg, E. P. Production of siderophore type chelates in Atlantic Ocean waters enriched with different carbon and nitrogen sources. *Mar. Chem.* **2011**, *124*, 90–99.
- (12) Bundy, R. M.; Boiteau, R. M.; McLean, C.; Turk-Kubo, K. A.; McIlvin, M. R.; Saito, M. A.; Van Mooy, B. A. S.; Repeta, D. J. Distinct Siderophores Contribute to Iron Cycling in the Mesopelagic at Station ALOHA. *Front. Mar. Sci.* **2018**, *5*, 61.
- (13) Boiteau, R. M.; Till, C. P.; Coale, T. H.; Fitzsimmons, J. N.; Bruland, K. W.; Repeta, D. J. Patterns of iron and siderophore distributions across the California Current System. *Limnol. Oceanogr.* **2019**, *64*, 376–389.
- (14) Huber, S. A.; Balz, A.; Abert, M.; Pronk, W. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND). *Water Res.* **2011**, *45*, 879–885.
- (15) Quentel, F.; Elleouet, C. Square-wave voltammetry of molybdenum-fulvic acid complex. *Electroanalysis* **2001**, *13*, 1030–1035.
- (16) Laglera, L. M.; Battaglia, G.; van den Berg, C. M. G. Determination of humic substances in natural waters by cathodic stripping voltammetry of their complexes with iron. *Anal. Chim. Acta* **2007**, *599*, 58–66.
- (17) Whitby, H.; van den Berg, C. M. G. Evidence for copper-binding humic substances in seawater. *Mar. Chem.* **2015**, *173*, 282–290.
- (18) Boyd, P. W.; Ellwood, M. J. The biogeochemical cycle of iron in the ocean. *Nat. Geosci.* **2010**, *3*, 675–682.
- (19) Sholkovitz, E. R. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. *Earth Planet. Sci. Lett.* **1978**, *41*, 77–86.
- (20) Witter, A. E.; Hutchins, D. A.; Butler, A.; Luther, G. W. Determination of conditional stability constants and kinetic constants for strong model Fe-binding ligands in seawater. *Mar. Chem.* **2000**, *69*, 1–17.
- (21) Muller, F. L. L. Exploring the Potential Role of Terrestrially Derived Humic Substances in the Marine Biogeochemistry of Iron. *Front. Earth Sci. China* **2018**, *6*, 159.
- (22) Krachler, R.; Krachler, R. F.; Wallner, G.; Hann, S.; Laux, M.; Cervantes Recalde, M. F.; Jirsa, F.; Neubauer, E.; von der Kammer, F.; Hofmann, T.; Keppler, B. K. River-derived humic substances as iron chelators in seawater. *Mar. Chem.* **2015**, *174*, 85–93.
- (23) Klunder, M. B.; Bauch, D.; Laan, P.; De Baar, H. J. W.; Van Heuven, S.; Ober, S. Dissolved iron in the Arctic shelf seas and surface waters of the central Arctic Ocean: Impact of Arctic river water and ice-melt. *J. Geophys. Res.: Oceans Atmos.* **2012**, *117*, C01027.
- (24) Watanabe, K.; Fukuzaki, K.; Fukushima, K.; Aimoto, M.; Yoshioka, T.; Yamashita, Y. Iron and fluorescent dissolved organic matter in an estuarine and coastal system in Japan. *Limnology* **2018**, *19*, 229–240.
- (25) Tani, H.; Nishioka, J.; Kuma, K.; Takata, H.; Yamashita, Y.; Tanoue, E.; Midorikawa, T. Iron(III) hydroxide solubility and humic-type fluorescent organic matter in the deep water column of the Okhotsk Sea and the northwestern North Pacific Ocean. *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **2003**, *50*, 1063–1078.
- (26) Bundy, R. M.; Abdulla, H. A. N.; Hatcher, P. G.; Biller, D. V.; Buck, K. N.; Barbeau, K. A. Iron-binding ligands and humic substances in the San Francisco Bay estuary and estuarine-influenced shelf regions of coastal California. *Mar. Chem.* **2015**, *173*, 183–194.
- (27) Dulaquais, G.; Waeles, M.; Gerringa, L. J. A.; Middag, R.; Rijkenberg, M. J. A.; Riso, R. The Biogeochemistry of Electroactive Humic Substances and Its Connection to Iron Chemistry in the North East Atlantic and the Western Mediterranean Sea. *J. Geophys. Res.: Oceans* **2018**, *123*, S481–S499.
- (28) Slagter, H. A.; Laglera, L. M.; Sukekava, C.; Gerringa, L. J. A. Fe-binding Organic Ligands in the Humic-Rich TransPolar Drift in the Surface Arctic Ocean using Multiple Voltammetric Methods. *J. Geophys. Res.: Oceans* **2019**, *124*, 1491–1508.
- (29) Sukekava, C.; Downes, J.; Slagter, H. A.; Gerringa, L. J. A.; Laglera, L. M. Determination of the contribution of humic substances to iron complexation in seawater by catalytic cathodic stripping voltammetry. *Talanta* **2018**, *189*, 359–364.
- (30) Benner, R.; Louchouart, P.; Amon, R. M. W. Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. *Global Biogeochem. Cycles* **2005**, *19*, GB2025. DOI: 10.1029/2004gb002398
- (31) Slagter, H. A.; Reader, H. E.; Rijkenberg, M. J. A.; Rutgers van der Loeff, M.; de Baar, H. J. W.; Gerringa, L. J. A. Organic Fe speciation in the Eurasian Basins of the Arctic Ocean and its relation to terrestrial DOM. *Mar. Chem.* **2017**, *197*, 11–25.
- (32) Nakayama, Y.; Fujita, S.; Kuma, K.; Shimada, K. Iron and humic-type fluorescent dissolved organic matter in the Chukchi Sea and Canada Basin of the western Arctic Ocean. *J. Geophys. Res.: Oceans* **2011**, *116*, C07031.
- (33) Hioki, N.; Kuma, K.; Morita, Y.; Sasayama, R.; Ooki, A.; Kondo, Y.; Obata, H.; Nishioka, J.; Yamashita, Y.; Nishino, S.; Kikuchi, T.; Aoyama, M. Laterally spreading iron, humic-like dissolved organic matter and nutrients in cold, dense subsurface water of the Arctic Ocean. *Sci. Rep.* **2015**, *4*, 6775.
- (34) Rijkenberg, M. J. A.; de Baar, H. J. W.; Bakker, K.; Gerringa, L. J. A.; Keijzer, E.; Laan, M.; Laan, P.; Middag, R.; Ober, S.; van Ooijen, J.; Ossebaer, S.; van Weerlee, E. M.; Smit, M. G. “PRISTINE”, a new high volume sampler for ultraclean sampling of trace metals and isotopes. *Mar. Chem.* **2015**, *177*, 501–509.
- (35) Rijkenberg, M. J. A.; Slagter, H. A.; Rutgers van der Loeff, M.; van Ooijen, J.; Gerringa, L. J. A. Dissolved Fe in the Deep and Upper Arctic Ocean With a Focus on Fe Limitation in the Nansen Basin. *Front. Mar. Sci.* **2018**, *5*, 88.
- (36) Cooper, L. W.; Benner, R.; McClelland, J. W.; Peterson, B. J.; Holmes, R. M.; Raymond, P. A.; Hansell, D. A.; Grebmeier, J. M.; Codispoti, L. A.; Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. *J. Geophys. Res.: Biogeosci.* **2005**, *110*, G02013. DOI: 10.1029/2005jg000031
- (37) van der Loeff, M. R.; Kipp, L.; Charette, M. A.; Moore, W. S.; Black, E.; Stimac, I.; Charkin, A.; Bauch, D.; Valk, O.; Karcher, M. isotopes across the Arctic Ocean show time scales of water mass ventilation and increasing shelf inputs. *J. Geophys. Res.: Oceans* **2018**, *123*, 4853–4873.
- (38) Chen, M.; Jung, J.; Lee, Y. K.; Hur, J. Surface accumulation of low molecular weight dissolved organic matter in surface waters and horizontal off-shelf spreading of nutrients and humic-like fluorescence in the Chukchi Sea of the Arctic Ocean. *Sci. Total Environ.* **2018**, *639*, 624–632.
- (39) Yang, R.; van den Berg, C. M. G. Metal Complexation by Humic Substances in Seawater. *Environ. Sci. Technol.* **2009**, *43*, 7192–7197.
- (40) Yang, R.; Su, H.; Qu, S.; Wang, X. Capacity of humic substances to complex with iron at different salinities in the Yangtze River estuary and East China Sea. *Sci. Rep.* **2017**, *7*, 1381.
- (41) Quentel, F.; Filella, M. Quantification of refractory organic substances in freshwaters: Further insight into the response of the voltammetric method. *Anal. Bioanal. Chem.* **2008**, *392*, 1225–1230.
- (42) Abualhaija, M. M.; van den Berg, C. M. G. Chemical speciation of iron in seawater using catalytic cathodic stripping voltammetry with ligand competition against salicylaldoxime. *Mar. Chem.* **2014**, *164*, 60–74.

- (43) Mahmood, A.; Abualhaja, M. M.; van den Berg, C. M. G.; Sander, S. G. Organic speciation of dissolved iron in estuarine and coastal waters at multiple analytical windows. *Mar. Chem.* **2015**, *177*, 706–719.
- (44) Muller, F. L. L.; Cuscov, M. Alteration of the Copper-Binding Capacity of Iron-Rich Humic Colloids during Transport from Peatland to Marine Waters. *Environ. Sci. Technol.* **2017**, *51*, 3214–3222.
- (45) Laglera, L. M.; Battaglia, G.; van den Berg, C. M. G. Effect of humic substances on the iron speciation in natural waters by CLE/CSV. *Mar. Chem.* **2011**, *127*, 134–143.
- (46) Mysak, L. A. Patterns of Arctic circulation. *Science* **2001**, *293*, 1269–1270.
- (47) Chen, M.; Wang, W. Accelerated uptake by phytoplankton of iron bound to humic acids. *Aquat. Biol.* **2008**, *3*, 155–166.
- (48) Sanders, R.; Brown, L.; Henson, S.; Lucas, M. New production in the Irminger Basin during 2002. *J. Mar. Syst.* **2005**, *55*, 291–310.
- (49) Nielsdóttir, M. C.; Moore, C. M.; Sanders, R.; Hinz, D. J.; Achterberg, E. P. Iron limitation of the postbloom phytoplankton communities in the Iceland Basin. *Global Biogeochem. Cycles* **2009**, *23*, GB3001. DOI: [10.1029/2008gb003410](https://doi.org/10.1029/2008gb003410)
- (50) Achterberg, E. P.; Steigenberger, S.; Marsay, C. M.; LeMoigne, F. A. C.; Painter, S. C.; Baker, A. R.; Connelly, D. P.; Moore, C. M.; Tagliabue, A.; Tanhua, T. Iron Biogeochemistry in the High Latitude North Atlantic Ocean. *Sci. Rep.* **2018**, *8*, 1283.
- (51) Pokrovsky, O. S.; Shirokova, L. S.; Viers, J.; Gordeev, V. V.; Shevchenko, V. P.; Chupakov, A. V.; Vorobieva, T. Y.; Candaudap, F.; Causserand, C.; Lanzasova, A. Fate of colloids during estuarine mixing in the Arctic. *Ocean Sci.* **2014**, *10*, 107–125.
- (52) Conrad, S.; Ingri, J.; Gelting, J.; Nordblad, F.; Engström, E.; Rodushkin, I.; Andersson, P. S.; Porcelli, D.; Gustafsson, Ö.; Semiletov, I.; Öhlander, B. Distribution of Fe isotopes in particles and colloids in the salinity gradient along the Lena River plume, Laptev Sea. *Biogeosci. Discuss.* **2018**, *2018*, 1–27.
- (53) Schuur, E. A. G.; McGuire, A. D.; Schädel, C.; Grosse, G.; Harden, J. W.; Hayes, D. J.; Hugelius, G.; Koven, C. D.; Kuhry, P.; Lawrence, D. M.; Natali, S. M.; Olefeldt, D.; Romanovsky, V. E.; Schaefer, K.; Turetsky, M. R.; Treat, C. C.; Vonk, J. E. Climate change and the permafrost carbon feedback. *Nature* **2015**, *520*, 171.
- (54) Peterson, B. J.; Holmes, R. M.; McClelland, J. W.; Vörösmarty, C. J.; Lammers, R. B.; Shiklomanov, A. I.; Shiklomanov, I. A.; Rahmstorf, S. Increasing River Discharge to the Arctic Ocean. *Science* **2002**, *298*, 2171–2173.