Distribution of Fe isotopes in particles and colloids in the salinity gradient along the Lena River plume, Laptev Sea

Sarah Conrad[1,*], Johan Ingri[1], Johan Gelting[1], Fredrik Nordblad[1], Emma Engström[1,2], Ilia Rodushkin[1,2], Per S. Andersson[3], Don Porcelli[4], Örjan Gustafsson[5], Igor Semiletov[6,7,8], and Björn Öhlander[1]

[1]Department of Chemical Engineering and Geosciences, Luleå University of Technology, Luleå, Sweden
[2]ALS Laboratory Group, ALS Scandinavia AB, Aurorum 10, Luleå, Sweden
[3]Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden
[4]Department of Earth Sciences, Oxford University, Oxford, United Kingdom
[5]Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, Sweden
[6]International Arctic Research Center (IARC), University of Alaska, Fairbanks, AK, USA
[7]Pacific Oceanological Institute (POI), Far Eastern Branch of the Russian Academy of Sciences (FEBRAS), Vladivostok, Russia
[8]Tomsk National Research Politechnical University, Tomsk, Russia

Correspondence to: Sarah Conrad (sarah.conrad@ltu.se)

Abstract. Riverine Fe input is the primary Fe source to the ocean. This study is focused on the distribution of Fe along the Lena River freshwater plume in the Laptev Sea using samples from a 600 km long transect in front of the Lena River mouth. Separation of the particulate (>0.22μm), colloidal (0.22μm – 1kDa), and truly dissolved (<1kDa) fractions of Fe was carried out. The total Fe concentrations ranged from 0.2 to 57 μM with Fe dominantly as particulate Fe. The loss of > 99% of particulate Fe and about 90% of the colloidal Fe was observed across the shelf, while the truly dissolved phase was almost constant across the Laptev Sea. Thus, the truly dissolved Fe could be an important source of bioavailable Fe for plankton in the central Arctic Ocean, together with the colloidal Fe. Fe-isotope analysis showed that the particulate phase and the sediment below the Lena River freshwater plume had negative $\delta^{56}Fe$ values (relative to IRMM-14). The colloidal Fe phase showed negative $\delta^{56}Fe$ values close to the river mouth (about -0.20‰) and positive $\delta^{56}Fe$ values in the outermost stations (about +0.10‰).

We suggest that the shelf zone acts as a sink for Fe particles and colloids with negative $\delta^{56}Fe$ values, representing chemically reactive ferrihydrites. While the positive $\delta^{56}Fe$ values of the colloidal phase within the outer Lena River freshwater plume, might represent Fe oxyhydroxides, which remain in the water column, and will be the predominant $\delta^{56}Fe$ composition in the Arctic Ocean.

1 Introduction

The cycling of Fe is a key component for understanding water quality and biogeochemical processes. Iron is the 4th most abundant element in the continental crust (Wedepohl, 1995). The concentration in seawater is low compared to riverine input (Martin and Gordon, 1991). The riverine input of Fe is one of the most important contribution to the oceanic Fe budget, as well as aeolian dust, recycled sediment, subglacial and iceberg meltwaters, and hydrothermal fluxes (Raiswell and Canfield, 2012). Estimations of filterable Fe (< 0.45 µm) fluxes to the Global Ocean reveal that about 140 of a maximum of 4800 Gg yr^{-1} is delivered by rivers (de Baar and de Jong 2001; Tagliabue et al. 2010). Particulate Fe supplied by rivers to the oceans is three orders of magnitude higher than filterable Fe (Martin and Meybeck, 1979). Iron behaves non-conservatively during the mixing of freshwater and seawater and is removed to sediments (Boyle et al., 1977; Eckert and Sholkovitz, 1976; Gustafsson et al., 2000; Sholkovitz, 1978, 1976) since Fe-rich particles and colloids flocculate and settle in this mixing zone (Sholkovitz, 1978).

It has been recognised that dissolved Fe is related to dissolved organic carbon (DOC) in freshwater (Perdue et al., 1976) and so to investigate the pathways for organic carbon (OC) in the Arctic, knowledge about Fe cycling and the coupling between the boreal-arctic watershed and the Arctic basin is crucial. Iron and OC in water samples can be separated using a variety of filtration techniques. These include both membrane filtration (0.22 to 0.7 µm) and ultrafiltration (1kDa, 10kDa, or 30kDa) and size fractions are thus often operationally defined as particulate matter (larger than 0.22µm or 0.7µm), colloidal (smaller than particles, but do not pass an ultrafilter) and truly dissolved phases (passing through an ultrafilter). Due to the technical complexity with ultrafiltration, including the extensive filtration time, there are few ultrafiltration Fe data available (Guo and Santschi, 1996; Ingri et al., 2000; Pokrovsky et al. 2012). Truly dissolved Fe data are scarce and deliver insights into this part of the Fe pool.

Previous studies showed that there is a relationship between Fe and OC in the dissolved fraction and found two main forms of Fe compounds: Fe-OC and Fe oxyhydroxides (Escoube et al., 2015; Hirst et al., 2017; Ilina et al., 2013; Ingri et al., 2006, 2000; Kritzberg et al., 2014; Pokrovsky et al., 2010, 2006; Pokrovsky and Schott, 2002; Raiswell and Canfield, 2012; Stolpe et al., 2013). It has also been shown that humic substances (HS) are associated with newly formed Fe oxyhydroxides in freshwater (Pédrot et al., 2011; Tipping, 1981). The behaviour of these Fe and OC particles and colloids during estuarine mixing depend on their chemical reactivity, which is defined by their size and speciation (Poulton and Raiswell, 2005; Tagliabue et al., 2017). Hirst et al. (2017) found that about 70% of the total suspended Fe in the Lena River to be in the form of reactive ferrihydrite. These ferrihydrites are independent particles within a network of amorphous particulate OC (POC) and are attached to the surfaces of primary organic matter and clay particles (Hirst et al., 2017).

Carbon-iron cycling is complex, and stable Fe isotope data show that the isotopic compositions might be used to investigate chemical pathways for Fe and Fe bound to OC during weathering and estuarine mixing in the boreal-arctic region (Dos Santos Pinheiro et al., 2014; Escoube et al., 2015, 2009; Ilina et al., 2013; Ingri et al., 2006; Mulholland et al., 2015; Poitrasson, 2006; Poitrasson et al., 2014). The $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios are defined relative to the international reference material IRMM-14 and are expressed as deviations from the standard in parts per thousand, or δ notation (in per mill ‰), as

$$\delta^{56}Fe = \left[\frac{\left(^{56}Fe/^{54}Fe\right)_{sample}}{\left(^{56}Fe/^{54}Fe\right)_{IRMM-14}} - 1 \right] * 10^3 \qquad (1)$$

$$\delta^{57}Fe = \left[\frac{\left(^{57}Fe/^{54}Fe\right)_{sample}}{\left(^{57}Fe/^{54}Fe\right)_{IRMM-14}} - 1 \right] * 10^3 \qquad (2)$$

Using this definition, the continental crust has a δ^{56}Fe value of 0.07±0.02‰. In low-temperature environments the δ^{56}Fe can vary by about 5‰ (Anbar, 2004; Beard et al., 2003; Fantle and DePaolo, 2004; Rouxel, Bekker, Edwards, 2005). The variations in δ^{56}Fe can be used to trace different Fe phases in rivers (Dos Santos Pinheiro et al., 2014; Ilina et al., 2013; Ingri et al., 2006; Poitrasson et al., 2014) and to map the origin of Fe (Conway and John, 2014). Isotope fractionation processes result in a δ^{56}Fe value that can be higher or lower compared to continental crust. The Fe isotopic composition is impacted by redox reactions (Wiederhold et al., 2006), complexation with organic ligands, and inorganic speciation of Fe, as well as the immobilization of Fe by precipitation and adsorption (Beard et al., 2003, 1999; Beard and Johnson, 2004; Brantley et al., 2001; Bullen et al., 2001; Icopini et al., 2004; Poitrasson and Freydier, 2005; Skulan et al., 2002; Welch et al., 2003). These processes can yield either negative or positive δ^{56}Fe values, depending on the initial Fe isotopic composition and the fractionation factor. Recent studies showed that subarctic and temperate rivers, with high Fe and OC concentrations, have low δ^{56}Fe values in the particulate phase, while the dissolved phase has high δ^{56}Fe (Escoube et al., 2015, 2009; Ilina et al., 2013; Ingri et al., 2006; Rouxel et al., 2008; Severmann et al., 2006). Also, high δ^{56}Fe values have been reported in the Low Molecular Weight (LMW) fraction (< 10kDa), while colloids and particles showed high δ^{56}Fe values (Ilina et al., 2013). Furthermore, seasonal variations in the Fe isotopic composition and Fe speciation have been reported (Allard et al., 2004; Escoube et al., 2015; Ingri et al., 2006).

This study presents Fe concentrations and Fe isotope compositions in the particulate and colloidal phase along the Lena River freshwater plume in the Laptev Sea, as well as Fe concentrations in the truly dissolved phase. The Lena River – Laptev Sea transect is stratified, with a freshwater layer that is on top of more saline and dense, deep waters and plays an important role in the transport of Fe and the distribution of Fe isotopes in the Arctic Ocean. The main objectives were to study the distribution of Fe in the Lena River – Laptev Sea transect and the variations in the partitioning of Fe between the different size fractions, as well as to identify the impact of processes such as mixing, transformation, and removal by settling on the export of Fe to the deeper ocean. Furthermore, Fe-isotope analysis of the colloidal and particulate fraction should help us to gain a better understanding of the composition of Fe particles and colloids transported out in the Arctic Ocean.

2 Sampling Site and Analytical Methods

2.1 Study Area

The Lena River is 4,387 km long and has the 8th largest discharge in the world. It is the 2nd largest river draining into the Arctic

Ocean and flows into the Laptev Sea (Fig. 1). The Lena watershed covers an area of 2.46 x 10^6 km^2 (Rachold et al., 1996) and is bound by the Verkhoyansk Mountain Ridge in the northeast and the central Siberian uplands in the west. Larch forests cover 72% of the watershed area and shrublands about 12% (Wagner, 1997; Walter and Breckle, 2002). Permafrost underlays 78–93% of the watershed (Zhang et al., 1999) and extends to depths of up to 1,500 m (Anisimov and Reneva, 2009). The annual discharge to the Arctic Ocean is 581 km^3 (Yang et al., 2002). During spring flood, late May to June, 31–45% of the annual runoff occurs (Amon et al., 2012). The Lena River delivers 5.6–5.8 Tg of DOC into the Arctic Ocean annually (Holmes et al., 2012; Raymond et al., 2007), along with about 0.4 Tg of particulate OC (Semiletov et al., 2011). More than 50% of the total OC (TOC) is delivered during a two-month period in summer, with 6.6 Tg year^{-1} in June (Le Fouest et al., 2013) and 3.5 Tg year^{-1} in July (Kutscher et al., 2017). The run-off from the Lena River accounts for more of 70% of the overall river inflow to the Laptev Sea (Antonov, 1967). The freshwater plume in the Laptev Sea is a mixing zone of about 600 km length and 50 km wide (Fig. 2). A low salinity freshwater plume overlies denser highly saline Arctic seawater (Alling et al., 2010). The Lena River plume can be divided into an inner and an outer plume based on a sharp increase in salinity, with salinities up to 5 in the inner plume and up to 15 in the outer plume (Alling et al., 2010). Both parts of the plume are separated by a strong halocline at about 10 m depth from the underlying dense Arctic sea water that has salinities up to 35 (Alling et al., 2010; Chester, 2003; Martin et al., 1993).

2.2 Sampling and Processing

The samples were collected in August 2008 during the International Siberian Shelf Study (ISSS-08) from the RV Yacob Smirnitskyi. The ISSS-08 was part of the International Polar Year (IPY) and the Arctic GEOTRACES programs. The sampling transect is 600 km long, stretching from off the Lena River mouth across the Laptev Sea, and samples from ten stations were collected after the GEOTRACES protocol (Fig. 1, Fig. 2 and Table 1), (Cutter et al., 2010). Additionally, surface sediment (upper 2 cm) samples were taken from the Kara, Laptev and East Siberian Seas (Fig. 1). Samples from this region collected during this cruise have also been studied for DOC (Alling et al., 2010; Bröder et al., 2016; Karlsson et al., 2016; Salvadó et al., 2017), dissolved inorganic carbon (Alling et al., 2012), POC (Karlsson et al. 2016; Sánchez-García et al., 2011), nutrients and alkalinity (Anderson et al., 2009; Pipko et al., 2017), and stable O isotopes (Rosén et al., 2015).

Table 1: Sampling stations in the Laptev Sea of the ISSS-08 research cruise. Temperature, salinity, pH and Oxygen data for the Lena River freshwater plume are obtained from waters at a depth of 4 m, whereas the data for the shelf sediment sample locations are obtained from the overlying bottom waters. The measurements were done with a CTD Seabird 19+. Salinity is based on the Practical Salinity Scale PSS-78.

	Station	Lat. (N)	Long. (E)	Date	Water depth	Salinity[+]	Temp.	pH	Oxygen	POC	DOC	TOC
		degrees (°) minutes (')	degrees (°) minutes (')		m		°C		%	µM	µM	µM
Lena River freshwater plume	YS-128	76°59.220	130°21.340	17/09/2008	51	29.13	-1.43	7.9	99.6	-	-	-
	YS-4*	75°59.220'	129°59.050'	23/08/2008	52	13.3	-1.54	7.7	99.4	8	320	-
	YS-5	75°15.590'	130°0.990'	24/08/2008	44	9.03	-1.56	7.6	99.5	12	434	503
	YS-6	74°43.440'	130°0.980'	24/08/2008	34	5.29	-1.61	7.6	100.5	13	440	543
	YS-7	74°7.920'	129°59.980'	24/08/2008	17	6.31	-1.26	7.6	100.6	11	432	454
	YS-8	73°33.940'	130°0.470'	24/08/2008	13	5.29	-0.78	7.6	99.4	15	391	-
	YS-9	73°21.980'	129°59.820'	25/08/2008	25	8.15	-1.13	7.6	101.7	11	397	437
	YS-10	73°11.040'	129°59.740'	25/08/2008	21	5.37	-0.89	7.6		36	414	441
	YS-11	73°1.110'	129°59.350'	25/08/2008	12	3.54	-0.32	7.5	94.6	53	435	468
	YS-14*	71°37.820'	130°2.970'	25/08/2008	8	1.08	11.14	-		89	442	476
Shelf sediment sample locations	YS-2	73°24.300'	72°59.710	19/08/2008	30	31.53	-1.09	7.5	67.9	20	544	-
	YS-3	73°29.520'	79°53.090'	19/08/2008	38	32.27	-1.06	7.6	70.5	-	-	-
	YS-13	71°58.080'	131°42.080'	26/08/2008	22	27.82	-1.03	-	-	10	453	-
	YS-26	72°27.590'	150°35.740'	31/08/2008	17	27.13	-0.72	7.3	62.3	5	185	-
	YS-28	72°39.050'	154°11.120'	01/09/2008	29	31.05	-0.86	7.2	42.9	4	94	-
	YS-30	71°21.460'	152°9.160'	01/09/2008	10	22.94	1.19	7.5	90.4	13	198	-
	YS-39	71°13.150'	169°22.370'	04/09/2008	46	32.41	-1.64	7.4	64.3	5	46	-

*   station was also sampled for surface sediment   0

[+]   salinity. pH. And oxygen saturation for shelf sediment samples are measured in bottom water

^   measured with a Hydrosonde M5

All water samples, besides YS-14, were collected between 2.5 m and 5.0 m depth using a peristaltic pump and acid-cleaned, silicon tubing. The tubing was attached to a flagpole, which was mounted to the bow of the ship. To avoid contamination from the ship, the flagpole was extended about 10 m in front of the ship. The samples were pumped into a 25 L container, which was rinsed with MQ water between each station. Station YS-14 was sampled at 4.0 m depth using a 60 L Go-Flo® water sampler. All equipment in contact with the samples were cleaned with 5% HNO₃, rinsed with MQ water, and dried in a HEPA-filtered clean air hood. Membrane filtration was carried out within 12 hours of sampling. All water samples were stored in

acid-cleaned polyethylene (PE) bottles and acidified with ultrapure HNO₃ to a pH <2, and all nitrocellulose filters (0.22µm, Millipore®) were stored at -18°C until further analysis (Ödman et al., 1999). Samples for particulate organic carbon were filtered with 0.7 µm GF/F glassfiber filters (Whatman®). The filters were pre-combusted for four hours at 450°C to limit the C blank.

5 Sediment samples were taken with a GEMAX gravity corer and a Van Veen grab sampler as described earlier (Vonk et al., 2012).

During cross-flow ultrafiltration the sample water (< 0.22µm) flows across a membrane surface at a constant pressure. This process prevents clogging, since while particles smaller than the membrane cut-off can pass, larger suspended particles remain circulating in the sample water. The sample water progressively decreases in volume as the permeate crosses the filter, and the

10 larger colloids and particles remain in the retentate, which therefore are progressively concentrated. The cross-flow ratio (CFR=Q_R/Q_P, where Q_R and Q_P are the flow rates of the retentate and permeate, respectively) (Forsberg et al., 2006; Ingri et al., 2000; Larsson et al., 2002) was kept between 60 and 100 to achieve an overall concentration factor larger than 10 (Conc. Fact.= $(V_P+V_R)/V_R$, where V_P and V_R are the final volumes of the permeate and retentate, respectively). For the concentration factors and cross-flow ratios, see Table 2. In this study, the water used for ultrafiltration was pre-filtered through a membrane

15 (<0.22µm) prior to introduction into the MilliPore® Prep/Scale ultrafiltration system, which had a cutoff of 1 kDa. Thus, the permeate is < 1 kDa, while the retentate includes colloids between < 0.22 µm and 1kDa.

Table 2: Cross-flow ultrafiltration details

Sample	Retentate (V_R) litre	Permeate (V_P) litre	Conc. Factor	Retentate Q_R (ml/min)	Permeate Q_P (ml/min)	Cross-flow ratio (CFR)
YS-128	0.97	16.4	18	>3,000	30-50	60-100
YS-4	1.14	11.8	11	3,000	30	100
YS-11	1.10	10.5	11	>3,000	30-50	60-100
YS-14	0.61	12.2	21	>3,000	30-50	60-100

2.3 Analytical Methods

20 Iron concentrations and isotopic compositions were measured at ALS Scandinavia AB. All sample manipulations were performed in a clean laboratory (Class 10 000) by personnel wearing clean room gear and following all general precautions to reduce contamination (Rodushkin, Engström, and Baxter, 2010). High purity Suprapure® acids were used throughout sample treatment and analysis. Organic carbon analyses were carried out at Stockholm University (for analytical details, see Alling et al., 2010; Sánchez-García et al., 2011).

25 For element analysis, the water samples (colloidal: 1 kDa to 0.22µm; truly dissolved: <1 kDa) were diluted (2-200 fold) with 10 % HNO₃. The degree of dilution was dependent on the salinity of the sample. At least two dilutions of each sample were carried out; one high dilution for determination of major elements and one low dilution for minor and trace elements. For Fe analysis, the samples were diluted by a factor of 50. In order to analyze the particles on the filters, the filters were treated with

a 1,000:1 mixture of HNO_3/HF overnight, followed by closed-vessel microwave-assisted digestion. Prior to analysis, the digests were further diluted in 10% HNO_3.

Multi-elemental analysis of the water and filter samples was performed on an Inductively Coupled Plasma Sector Field Mass Spectrometer (ICP-SFMS, ELEMENT2 Thermo Scientific) at ALS Scandinavia AB. The measurement procedure combines internal standardization and external calibration. For internal standardization, indium was added to all the solutions (Rodushkin et al., 2005; Rodushkin and Ruth, 1997). The analytical procedure was validated with different reference materials (SLRS-4 River Water CRM for Trace Metals, SLEW-2 Estuarine Water CRM for Trace Metals and NASS-4 open ocean water (all supplied from National Research Council, Ottawa, Canada) (Rodushkin et al., 2005; 2016).

The blanks of digested filters (0.22µm) for Fe were 2.79 µg/L, which is about 0.25% of the average Fe concentration in the samples for the Lena River sampling transect. Replicated measurements of sample concentrations showed a precision of ±3% (n=4). The limit of detection for Fe in seawater (salinity 35) is 250ppt, the salinity in the analyzed samples were much lower, which decreases the limit of detection. Fe concentrations for the particulate, colloidal and truly dissolved phase are reported in Table 3. Aluminum and titanium concentrations can be found in the supplement.

For the Fe isotope ratio measurements, water samples (colloidal: 1 kDa to 0.22µm) and digested filters were evaporated to dryness, and the residue was re-dissolved in 1 mL 9M HCl. Iron was separated from the matrix elements by using an AG-MP-1M ion-exchange resin (Ingri et al., 2006; Roduhskin and Ruth, 1997). After the sample was loaded, the matrix was washed with 9.6 M HCl, and Cu was eluted with 8 ml 5M HCl. Afterwards, Fe was eluted with 6 ml 2 M HCl and can be used for further steps (Rodushkin et al. 2016). After evaporating to dryness, 50 µL of concentrated HNO_3 was pipetted directly to the residue followed by the addition of 5 mL MQ-water. Samples with high Fe content were diluted with 0.2M HNO_3 to a concentration of 2 mgL^{-1} in the measurement solutions. Low Fe concentration water samples were further diluted to 40-50 µgL^{-1} and measured using high-efficiency desolvation nebulizer (Aridus) in a separate analytical sequence. Iron was separated from the matrix by ion exchange, with a recovery rate above 95%. The Fe isotope compositions in separated fractions from filters and water samples were measured using a Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS, NEPTUNE PLUS®, Thermo Scientific) equipped with micro-concentric nebulizer and tandem cyclonic/Scott double pass spray chamber. Instrumental mass biases were corrected by sample-standard bracketing using IRMM-14 CRM, while an internal standard (Ni) was added to all samples and used to correct for instrumental drift. Each sample was measured twice with the sample-standard bracketing method. Detailed information on the correction procedures can be found in Baxter et al. (2006). During the Fe isotope analysis, $\delta^{56}Fe$ and $\delta^{57}Fe$ were measured. In the three isotopes plot of $\delta^{56}Fe$ and $\delta^{57}Fe$ all samples plot on a single mass fractionation line (Fig. S1). We only discuss the $\delta^{56}Fe$ in this study, although all Fe isotope data are reported in Table 4 including 2σ (n=4;).

Table 3: Iron concentrations of the different fractions for the Lena River freshwater plume. Station

	Location	Particulate	Colloidal	Truly dissolved	Total	pFe/cFe
		μM	μM	nM	μM	mol ratio
YS-128	Lena transect; Laptev Sea	0.1	0.1	8	0.2	1
YS-4	Lena transect	0.5	0.3	7	0.8	2
YS-5	Lena transect	-	-	-	-	-
YS-6	Lena transect	0.7	0.6	-	1.3	1
YS-7	Lena transect	-	-	-	-	-
YS-8	Lena transect	0.9	0.8	-	1.7	1
YS-9	Lena transect	-	-	-	-	-
YS-10	Lena transect	-	-	-	-	-
YS-11	Lena transect	34.0	0.6	9	35.0	56
YS-14	Lena transect; Mohtaba Island	56.0	0.6	1	57.0	90

Total Fe is calculated as a sum of particulate, colloidal, and truly dissolved Fe

Table 4: Fe isotope data for the particulate and the colloidal phase, as well as Fe isotope data for the surface sediments.

Particulate >0.22μm

Station	$\delta^{56/54}Fe$	2σ	$\delta^{57/54}Fe$	2σ
	‰	‰	‰	‰
YS-128	-0.289	0.050	-0.487	0.024
YS-4	-0.406	0.126	-0.735	0.114
YS-6	-0.360	0.014	-0.644	0.082
YS-8	-0.130	0.008	-0.266	0.136
YS-11	-0.067	0.040	-0.106	0.008
YS-14	-0.048	0.106	-0.097	0.114

Colloidal 1kDa-0.22μm

Station	$\delta^{56/54}Fe$	2σ	$\delta^{57/54}Fe$	2σ
	‰	‰	‰	‰
YS-128	0.112	0.069	0.233	0.050
YS-4	0.102	0.079	0.277	0.038
YS-11	-0.227	0.089	-0.312	0.298
YS-14	-0.171	0.015	-0.267	0.030

Surface Sediment

Station	$\delta^{56/54}Fe$	2σ	$\delta^{57/54}Fe$	2σ
	‰	‰	‰	‰
YS-13	-0.233	0.070	-0.324	0.006
YS-4	-0.220	0.040	-0.355	0.028
YS-26	-0.209	0.002	-0.298	0.116
YS-14	-0.250	0.110	-0.404	0.100
YS-2	-0.351	0.150	-0.439	0.102
YS-3	-0.230	0.024	-0.396	0.106
YS-11	-0.083	0.022	-0.209	0.094
YS-28	-0.131	0.074	-0.220	0.118
YS-30	-0.102	0.028	-0.185	0.088
YS-39	-0.241	0.086	-0.403	0.124

3 Results

The average pH for the water samples was 7.6 ± 0.1(1SD) and the oxygen saturation was 99.4 ± 2.1% (Tab. 1), (Andersson and Jutterstrøm, 2008). Within the Lena River freshwater plume the pH ranged from 7.5 to 7.9. The methodology for pH and oxygen measurements is described in the supplement (after Dudarev, 2008).

3.1 Organic Carbon distributions in the Lena River plume

The DOC concentrations show a small variation between 320 and 442 µM in the surface waters of the inner and outer plume (Tab. 1; Fig. 3). The average DOC concentration of 410 µM in the surface water of the Lena River freshwater plume has been reported by Alling et al. (2010) and is similar to previous studies (Cauwet and Sidorov, (1996): 300–600µM). It has been

10   shown that DOC is behaving conservatively during mixing between Lena River water and Arctic Ocean water along the sampling profile (Alling et al., 2010; Opsahl et al., 1999; Pugach et al., 2018). The POC concentrations decrease from high values (89 µM) close to the coast to low values (8 µM) in the outer plume (Fig. 3). In the inner plume (YS-14 to YS-10) the POC concentrations are high, between 89 µM and 36 µM, whereas in the outer plume the POC concentrations were almost constant, with an average value of about 12 µM. The overall average POC concentration of about 28 µM has been earlier

15   reported by Sánchez-García et al. (2011).

3.2 Iron concentrations in the Lena River freshwater plume

Three size fractions were analyzed for Fe: particulate Fe (PFe, > 0.22 µm), colloidal Fe (CFe, 1kDa-0.22 µm), and truly dissolved Fe (DFe, < 1 kDa). The total Fe (TFe) concentration was calculated as the sum of PFe, CFe, and DFe (Tab. 3). The PFe concentration decreased from 56 to 0.1 µM along the Lena River freshwater plume (Fig. 4). Between the inner and

20   the outer plumes (i.e. between YS-11 and YS-8), the PFe concentration dropped to 0.9 µM, a loss of > 99% of PFe. The loss of Fe was estimated as fraction of the maximum Fe concentration of each size fraction (details can be found in the supplement). The CFe concentration decreased from 0.6 to 0.1 µM along the freshwater plume, a loss of about 90% CFe (Fig 4). The concentration of DFe was low, at around 8 nM, and relatively constant along the plume (Fig. 4). In total, a loss of >99% TFe was observed between the first station (YS-14) and the last station (YS-128).

25   We observed non-conservative behaviour of PFe during mixing between Lena River water and Arctic Ocean water, while CFe showed generally conservative behaviour, with an almost linear correlation with salinity (Fig. 5). The PFe concentrations below 1 µM also showed an almost linear correlation at salinities above 5 in the outer plume. In the inner plume, at salinities below 5, the PFe showed non-conservative behaviour.

3.3 Iron isotopes in the Lena River freshwater plume

30   The Fe isotope compositions in the particulate and the colloidal phases, as well as in the surface sediments, are reported in Fig. 6. The $\delta^{56}Fe$ values in the particulates varied between -0.05 ± 0.11‰ (YS-14) in the inner plume and -0.41 ± 0.12‰ (YS-4) in

the outer plume (Fig. 6), with the δ^{56}Fe values in the outer plume all lower compared to the inner plume. The CFe show negative δ^{56}Fe values (average -0.20 ± 0.06‰) in the inner plume and positive δ^{56}Fe values (average 0.11 ± 0.08‰) in the outer plume. The surface sediments from the Laptev Sea had negative δ^{56}Fe values (-0.23 ± 0.08‰ and -0.25 ± 0.12‰). Surface sediments obtained from 10 samples in other parts of the East Siberian Arctic Schelf (ESAS) showed only small variations (Fig 1 and Fig. 6; Tab. 4; Tab. S2).

4 Discussion

In the Laptev Sea close to the river mouth about 18% of the total OC was present as POC and this was apparently rapidly lost during mixing (Fig. 3). In the outer plume only about 2% of the total OC was present as POC. It has been suggested that POC in the Lena River freshwater plume is transported in different forms, including large particles, which can sink, and almost neutrally buoyant flocculates of humic substances (Gustafsson and Gschwend, 1997; Gustafsson et al., 2000; Sánchez-García et al., 2011). The POC, which is associated with larger particles (> 0.7µm), will settle close to land, whereas the humic substance flocculates will travel further out (Vonk et al., 2010).

4.1 Iron behaviour in the Lena River freshwater plume

The PFe concentrations found in the Laptev Sea close to the shore are higher than the average PFe concentration in the Lena River, but similar to the highest PFe river values up to 32 µM (Hirst et al., 2017). The CFe and DFe in the Lena River (Hirst et al., 2017) showed higher average concentrations (CFe: 1.5 µM; DFe: 54 nM) than concentrations found in the Lena River – Laptev Sea transect. Most likely some of the CFe and DFe from Lena River already flocculated at salinities below 1, where the first sample of our sampling profile was taken (YS-14). Within the Arctic Ocean, dissolved Fe (CFe + DFe) concentrations vary between 0.2 and 63 nM and the concentrations depend on distance to the shore and depths of sampling, with generally higher values in surface waters as well as close to the bottom sediment, which might be related to resuspension, sinking of brines, or resuspension from the sedimentary Fe (Klunder et al., 2012; Thuróczy et al., 2011). The CFe concentrations are higher close to the coast and decreasing in the outer plume to values that are similar to CFe concentrations reported from further out in the Arctic Ocean (e.g. Thuróczy et al., 2011). Estuarine processes, including flocculation and sedimentation (e.g. Boyle et al. 1977; Sholkovitz, 1978), are the primary cause for the sharp decrease of particulate and dissolved Fe concentrations along the transect from the river towards the open Arctic Ocean. Within the estuaries, the destabilization of the Fe-rich colloids and particles by seawater cations causes flocculation along the salinity gradient (Escoube et al. 2009; Gerringa et al. 2007; Mosley, Hunter, and Ducker 2003) and successively sedimentation of the newly built flocculates (Daneshvar, 2015). The distribution of Fe between the different phases show that PFe is the dominant Fe-phase in the inner plume system (with a PFe/CFe ratio of about 90). However, most of the PFe is lost in the inner plume close to the shore and the ratio PFe/CFe decreases towards a ratio of about 1 in the outer plume.

We observed non-conservative mixing of PFe at salinities lower than 5 and conservative mixing at salinities higher than 5 (Fig. 5). Recent studies showed that the majority of PFe (70±15%) coming from the Lena River is in the form of chemically

reactive ferrihydrite (Hirst et al., 2017). Organic C hinders the coagulation of the particles during riverine transport, but in the estuarine mixing zone the negatively charged iron-bearing particles will react with seawater cations and form larger aggregates (Boyle et al., 1977). The larger aggregates sink more readily to the sediments in the Lena River – Laptev Sea transect and can thus explain the observed non-conservative behaviour (Martin et al., 1993). This process is a common feature for Fe that is

5   observed in other estuaries and is responsible for at least 80% loss of "dissolved" riverine Fe (Boyle et al., 1977; Figuères, Martin, and Meybbeck, 1978; Guieu et al., 1996; Windom, Beck, and Smith, 1971). The large amount of PFe (99%) lost in the inner Lena River freshwater plume is likely due to removal of chemically reactive ferrihydrite, which is the main form of PFe in the Lena River. Furthermore, it has been shown that about 20% of OC in the Eurasian Arctic Shelf is bound to reactive Fe phases (Salvadõ et al., 2015). It has also been shown that part of the ferrihydrite might be transported via surface attachment

10   to POC in a network of organic fibrils (Hirst et al., 2017). The attachment of POC to the ferrihydrite possibly reduces the density of Fe-oxyhydroxides (Passow, 2004), allowing both POC and PFe to be transported into the Arctic Ocean, where they are present at about 2% of their initial concentration in rivers. Concentrations of PFe at salinities >5 and CFe along the whole salinity gradient show a linear correlation with salinity, suggesting that these particles and colloids are less affected by changes in ionic strength and therefore might be mainly in the form of Fe-oxyhydroxides. Gregor et al. (1997) showed that the optimal

15   range for cationic flocculation is a pH between 6 and 7. At higher pH, more cations are needed for achieve the same efficiency of flocculation. Anyhow, Asmala et al. (2014) showed that the pH range is important at salinies below 1-2, but at higher salinities the pH is negligible. Furthermore, they showed that it is likely that high Fe concentrations are a more significant factor and will yield to the same flocculation rates. The DFe (<1kDa) concentrations along the freshwater plume are almost constant around 8nM (except station YS-14, 1 nM). The average DFe concentration in the Lena River is about 54 nM (Hirst

20   et al., 2017). These data suggest a loss of DFe at low salinities (<1.3) before the concentration stabilize around 8 nM in the Lena River freshwater plume. These observations are in accordance with previous studies in the Laptev Sea where dissolved Fe concentrations of 3 to10 nM in the upper 20 m has been reported (Klunder et al., 2012). It has also been reported that about 74 to 83% of the dissolved Fe is present in the truly dissolved phase in the Arctic Ocean (Thuróczy et al., 2011). Slagter et al. (2017) report dissolved Fe concentration of 2.6 nM in the Transpolar Drift, which is transporting surface water from Siberian

25   great rivers, e.g. Lena River, across the Arctic Ocean into the Atlantic. Available evidence indicates that the Ob River similarly contributes Fe into the open Arctic Ocean. Along the Ob River, the DFe shows relatively constant DFe concentrations of 36 to 44 nM in the 10kDa fraction (Dai and Martin, 1995), which are somewhat higher than reported here for the Lena possibly due to a larger ultrafiltration cutoff size. The overall trend of this and earlier studies suggests a loss of DFe from the Lena River to the Lena River freshwater plume and almost constant concentrations along the freshwater plume. The conservative

30   behaviour of DFe concentrations along a salinity gradient has been examined in estuarine mixing experiments, and it has been shown that freshwater Fe oxyhydroxide colloids aggregate into much larger particles in contact with seawater, whereas the truly dissolved phase was virtually unaffected (Gustafsson et al., 2000; Stolpe and Hassellöv, 2007). The observation that the truly dissolved phase is less affected by the increase in salinity suggests that this phase can be transported through estuaries and further out into the open ocean (Laglera and Van Den Berg, 2009).

35   River water is the most important source of Fe for the central Arctic Ocean (Klunder et al., 2012) and estuarine processes

significantly modify the amount and distribution of Fe between different fractions, and therefore also the bioavailability of the river-derived Fe. Slomp et al. (2013) showed that Fe concentrations are likely to affect the sedimentation of organic matter and P in sediments of lakes and coastal seas. Therefore, the loss of Fe-OC aggregates close to the shoreline might also cause a great loss of phosphorous and thus contribute to the suggested "rusty carbon sink" (Lalonde et al., 2012; Salvadõ et al., 2015).

4.2 Iron isotopes in the Lena River freshwater plume

The measured δ^{56}Fe compositions in the Lena River plume are broadly similar to those reported in previous studies in other arctic/subarctic regions (e.g. Escoube et al. 2009; Staubwasser et al. 2013). In these areas, within the fully oxidized water column, the PFe phase show negative δ^{56}Fe values, while the dissolved phase generally shows values, enriched in Fe(III) compared to the PFe phase (Escoube et al., 2015; 2009; Ingri et al., 2006; Staubwasser et al., 2013; Zhang et al., 2015). It has been shown that the Fe isotope composition is affected by seasonal variations of water flow pathes to the river (Hirst et al., 2017). Ingri et al. (accepted at GCA) showed that the Fe isotope composition is an indiactor for different Fe aggregates and for changing primary Fe sources throughout the season. Along the freshwater plume the CFe phase has two different Fe isotope compositions, positive and negative δ^{56}Fe values, therefore it might also represent water masses from different seasons. This would suggest that the water masses in the inner plume represent spring flood discharge, whereas the water masses in the outer plume represent summer flow discharge. In contrast, Alling et al. (2010), claim that the age of the entire freshwater plume is approximately two months. All measured DOC samples (400-420 µM) from their study plot on a mixing line of Lena River water measured in August and Arctic Deep water. If the water would represent spring flood discharge, which has much higher DOC concentrations (1170 µM), their samples would plot on a different mixing line (Alling et al., 2010).

Sundman et al., (2014) measured the speciation of Fe in stream water samples with X-ray absorption spectroscopy and found iron-organic complexes with mixed speciation states of Fe as Fe(II, III)-OC and Fe(III)oxyhydroxides associated to OC. The variations in the distributions of Fe between the different species in the iron-organic complexes are controlled by pH and OC concentrations (Neubauer et al., 2013; Sundman et al., 2013). The Fe speciation of these complexes regulate the Fe isotopic composition. When Fe(II) is oxidized to Fe(III), the heavy ^{56}Fe is enriched in the Fe(III) phase whereas Fe(II) becomes depleted in the ^{56}Fe isotope (Bullen et al., 2001; Homoky et al., 2012; Rouxel et al., 2008; Severmann et al., 2006; Welch et al., 2003; Wu et al., 2011). Laboratory experiments showed the existence of oxidative precipitation of Fe(II) to Fe(III) (e.g. Welch et al. 2003), which can occur in natural streams. Bullen et al. (2001) measured an overall fractionation factor of about 0.9 in natural streams. Hence, Fe(III)oxyhydroxides should show a enrichment of ^{56}Fe in oxidized river water, while Fe(II, III)-OC complexes should show a depletion of ^{56}Fe. The differences of the Fe isotope composition in the PFe and CFe fraction clearly indicates different sources for the two phases, as flocculation of CFe into PFe would result in PFe with the same isotopic composition (e.g. Escoube et al. 2009). The existence of two different Fe colloid pools, composed of organic-rich and Fe rich particles, was shown by Pokrovsky and Schott (2002) in small boreal rivers. Fe-isotope data from this study show the existence of two colloidal Fe phases with different δ^{56}Fe within the Lena River – Laptev Sea transect. The Fe isotope values of CFe and PFe along the plume and the composition of the surface sediment suggest that the chemically reactive ferrihydrite represent

colloids and particles, with a negative δ^{56}Fe value, sedimenting close to the shoreline. The Fe oxyhydroxides that remain in the water column could then be responsible for the positive δ^{56}Fe values in the colloidal phase in the outer plume. Therefore, in this case the Lena River is an important source of positive δ^{56}Fe values to the Arctic Ocean, along with small OC-rich arctic and subarctic rivers (Ilina et al., 2013; Pokrovsky et al., 2014).

5   The surface sediments in the shelf areas along the Laptev Sea have δ^{56}Fe values of -0.2‰ (Figure 6). This value results from the removal of particulate and colloidal Fe(II, III)oxyhydroxides from the water column and burial in the sediment. As seen in earlier studies, flocculation during estuarine mixing did not fractionate the Fe isotopic composition of the colloids and particles (Bergquist and Boyle, 2006; Escoube et al., 2009; Fantle and DePaolo, 2004; Poitrasson et al., 2014). Other processes, as resuspension of sediment and non-reductive dissolution of sediment to the seawater (Radic et al., 2011) would lead to a much

10   more negative (-3.3‰ to -1.7‰) Fe isotope composition of the sediment (Homoky et al., 2009; Severmann et al., 2006; 2010). Therefore, the δ^{56}Fe of the uppermost sediment reflecting the δ^{56}Fe of the sedimenting colloids and particles from the water column seems reasonable.

5. Conclusions

15   Close to the coast and within the inner part of the river plume, the concentration of PFe dominates the total Fe budgets. In the outer part of the plume, the PFe and CFe concentrations are almost equal, as more than 99% of the total Fe is lost. The loss of PFe, most likely in the form of chemically reactive ferrihydrite, results from increasing ionic strength, due to increasing salinities, which promotes flocculation. The coagulation and removal appear at the beginning of the mixing zone at low salinities (0-5). Colloidal Fe concentrations are almost constant along the inner plume and the decrease along the outer plume

20   due to conservative mixing. The truly dissolved Fe shows little variation along the Lena River freshwater plume. Therefore, the river-derived truly dissolved fraction could be an important source of bioavailable Fe, along with colloidal Fe, which may affect the primary production in the central Arctic Ocean.

The Fe isotope compositions in the Lena River freshwater plume provide clear indications on which forms of Fe reach the deep ocean basin. There are significant differences between the particulate and colloidal phases. The negative δ^{56}Fe values,

25   found in the colloidal and particulate phases, are lost during estuarine mixing and buried in the sediment. These negative δ^{56}Fe values seem to represent chemically reactive ferrihydrite. Within the colloidal phase, we measured positive δ^{56}Fe values further out in the plume, which likely represent Fe-oxyhydroxide, which remain buoyant in the water column, transported along the Lena River freshwater plume into the Arctic Ocean.

Competing interests

30   The authors declare that they have no conflict of interest.

Acknowledgment

The ISSS-08 program was supported by the Knut and Alice Wallenberg Foundation, the Far Eastern Branch of the Russian Academy of Sciences, the Swedish Research Council (621-2004-4039 and 211-621-2007), the U.S. National Oceanic and Atmospheric Administration, the Russian Foundation for Basic Research, the Swedish Polar Research Secretariat, and the Stockholm University Bert Bolin Centre for Climate Research. Ö.G. also acknowledge a Distinguished Professor Grant from the Swedish Research Council (VR Contract No. 2017-05687), an Advanced Grant from the European Research Council (ERC-AdG CC-TOP project #695331). I.S. acknowledges the Russian Government (grant No. 14.Z50.31.0012). The ISSS-08 program is part of the IPY (International Polar Year) and the GEOTRACES program.

References

Allard, T., Menguy, N., Salomon, J., Calligaro, T., Weber, T., Calas, G., Benedetti, M.F., 2004. Revealing forms of iron in river-borne material from major tropical rivers of the Amazon Basin (Brazil). Geochim. Cosmochim. Acta 68, 3079–3094. https://doi.org/10.1016/J.GCA.2004.01.014

Alling, V., Sanchez-Garcia, L., Porcelli, D., Pugach, S., Vonk, J.E., Van Dongen, B., Mörth, C.M., Anderson, L.G., Sokolov, A., Andersson, P., Humborg, C., Semiletov, I., Gustafsson, Ö., 2010. Nonconservative behavior of dissolved organic carbon across the Laptev and East Siberian seas. Global Biogeochem. Cycles 24, 1–15. https://doi.org/10.1029/2010GB003834

Alling, V., Porcelli, D., Mörth, C.M., Anderson, L.G., Sanchez-Garcia, L., Gustafsson, Ö., Andersson, P.S., Humborg, C., 2012. Degradation of terrestrial organic carbon, primary production and out-gassing of CO_2 in the Laptev and East Siberian Seas as inferred from $\delta 13C$ values of DIC. Geochim. Cosmochim. Acta 95, 143–159. https://doi.org/10.1016/j.gca.2012.07.028

Amon, R.M.W., Rinehart, A.J., Duan, S., Louchouarn, P., Prokushkin, A., Guggenberger, G., Bauch, D., Stedmon, C., Raymond, P.A., Holmes, R.M., McClelland, J.W., Peterson, B.J., Walker, S.A., Zhulidov, A. V., 2012. Dissolved organic matter sources in large Arctic rivers. Geochim. Cosmochim. Acta 94, 217–237. https://doi.org/10.1016/j.gca.2012.07.015

Anbar, A.D., 2004. Iron stable isotopes: Beyond biosignatures. Earth Planet. Sci. Lett. 217, 223–236. https://doi.org/10.1016/S0012-821X(03)00572-7

Andersson, Leif; Jutterstrøm, Sara (2008): Seawater carbonate chemistry and nutrients measured on water bottle samples during the International Siberian Shelf Study 2008 (ISSS-08) in the Laptev, East Siberian and Chukchi Seas. Department of Chemistry, University of Gothenburg, PANGAEA, https://doi.org/10.1594/PANGAEA.715045

Anderson, L.G., Jutterstrøm, S., Hjalmarsson, S., Wåhlström, I., Semiletov, I.P., 2009. Out-gassing of CO_2 from Siberian Shelf seas by terrestrial organic matter decomposition. Geophys. Res. Lett. 36, L20601. https://doi.org/10.1029/2009GL040046

Anisimov, O., Reneva, S., 2009. Permafrost and Changing Climate: The Russian Perspective. http://dx.doi.org/10.1579/0044-7447(2006)35[169:PACCTR]2.0.CO;2. https://doi.org/10.1579/0044-7447(2006)35[169:PACCTR]2.0.CO;2

Antonov, V.S., 1967. The Mouth Area of the Lena, in: The Hydrographic Review. Gidrometeoizdat, Leningrad.

Baxter, D.C., Rodushkin, I., Engström, E., Malinovsky, D., 2006. Revised exponential model for mass bias correction using an internal standard for isotope abundance ratio measurements by multi-collector inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 21, 427. https://doi.org/10.1039/b517457k

Asmala, E., Bowers, D., Autio, R., Kaartokallio, H., Thomas, D.N., 2014. Qualitative changes of riverine dissolved organic matter at low salinities due to flocculation. J. Geophy. Res.: Biogeosci. 119,1919–1933, doi:10.1002/ 2014JG002722.

Beard, B.L., Johnson, C.M., 2004. Ancient Earth and Other Planetary Bodies. Rev. Mineral. 55, 319–357. https://doi.org/10.2138/gsrmg.55.1.319

Beard, B.L., Johnson, C.M., Cox, L., Sun, H., Nealson, K.H., Aguilar, C., 1999. Iron isotope biosignatures. Science (80-.). 285, 1889–1891. https://doi.org/10.1126/science.285.5435.1889

Beard, B.L., Johnson, C.M., Von Damm, K.L., Poulson, R.L., 2003. Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. Geology 31, 629–632. https://doi.org/10.1130/0091-7613(2003)031<0629:IICOFC>2.0.CO;2

Bergquist, B.A., Boyle, E.A., 2006. Iron isotopes in the Amazon River system: Weathering and transport signatures. Earth Planet. Sci. Lett. 248, 39–53. https://doi.org/10.1016/j.epsl.2006.05.004

Boyle, E.A., Edmond, J.M., Sholkovitz, E.R., 1977. The mechanism of iron removal in estuaries. Geochim. Cosmochim. Acta 41, 1313–1324. https://doi.org/10.1016/0016-7037(77)90075-8

Brantley, S.L., Liermann, L., Bullen, T.D., 2001. Fractionation of Fe isotopes by soil microbes and organic acids. Geology 29, 535. https://doi.org/10.1130/0091-7613(2001)029<0535:FOFIBS>2.0.CO;2

Bröder, L., Tesi, T., Salvadó, J.A., Semiletov, I.P., Dudarev, O.V., Gustafsson, Ö. 2016. Fate of terrigenous organic matetr across the Laptev Sea from the mouth of the Lena River to the deepp sea of the Arctic interior. Biogeosci. 13, 17, 5003-5019. https://doi.org/10.5194/bg-13-5003-2016

Bullen, T.D., White, A.F., Childs, C.W., Vivit, D. V, Schultz, M.S., 2001. Demonstration of a significant iron isotope fractionation in nature. Geology 29, 699–702. https://doi.org/10.1130/0091-7613(2001)029<0699:DOSAII>2.0.CO;2

Cauwet, G., Sidorov, I., 1996. The biogeochemistry of Lena River: organic carbon and nutrients distribution. Mar. Chem. 53, 211–227. https://doi.org/10.1016/0304-4203(95)00090-9

Chester, R. (Roy), 2003. Marine geochemistry, 2. [rev.] ed. ed. Blackwell Pub, Malden.

Conway, T.M., John, S.G., 2014. Quantification of dissolved iron sources to the North Atlantic Ocean. Nature 511, 212–215. https://doi.org/10.1038/nature13482

Cutter, G., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H., Rutgers, M. (2010). Sampling and sample-handling protocols for GEOTRACES cruises, [Miscellaneous]. 10013/epic.42722

Dai, M.-H., Martin, J.-M., 1995. First data on trace metal level and behaviour in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia. Earth Planet. Sci. Lett. 131, 127–141. https://doi.org/10.1016/0012-821X(95)00021-4

Daneshvar, E. (2015) Dissolved Iron Behavior in the Ravenglass Estuary Waters, An Implication on the Early Diagenesis. Universal Journal of Geoscience 3(1): 1-12. DOI: 10.13189/ujg.2015.030101

de Baar, H.J.W. and de Jong, J.T.M, 2001. Distributions, sources and sinks of iron in seawater. In Turner D.R., Hunter, K.A. (Eds) Biogeochemistry of Iron in Seawater. Wiley, New York, pp. 123-253.

Dos Santos Pinheiro, G.M., Poitrasson, F., Sondag, F., Cochonneau, G., Vieira, L.C., 2014. Contrasting iron isotopic compositions in river suspended particulate matter: The Negro and the Amazon annual river cycles. Earth Planet. Sci. Lett. 394, 168–178. https://doi.org/10.1016/j.epsl.2014.03.006

Dudarev,O., 2008. Cruise report International Siberian Shelf Study 2008 (ISSS-08). Swedish Knut and Alice Wallenberg Foundation, the Far-Eastern Branch of the Russian Academy of Sciences, the Swedish Research Councli, the Russian Foundation for Basic Research, NoAA, and the Swedish Polar Research Secretariat, Bremerhaven, PANGAEA. Hdl:10013/epic32714

Eckert, J.M., Sholkovitz, E.R., 1976. The flocculation of iron, aluminum and humates from river water by electrolytes. Geochim. Cosmochim. Acta 40, 847–848.

Escoube, R., Rouxel, O.J., Pokrovsky, O.S., Schroth, A., Max Holmes, R., Donard, O.F.X., 2015. Iron isotope systematics in Arctic rivers. Comptes Rendus - Geosci. 347, 377–385. https://doi.org/10.1016/j.crte.2015.04.005

Escoube, R., Rouxel, O.J., Sholkovitz, E., Donard, O.F.X., 2009. Iron isotope systematics in estuaries: The case of North River, Massachusetts (USA). Geochim. Cosmochim. Acta 73, 4045–4059. https://doi.org/10.1016/j.gca.2009.04.026

Fantle, M.S., DePaolo, D.J., 2004. Iron isotopic fractionation during continental weathering. Earth Planet. Sci. Lett. 228, 547–562. https://doi.org/10.1016/j.epsl.2004.10.013

Figuères, G., Martin, J.M., Meybeck, M., 1978. Iron behaviour in the Zaire Estuary. Netherlands J. Sea Res. 12, 329–337.

Forsberg, J., Dahlqvist, R., Gelting-Nyström, J., Ingri, J., 2006. Trace metal speciation in brackish water using diffusive gradients in thin films and ultrafiltration: comparison of techniques. Environ. Sci. Technol. 40, 3901–5. https://doi.org/10.1021/es0600781

Gerringa, L.J.A., Rijkenberg, M.J.A., Wolterbeek. H.Th:. Verburg, T.G., Boye, M., de Abar, H.J.W., 2007. Kinetic study reveals weak Fe-binding ligand, which affects the solubility of Fe in the Scheldt estuary. Mar. Chem. 103, 30-45. https://doi.org/ 10.1016/j.marchem.2006.06.002

Gregor, J. E., Nokes, C.J., and Fenton, E. (1997), Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation, Water Res., 31(12), 2949–2958.

Guieu, C., Huang, W.W., Martin, J.M., Yong, Y.Y., 1996. Outflow of trace metals into the Laptev Sea by the Lena River. Mar. Chem. 53, 255–267. https://doi.org/10.1016/0304-4203(95)00093-3

Guo, L., Santschi, P., 1996. A critical evaluation of cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater. Mar. Chem. 55, 113-127. https://doi.org/10.1016/S0304-4203(96)00051-5

Gustafsson, C., Gschwend, P.M., 1997. Aquatic colloids: Concepts, definitions, and current challenges. Limnol. Oceanogr. 42, 519–528. https://doi.org/10.4319/lo.1997.42.3.0519

Gustafsson, Ö., Widerlund, A., Andersson, P.S., Ingri, J., Roos, P., Ledin, A., 2000. Colloid dynamics and transport of major elements through a boreal river - Brackish bay mixing zone. Mar. Chem. 71, 1–21. https://doi.org/10.1016/S0304-4203(00)00035-9

Hirst, C., Andersson, P.S., Murphy, M.J., Mörth, C.M., , Kutscher, L., Schmitt, M., Petrov, R.E., Maximov, T., Porcelli, D., 2017 Seasonal variations in the sources and formation of Fe-bearing particles in the Lena River basin; evidence from iron isotopes. Goldschmidt abstract.

Hirst, C., Andersson, P.S., Shaw, S., Burke, I.T., Kutscher, L., Murphy, M.J., Maximov, T., Pokrovsky, O.S., Mörth, C.M., Porcelli, D., 2017. Characterisation of Fe-bearing particles and colloids in the Lena River basin, NE Russia. Geochim. Cosmochim. Acta 213, 553–573. https://doi.org/10.1016/j.gca.2017.07.012

Holmes, R.M., McClelland, J.W., Peterson, B.J., Tank, S.E., Bulygina, E., Eglinton, T.I., Gordeev, V. V., Gurtovaya, T.Y., Raymond, P.A., Repeta, D.J., Staples, R., Striegl, R.G., Zhulidov, A. V., Zimov, S.A., 2012. Seasonal and Annual Fluxes of Nutrients and Organic Matter from Large Rivers to the Arctic Ocean and Surrounding Seas. Estuaries and Coasts 35, 369–382. https://doi.org/10.1007/s12237-011-9386-6

Homoky, W.B., Severmann, S., Mills, R.A., Statham, P.J., Fones, G.R., 2009. Proe-fluid Fe isotopes reflect the extent of benthic Fe redoc recycling: Evidence from continental shelf and deep.sea sediments. Geology 37, 751-754. https://doi.org/ 10.1130/G25731A.1

Homoky, W.B., Severmann, S., McManus, J., Berelson, W.M., Riedel, T.E., Statham, P.J., Mills, R.A., 2012. Dissolved oxygen and suspended particles regulate the benthic flux of iron from continental margins. Mar. Chem. 134–135, 59–70. https://doi.org/10.1016/j.marchem.2012.03.003

Icopini, G.A., Anbar, A.D., Ruebush, S.S., Tien, M., Brantley, S.L., 2004. Iron isotope fractionation during microbial reduction of iron: The importance of adsorption. Geology 32, 205–208. https://doi.org/10.1130/G20184.1

Ilina, S.M., Poitrasson, F., Lapitskiy, S.A., Alekhin, Y. V, 2013. Extreme iron isotope fractionation between different size colloids of boreal organic-rich waters. Geochim. Cosmochim. Acta 101, 96–111. https://doi.org/10.1016/j.gca.2012.10.023

Ingri, J., Widerlund, A., Land, M., Gustafsson, Ö., Andersson, P., Öhlander, B., 2000. Temporal variations in the fractionation of the rare earth elements in a Boreal river; the role of colloidal particles. Chem. Geol. 166, 23–45. https://doi.org/10.1016/S0009-2541(99)00178-3

Ingri, J., Malinovsky, D., Rodushkin, I., Baxter, D.C., Widerlund, A., Andersson, P., Gustafsson, Ö., Forsling, W., Öhlander, B., 2006. Iron isotope fractionation in river colloidal matter. Earth Planet. Sci. Lett. 245, 792–798. https://doi.org/10.1016/j.epsl.2006.03.031

Ingri, J., Conrad, S., Lidman, F., Nordblad. F., Engström. E., Rodushkin. I., Porcelli. D., accepted. Iron pathways in the boreal landscape: role of the riparian zone. Geochim. Cosmochim. Acta

Karlsson, E., Gelting, J., Tesi, T., van Dongen, B., Andersson, A., Semiletov, I., Charkin, A., Dudarev, O., Gustafsson, Ö., 2016. Different sources and degradation state of dissolved, particulate, and sedimentary organic matter along the Eurasian Arctic coastal margin. Global Biogeochem. Cycles, 30,898–919, doi:10.1002/2015GB005307

Klunder, M.B., Bauch, D., Laan, P., De Baar, H.J.W., Van Heuven, S., Ober, S., 2012. 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. Ocean. 117, 1–18. https://doi.org/10.1029/2011JC007133

Kritzberg, E.S., Villanueva, A.B., Jung, M., Reader, H.E., 2014. Importance of boreal rivers in providing iron to marine waters. PLoS One 9. https://doi.org/10.1371/journal.pone.0107500

Kutscher, L., Mörth, C.M., Porcelli, D., Hirst, C., Maximov, T.C., Petrov, R.E., Andersson, P.S., 2017. Spatial variation in concentration and sources of organic carbon in the Lena River, Siberia. J. Geophys. Res. Biogeosciences 122, 1999–2016. https://doi.org/10.1002/2017JG003858

Laglera, L.M., Van Den Berg, C.M.G., 2009. Evidence for geochemical control of iron by humic substances in seawater. Limnol. Oceanogr. 54, 610–619. https://doi.org/10.4319/lo.2009.54.2.0610

Lalonde, K., Mucci, A., Ouellet, A., Gélinas, Y., 2012. Preservation of organic matter in sediments promoted by iron. Nature 483, 198–200. https://doi.org/10.1038/nature10855

Larsson, J., Ingri, J., Gustafsson, Ö., 2002. Evaluation and optimization of two complementary cross-flow ultrafiltration systems toward isolation of coastal surface water colloids. Environ.Sci.Technol., Vol. 36, No. 10, 2236-2241. https://doi.org/10.1021/ES010325V

Le Fouest, V., Babin, M., Tremblay, J.-É., 2013. The fate of riverine nutrients on Arctic shelves. Biogeosciences 10, 3661–3677. https://doi.org/10.5194/bg-10-3661-2013

Martin, J.M., and Meybeck, M., 1979. Elemental mass-balance or material carried by major world rivers. Mar. Chem. 7, 173-206.

Martin, J.M., Guan, D.M., Elbazpoulichet, F., Thomas, A.J., Gordeev, V. V, 1993. Preliminary Assessment of the Distributions of Some Trace-Elements (as, Cd, Cu, Fe, Ni, Pb and Zn) in a Pristine Aquatic Environment - the Lena River Estuary (Russia). Mar. Chem. 43, 185–199. https://doi.org/Doi 10.1016/0304-4203(93)90224-C

Martin J.H., Gordon M.R., F.E.S., 1991. Iron Limitation? Limnol. Ocean. 36, 1793–1802. https://doi.org/10.4319/lo.1991.36.8.1793

Mosley, L.M., Hunter, K.A., Ducker, W.A., 2003. Forces between colloid particles in natural waters. Environ. Sci. Technol. 37, 3303-3308. https://doi.org/ 10.1021/es026216d

Mulholland, D.S., Poitrasson, F., Boaventura, G.R., Allard, T., Vieira, L.C., Santos, R.V., Mancini, L., Seyler, P., 2015. Insights into iron sources and pathways in the Amazon River provided by isotopic and spectroscopic studies. Geochim. Cosmochim. Acta 150, 142–159. https://doi.org/10.1016/j.gca.2014.12.004

Neubauer, E., Köhler, S.J., Von Der Kammer, F., Laudon, H., Hofmann, T., 2013. Effect of pH and stream order on iron and arsenic speciation in boreal catchments. Environ. Sci. Technol. 47, 7120–7128. https://doi.org/10.1021/es401193j

Ödman, F., Ruth, T., Pontér, C., 1999. Validation of a field filtration technique for characterization of suspended particulate matter from freshwater. Part I. Major elements. Appl. Geochemistry 14, 301–317. https://doi.org/10.1016/S0883-2927(98)00050-X

Opsahl, S., Benner, R., Amon, R.M.W., 1999. Major flux of terrigenous dissolved organic matter through the Arctic Ocean. Limnol. Oceanogr. 44, 2017–2023. https://doi.org/10.4319/lo.1999.44.8.2017

Passow, U., 2004. Switching perspectives: Do mineral fluxes determine particulate organic carbon fluxes or vice versa? Geochemistry, Geophys. Geosystems 5, n/a-n/a. https://doi.org/10.1029/2003GC000670

Pédrot, M., Boudec, A. Le, Davranche, M., Dia, A., Henin, O., 2011. How does organic matter constrain the nature, size and availability of Fe nanoparticles for biological reduction? J. Colloid Interface Sci. 359, 75–85. https://doi.org/10.1016/j.jcis.2011.03.067

Perdue, E.M., Beck, K.C., Helmut Reuter, J., 1976. Organic complexes of iron and aluminium in natural waters. Nature 260, 418–420. https://doi.org/10.1038/260418a0

Pipko, I.I., S.P. Pugach, I.P. Semiletov, L.G. Anderson, N.E. Shakhova, Ö. Gustafsson, I.A. Repina, E. A. Spivak, A. N. Charkin, A. N. Salyuk, K. P. Shcherbakova, E. V. Panova, and Dudarev O. V.: The dynamics of the carbon dioxide system in the outer shelf and slope of the Eurasian Arctic Ocean //Ocean Sci., 13, 997–1016, 2017, https://doi.org/10.5194/os-13-997-2017

Pugach, S.P., Irina I. Pipko, Natalia E. Shakhova, Evgeny A. Shirshin, Irina V. Perminova, Örjan Gustafsson, Valery G. Bondur, and Semiletov I. P. DOM and its optical characteristics in the Laptev and East Siberian seas: Spatial distribution and inter-annual variability (2003–2011) // Ocean Sci., 14, 87–103, 2018, https://doi.org/10.5194/os-14-87-2018

Poitrasson, F., 2006. On the iron isotope homogeneity level of the continental crust. Chem. Geol. 235, 195–200. https://doi.org/10.1016/j.chemgeo.2006.06.010

Poitrasson, F., Freydier, R., 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. Chem. Geol. 222, 132–147. https://doi.org/10.1016/j.chemgeo.2005.07.005

Poitrasson, F., Cruz Vieira, L., Seyler, P., Márcia dos Santos Pinheiro, G., Santos Mulholland, D., Bonnet, M.P., Martinez, J.M., Alcantara Lima, B., Resende Boaventura, G., Chmeleff, J.Ô., Dantas, E.L., Guyot, J.L., Mancini, L., Martins Pimentel, M., Ventura Santos, R., Sondag, F., Vauchel, P., 2014. Iron isotope composition of the bulk waters and sediments from the Amazon River Basin. Chem. Geol. 377, 1–11. https://doi.org/10.1016/j.chemgeo.2014.03.019

Pokrovsky, O.S., Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). Chem. Geol. 190, 141–179. https://doi.org/10.1016/S0009-2541(02)00115-8

Pokrovsky, O.S., Schott, J., Dupré, B., 2006. Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in Central Siberia. Geochim. Cosmochim. Acta 70, 3239–3260. https://doi.org/10.1016/j.gca.2006.04.008

Pokrovsky, O.S., Viers, J., Shirokova, L.S., Shevchenko, V.P., Filipov, A.S., Dupré, B., 2010. Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina River and its tributary. Chem. Geol. 273, 136–149. https://doi.org/10.1016/j.chemgeo.2010.02.018

Pokrovsky, O.S., Shirokova, L.S., Zabelina, S.A., Vorobieva, T.Ya., Moreva, O.Yu., Klimov, S.I., Chupakov, A.V., Shorina, N.V., Kokryatskaya, N.M., Audry, S., Viers, J., Zoutien, C., Freydier, R., 2012. Size fractionation of trace elements in a seasonally stratified boreal lake: control of organic matter and iron colloids. Aquat. Geochem. 18, 115-139. https://doi.org/10.1007/s10498-011-9154-z

Pokrovsky, O.S., Shirokova, L.S., Viers, J., Gordeev, V. V., Shevchenko, V.P., Chupakov, A. V., Vorobieva, T.Y., Candaudap, F., Causserand, C., Lanzanova, A., Zouiten, C., 2014. Fate of colloids during estuarine mixing in the Arctic. Ocean Sci. 10, 107–125. https://doi.org/10.5194/os-10-107-2014

Poulton, S.W., Raiswell, R., 2005. Chemical and physical characteristics of iron oxides in riverine and glacial meltwater sediments. Chem. Geol. 218, 203–221. https://doi.org/10.1016/j.chemgeo.2005.01.007

Rachold, V., Alabyan, A., Hubberten, H.-W., Korotaev, V.N., Zaitsev, A.A., 1996. Sediment transport to the Laptev Sea–hydrology and geochemistry of the Lena River. Polar Res. 15, 183–196. https://doi.org/10.3402/polar.v15i2.6646

5 Radic, A., Laca, F., Murray, J.W., 2011. Iron isotopes in the seawater of the equatorial Pacif Ocean: New constraints for the oceanic iron cycle. Earth Planet. Sci. Lett. 306, 1-10. https://doi.org/ 10.1016/j.epsl.2011.03.015

Raiswell, R., Canfield, D.E., 2012. The Iron Biogeochemical Cycle Past and Present. Geochemical Perspect. 1, 1–220. https://doi.org/10.7185/geochempersp.1.1

Raymond, P.A., McClelland, J.W., Holmes, R.M., Zhulidov, A. V., Mull, K., Peterson, B.J., Striegl, R.G., Aiken, G.R.,
10 Gurtovaya, T.Y., 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochem. Cycles 21, 1–9. https://doi.org/10.1029/2007GB002934

Rodushkin, I., Nordlund, P., Engström, E., Baxter, D.C., 2005. Improved multi-elemental analyses by inductively coupled plasma-sector field mass spectrometry through methane addition to the plasma. J. Anal. At. Spectrom. 20, 1250–1255. https://doi.org/10.1039/b507886e

15 Rodushkin, I., Ruth, T., 1997. Determination of Trace Metals in Estuarine and Sea-water Reference Materials by High Resolution Inductively Coupled Plasma Mass Spectrometry. J. Anal. At. Spectrom. 12, 1181–1185. https://doi.org/10.1039/a702486j

Poitrasson, F., Viers, J., Martin, F., Braun, J.J., 2008. Limited iron isotope variations in recent lateritic soils from Nsimi, Cameroon: Implications for the global Fe geochemical cycle. Chem. Geol. 253, 54–63.
20 https://doi.org/10.1016/j.chemgeo.2008.04.011

Rodushkin, I., Engström, E., Baxter, D., 2010. Sources of contamination and remedial strategies in the multi-elemental trace analysis laboratory. Anal. Bioanal. Chem. 396, 365-377. DOI 10.1007/s00216-009-3087-z

Rodushkin, I., Pallavicini, N., Engström, E., Sörlin, D., Öhlander, B., Ingri, J., Baxter, D.C., 2016. Assessment of the natural variability of B, Cd, Cu, Fe, Pb, Sr, Tl, and Zn concentrations and isotopic compositions in leaves, needles, and mushrooms
25 using single sample digestion and two-column matrix separation. J. Anal. At. Spectrom. 31, 220-233. https://doi.org/10.1039/C5JA00274E

Rosén, P.-O., Andersson, P.S., Alling, V., Mörth, C.-M., Björk, G., Semiletov, I., Porcelli, D., 2015. Ice export from the Laptev and East Siberian Sea derived from δ ^{18} O values. J. Geophys. Res. Ocean. 120, 5997–6007. https://doi.org/10.1002/2015JC010866

30 Rouxel, O., Sholkovitz, E., Charette, M., Edwards, K.J., 2008. Iron isotope fractionation in subterranean estuaries. Geochim. Cosmochim. Acta 72, 3413–3430. https://doi.org/10.1016/j.gca.2008.05.001

Rouxel A. Bekker, K.J. Edwards, O.J., 2005. Iron isotope constraints on the Archaen and Paleoproterozoic Ocean redox state. Science (80-.). 307, 1088–1091.

Salvadó, J.A., Tesi, T., Andersson, A., Ingri, J., Dudarev, O. V., Semiletov, I.P., Gustafsson, Ö., 2015. Organic carbon remobilized from thawing permafrost is resequestered by reactive iron on the Eurasian Arctic Shelf. Geophys. Res. Lett. 42, 8122–8130. https://doi.org/10.1002/2015GL066058

Salvadó, J.A., Bröder, L., Andersson, A., Semiletov, I.P., Gustafsson, Ö., 2017. Release of black carbon from thawing permafrost estimated by sequestration fluxes in the East Siberian Arctic Shelf recipient. Global Biogeochemical Cycles, 31, 1501–1515. https://doi.org/10.1002/ 2017GB005693

Sánchez-García, L., Alling, V., Pugach, S., Vonk, J., Van Dongen, B., Humborg, C., Dudarev, O., Semiletov, I., Gustafsson, Ö., 2011. Inventories and behavior of particulate organic carbon in the Laptev and East Siberian seas. Global Biogeochem. Cycles 25, 1–13. https://doi.org/10.1029/2010GB003862

Semiletov, I.P., Pipko, I.I., Shakhova, N.E., Dudarev, O. V., Pugach, S.P., Charkin, A.N., Mcroy, C.P., Kosmach, D., Gustafsson, Ö., 2011. Carbon transport by the Lena River from its headwaters to the Arctic Ocean, with emphasis on fluvial input of terrestrial particulate organic carbon vs. carbon transport by coastal erosion. Biogeosciences 8, 2407–2426. https://doi.org/10.5194/bg-8-2407-2011

Severmann, S., Johnson, C.M., Beard, B.L., McManus, J., 2006. The effect of early diagenesis on the Fe isotope compositions of porewaters and authigenic minerals in continental margin sediments. Geochim. Cosmochim. Acta 70, 2006–2022. https://doi.org/10.1016/J.GCA.2006.01.007

Severmann, S., McManus, J., Berelson, W.M., Hammond, D.E., 2010. The continental shelf benthic iron flux and its isotope composition. Geochim. Cosmochim. Acta 74, 3984-4004. https://doi.org/ 10.1016/j.gca.2010.04.022

Sholkovitz, E.R., 1978. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. Earth Planet. Sci. Lett. 41, 77–86. https://doi.org/10.1016/0012-821X(78)90043-2

Sholkovitz, E.R., 1976. Floculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim. Cosmochim. Acta 40, 831–845.

Skulan, J.L., Beard, B.L., Johnson, C.M., 2002. Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(III) and hematite. Geochim. Cosmochim. Acta 66, 2995–3015. https://doi.org/10.1016/S0016-7037(02)00902-X

Slagter, H.A., Reader, H.E., Rijkenberg, M.J.A., Rutgers van der Loeff, M., De Baar, H.J.W.W., Gerringa, L.J.A., Salvadõ, J.A., Tesi, T., Andersson, A., Ingri, J., Dudarev, O. V., Semiletov, I.P., Gustafsson, Ö., Kutscher, L., Mörth, C.M., Porcelli, D., Hirst, C., Maximov, T.C., Petrov, R.E., Andersson, P.S., Klunder, M.B., Bauch, D., Laan, P., De Baar, H.J.W.W., Van Heuven, S., Ober, S., Forsberg, J., Dahlqvist, R., Gelting-Nyström, J., Ingri, J., Pokrovsky, O.S., Shirokova, L.S., Viers, J., Gordeev, V. V., Shevchenko, V.P., Chupakov, A. V., Vorobieva, T.Y., Candaudap, F., Causserand, C., Lanzanova, A., Zouiten, C., 2017. Trace metal speciation in brackish water using diffusive gradients in thin films and ultrafiltration: comparison of techniques. J. Geophys. Res. Biogeosciences 40, 8122–8130. https://doi.org/10.1016/j.marchem.2017.10.005

Slomp, C.P., Mort, H.P., Jilbert, T., Reed, D.C., Gustafsson, B.G, Wolthers, M., 2013. Coupled dynamics of iron and phosphorous in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane. PLoS ONE 8(4): e62386. doi:10.1371/journal.pone.0062386

Staubwasser, M., Schoenberg, R., Von Blanckenburg, F., Krüger, S., Pohl, C., 2013. Isotope fractionation between dissolved and suspended particulate Fe in the oxic and anoxic water column of the Baltic Sea. Biogeosciences 10, 233–245. https://doi.org/10.5194/bg-10-233-2013

Stolpe, B., Guo, L., Shiller, A.M., 2013. Binding and transport of rare earth elements by organic and iron-rich nanocolloids in alaskan rivers, as revealed by field-flow fractionation and ICP-MS. Geochim. Cosmochim. Acta 106, 446–462. https://doi.org/10.1016/j.gca.2012.12.033

Stolpe, B., Hassellöv, M., 2007. Changes in size distribution of fresh water nanoscale colloidal matter and associated elements on mixing with seawater. Geochim. Cosmochim. Acta 71, 3292–3301. https://doi.org/10.1016/j.gca.2007.04.025

Sundman, A., Karlsson, T., Laudon, H., Persson, P., 2014. XAS study of iron speciation in soils and waters from a boreal catchment. Chem. Geol. 364, 93–102. https://doi.org/10.1016/j.chemgeo.2013.11.023

Sundman, A., Karlsson, T., Persson, P., 2013. An experimental protocol for structural characterization of Fe in dilute natural waters. Environ. Sci. Technol. 47, 8557–8564. https://doi.org/10.1021/es304630a

Tagliabue, A., Bopp, L., Dutay, J.-C., Bowie, A.R., Chever, F., Jean-Baptiste, P., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., Jeandel, C., 2010. Hydrothermal contribution to the oceanic dissolved iron inventory. Nature Geoscience 3, 252-256. https://doi.org/10.1038/ngeo818

Tagliabue, A., Bowie, A.R., Boyd, P.W., Buck, K.N., Johnson, K.S., Saito, M.A., 2017. The integral role of iron in ocean biogeochemistry. Nature 543, 51–59. https://doi.org/10.1038/nature21058

Thuróczy, C.-E., Gerringa, L.J.A., Klunder, M., Laan, P., Le Guitton, M., de Baar, H.J.W., 2011. Distinct trends in the speciation of iron between the shallow shelf seas and the deep basins of the Arctic Ocean. J. Geophys. Res. 116, C10009. https://doi.org/10.1029/2010JC006835

Tipping, E., 1981. The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta 45, 191–199. https://doi.org/10.1016/0016-7037(81)90162-9

Vonk, J.E., van Dongen, B.E., Gustafsson, Ö., 2010. Selective preservation of old organic carbon fluvially released from sub-Arctic soils. Geophys. Res. Lett. 37, n/a-n/a. https://doi.org/10.1029/2010GL042909

Vonk, J.E., Sánchez-García, L., van Dongen, B.E., Alling, V., Kosmach, D., Charkin, A., Semiletov, I.P., Dudarev, O.V., Shakhova, N., Roos, P., Eglinton, T.I., Andersson, A., Gustafsson, Ö., 2012. Activation of old carbon by erosion of coastal and subsea permafrost in Arctic Siberia. Nature 489, 137-140. https://doi.org/ 10.1038/nature11392

Wagner, V., 1997. Analysis of a Russian landscape map and landscape classification for use in computer-aided forestry research. IIASA Interim Report IR-97-54. 56.

Walter, H., Breckle, S.-W., 2002. Walter's Vegetation of the earth : the ecological systems of the geo-biosphere. Springer.

Wedepohl, K.H., 1995. INGERSON LECTURE The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217–1232. https://doi.org/10.1016/0016-7037(95)00038-2

Welch, S.A., Beard, B.L., Johnson, C.M., Braterman, P.S., 2003. Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(II) and Fe(III). Geochim. Cosmochim. Acta 67, 4231–4250. https://doi.org/10.1016/S0016-7037(03)00266-7

Wiederhold, J.G., Kraemer, S.M., Teutsch, N., Borer, P.M., Halliday, A.N., Kretzschmar, R., 2006. Iron isotope fractionation during proton-promoted, ligand-controlled, and reductive dissolution of goethite. Environ. Sci. Technol. 40, 3787–3793. https://doi.org/10.1021/es052228y

Windom, H. L., Beck, K., Smith, R., 1971. Transport of trace metals to the Atlantic Ocean by three southeastern rivers. Southeast Geol. 12, 169–181.

Wu, L., Beard, B.L., Roden, E.E., Johnson, C.M., 2011. Stable Iron Isotope Fractionation Between Aqueous Fe(II) and Hydrous Ferric Oxide. Environ. Sci. Technol. 45, 1847–1852. https://doi.org/10.1021/es103171x

Yang, D., Kane, D.L., Hinzman, L.D., Zhang, X., Zhang, T., Ye, H., 2002. Siberian Lena River hydrologic regime and recent change. J. Geophys. Res. Atmos. 107, ACL 14-1-ACL 14-10. https://doi.org/10.1029/2002JD002542

Zhang, F., Zhu, X., Yan, B., Kendall, B., Peng, X., Li, J., Algeo, T.J., Romaniello, S., 2015. Oxygenation of a Cryogenian ocean (Nanhua Basin, South China) revealed by pyrite Fe isotope compositions. Earth Planet. Sci. Lett. 429, 11–19. https://doi.org/10.1016/J.EPSL.2015.07.021

Zhang, T., Barry, R.G., Knowles, K., Heginbottom, J.A., Brown, J., 1999. Statistics and characteristics of permafrost and ground-ice distribution in the Northern Hemisphere [1]. Polar Geogr. 23, 132–154. https://doi.org/10.1080/10889379909377670
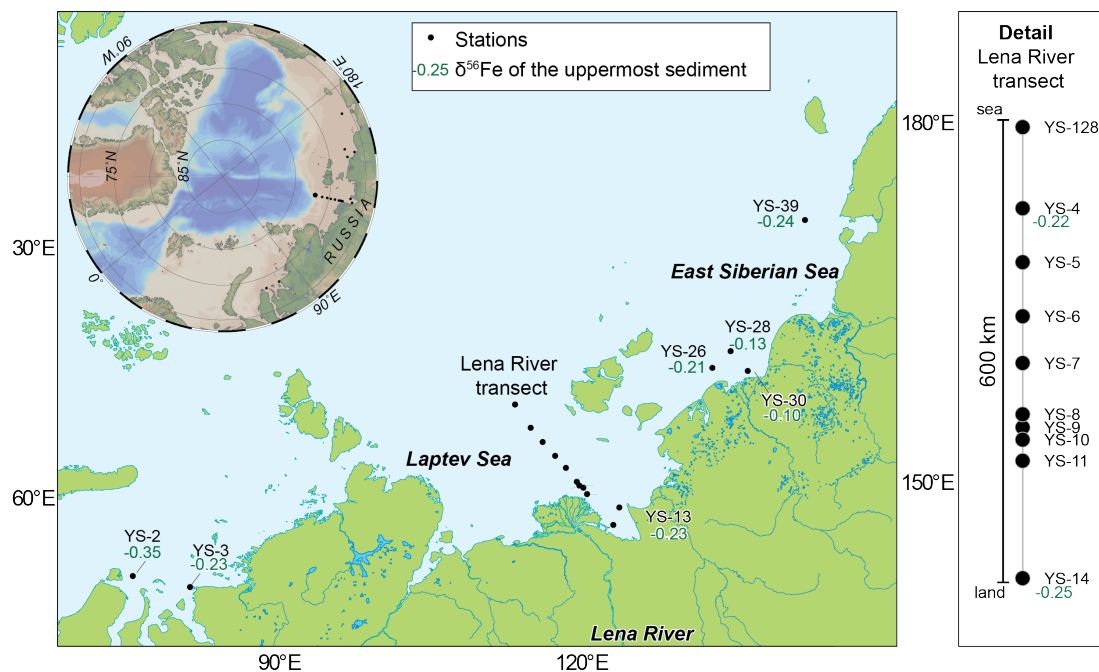
Figure 1: Sampling stations in the Arctic Ocean. Black dots mark the stations in the detailed East Siberian Arctic Shelf map. Along the Lena River-Laptev Sea transect membrane filtration and/or ultrafiltration was carried out. The sampling stations of this study follow the Lena River freshwater plume. The green numbers display δ56Fe values, measured in the uppermost sediment.
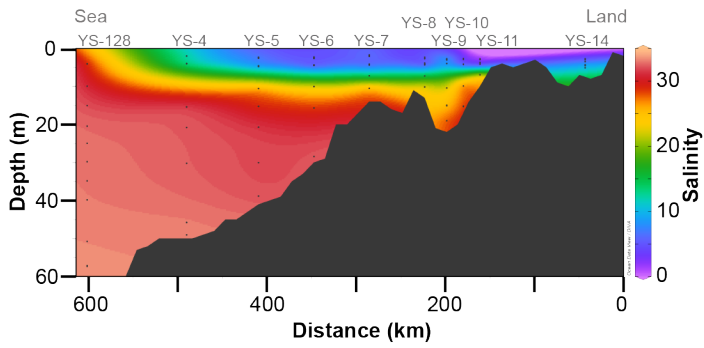
Figure 2: The salinity gradient along the Lena River-Laptev Sea transect. Salinity is based on the Practical Salinity Scale PSS-78. The freshwater builds an almost 10 m thick surface layer in the Laptev Sea, and the plume itself extends over an area of about 50 times 600 km. The plume is divided into an inner and outer plume between station YS-8 and YS-11 by a sharp increase of salinity.
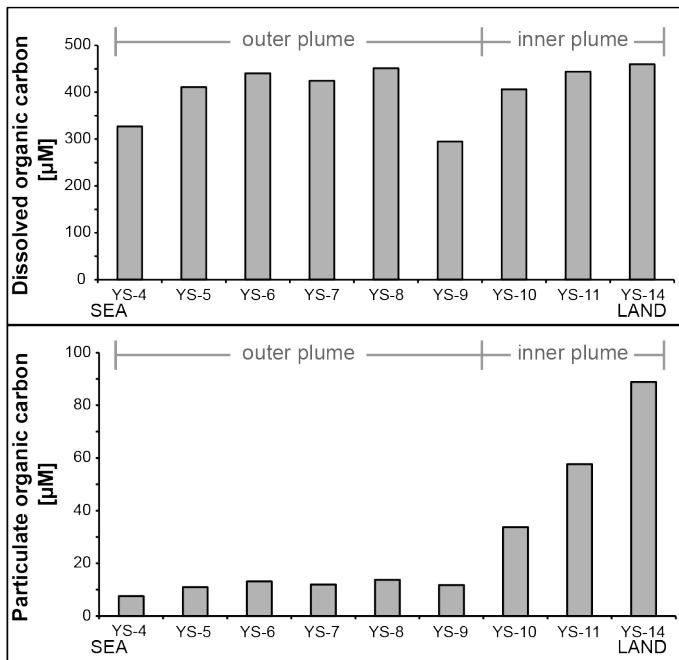
Figure 3: Dissolved (< 0.70 µm) and particulate (> 0.70 µm) organic carbon concentrations along the Lena River-Laptev Sea transect. Close to the Lena River mouth POC constitutes about 18% of the TOC input, while at the outermost station it is only 2% of the TOC.
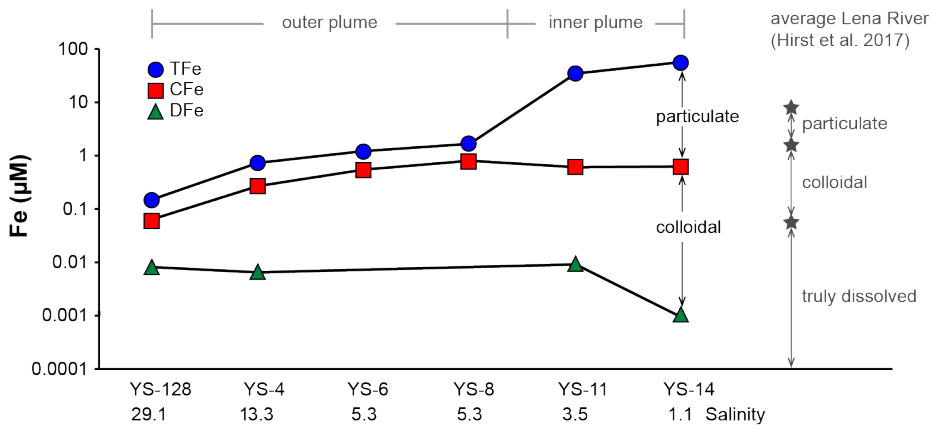
Figure 4: Total, colloidal and truly dissolved Fe concentrations along the Lena River freshwater plume. Concentrations of PFe and CFe decreased along the salinity gradient, while the concentrations of DFe is almost constant. Note the logarithmic scale and the sharp decrease of PFe between the inner and the outer plume. The reference for the Lena River is an average of all analysed samples (PFe n=3; CFe and DFe n=5) by Hirst et al. 2017.
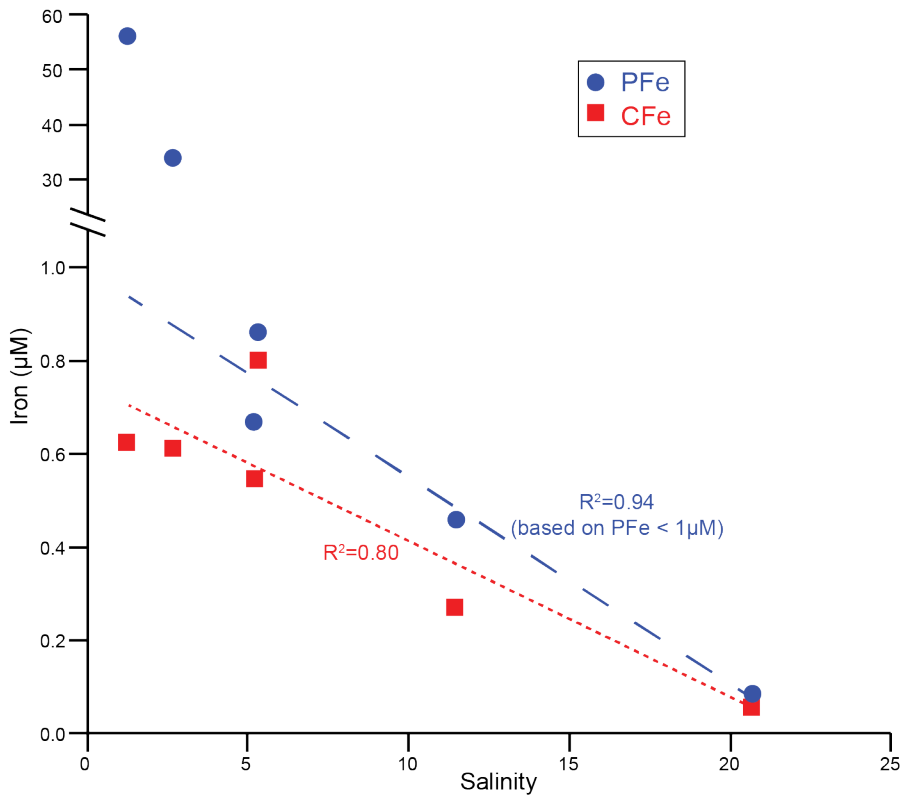
Figure 5: The colloidal and particulate Fe concentrations plotted versus salinity. Salinity is based on the Practical Salinity Scale PSS-78. Note the y-axis break due to the high range of PFe in the inner plume. The linear correlation between PFe and salinity is based on the data points below 1μM PFe. In the low salinity environment, the PFe is much higher compared to the CFe, whereas at salinities above 5 the differences are smaller.
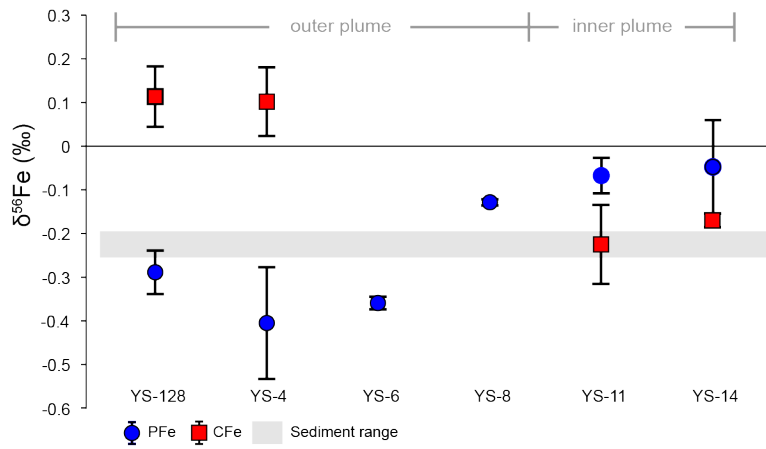
Figure 6: Iron isotope values along the Lena River freshwater plume and the uppermost sediment of the East Siberian Arctic Shelf (ESAS). The error bars represent ±2 σ, in some cases the symbol is larger than the error. The δ⁵⁶Fe values of PFe are negative at all stations, values close to zero close to the coast and more negative towards the open sea. The δ⁵⁶Fe values of the CFe are negative in the inner plume and positive in the outer plume. The δ⁵⁶Fe of the sediment samples were around -0.2 ‰, displaying the overall composition of the entire ESAS area.