Biogeosciences Discuss., 6, 6491–6537, 2009
www.biogeosciences-discuss.net/6/6491/2009/

Biogeosciences
Discussions

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Fractionation of iron species and iron isotopes in the Baltic Sea euphotic zone

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Received: 10 June 2009 – Accepted: 23 June 2009 – Published: 2 July 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Measurements of the physiochemical speciation of Fe in the euphotic zone were performed at three different locations, over a well defined salinity gradient, during spring and summer in the Baltic Sea. The average of total Fe changed from 114 nM in the Bothnian Sea, 44 nM at Landsort Deep and 15 nM at Gotland Deep. Particulate Fe (PFe) was the dominating phase at all stations and on average accounted for 75–85% of the total Fe pool. At all three locations, a decrease in total Fe of 80–90% from initial measurements compared to the summer was found. A strong positive correlation between PFe and chl-*a* was observed. Hence, primary production strongly regulates cycling of suspended Fe. However, this relation is not dominated by active uptake of Fe in phytoplankton; instead this reflects cycling of phosphorus, growth of diatoms, and removal of PFe during phytoplankton sedimentation. The average colloidal iron fraction, CFe, showed decreasing concentrations along the salinity gradient; Bothnian Sea 15 nM; Landsort Deep 1 nM and Gotland Deep 0.5 nM. Field Flow Fractionation data indicate that the main colloidal carrier phase for Fe in the Baltic Sea is a carbon-rich fulvic acid associated compound, likely of riverine origin. The Fe isotope composition (δ^{56}Fe) of the PFe showed constant positive values in the Bothnian Sea surface waters (+0.08 to +0.20‰). Enrichment of heavy Fe in the Bothnian Sea PFe is most likely associated to input of aggregated land derived Fe-oxyhydroxides and a rapid overturn of Fe(II). At the Landsort deep, the fractionation of PFe changed between −0.08‰ to +0.28‰. The negative values, in early spring, probably indicate exchange over the oxic-anoxic boundary at ~80 m depth.

1 Introduction

Iron, the fourth most abundant element of the Earth's crust, has a dynamic and fundamental role in all earth surface systems. It is essential as micronutrient to all living organisms, as it is required for photosynthesis and respiratory electron transport, for nitrate, nitrite and sulphate reduction and for nitrogen fixation (Whitfield, 2001). The role of iron as a regulating element for phytoplankton in large regions of the world ocean, also referred to as the High Nutrient, Low Chlorophyll regions, is now well established (de Baar et al., 2005; Boyd et al., 2007). In costal and estuarine regions Fe depletion is not considered at first hand, but due to the extremely low solubility and the high degree of organic complexation (Rue and Bruland, 1995), the actual bioavailable amount of iron may be very low. Findings in coastal California suggest that Fe might be a limiting factor also in near shore waters (Hutchins and Bruland, 1998; Bruland et al., 2001).

Iron is also an important determinant of trace metal speciation in soils and natural waters due to the highly reactive properties of hydrous ferric oxides (Dzombak and Morel, 1990), which affect the bioavailability of other elements. Control on adsorption and competition of ligands to other trace elements also gives iron an essential role in these environments (Tipping et al., 2002; Warren and Haack, 2001). Colloidal size distributions of iron and other elements determined by Field Flow Fractionation coupled to Inductively Coupled Plasma Mass Spectrometry (FFF-ICPMS) in a number of studies, ranging from river water (Dahlqvist et al., 2007; Lyvén et al., 2003), estuarine mixing (Stolpe and Hassellöv, 2007), and surface seawater from the brackish Bothnian Sea (salinity ~4.7) through the Baltic Proper (this study) and the Skagerrak coast (Salinity 5–>20) at the North Sea boundary (Fig. 1) (Stolpe and Hassellöv, 2009). In river water, colloid-associated iron is mainly distributed between 0.5–4 nm macromolecules of humic-type fluorescent organic matter (presumed fulvic acid) and 3–50 nm iron rich colloids (presumed Fe(III)-hydroxide/oxyhydroxide) (Hassellöv and von der Kammer, 2008). The occurrence and relative importance of the iron oxyhydroxide colloids in relation to iron complexed by fulvic acid depend on catchment geology and water chemistry (e.g. pH, dissolved organic carbon (DOC) concentration, suspended particulate matter (SPM), and total iron concentration). The physicochemical fractionation of iron between iron oxyhydroxide and fulvic acid showed drastic seasonal variations in the Kalix river, a typical boreal river that is one of the major contributors of fresh water to the Baltic Sea (Dahlqvist et al., 2007). During the winter, when the top soil is frozen and groundwater is the major source of water in the river, the colloidal iron is dominated by iron oxyhydroxide (Fig. 1a). During the snow melt and following spring flood, colloid-associated iron is mainly complexed to fulvic acid that is carried from mires and eroded from the forest top soils by the snowmelt water (Dahlqvist et al., 2007). It has been suggested (Ingri et al., 2006) that iron isotopes could be used to roughly identify these two phases.

The general conception of Fe behaviour in estuarine systems, is that Fe is rapidly removed by aggregation at higher salinities (e.g. Dai and Martin, 1995; Boyle et al., 1977; Guieu et al., 1996) but exceptions to this have also been observed (Shiller and Boyle, 1991). In estuarine mixing experiments, it was shown that the iron oxyhydroxide colloids from river water aggregate into much larger particles in contact with seawater, while the fulvic acid phase was virtually unaffected (Stolpe and Hassellöv, 2007), similar to the results from previous mixing experiments (Sholkovitz, 1976). This will lead to an enrichment of heavy Fe in the aggregated fraction (Bergquist and Boyle, 2006). The aggregation of iron oxyhydroxide colloids can be explained by compression of the electrical double layer due to high ionic strength and by charge neutralization due to surface complexation of Ca^{2+} and Mg^{2+} to the colloids (Hunter, 1983). The fact that fulvic acid macromolecules are less affected by the increase in salinity is likely to be a consequence of their higher charge densities. Fulvic acid from rivers can therefore be expected to be transported through estuaries and out in the sea. Recent findings from Laglera and van den Berg (2009), suggest that it is possible that terrestrial humic matter may reach the open ocean and account for a significant proportion of the Fe binding ligands.

The Baltic Sea is a semi-enclosed shelf sea and the largest brackish water body in the world. The environment and chemistry of this large estuary is complex due to strong influences from land combined with the occasional Atlantic water salinity pulses through the Danish straights. The Baltic Sea has been given growing attention due to changes in the ecosystem (e.g. Larsson et al., 1985; Bianchi et al., 2000) and recent satellite monitoring studies have shown abundances of intense, yet varying, cyanobacterial blooms (Kahru et al., 2007). Nitrogen fixation by cyanobacteria contributes to 20–40% of the nitrogen supply to the Baltic Sea (Larsson et al., 2001). Nitrogen fixation is favoured by low N:P ratios and cyanobacterial blooms generally develop during the summer after eukaryotic phytoplankton has depleted dissolved nitrogen sources. The recent increase in cyanobacteria occurrence and density has been attributed to eutrophication (Finni et al., 2001). Alternatively, up-welled phosphorus from deep waters may stimulate growth of cyanobacteria (Kononen et al., 1996; Stal et al., 2003). Iron as a potentially limiting nutrient for cyanobacterial bloom development and nitrogen fixation in the Baltic Sea has been suggested (Stal et al., 1999; Stolte et al., 2006). Nitrogen-fixing cyanobacteria have a Fe demand that is 4–6 times higher than other phytoplanktonn (Kustka et al., 2002; Sanudo-Wilhelmy et al., 2001), hence the development of cyanobacterial blooms may to some degree be regulated by iron bioavailability.

Ingri et al. (2004) showed that the LMW fraction (<5 kDa) of several trace metals was depleted during a spring bloom in a coastal bay of the Baltic Sea. The levels of Fe were depleted below detection limit in the <5 kDa fraction (Ingri, unpublished data). That study suggested a very slow exchange between the particulate, colloidal and the truly dissolved fraction. Very limited data on size-fractionated iron concentrations and its temporal variation in the Baltic Sea can be found in the literature.

Our objective in this study was to investigate the physicochemical speciation of Fe over several months in the euphotic zone at three different locations in the Baltic Sea, using a wide set of methods. We investigate the processes affecting Fe speciation during transport from lower to higher salinity. In order to assess the transport and contribution of Fe from continental sources to the world ocean, one key question is how much Fe will be left in the LMW fraction. As pointed out by for instance Boyd et al. (2007), not only low Fe open ocean systems are of interest for the understanding of Fe biogeochemistry, but also knowledge about Fe cycling in high-Fe regimes. An improved understanding of estuarine processes controlling Fe speciation in the Baltic Sea is also of general Fe in the Baltic Sea would also be of general use for estimating fluxes of Fe to coastal waters.

2 Materials and methods

2.1 Sampling

Samples were taken at three locations in the Baltic Sea; the Bothnian Sea (station C3), Landsort Deep (BY31) and Gotland Deep (BY15) which all are shown on the map (Fig. 2).

Water samples for subsequent filtration were taken at 5 m depth (approximately the middle of the upper mixed layer) from M/S Fyrbyggaren during March to October 2004 at the Landsort Deep station. Samples in the Bothnian Sea were taken from M/S KBV005 from April to September 2006 and at the BY15 station during 2007, samples were taken from M/S Fyrbyggaren, from May to August, also at 5m depth. To avoid iron contamination from the hull, a piece of tubing was attached to a flagpole that was pointing out vertically 10 m from the bow of the ship. Having this set-up during the ship slow steaming, the opening of the tubing was at least 10 m from the hull. Water was pumped through the tubing by a peristaltic pump (Masterflex, Colepalmer) into 25 L poly-ethylene (PE) containers. Prior to use, all sampling tubing and containers used for metal analysis were acid-cleaned in 5% HCl with subsequent wash in purified water (Millipore, $>18.2\,\mathrm{M\Omega}$). Water samples were taken where taken from 0.5, 5, 10 and 40 m depth using a Niskin-type water sampler from General Oceanics. These were afterwards analyzed for elemental composition without filtration. Sediment traps were deployed at 30 m depth at the C3 and BY31 station. The design and set-up was slightly modified from Larsson et al. (1986).

2.2 Filtration

Immediately after collecting water from the flagpole system, membrane filtration (0.22 μm pore size, 142 mm diameter, Millipore mixed cellulose esters) of the water sample was carried out. The first filter was completely clogged; the filtrate volume was measured and then discarded. New filters were then used to collect the particulate fraction from seawater, through which only half the clogging volume was pumped. The reason for this was to reduce the removal of colloids that is caused by clogging of filters, i.e. colloids will be discriminated in the filtrate when the filter gets clogged (Morrison and Benoit, 2001). Filtrate from several filtrations was collected in 25 L polyethylene containers from which sub samples for analysis were taken. All tubing and containers were acid-cleaned in 5% HCl with subsequent wash in MilliQ water (Millipore, >18.2 MΩ) prior and after sampling. Prior to use, filters were washed in 5% acetic acid, as described by Ödman et al. (1999). Cross-flow ultrafiltration started within 5 to 24 h after the samples were collected and was performed on water samples taken at five meters depth. Prior to ultrafiltration the water samples were filtered through a 0.22 μm nitrocellulose filter membrane. Ultrafiltration was carried out on a Millipore Prep/Scale system (Prep/Scale Spiral Wound TFF-6 module) with 1 kDa cut-off size. Approximately 12 l of sample water were used for ultrafiltration. Before the ultrafiltration procedure began, sample water was circulated through the filter to precondition the system. Half a litre of permeate was collected and the system was emptied where upon the actual filtration begun. The concentration factor of the retentate was above 10 to achieve good recovery, as recommended by Larsson et al. (2002). The cross flow ratio (retentate flow/permeate flow) was between 60 and 80. After every ultrafiltration the system was washed with base and acid solutions and Milli-Q water, following a procedure described by Larsson et al. (2002), with the slight modification that both the solutions had a concentration of 0.01 M.

2.3 Diffusive gradients in thin films

DGT samplers with Chelex 100 binding gels were manufactured during 2004, but thereafter purchased from DGT Research Inc (Lancaster, UK). The thickness of the diffusive gels were specified by the manufacturer to be 0.8 mm. All DGT sampling was carried out in situ, at several depths and DGT samplers were deployed in duplicates. The exposure time for DGT samplers varied from location to location between 14 days and up to two months. A temperature logger (StowAway TidbiT, Onset Computer Corporation) was attached along with the DGT units, logging the temperature every fifth hour. The mean temperature of the deployment period was used to recalculate the diffusion coefficient in the gel. DGT concentrations ($[Fe]_{DGT}$) were calculated assuming a 0.23 mm diffusive boundary layer (DBL), which is reasonable to expect in moderate to well mixed waters (Warnken et al., 2006). The accumulation area was assumed to be equal to 3.8 cm^2 (Warnken et al., 2006). Diffusion coefficients in the gels were taken from DGT Research Inc (www.DGTresearch.com).

2.4 Elemental analyses

Analytical work for trace metal analysis of water and DGT samples was performed in class 100 clean room conditions. After sampling, DGT devices were disassembled in the laboratory and the gels were eluted in 5 ml of 5 M HNO_3 (suprapur). Concentrations of elements in DGT eluents, unfiltered samples, and 0.22 μm and 1 kDa filtrate were measured with an Inductively Coupled Plasma SectorField Mass Spectrometer (ICP-SFMS, Element, ThermoFinnigan, Bremen, Germany) at ALS Scandinavia (Luleå, Sweden). For details about the instrument operation, see Rodushkin and Ruth (1997). Prior to analysis, water samples were diluted 4-fold with 0.16 M HNO_3 (suprapur) in MilliQ water. Matrix induced signal variations and signal instabilities were corrected for using internal standards (25 ppb In and Tl) added to samples, blanks, and elemental standards. Quality control was accomplished by regular analyses of in-house control samples. For six some samples close to or below detection limit of ICP-SFMS, Chemiluminescent Flow Injection Analysis (CL-FIA) with a luminol (5-amino-2,3-dihydro-1,4-phthalazine-dione) reagent was used to determining total Fe in samples. For details see the Bowie et al. (1998). Overlapping measurements from CL-FIA and ICP-SFMS, showed less than 10% difference.

The 0.22 μm nitrocellulose filters and sediment trap material were analyzed by ALS Scandinavia AB in Luleå and prepared according to the procedure described by Ödman et al. (1999). Dried filters with particulate material were wet-ashed with concentrated nitric acid in a platinum crucible at 50°C and dry-ashed at 550°C. The residue was weighted, average ashed weight subtracted, giving the ash weight of suspended material. The sample was subsequently digested with an equal amount of dried lithium-metaborate at 1045°C for 45 min, giving a bead which was dissolved in 5% HNO_3. Analysis was then performed by atomic emission spectroscopy with inductively coupled plasma as excitation source (ICP-AES) for major elements.

Nitrogen and phosphorous were simultaneously oxidized using a modification of the method of Koroleff (1983). Standard flow injection analysis (QuickChem® 8000 method 31-115-01-3-A, 31-107-06-1-A, Lachat Instruments) was used to measure dissolved inorganic phosphorous (DIP) and dissolved inorganic nitrogen (DIN; ($NH_4^+ + NO_2^- + NO_3^-$)). For chlorophyll-*a* (chl-*a*) determinations, 2 L of sea water were filtered on 47 mm Whatman GF/F filters, which were stored frozen and extracted by acetone before spectrophotometric measurements at 664 nmol L-1 (SS 02 81 46). At BY31 and BY15, this was done for samples from discrete depths, at the C3 station an in integrated sample of the upper 10 m were taken. Total organic carbon (TOC) content was analysed at Umeå Marine Science Centre (Norrbyn, Sweden) using high-temperature catalytic oxidation instrument (Shimadzu TOC 5000). The analytical protocols for dissolved organic carbon (DOC) samples have been described in detail by Gustafsson et al. (2001). The 10 mL DOC samples were acidified with 200 μL of 1.2 M HCl to remove inorganic carbon and were quantified with a high-temperature catalytic oxidation instrument (Shimadzu TOC 5000).

2.5 FlFFF

Flow field-flow fractionation (FlFFF) is a chromatography-like elution technique for the characterization of colloids, where the retention of colloids depends on their ability to diffuse against a flow of liquid in an open channel. The diffusion coefficient, and thereby the hydrodynamic diameter, can be calculated from the retention time (Giddings, 1993). The on-line coupling of FlFFF to UV-absorbance and fluorescence detectors and to inductively coupled plasma mass spectrometry (for simplicity hereafter abbreviated as FFF-ICPMS) has been described previously (Hassellöv et al., 1999; Stolpe et al., 2005). By this combination of techniques, the continuous colloidal size distribution of chromophores, fluorophores and different elements can be determined, information which is valuable for the identification of the different types of colloids present in a sample, and for investigating their importance as carriers of iron and other elements in aquatic systems.

2.6 Iron isotopic measurements

Suspended matter from clogged 0.22 μm nitrocellulose filters collected at the C3 and BY31 stations (5 m depth) and sediment trap material from the BY31 station were analysed with regard to Fe isotopic composition. Fe-isotope ratio measurements were performed with a double focusing high resolution MC-ICPMS instrument (Neptune, Thermo Finnigan, Germany) with detailed procedures described in Ingri et al. (2006). Results are presented using the δ-notation, defined as

$$\delta^{56}\mathrm{Fe} = \left[\left({}^{56}\mathrm{Fe}/{}^{54}\mathrm{Fe}\right)_{\mathrm{sample}} / \left({}^{56}\mathrm{Fe}/{}^{54}\mathrm{Fe}\right)_{\mathrm{standard}} - 1\right] \times 1000$$

where the (^{56}Fe/^{54}Fe) standard is the ratio for IRMM-014, corrected for instrumental mass discrimination using Ni. Similar notations were also used for the ^{57}Fe/^{54}Fe and ^{57}Fe/^{56}Fe ratios.

2.7 Optical measurements

To measure the concentration of humic substances (HS), a Jasco FP-777 spectrophotometer with a quartz-cell was used. Intensity was read at an emission at 350 nm from excitation at 450 nm and was then converted to HS concentration by comparison with a standard curve of Quinine Sulphate. The samples were collected in clean amber glass bottles and refrigerated before reading. The flourometer cell was rinsed with deionised water and sample before every reading. The molar extinction coefficient at 280 nm (ε280) was derived from normalizing the absorbance at 280 nm (A280) to the TOC content of the sample. This parameter represents the $\pi-\pi*$ transition of aromatic carbon atoms of the organic matter (Gauthier et al., 1987; Chin et al., 1994). Absorbance measurements (2 nm bandwidth) were carried out on a UV/VIS absorption spectrophotometer having two parallel light paths. Both sample and distilled water reference were probed in 1-cm quartz cuvettes.

3 Results and Discussion

An overview of Fe concentrations in different fractions, and average salinities at the three stations is presented in Table 1. In Table 2 the percentage of different fractions (as % of TFe) is given. We discuss the results with particular respect to the aspects of the high Fe concentrations measured in the spring, the role of riverine input versus upwelling as a source of Fe, the observed strong correlation of PFe and chlorophyll, and the size fractionation and isotopic fractionation during Fe transport through the Baltic Sea.

Generally, the sources of the initial high Fe concentrations at C3 and BY31 (Figs. 4 and 8 respectively) could be primarily terrestrial input, lateral transport of water from other basins and vertical mixing. Atmospheric input or diffusive flux of Fe is unlikely, especially at the BY31 station where changes take place within two weeks. In detail, the processes affecting Fe transport and cycling at the separate stations are discussed below.

3.1 Bothnian Sea

3.1.1 Biogeochemical framework

At the C3 station, a weak stratification was developed in May, which became stronger towards the end of sampling period (Fig. 3). A very weak permanent halocline was observed at about 50–70 m depth during the course of the study (Fig. 3), which is quite typical for the Bothnian Sea (Kullenberg, 1981). A minimum on salinity was observed on 23 May, where the water column down to 12 m was below 4.4. A chl-*a* maximum of 6.7 μg/L (integrated value for the upper 10 m) was measured in April, and after that date, the concentration was gradually deceasing down to 1.3 μg/L in late June. Then the amount of chl-*a* was quite stable above 1 μg/L until September. TOC was rather stable around 350 μM, where the colloidal fraction comprised about 130 μM. Both ε280 and HS showed a small increase from April to May and were then continuously decreasing until September.

3.1.2 Iron speciation

During the whole measured period, the iron in surface waters of the C3 station was dominated by the particulate fraction; DFe was only 9% of TFe initially and was then increasing its proportion (Table 2). TFe decreased 89% from April to mid August (309 nM to a minimum of 34 nM), followed by a slight increase in early September (Fig. 4a).

When minimum salinity was observed on 23 May (4.3), the highest levels of unfiltered Fe and P were measured, and at the same time a minima of major elements like Na, Ca and Mg were observed (Fig. 5) After this date, salinity was continuously increasing along with the major elements, whilst Fe, Al, P and Mn decreased. This is reflected in a clear negative correlation between salinity and TFe (R^2=0.83), if the value from April is excluded (Fig. 4b).

A clear positive correlation was also observed between unfiltered Fe, ε280 and humic substances. Both the total and the dissolved Fe showed this correlation. PFe had a clear correlation to chl-*a* during the whole sampling period (r^2=0.98, Fig. 4c). The filtered fractions also showed a clear decline (Fig. 4d), where <0.22 μm (DFe) decreased 69% (28 nM to 8.7 nM) and <1 kDa (SFe) 43% from April to August (10 nM to 3.2 nM). The colloidal bound Fe (CFe) was clearly decreasing during the sampled period, which is indicated by the differences between SFe and DFe fractions (Fig. 4d). The amount of CFe was higher than the BY31 and BY15 stations, and also the proportion CFe of

TFe (Table 2). This is possibly connected to higher amount of colloidal C from riverine input, FFF-ICPMS-data (Fig. 1b, discussed further down in the text) are also indicating the presence of a much larger fraction of carbon-bound colloidal Fe organic bound colloidal fraction, compared to the two stations in the open Baltic Proper. The decline for the DFe and SFe fractions are clearly not as pronounced as the PFe fraction, but they follow a similar pattern. Removal of these two fractions is likely to follow that same process as the removal of suspended Fe, see discussion below.

The turnover of water of the Bothnian Sea is mainly governed by the inflow of surface water from the Baltic Proper (Marmefelt and Omstedt, 1993), and not by thermohaline circulation.

Since the most of the bottom water is renewed annually in the Bothnian Sea (Kullenberg, 1981), a considerable amount of Fe and associated elements are likely to be supplied from this deep water. But because of the coincidental peak in total Fe concentration and dip in salinity during this study (Fig. 4b), it is likely that, at least partly, riverine input is responsible for the elevated concentrations in May. Spring flood from Swedish rivers at the same latitude peaks at this time Bergström and Carlsson (1994). The positive correlation between terrestrial biomarkers such as HS and ε280 to unfiltered iron, also suggests terrestrial influence. The negative correlation between TFe and salinity, further supports that conditions at the C3 station are governed by mainly a two component mixing of a freshwater compound (that has a high concentration of nutrients and Fe), and a seawater compound, that is diluting the concentration of Fe.

Since the particulate Fe phase is dominating the system at this station, it is motivated to further evaluate the changes in this fraction during the studied period. A strong correlation of chl-*a* and PFe was observed (Fig. 4c). This correlation is not driven by active phytoplankton Fe uptake, because stoichiometrically the Fe concentrations are much too high. Phosphorous is the limiting nutrient for the bloom, and is supplied to the surface waters via similar pathways as iron. It is especially in the suspended phase that phosphorus and iron have linked hydrogeochemical pathways; P is transported adsorbed on or co-precipitated with Fe oxyhydroxides in river systems (Fox, 1989;

Pokrovsky and Schott, 2002). The removal of dissolved P and Fe during estuarine aggregation has in previous studies shown to be coincidental; formed Fe oxyhydroxides incorporate phosphate which drastically diminish the dissolved P concentration through a salinity gradient (Gunnars et al., 2002). In this study, both suspended P and PO_4^{2-} are correlated to PFe (r^2=0.90 and 0.82 respectively). Probably, Fe-oxyhydroxides can act as P scavengers, and remove P from the euphotic zone. High levels of chlorophyll-*a* in April indicate growth of phytoplankton. Phytoplankton cells can serve as surfaces to which iron in different forms may adsorb. This process may be related to the occurrence of sticky exudates from the plankton (transparent exopolymer particles, TEP) (Passow, 2002), that scavenges suspended and colloidal Fe in the water. We suggest that suspended Fe is supplied to the C3 station mainly by a terrestrial component, which also is enriched in P. As the bloom declines, P is consumed from the water, and at the same time Fe is attached to cell surfaces and lost form the surface water. Sediment trap data (not shown) indicate a correlation between C, N, and P removal. While the amount of PFe at 5 m depth is decreasing during the summer, the amount of sedimenting Fe is fairly constant from May to August (~50 μmoles/day/m^2). There has to be an additional source of PFe, since the sum of the loss in the upper 30 m does not budget the amount collected in the sediment traps. Taken together with the fact that sediment traps usually are underestimating the sedimenting material (Gustafsson et al., 2004), data indicate that there is a continuous, yet diminishing supply of PFe during the whole measured period.

3.1.3 Isotopic signatures

Isotope signatures in PFe were throughout the measured period positive, i.e. enriched in heavy isotopes relative the IRMM-014 standard (Fig. 6a). The lowest δ^{56}Fe was measured from a sample collected on 23 May (0.07‰) and the highest (0.20‰) was measured on 30 June. The Fe/Ti (w/w) ratio was above 23 during the whole measured period, which may be compared to the average crust ratio of 10.2 (Rudnick et al., 2003). If the suspended Ti represents lithogenic, detrital particles, then the excess Fe/Ti (above the crustal average) represents non-detrital particles. The most common normalization in these cases is to Al, and although the relationship between Al and Ti appears to be almost linear for all filters collected, there are indications from our data that Al does not at all times have a conservative behaviour. Al may be associated with the humic fraction (Ingri et al., 2006; Warren and Haack, 2001), and since this fraction may also be a carrier for Fe, Al can neither be regarded to always behave conservative nor to only represent the lithogenic phase. Throughout this paper, Fe/Ti ratios are used. The isotopic composition of the suspended matter shows a linear positive correlation with the Fe/Ti ratio (Fig. 6b). Findings from Ingri et al. (2006) suggest that the isotopic signature of riverine Fe-oxyhydroxides is heavy (positive δ^{56}Fe), while carbon-rich colloidal material with high Fe content have a negative δ^{56}Fe. Following this model, the Bothnian Sea suspended phase is dominated by oxyhydroxides. However, the intercept of the regression line on the Fe/Ti axis shows a value of 17, clearly above average crust. Hence, the iron isotope signature is also influenced by a phase with a negative value. If the regression line is extrapolated to the average crust Fe/Ti value, δ^{56}Fe is approximately −0.07‰, a value close to what has been measured in the Kalix river during spring flood (Ingri et al., 2006). These low δ^{56}Fe were attributed to Fe-C colloids. Stolpe and Hassellöv (2007) suggested that this phase mainly consists of fulvic acids due to its low tendency to form aggregates at increasing salinities. River water-seawater mixing experiments by Bergquist and Boyle (2006) showed that aggregated Fe was enriched in heavy isotopes. Hence, aggregation and sedimentation of the oxyhydroxide fraction during estuarine mixing should remove heavy isotopes from surface suspended matter, resulting in a more negative isotopic signature in the remaining suspended phase. The general pattern of positive δ^{56}Fe at the C3 station is probably caused by strong terrestrial influences.

The filters analyzed in this study were clogged to collect some of the colloidal Fe, which is believed to consist of both the Fe-carbon rich phase and the Fe-oxyhydroxide phase (Lyvén et al., 2003). Probably, the removal of Fe-oxyhydroxides is still not very high at these salinities (4.7) and this phase is dominating to such an extent that it masks the isotopic signature from the Fe-C colloids. Stolpe and Hassellöv (Gustafsson et al., 2000) concluded that most of the removal of Fe colloids takes place at salinities below 2.5‰. In our study, the case might be that Fe-oxyhydroxides are aggregated, but still present as suspended matter due to a relatively slow sedimentation. Findings in the Kalix river estuary (Gustafsson et al., 2000) indicate that the low presence of "sinkers", i.e. detrital particles, inhibited sedimentation even though aggregation took place trough the salinity gradient. The situation could be similar for the Bothnian Sea station. Except for the supply of riverine Fe-oxyhydroxides, in-situ redox cycling may cause enrichment of ^{56}Fe in Bothnian Sea surface waters. In the Baltic Proper a high persistent standing stock of Fe(II) recently was measured in the summer (Breitbarth et al., 2009). Studies have shown that non-biogenic oxidation of Fe(II) generates Fe-oxyhydroxides enriched in ^{56}Fe (Bullen et al., 2001). If the levels of Fe(II) in the Bothnian Sea are similar to the standing stock of 0.25–0.5 nM in the Baltic Proper (Breitbarth et al., 2009), and the half-life is in the same order of magnitude (minutes to seconds), then the redox cycle of Fe in the euphotic zone may affect the isotopic composition of the suspended matter as much as the riverine input. Probably a large portion of the oxidized Fe is recycled back to Fe(II), but if only 10% take part in the formation of PFe, this process will contribute to the fractionation of several tenths of nanomolar per day.

3.2 Landsort Deep

3.2.1 Biogeochemical framework

During the whole sampling period the water column down to about 60 m depth was oxygenated close to saturation, which also was the level of the permanent halocline (Fig. 7). Generally, the Baltic Sea has a relatively constant halocline at about 70 m depth (Kullenberg, 1981). Salinity decreased by ~0.8 units from March to mid August in the integrated upper 10 m of water, but was much more stable at 40 m depth (Fig. 7). From rather well mixed water above the halocline in March, conditions changed to a more stratified situation in June to September, where the upper mixed layer was about 10–20 m (Fig. 7). Chl-*a* demonstrated a peak in the upper 10 m on 24 March, reflecting the spring bloom (Fig. 7). This peak was followed by a peak during mid-April and rising and falling values from mid-June to September, indicating the presence of cyanobacteria.

Phosphate had similar concentrations from the surface down to 40 m in early March, but then decreased drastically at 0–10 m during spring and summer (Fig. 7). Levels at 40 m remained high, around 25 g/L, throughout the measured period. The initial concentrations were elevated down to 40 m due to mixing with high phosphate containing underlying water masses during wintertime. In this part of the Baltic Sea, active uptake by phytoplankton has been shown to be the mechanism that decreases the amount of PO_4^{2-} during March and April. This pattern has been observed to be consistent interannually at the Landsort Deep, even though the absolute concentrations of PO_4^{2-} differ (Larsson et al., 2001). TOC did not show great variations during the season. Concentrations were between 310 and 350 μM, with a trend of somewhat lower concentrations during June–August. Colloidal organic carbon was rather stable, with an average of 90 μM.

3.2.2 Iron speciation

High initial concentrations of Fe were observed (Fig. 8a), a similar pattern as for the Bothnian Sea. Around 80% of TFe was removed after the spring bloom. A clear correlation between chl-*a* and PFe was observed for the first 5 sampling occasions (69% and 64% respectively, Fig. 8c). The decrease for the DFe and SFe fraction from 10 March to 4 May was almost similar 69% and 64% respectively (Fig. 8c). The decrease in DFe was similar to the Bothnian Sea. Patterns in the SFe fraction though indicate a clear difference in colloidal speciation. Even though the DFe concentration at the BY31 station was less than half the one in the Bothnian Sea, the SFe concentrations were almost similar. Data on SFe are partly missing from the summer, but the data we have suggest that the CFe pool is almost depleted from May on. There was no correlation between TFe and salinity. A peak of DFe (and SFe) was observed at 26 July (Fig. 8c), correlates with an elevated from 4 to 14 nM in one month time. This peak correlate to an elevated level of ε280 during the summer, while no other measured parameter showed this drastic change.

The origin of the high Fe levels in at the Landsort Deep in March could be explained by direct terrestrial input or by the transport of lower saline water from the Bothnian Sea via the southward current along the Swedish east-coat. However, station BY31 is far from any major river, and the average peak of riverine freshwater contribution to the Baltic Proper until April (Bergström and Carlsson, 1994). During this study, most of the Fe in the surface water was already lowered considerably in April. A riverine source, as well as lateral transport of Bothnian Sea surface water, would also probably affect the salinity and the concentrations of the major elements, not causing maximum levels as observed here. The pattern of higher Na concentrations at the same time as elevated levels of Fe and P (Fig. 9) indicate that the supply of Fe (and associated elements) is from mixing of deeper laying water masses with higher salinity. A strong relationship between P and Mn was observed during 2004 at the BY31 station (Gelting et al., 2009), where the high initial concentration of these elements were suggested to be supplied from deeper levels. It is also clear from salinity and density data that the water column above the halocline was well mixed in March and April. The area where this station is located also belongs to an upwelling regime (Myrberg and Andrejev, 2003), which supports that iron is supplied by vertical mixing. According to Eilola and Stigebrandt (1998), the input of juvenile freshwater to the Baltic Sea (water from the Bothnian Sea) has its second highest monthly average during March. Probably this input of Bothnian Sea water has some importance, but from our data, the vertical mixing appears to be the dominant source.

Similar to the Bothnian Sea, there is a correlation between chl-*a* and particulate Fe, but at the Landsort Deep, this relationship only exists during the first five sampling occasions (Fig. 8b). The explanation to this phenomenon is similar to the one in the

Bothnian Sea. Changes in chl-*a* reflect changes in the phytoplankton biomass. Phytoplankton provides surfaces and also exudates onto which Fe and other elements can adsorb. Measurements of TEP at the BY31 station were made, but no clear correlation with suspended or sedimenting Fe was observed. Still, exudates from plankton may be of importance, since they exist over a continuum of size ranges (Verdugo et al., 2004), and the TEP method only measures those $>0.45\,\mu$m. Stolpe and Hassellöv (2009) found significant amounts of Fe associated to colloidal biopolymers in surface seawater in the Skagerack Sea after periods of high primary production. However, FFF-ICPMS data (Fig. 1c, see also Sect. 3.4) from the BY31 station does not indicate presence of such colloids.

Initially, on 10 March, chl-*a* and PFe are relatively low, but chl is increasing fourfold, and PFe almost tripled in two weeks time. We suggest that Fe is supplied in a similar way as the supplied of P that feeds the spring bloom, namely from mixing with deeper layers of high P and Fe. Further, the decrease of PFe after the peak of the spring bloom appears to be due to the sedimentation of dead phytoplankton cells and adsorbed elements. The decrease in the DFe and SFe fractions are possibly coupled to this process, where soluble and colloidal Fe aggregate during the spring bloom and are rapidly removed together with fast sinking diatom shells. As indicated by Fig. 8d, the formation of non-detrital Mn seems not to be coupled to the formation of non-detrital Fe. The Fe/Ti (w/w) ratio in suspended matter was above 15 during the whole measured period, except for 26 July when the ratio reached 13.4. This indicates an enrichment of Fe in the suspended matter, since the average crust ratio is 10.2 (Rudnick et al., 2003). Elevated Fe/Ti ratios in PFe on 30 June and 15 July, occur at the same time as the peak of cyanobacteria (Walve et al., unpublished data), which indicate that there may be a coupling to the formation of particulate non-detrital Fe. The vertical flux of Fe to the sediment traps were decreasing from 131 in April to $6.9\,\mu$moles/day/m^2 in August (Fig. 10), which means that the sedimenting Fe follows roughly the same temporal trend as the PFe at 5 m depth. As for the C3 station, the sedimenting amount is higher than the decrease in PFe at 5 m, which indicates a continuous supply of suspended

Fe.

During the highest level of DFe (26 July, Fig. 8c), the Fe/Ti ratio in the particulate phase, which is a sign of a connection between the processes regulating PFe and DFe. The reason of the sharp increase during the summer may be explained by terrestrial input, due to the coincidental high levels of ε280. One other possible source is addition by rain. Measurements from the Polish coast showed that rainwater in Gdansk contained on average about 7 μmol per mm of precipitation (data from Falkowska et al., 2008). If this holds for the open Baltic Sea, this is a potential major contributor of Fe. An evaluation of precipitation data from the Swedish Hydrological and Metrological Institute (SMHI) does, however, not support this since the precipitation in late June–July does not significantly differ from the previous or subsequent periods of the summer. Lower salinity (Fig. 7) and lower concentration of the major elements (exemplified by Na in Fig. 9) suggests a dilution that may be caused either by fresh- or rainwater input. The increasing population of cyanobacteria during the summer may also be responsible for keeping Fe in solution and extract DFe from PFe by siderophore-like pathways. The amount of cyanobacteria reached its peak on 15 July (Walve et al., unpublished data), and the elevated levels of DFe and SFe on 26 July could possibly origin from remineralization by cyanobacteria. The stratified conditions (Fig. 7) suggest that no vertical mixing took place at this event of high DFe in the summer.

3.2.3 Isotopic signature of PFe and sediment trap material

The isotopic signature of PFe is changing drastically during the spring bloom, from −0.10 to +0.25‰ in only 2 weeks (Fig. 11a). During the summer, the δ^{56}Fe is positive at all measured occasions. At 6 October, the δ^{56}Fe decreased back to zero. Staubwasser (2006) found that the composition of the PFe in the anoxic bottom waters of the Gotland Deep were about half a permille lower than the samples from oxic deep water, which were close to zero. They also presented data from the upper 50 m, which showed the lowest δ^{56}Fe values close to the surface. In more recently presented data (Staubwasser et al., 2008), also from the Gotland Deep, a change in the isotopic composition of the suspended matter was attributed to the surface cyanobacterial bloom. The authors hypothesize that the low initial values are originating from water diffusing up from the basin margin sediments after suboxic early-diagenetic remineralization, since such a process commonly generate low δ^{56}Fe values. This hypothesis follows the findings of fractionation of Fe during redox processes, both by abiotoc processes (Bullen et al., 2001) and microbially mediated (Balci et al., 2006). The initial PFe at the surface water of the Landsort Deep has a low δ^{56}Fe, probably originating from the suboxic zone, and it then rapidly changed when the bloom alters the pool of PFe. Between 9 and 21 September, salinity was increasing from 6.0 to 6.7 at 5 m depth, and total P increased from 14.6 to 25.5 μg/L. This is clearly indicating an event of vertical mixing, which also explains the lowering of the δ^{56}Fe from +0.28‰ 15 July to zero at 6 October (Fig. 11a). There seems not to be a correlation between the Fe/Ti ratios and the δ^{56}Fe value, as for the Bothnian Sea (Fig. 11b). One probable reason for this is that the suspended material in the surface water of the BY31 station is less homogeneous and more affected by the processes occurring in the suboxic zone. The conditions in the Bothnian Sea, on the other hand, may to a higher extent be affected by the higher load of suspended material of terrestrial origin, and by the case that the whole water column is oxygenated. From a study of the isotopic composition of dissolved Fe in the Sheldt estuary, de Jong et al. (2007) pointed out the importance of local sinks and sources. In the case of the Baltic Sea, the anoxic conditions below the halocline would fall into that category, since this is a mixing of at least tree different non-detrital Fe phases. In the Bothnian Sea, the original model of two carrier phases with two different isotopic signatures seems to be valid (Ingri et al., 2006).

The Fe removal during the spring bloom can clearly be detected in the sediment traps, as well as elevated levels of P and Si (data not shown). Fe isotopic signatures of the sedimenting material are at all measured occasions negative (Fig. 11c) and show a trend of more negative values towards the summer (with the exception of 23 June). No linear correlation between Fe/Ti and the δ^{56}Fe value could be observed (Fig. 11d). It is notable, that while the Fe/Ti ratio in the sedimenting material is close to the average crust value of 10.2 at all except the last two occasions (Fig. 10b), the δ^{56}Fe value is the entire time negative. A PFe phase with a Fe/Ti value close to average crust ratio would be regarded as mainly composed of lithogenic particles and is predicted to have a δ^{56}Fe of 0. This is not the case here, which means that the use if elemental ratios should be carefully evaluated. The suspended matter at 5 m depth is much more enriched in Fe, as reflected by the higher Fe/Ti values (Fig. 10b). These ratios are intermediates of those in the sediment traps and what was measured in the Bothnian Sea suspended matter. In July, during the drop in Fe/Ti in PFe, the sediment trap data show an increased ratio, which indicates that the particles formed at surface (high Fe/Ti) end up in the sediment trap with some lag. Furthermore, the δ^{56}Fe value changes from −0.08 to +0.28 whereas the Fe/Ti ratio is constant at approximately 16 (Fig. 11b)

The general negative values of δ^{56}Fe in the sediment trap seem at least initially to be connected to the light signature of the suspended matter at 5 m depth that is removed from the euphotic zone and collected in the sediment trap. The reason for the persisting negative δ^{56}Fe in the sediment traps when suspended PFe in surface water is enriched in heavy Fe isotopes, is not easy to explain. Not only isotope data, but also the Fe/Ti ratios indicate that the composition of the sedimenting material is different from the PFe in the surface. Phytoplankton was shown to fractionate Fe isotopes to a relative high extent. Bergquist and Boyle (2006) measured δ^{56}Fe values of –0.24‰ for Amazon plume plankton tows, where they attributed this signature to both intra- and extracellular bound Fe. This is an likely explanation, but there may also be a component of Fe(II) enriched in light Fe, diffusing from the suboxic deeper water and perturbing the δ^{56}Fe value of sedimenting material.

3.3 Gotland Deep

3.3.1 Biogeochemical framework

At 5 m depth, salinity was rather stable around 7, but showed a slightly lower value in the end of June and a maximum in mid August. Chl-*a* was rising throughout the whole sampling period to reach the highest value of 4.13 μg/L in mid August. Surface temperatures increased from 15.4 to 19.7°C during the sampled period. As for the BY31 station, BY15 is characterized by a ~60 m deep layer of low salinity ($S<7.5$) surface water and an intermediate boundary water layer ($S=7.5$–11, 60–100 m) overlaying more saline deep water. A differentiation between oxygenated surface water and oxygen-depleted deeper water, separated by a redox-cline at ~80 m, was present throughout the sampling period (Fig. 12). Salinity and temperature indicate a mixed layer depth of 16 to 21 m (Fig. 12).

TOC concentrations were stable around 400 μM, having a colloidal fraction that varied from 70 to 120 μM during the summer.

3.3.2 Iron speciation

Changes of Fe concentrations were less pronounced compared to the other two stations (Table 1 and Fig. 13). Initial concentrations of TFe are higher, but the DFe and SFe fractions are rather stable through the sampling period. Concentrations are changing during the measured period, but the differences are not as large as for the other two stations. TFe is 24.4 nM in May and deceases to a minimum of 7 nM in July. The correlation between suspended Fe and chl-*a* was not seen at this station.

We can observe similar declining patterns of the measured Fe fractions at this station, as for the other two at lower salinities (Fig. 13), but the total concentrations are clearly lower. This is mainly due to a much lower abundance of PFe at this location, while the DFe and SFe fractions are less different than at the BY31 station. Due to the remoteness from land, the costal upwelling is probably much weaker in the Gotland basin. Vertical mixing and contribution from land may be important sources of Fe also in this area of the Baltic Sea, but we find no clear evidence of this in our measurements. The sampling for this station started later than for C3 and BY31, which means that the peak in spring time would possibly have been higher if sampling stared already in March or April.

3.4 Colloidal iron size distributions determined by FFF-ICPMS

The results from the FFF-ICPMS (Fig. 1) suggest that terrestrial fulvic acid associated Fe is the major colloidal component. This hypothesis has been confirmed in seawater samples from several stations along the Swedish west coast, where 0.5–4 nm humic-type fluorescent organic matter has been found to bind most trace elements. In addition, different types of larger (3–50 nm) colloidal biopolymers have been found to form in surface seawater after periods of high primary production (Stolpe and Hassellöv, 2009). In the Bothnian Sea, although these types of biopolymers occurred during summer, iron was found to be exclusively associated to fulvic acid from terrestrial sources (Fig. 1b). Similar results were obtained in surface water of the Baltic Sea, both in offshore samples (Fig. 1c) and in the coastal Baltic Proper (Fig. 1d). Data from the Gotland Deep is very similar to the obtained fractogram from the Landsort Deep station (Fig. 1c). In contrast, in the more marine coastal system of the Gullmarsfjord on the Swedish west coast, where the influence of rivers is less strong, iron was found to associate to biopolymer nanofibrils during the summer (Fig. 1e) (Stolpe and Hassellöv, 2009). By the use of Atomic Force Microscopy (AFM) the sizes of these nanofibrils were determined to 50–250 nm in length and 0.5–1.1 nm in thickness.

3.5 DGT measurements

During 2004 the DGT measurements at Landsort Deep were conducted at a temporal resolution, which affected the precision of the method. During the short time of deployment (2–3 weeks) the amount of accumulated Fe was often very low, and the blank contribution made it difficult to interpret any temporal changes in $[Fe]_{DGT}$, even tough an average for the whole sampling period could be obtained. The DGT-labile fraction was low at all stations compared to SFe (less than 10% on average, Table 1). If assuming that all DGT-labile Fe ($[Fe]_{DGT}$) was bound to fulvic acids the concentrations becomes about 5 times higher, but still lower than SFe. Breitbarth et al. (2009), showed that the DGT labile fraction is very similar to the Fe(II) concentration.

Clearly, the average $[Fe]_{DGT}$ was deceasing from the Bothnian Sea (1.1 nM) to about 1/3, with similar concentrations at the Landsort Deep and Gotland Deep stations (0.35 nM). This means that, as well as for the TFe, DFe and SFe fractions, there is a terrestrial proximity-salinity dependency on the fraction. We were able to detect a 30–40% decrease in $[Fe]_{DGT}$ from from the spring towards later in the season at the C3 and BY15 stations This change from low to higher salinity, and from spring to summer, is possibly connected to the amount of complexed Fe that changes along this gradient. As discussed above, FFF-ICPMS data (Fig. 1), indicate that most colloidal Fe is bound to fulvic acid, and also that this compound is decreasing from C3 to similar levels at BY31 and BY15. It has been shown in several studies (e.g. Scally et al., 2006), that complexes between metals and fulvic acids may pass through the diffusive gel and are thus measured by the DGT technique.

4 Conclusions

We conclude three major findings from our study:

1. All three studied locations showed a steadily decreasing pattern of Fe in the measured fractions TFe, DFe, SFe and $[Fe]_{DGT}$, from the first measurement in spring towards the summer. From FFF-ICPMS measurements, a significant, but decreasing, carbon fraction (most likely fulvic acid) dominated colloid bound Fe at all locations. This is analogous to the findings of humic substances (HS) controlling Fe in the coastal and open ocean (Laglera and van den Berg, 2009).

2. The relatively high level of Fe in the <1 kDa fraction at all sampled stations (above 2 nM) indicate that the levels of SFe are sufficient for Fe-replete phytoplankton growth. Calculations of Fe uptake by Baltic phytoplankton are orders of magnitude lower than this number. In spite of this, a strong correlation was observed between chl-*a* and PFe. This was not attributed to active uptake, but a common cycling of Fe and P; similar sources, growth of phytoplankton onto which PFe attach and removal of PFe during sedimentation. Hence, primary production strongly regulates cycling of suspended Fe.

3. Iron isotope data reveal systematic temporal variations in the Fe-isotope signature, the δ^{56}Fe value changed from −0.08 to +0.25‰ during three weeks in March and April at the Landsort Deep. This change was related to spring-bloom (diatoms) and subsequent sedimentation of iron with a negative isotope signature. All sediment trap data from the Landsort Deep showed a negative iron isotope value. During summer a relatively stable positive δ^{56}Fe value was measured in suspended matter both in the Bothnian Sea and at the Landsort Deep. This positive value probably is a combination of river introduced aggregated oxyhydroxides and particulate iron formed from oxidation of dissolved Fe(II) in the euphotic zone. Hence, aggregated but still suspended Fe-oxyhydroxides might be spread over large areas in the Gulf of Bothnia. Iron isotope data clearly show that a δ^{56}Fe value around zero does not mean that the sample consist of mainly detrital rock fragments, usually the value is reflecting a mixture of iron particles with positive and negative values.

Acknowledgements. This work has been carried out with financial support from the Swedish Research Council #621-2003-2523 and #621-2005-3680, Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) #217-2005-1879, Kempestiftelsen and Umeå Marine Research Center (UMF). Bernt Abrahamsson, Amund Lindberg, Leif Lundgren, Fredrik Nordblad, Carl-Henrik Stangenberg, Jakob Walve, Johan Wikner, and the crew of M/F Fyrbyggaren and R/V KBV005 are acknowledged for their assistance during sampling. Thanks also to Murat V. Ardelan for analyzing some of the water samples on the CL-FIA

instrument. Dimitry Malinovsky, Ilia Rodushkin and ALS Scandinavia are greatly acknowledged for performing the Fe isotopic measurements.

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Table 1. Iron concentrations at 5 m depth in different fractions at the three studied stations in the Baltic Sea. All Fe concentrations are given in nM. The ± notations indicate the standard deviation for mean values. For maximum and minimum ± indicate the precision of the measurement.

Station	C3 (Bothnian Sea) *n*=8	BY31 (Baltic Proper) *n*=15	BY15 (Baltic Proper)*n*=5
Mean Salinity	4.69±0.23	6.29±0.30	7.03±0.10
Mean TFe	114±87	44±30	15±2.5
Max TFe	309±11	108±1	24±0.3
Mean DFe	21.3±10	7.0±3.8	3.8±1.8
Max DFe	32.4±2.5	13.7±0.41	7.0±4.0
Min DFe	6.0±0.09	1.9±0.11	2.7±0.17
Mean SFe	6.2±2.5	5.9±3.0	3.2±0.96
Max SFe	10±1.8	13.1±0.78	4.4±1.8
Min SFe	3.2±0.18	2.7±0.19	2.1±0.12
DGT (top 40m average)	1.3 in spring, 0.9 during summer	0.35 on average, but no clear tend during the year	0.44 May–June 0.26 July–August

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Table 2. Different fractions of Fe expressed as percentage of total Fe (TFe).

	DFe (<0.22 µm)	SFe (<1 kDa)	CFe (1 kDa–0.22 µm)
C3	9% of TFe in April, 20–30% May–August	3.2% of TFe in April, 6.5–13% May–August	5.8 % of TFe in April, 16–20%, May–August
BY31	27% of TFe in March 10–22% during April–May, varying during June–October, showing a maximum of 50%	Initially 15% of TFe in March. 5–10% during spring and a few high numbers June–October (max ∼50%)	12.6 % of TFe in March, 3.6–10% during spring, 0–8% June–October
BY15	23–54% of TFe	18–41% of TFe	5–10% of TFe

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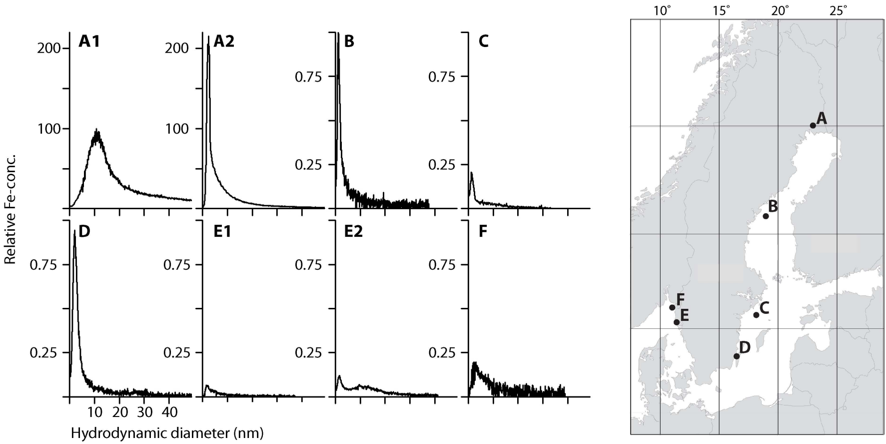

Fig. 1. 0.5–50 nm colloidal size spectra of iron in: (A) Kalix River at Kamlunge on 9 April 2002 (A1) and during maximum spring flood on 1 May 2002 (A2). (B) Bothnia Sea at 5 m depth on 19 July 2006. (C) Baltic Sea (offshore) at 5 m depth on 14 April 2004. (D) Baltic Sea at Kalmar Sound (near shore) at 1 m depth on 5 September 2005, (E) Gullmarsfjord at 10 m depth on 21 March 2005 (E1) and on 22 June 2005 (E2). (F) Skagerrak Sea (nearshore) at 1 m depth on 30 June 2005. Relative Fe-concentrations shown on y-axis are proportional to, but not equal to, concentrations in the samples.

Fig. 2. Map of the sampling stations.

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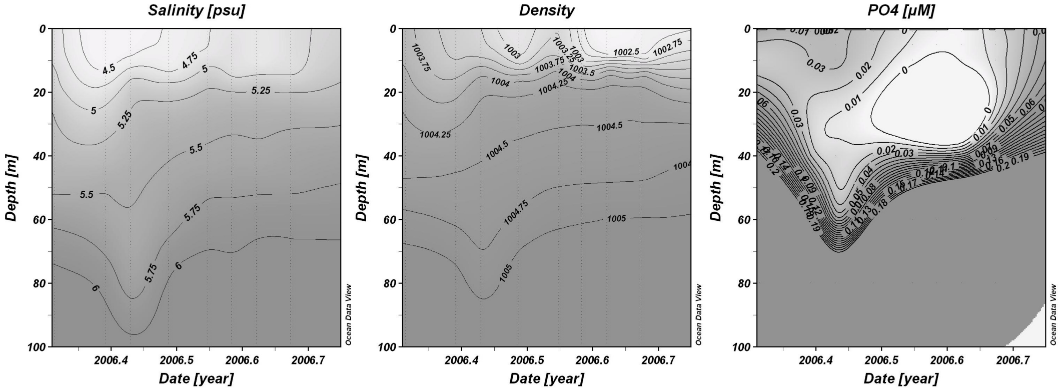

Fig. 3. Time series of salinity, density and PO_4^{2-} in the upper 100 m at the C3 station (Bothnian Sea) during 2006. Date format is decimal year. This figure was prepared with Ocean Data View using DIVA gridding.

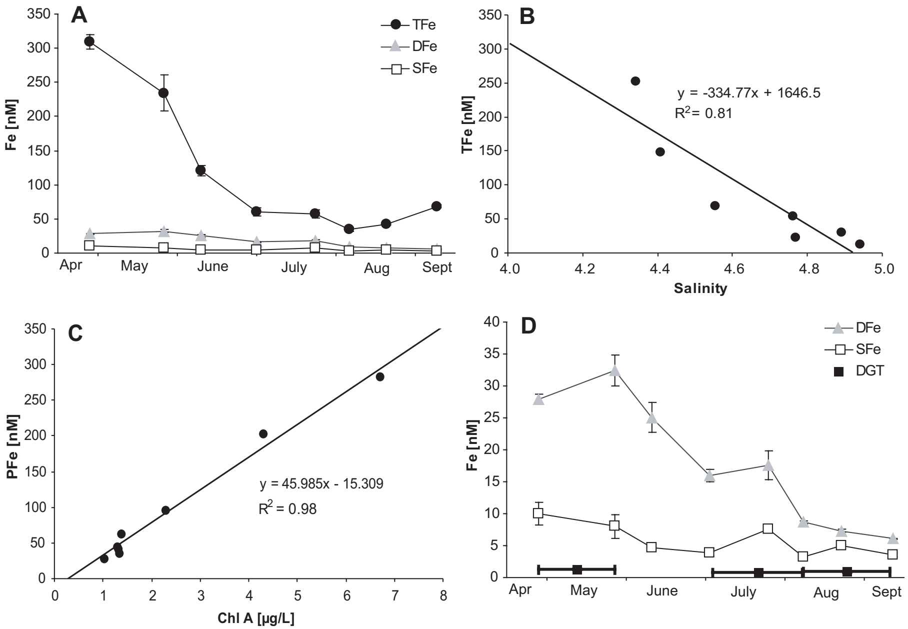

Fig. 4. Bothnian Sea (C3 station) 2006. Concentrations of TFe (total Fe), DFe (<0.22 *µ*m) and SFe (<1 kDa) **(A)**. Regression between unfiltered Fe and Salinity at 5 m depth, May to September **(B)**. Regression between chlorophyll-*a* and suspended Fe (PFe) **(C)**. Concentrations of DFe(<0.22 *µ*m), SFe(>1 kDa) and DGT-labile Fe ($[\mathrm{Fe}]_{\mathrm{DGT}}$) **(D)**. For DGT measurements, the vertical lines indicate the time period for the measurement, and the filled squares represent the mid-date.

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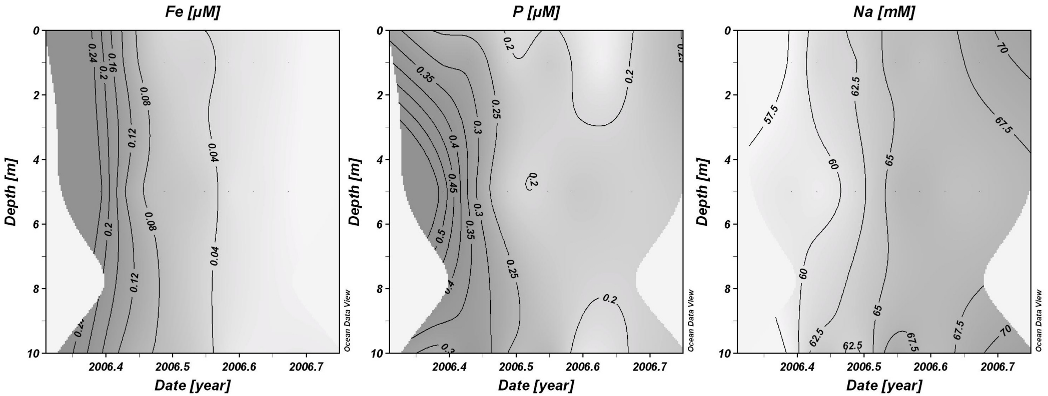

Fig. 5. Variations of total Fe (unfiltered samples), phosphorus (P) and sodium (Na) for the uppermost 10 m at the C3 station. Date format is decimal year. This figure was prepared with Ocean Data View using DIVA gridding for samples taken at 0.5, 5 and 10 m depth.

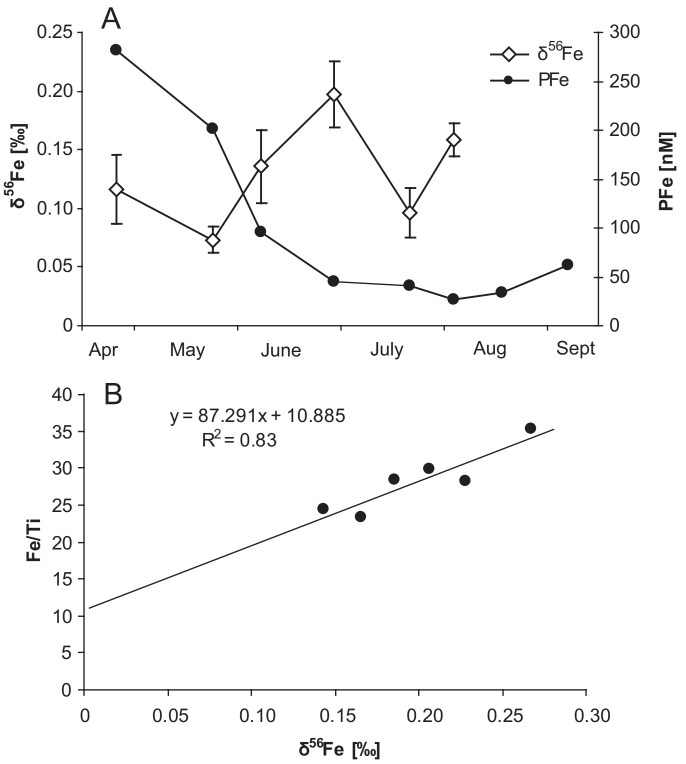

Fig. 6. PFe in the C3 station (Bothnian Sea) 2006 (filled dots) and Fe isotopic signatures of the suspended matter (open diamonds) **(A)**. Regression between Fe isotopic signature and Fe/Ti ratios of the suspended matter (PFe) **(B)**.

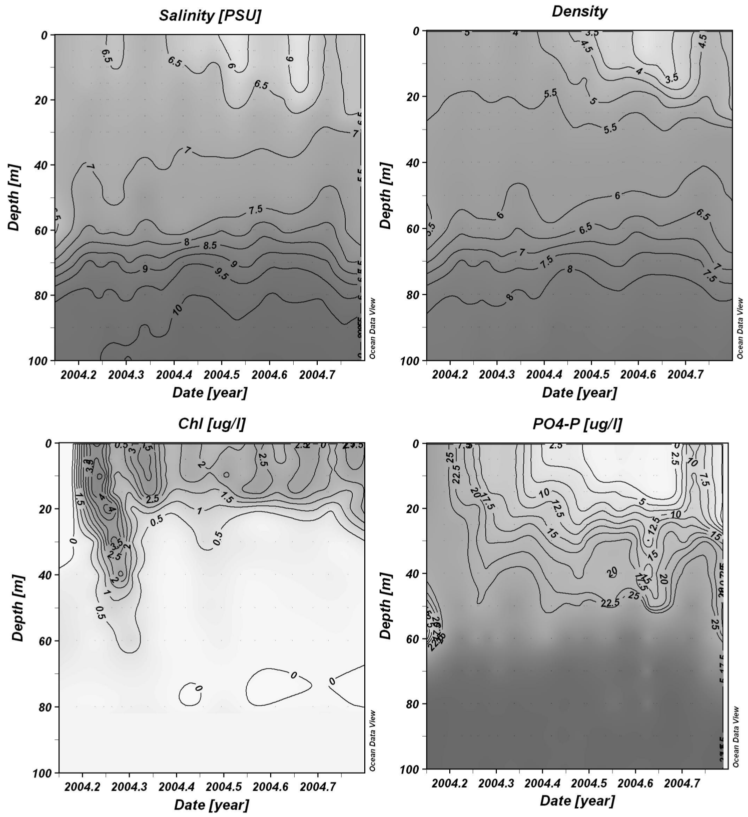

Fig. 7. Time series of salinity, density, chl-*a* and PO_4^{2-} in the upper 100 m at the BY31 station (Landsort Deep) during 2004. Date format is decimal year. This figure was prepared with Ocean Data View using DIVA gridding.

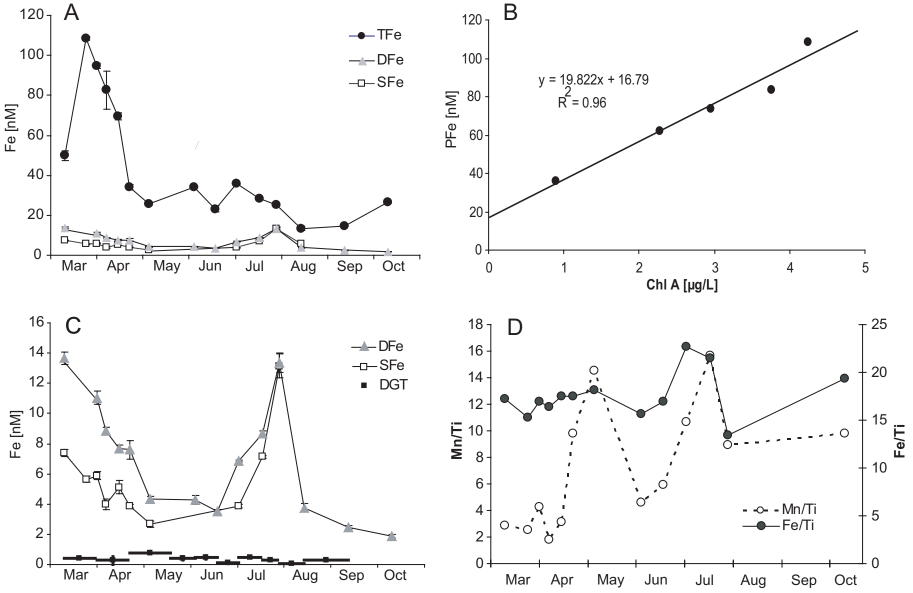

Fig. 8. Landsort deep (BY31 station) 2004. Concentrations TFe (total Fe), DFe ($<0.22\,\mu$m) and SFe (<1 kDa) **(A)**. Regression between unfiltered Fe and Salinity at 5 m depth, the five first sampling occasions **(B)**. Concentrations of DFe($<0.22\,\mu$m), SFe(>1 kDa) and DGT-labile Fe ($[\text{Fe}]_{\text{DGT}}$) **(C)**. For DGT measurements, the vertical lines indicate the time period for the measurement, and the filled squares represent the mid-date. Temporal variations of Mn/Ti and Fe/Ti in the suspended phase at 5 m depth **(D)**.

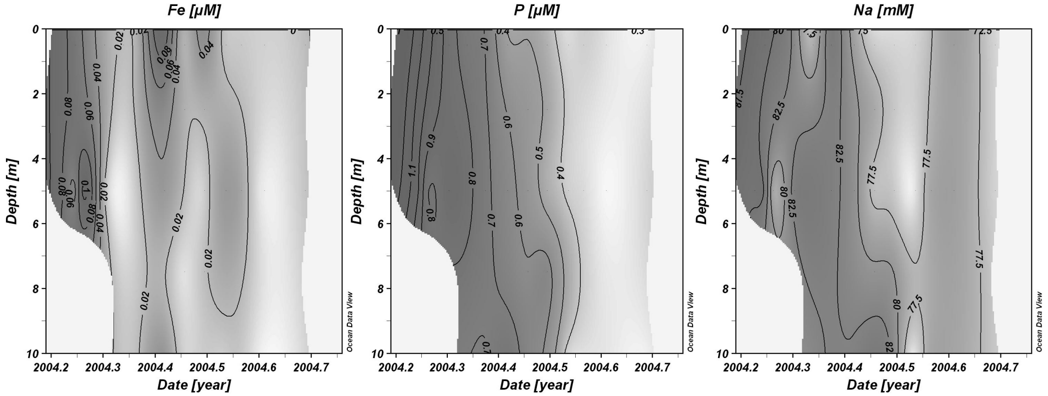

Fig. 9. Variations of total Fe (unfiltered samples), phosphorus (P) and sodium (Na) for the uppermost 10 m at the BY31 station. Date format is decimal year. This figure was prepared with Ocean Data View using DIVA gridding for samples taken at 0.5, 5 and 10 m depth.

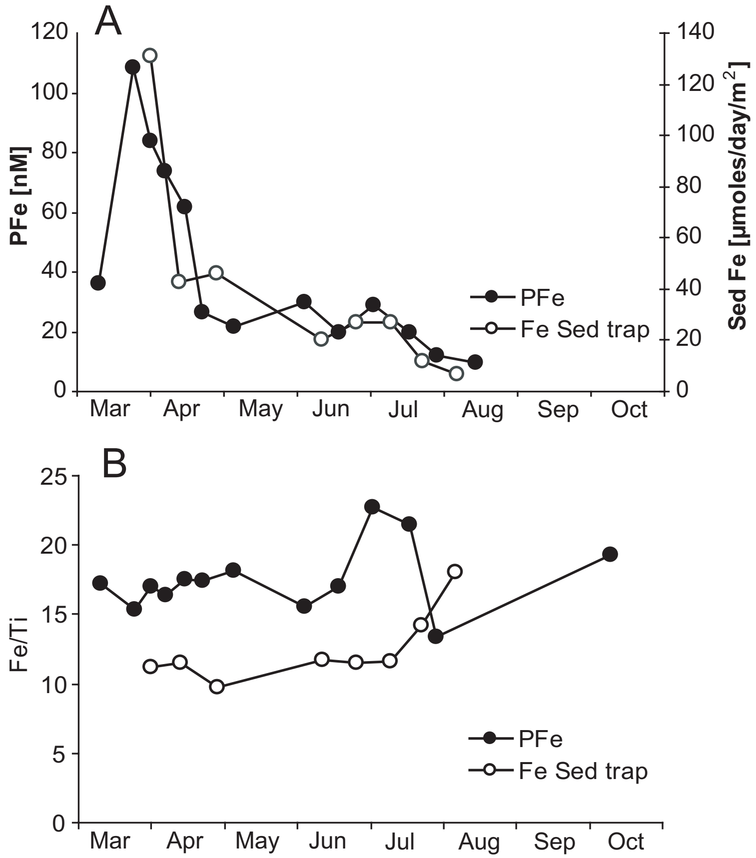

Fig. 10. Suspended Fe (PFe) at 5 m depth and sediment trap collected Fe at 30 m depth at Landsort Deep (BY31) 2004 **(A)**. Fe/Ti in PFe at 5 m depth and in sediment trap collected material **(B)**.

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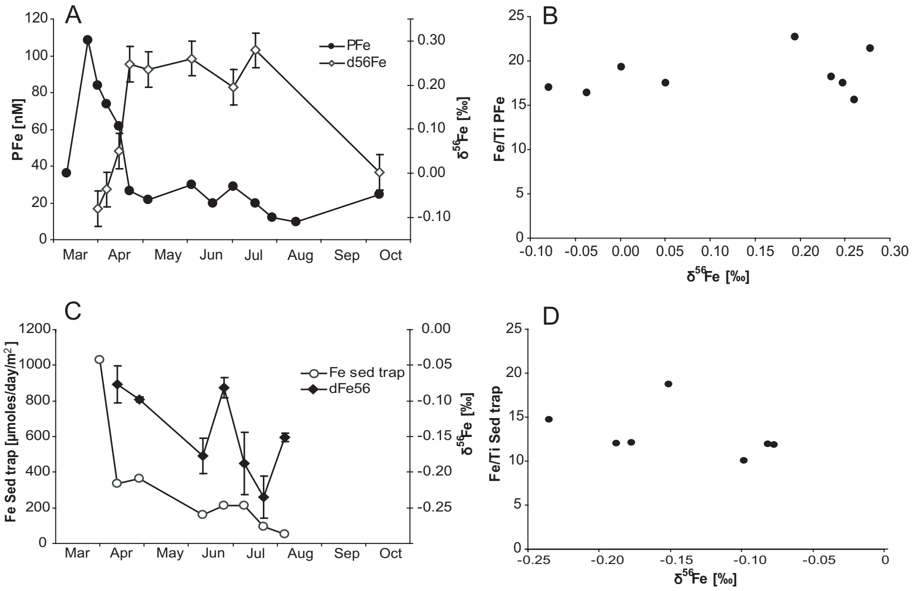

Fig. 11. Isotopic signatures of suspended Fe (PFe) at 5 m depth and sediment trap collected material at 30 m depth, all data from Landsort Deep 2004. The seasonal variation of δ^{56}Fe in PFe and the PFe concentration **(A)**. δ^{56}Fe plotted against Fe/Ti in PFe **(B)**. Temporal variation of δ^{56}Fe in sediment trap collected material and amount of sedimenting Fe **(C)**. δ^{56}Fe plotted against Fe/TI in the sediment trap collected material **(D)**.

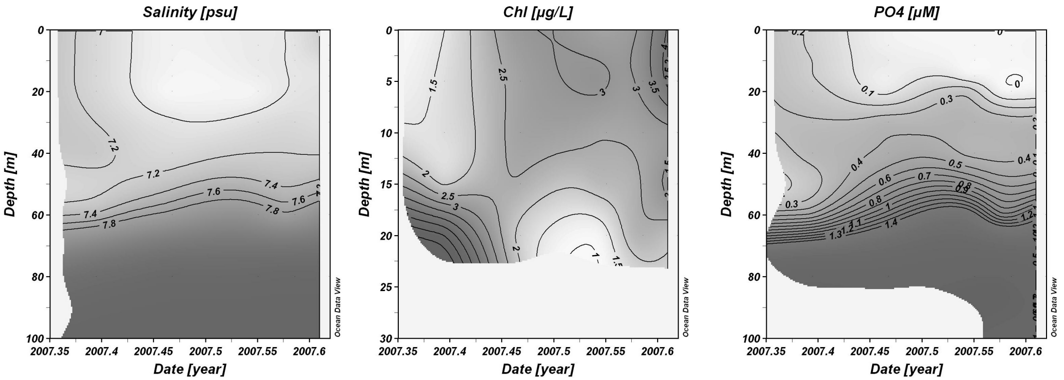

Fig. 12. Time series of salinity, density, chl-*a* and PO$_4^{2-}$ at the BY15 station (Gotland Deep) during 2007. Note the differences in depth scale. Date format is decimal year. This figure was prepared with Ocean Data View using DIVA gridding.

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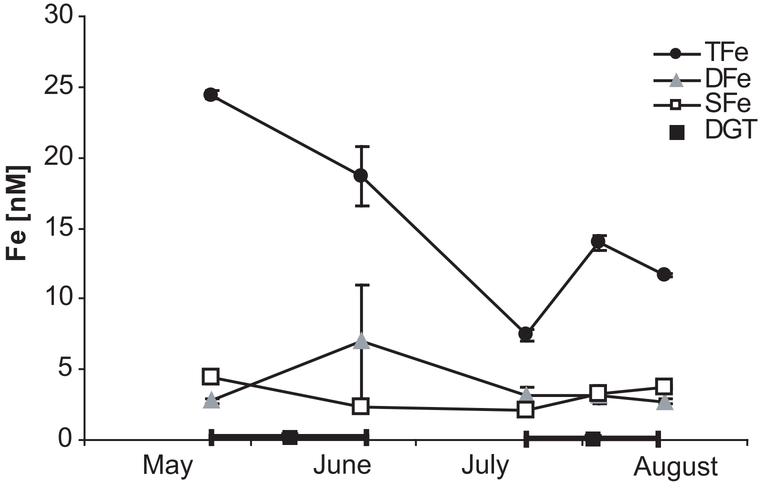

Fig. 13. Temporal variations of TFe (total Fe), DFe (<0.22 µm), SFe (<1 kDa) and DGT-labile Fe ($[\mathrm{Fe}]_{\mathrm{DGT}}$) at the Gotland Deep (station BY15) euphotic zone. For DGT measurements, the vertical lines indicate the time period for the measurement and the filled square represent the mid-date.